

Evaluating Nonlinear Sorption of Four Substituted Phenols to Agriculture Soils Using Expanded Polyparameter Linear Free Energy Relationship

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Abstract Nonlinear sorption of substituted phenols (degradation products of several pesticides) onto soils was often observed. This sorption nonlinearity at low solute concentration ranges could result in higher soil organic carbon-water distribution coefficient (K_{oc}) values than those predicted by their hydrophobicity (K_{ow}). In this study, nonlinear sorption characteristic of four substituted phenols (2,6-dimethylphenol, 2-chlorophenol, 2-nitrophenol, and 2,4-dichlorophenol) onto two agricultural soils was investigated. The sorption nonlinearity gradually approached apparent saturation at low solute activity ranges (e.g., $a_i < 0.01$). At high a_i ranges, linear sorption was observed. Thus, partition and adsorption of solutes were successfully evaluated by a dual-mode sorption model. The concentrations of substituted phenols in the environment are pretty low (e.g., usually lower than 1 mg/L). According to our results, nonlinear adsorption is dominant in such low concentration ranges in the environment. To predict

varied $\log K_{oc}$ values resulted from nonlinear adsorption, especially for low a_i range, an expanded polyparameter linear free energy relationship (pp-LFER) is established: $\log K_{oc} = [(1.829 \pm 0.488) + (3.481 \pm 0.462) \log a_i]E + [(-4.307 \pm 0.466) \log a_i]S + [(-0.876 \pm 0.138) \log a_i]A + [(-0.086 \pm 0.529) + (1.209 \pm 0.218) \log a_i]B + (6.280 \pm 0.649)V - (6.814 \pm 0.917)$ (E , the excess molar refraction; S , the dipolarity/polarizability parameter; A , the solute H-bond acidity; B , the solute H-bond basicity; and V , the molar volume). This model can provide a better prediction (within 0.3 log unit) than previous models. This study provides essential parameters for predicting and understanding the environmental behavior of substituted phenols in agricultural soils.

Keywords Partition · Adsorption · Soil · Substituted phenols · Polyparameter linear free energy relationship

1 Introduction

Increasing organic pollution in surface water and groundwater is a crucial environmental problem facing human society (Fenner et al. 2013; Schwarzenbach et al. 2006). Sorption to soils/sediments is one of the most important processes controlling the temporal and spatial extent of these organic pollutants in soil-water environment. Soil or sedimentary organic matter (SOM) is the major environmental sorbent for the sorption of neutral compounds (Aeschbacher et al. 2012; Chen et al. 2005;

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Han et al. 2014; Tremolada et al. 2012). To evaluate the sorption of organic pollutants in soil-water environment, soil organic carbon-water distribution coefficient (K_{oc} , L/kg) is required. It is calculated by the following equation:

$$K_{oc} = K_d/f_{oc} = (q/C_e)/f_{oc} \quad (1)$$

where K_d (L/kg) is the sorption distribution coefficient between the sorbent and water, f_{oc} is the content of soil organic carbon by weight, q (mg/kg) is the overall sorption by solid, and C_e (mg/L) is the equilibrium solute concentration.

Since one-parameter linear free energy relationships using octanol/water partition constant (K_{ow}) or the water solubility (S_w) often fail to predict sorption distribution coefficients (Goss and Schwarzenbach 2001), polyparameter linear free energy relationships (pp-LFERs) have been shown to provide good predicted K_{oc} values instead (Endo and Goss 2014; Endo et al. 2009; Nguyen et al. 2005). The most widely used pp-LFER model was developed by Abraham (Abraham 1993; Abraham et al. 2004) as follows:

$$\text{Log}K_{oc} = c + eE + sS + aA + bB + vV \quad (2)$$

The capital letters are used for the solute descriptors: E , excess molar refraction; S , polarizability/dipolarity parameter; A , solute H-bond acidity; B , solute H-bond basicity; V , McGowan molar volume with units of ($\text{cm}^3 \text{mol}^{-1}$)/100. The regression coefficients e , s , a , b , and v and the constant c are determined by the multiple linear regression analysis.

Among the top priority pollutants, phenolic compounds are often detected in surface water and groundwater (Dolatto et al. 2016; Li et al. 2015; Xiao et al. 2016). Substituted phenols are the degradation products of pesticides (Boyd 1982) and pose a threat to human health and aquatic ecosystem in agricultural region. Therefore, sorption of phenols with geosorbents draws more and more attention. With respect to the sorption of phenolic compounds to SOM, hydrophobic partitioning of undissociated phenolic species into SOM should be dominant, e.g., chlorophenols partitioning into particulate soil organic matter (Frankki and Skyllberg 2006) or marine sediments (Fytianos et al. 2000). However, it should be noted that phenolic compounds contain one or several polar functional groups (like $-\text{OH}$, $-\text{Cl}$, and

$-\text{NO}_2$). Hence, specific interactions could occur and enhance sorption nonlinearity. As a result, nonlinear sorption isotherms of phenols to soils (Gao et al. 2012; Khan and Anjaneyulu 2005; Liu et al. 2010; Selig et al. 2003) or humic acid particles (Sagbas et al. 2014) were often reported. In these studies, phenols are undissociated or partly dissociated. Therefore, partition and adsorption were supposed to play roles together. Identifying partition and adsorption is of great importance because different sorption mechanisms showed different influence on the long-term persistence and biodegradation accessibility of organic pollutants (Cornelissen et al. 2005). However, partition and adsorption of phenols are barely identified in nonlinear sorption isotherms previously.

Because the phenolic $-\text{OH}$ group could form H-bond with soil, water solubility (S_w) has been shown to be inaccurate to predict K_{oc} values for substituted phenols (Boyd 1982). Meanwhile, $\text{log} K_{oc}$ values in nonlinear sorption could vary significantly and bring challenge to the application of pp-LFERs. So far, the attempts to deal with nonlinear sorption by modified pp-LFERs were made for some model sorbents, such as activated carbon, diesel soot, and wood char (Apul et al. 2013; Lu et al. 2016; Shih and Gschwend 2009).

Hence, the main objects of this study were (1) to quantitatively evaluate the contributions of partition and adsorption to the overall sorption of substituted phenols to agricultural soils and (2) to develop an expanded pp-LFER model to predict varied $\text{log} K_{oc}$ in nonlinear sorption. We especially focused on the adsorption at low solute concentration ranges, which are more environmentally relevant. To this end, batch sorption experiments were carried out. Two agricultural soils (black soil and fluvo-aquic soil) with different f_{oc} values served as natural sorbents. Four substituted phenols, 2,6-dimethylphenol, 2-chlorophenol, 2-nitrophenol, and 2,4-dichlorophenol, were chosen as representative phenols because they carried different substituted groups ($-\text{CH}_3$, $-\text{Cl}$, and $-\text{NO}_2$). Sorption isotherms were determined with equilibrium solute concentration ranges covering 2 ~ 3 orders of magnitudes. Thus, partition and adsorption could be evaluated according to the characteristics of sorption isotherms. Then, expanded pp-LFER model was developed for soil systems to identify the molecular interactions controlling

phenols sorption to soils and to predict varied K_{oc} values in nonlinear sorption processes.

2 Materials and Methods

2.1 Materials

2,6-dimethylphenol (2,6-DMP, > 99%, TCI), 2-chlorophenol (2-CP, > 99%, TCI), 2-nitrophenol (2-NP, > 99%, Sigma), and 2,4-dichlorophenol (2,4-DCP, > 98%, TCI) were used as tested sorbates in sorption experiments. 2-CP is liquid and the rest are solids at room temperature. The liquid density is 1.241 g/mL for 2-CP at 25 °C. Other physicochemical properties of these organic compounds are listed in Table 1 and Table S1 in the supporting information (SI). According to solute pK_a values, speciation of phenols as a function of pH can be seen in Fig. S1. Black soil (Bsoil) from Heilongjiang Province and fluvo-aquic soil (Fsoil) from Anhui Province were chosen as sorbents. Both agricultural soils were obtained from Langfang Institute of Geochemistry and Geophysics, Chinese Academy of Geosciences. Soils were used as received. Values of organic matter content (f_{om}) are 3.45% for Bsoil and 1.7% for Fsoil, respectively. According to the empirical equation ($f_{oc} = 0.59 f_{om}$), the contents of soil organic carbon are 2.04 and 1.03% for Bsoil and Fsoil, respectively. Soil pH values are 6.14 for Bsoil and 8.18 for Fsoil, respectively.

Table 1 Physicochemical properties of investigated organic compounds

Compound	Structure	Log K_{ow}^a	pK_a^a	S_w^a (g/L)	$S_{w,sub}^b$ (g/L)	S_w^a (g/L)
2,6-DMP		2.36	10.62	6.05	9.87	6.05
2-CP		2.15	8.56	11.3	/	11.3
2-NP		1.79	7.23	2.5	3.96	2.5
2,4-DCP		3.06	7.89	5.55	8.40	5.55

^aData were collected from database SRC

^bSubcooled liquid solubility ($S_{w,sub}$) was calculated as shown in S1 in the supporting information. Since 2-CP is liquid and 2,6-DMP, 2-NP, and 2,4-DCP are solids at 25 °C, S_w for 2-CP and $S_{w,sub}$ for 2,6-DMP, 2-NP, and 2,4-DCP were used to calculate their activities (a_i)

2.2 Batch Sorption Experiments

Sorption experiments of solutes with Bsoil and Fsoil were carried out by a batch equilibrium method. Organic solute was dissolved in methanol (> 99.9%, Thermo Fisher Scientific), and then, different concentrations of organic solute were prepared in a background solution with 0.01 mol/L $CaCl_2$ in ultrapure water. The methanol carrier in background solution was kept at < 0.1% (v/v) to avoid co-solvent effects. Initial solution pH was adjusted to 7 ± 0.2 by 0.1 mol/L NaOH or HCl. Initial solute concentrations ranged from 0.5 to 233 mg/L for 2,6-DMP, 6 to 249 mg/L for 2-CP, 5 to 245 mg/L for 2-NP, and 10 to 432 mg/L for 2,4-DCP, respectively. Certain amounts of each soil (0.5 g) were added in 10-mL vials and mixed with 10 mL organic pollutant solution, leaving the vial a minimum headspace to avoid the volatile loss. All vials were tightly sealed by a Teflon screw cap. Samples were run in duplicate. One control (without sorbents) was prepared to monitor the loss of solute during the sorption experiment. All samples were placed on a reciprocal shaker at 175 rpm (25 °C) for 7 days. According to sorption kinetics, 7 days were long enough for solutes to reach the apparent equilibrium. After centrifugation at 3000 rpm for 15 min, concentrations of organic solutes were determined by high-performance liquid chromatography (HPLC, Shimadzu LC-20AT) with a UV detector and an Inert Sustain Swift C18 column (4.6 × 250 mm) at 30 °C. Details about the HPLC method are presented in Table S2 in SI. Controls (without sorbents) showed no significant mass loss during the whole experiments. Therefore, the sorbed amount of investigated solutes can be calculated by mass balance according to the solute concentration in water of the control sample and studied sample.

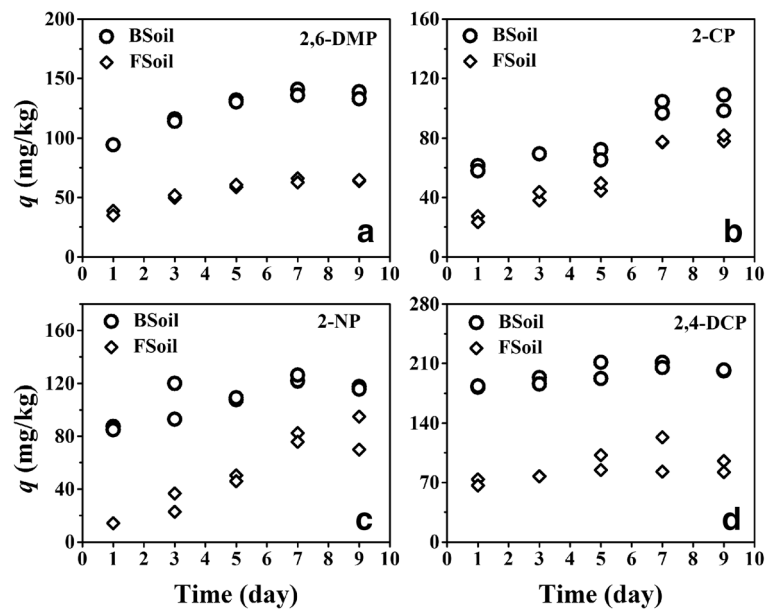
2.3 Data Analysis

The dual-mode sorption model was applied to analyze the sorption isotherms, which is described by

$$q = K_{d,part} C_e + K_L Q_{max} / (1 + K_L C_e) \quad (3)$$

where q and C_e were described in Eq. 1, $K_{d,part}$ (L/kg) is sorbate partition coefficient between the partition phase (e.g., SOM) and aqueous phase, and K_L and Q_{max} (parameters in the Langmuir model) are the affinity constant (L/mg) and the maximum adsorption capacity (mg/kg), respectively.

Fig. 1 Sorption kinetics of 2,6-DMP, 2-CP, 2-NP, and 2,4-DCP to two soils. Initial solute concentration was 50 mg/L



3 Results

3.1 Sorption Kinetics

Sorption kinetics experiments were carried out in 9 days. During the experimental period, Bsoil (f_{oc} , 2.04%) with higher content of organic matter showed stronger sorption ability than Fsoil (f_{oc} , 1.03%) (Fig. 1). It took 1 day and 5 days for 2,4-DCP and 2,6-DMP to approach sorption equilibrium, respectively, while it took 7 days for 2-CP and 2-NP. Larger $\log K_{ow}$ of solute resulted in faster sorption rate, suggesting hydrophobic partition plays an important role in their sorption process. In the following sorption experiments, 7 days were taken as the time of equilibrium.

3.2 Sorption Isotherms

Sorption isotherms are depicted in Fig. 2 for four substituted phenols on two soils. Sorption affinity of Bsoil was stronger than that of Fsoil. Sorption of organic solute to soils is commonly assumed to be controlled by SOM when its content is above 0.1% by weight (Haderlein and Schwarzenbach 1993; Schwarzenbach and Westall 1981). The soil mineral matter is practically inert to the solute because of the adsorptive suppression by water (Chiou et al. 2015). Uptake of four phenols all showed

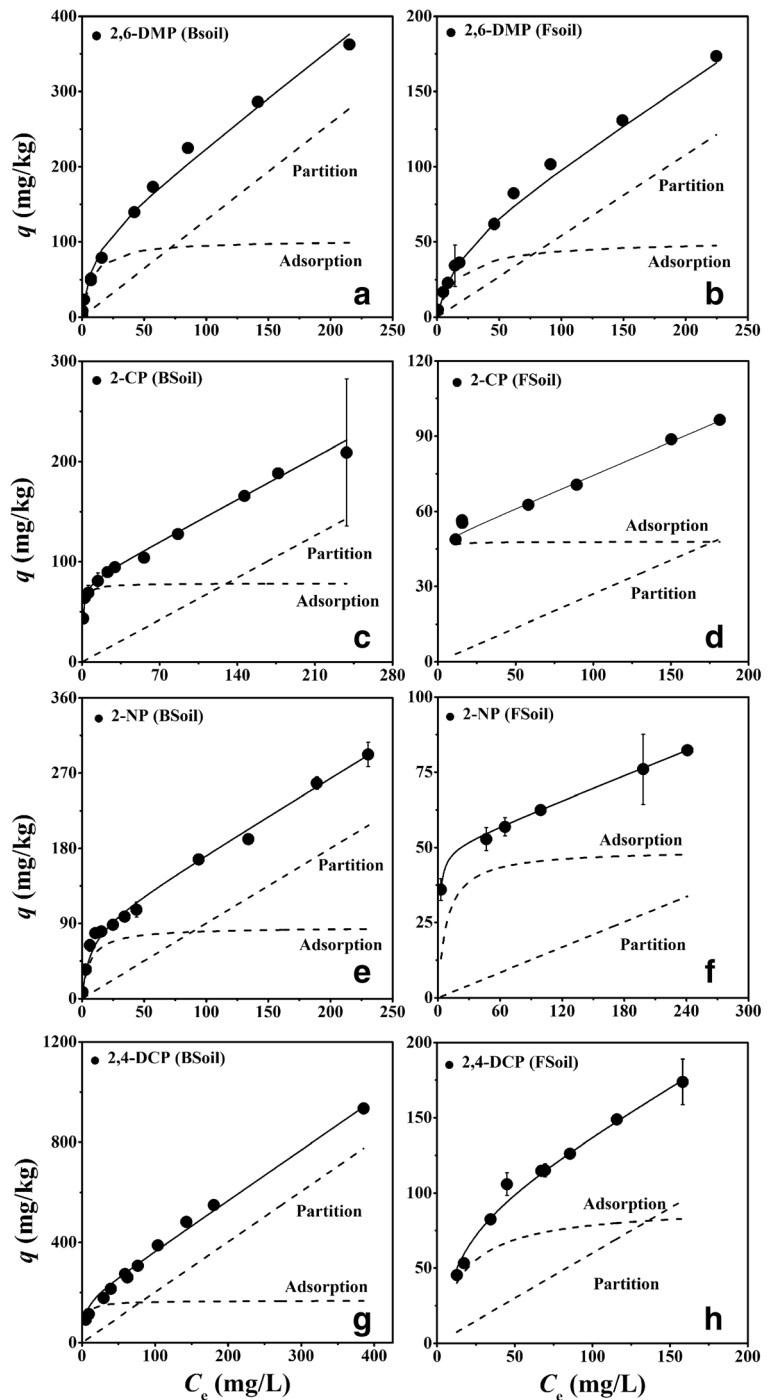
nonlinearity, indicating specific interactions occurred in addition to absorptive partition. The dual-mode model (Eq. 3) is applied to fit sorption data and to identify contributions of partition and adsorption to overall sorption. Fitting results indicated that sorption of phenols can be well described by the dual-mode model (all $R^2 > 0.99$) (Table 2). Since specific interactions (e.g., polar interaction and H-bonding) are more powerful molecular forces than nonpolar forces (Chiou and Kile 1994), adsorption, rather than partition, was dominant especially at low C_e ranges. Site-specific adsorption gradually got saturated with increasing C_e and only partition contributed to overall sorption at high C_e level. Hence, linear sorption can be seen at high solute concentration ranges. The concentrations of substituted phenols in the environment are pretty low, for example, usually lower than 1 mg/L in river (Li et al. 2015). According to our results, nonlinear adsorption is dominant in such low concentration ranges.

4 Discussion

4.1 Partition and Adsorption of Four Substituted Phenols

Partition and adsorption to soils play roles together in the overall sorption. The sorption isotherms display

Fig. 2 Sorption of four substituted phenols to two agricultural soils. The solid lines were fitted by the dual-mode model. The linear dash lines represent partition and the nonlinear dash lines represent adsorption according to the dual-mode model. Data are an average of two replicates. Error bars are shown but generally are smaller than the label



concave-downward nonlinear sorption at low solute activity (e.g., $< 0.01 C_e/S_w$ (or $C_e/S_{w,sub}$), the ratio of equilibrium concentration to aqueous solubility or subcooled liquid solubility) whereas exhibit linear

sorption at high concentration. This has also been observed in previous studies for other hydrophobic pollutants (Accardi-Dey and Gschwend 2002; Allen-King et al. 2002; Chiou and Kile 1998). Chiou and Kile

Table 2 Fitted parameters by the dual-mode model for phenols sorption to Bsoil (f_{oc} , 2.04%) and Fsoil (f_{oc} , 1.03%)

Sorbents	Organic pollutants	$K_{d,part}$ (L/kg)	K_L (L/mg)	Q_{max} (mg/kg)	Dual-mode R^2
Bsoil	2,6-DMP	1.29	0.13	102.1	0.996
	2-CP	0.60	1.07	78.4	0.997
	2-NP	0.90	0.16	85.4	0.996
	2,4-DCP	2.01	0.27	167.5	0.997
Fsoil	2,6-DMP	0.54	0.06	51.0	0.998
	2-CP	0.27	4.12	47.9	0.992
	2-NP	0.14	0.85	49.3	0.999
	2,4-DCP	0.60	0.07	87.0	0.993

(1998) studied the adsorption and partition of 3,5-dichlorophenol to soils and found that nonlinear capacity of 3,5-dichlorophenol exceeds greatly the amount accountable by the small surface area of the soil. Thus, they attributed the adsorption of 3,5-dichlorophenol to the interactions which occurred within the interior network of SOM. In this study, adsorption capacities (Q_{max} in Table 2) normalized by soil organic content for the given sorbate are comparable on two soils, which are 4.95 and 5.00 mg/g for 2,6-DMP, 4.65 and 3.84 mg/g for 2-CP, 4.79 and 4.19 mg/g for 2-NP, and 8.44 and 8.21 mg/g for 2,4-DCP on Bsoil and Fsoil, respectively. It demonstrates that adsorption of four phenols onto soils was also controlled by SOM content.

In this case, amorphous organic matter serves as the absorptive partition phase. Nonlinear adsorption is attributed to specific interaction between sorbate and condensed carbonaceous materials (Allen-King et al. 2002), which have high surface areas. Condensed carbonaceous materials including black carbon, unburned coal, and kerogen are ubiquitous in sediments and soils. For example, as reviewed by Cornelissen et al. (2005), there is 5 ~ 18% black carbon in total organic matter of sediments and 2 ~ 13% in that of soils. In fire-impacted soils, this ratio could be up to 30 ~ 45%.

Han et al. (2013) studied the effect of SOM composition on the sorption behavior of toluene in three soils including black soil from Heilongjiang Province and fluvo-aquic soil from Beijing. By removing “soft” SOM, the residual “hard” SOM showed slower sorption rate. Higher content of “hard” SOM increased sorption nonlinearity. The “soft” and “hard” SOM could account for the partition and adsorption behaviors of phenols to investigated soils in this study.

4.2 K_{oc} Values Predicted by Models from Literatures

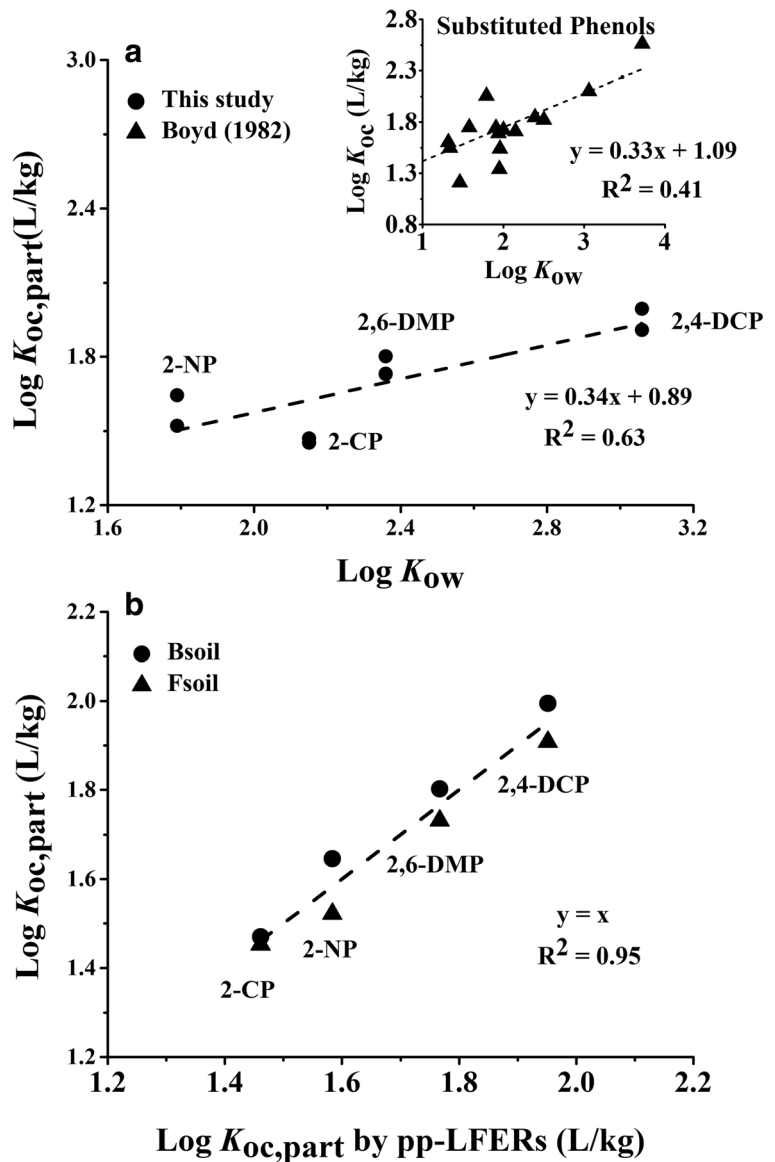
Partition is attributed to the undissociated sorbate molecules. The equilibrium solution pH values in Bsoil (soil pH = 6.14) systems ranged from 5.9 to 6.1, leaving four phenols in undissociated form (Fig. S1). The $K_{d,part}$ values followed the order: 2,4-DCP > 2,6-DMP > 2-NP > 2-CP. However, the equilibrium solution pH values in Fsoil (soil pH = 8.18) system ranged from 7.18 to 7.43, causing 2-NP (pK_a , 7.23) to form large dissociated species (Fig. S1). As a result, the partition coefficient of 2-NP into Fsoil decreased. Meanwhile, the other three phenols still stay non-ionic in the Fsoil system. Thus, the order of $K_{d,part}$ in Fsoil can be found as: 2,4-DCP > 2,6-DMP > 2-CP > 2-NP. Since the species of 2-NP in two soil systems were different, the organic carbon-normalized linear partition coefficients ($K_{oc,part}$, L/kg) should be calculation as follows:

$$K_{oc,part} = (K_{d,part}/f_{oc})/f_0 \quad (4)$$

where f_0 is the percentage of undissociated solute. Log $K_{oc,part}$ values of given solutes on two soils were comparable as expected (Fig. 3). No good correlation was observed between log $K_{oc,part}$ (or log K_{oc}) and log K_{ow} in our results or in previous study (Boyd 1982) (Fig. 3). Although 2-CP has a higher log K_{ow} value (2.15) than 2-NP (1.79), the log K_{oc} value of 2-CP was observed to be smaller than that of 2-NP (Boyd 1982; Graber and Borisover 2005). It may be partly attributed to the higher water solubility of 2-CP (11.3 g/L) than that of 2-NP (2.5 g/L).

One-parameter linear free energy relationships (log K_{ow}) failed to predict measured log $K_{oc,part}$ (Fig. 3a) while pp-LFERs showed good predictive ability (Fig. 3b). Non-specific interactions are the driving forces for solute

Fig. 3 Log $K_{oc,part}$ (or log K_{oc}) values predicted by log K_{ow} (a) and pp-LFER model (b). Literature data in the panel of (a) were from Boyd (1982). The pp-LFER model for log $K_{oc,part}$ prediction can be seen in Eq. 5



partitioning into SOM. Thus, there is no surprise that good correlation was shown between log $K_{oc,part}$ and terms representing nonspecific interactions (E , S , and V terms) (Eq. 5).

$$\text{Log}K_{oc,part} = 2.319E - 1.896S + 0.995V - 0.265 \quad (5)$$

$$(R^2 = 0.95, N = 8)$$

It implied that these three terms can represent van der Waals better than the parameter of log K_{ow} .

Log $K_{oc,part}$ values of the investigated phenols were lower than log K_{oc} values reported in literature by up to

1 order of magnitude (Table S3 and Fig. S2), indicating that both partition and adsorption contributed to measured log K_{oc} values (Endo and Goss 2014). Because of the sorption nonlinearity, log K_{oc} values were 1.87 ~ 2.83 for 2,6-DMP, 1.63 ~ 3.11 for 2-CP, 1.52 ~ 3.06 for 2-NP, and 2.03 ~ 2.93 for 2,4-DCP, respectively. Prediction models for log K_{oc} can be obtained. For example, EPISuite's KOCWIN can provide predicted log K_{oc} values in two ways. One is mainly based on K_{ow} and the other applies a molecular connectivity index (MCI) (Schenzel et al. 2012). Predicted values by EPISuite's KOCWIN were not consistent with experimental data (Table S4). Endo et al. (2009) found

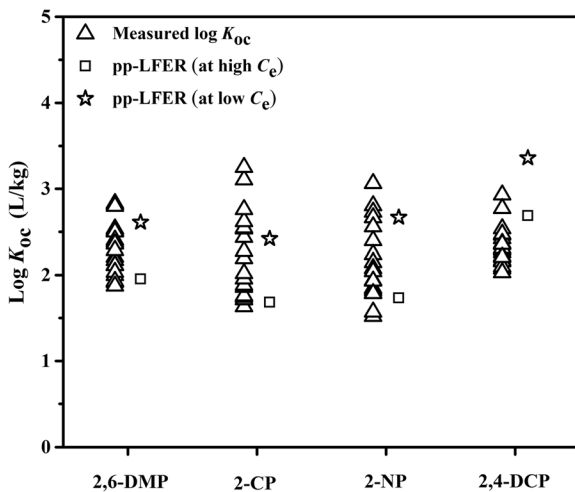


Fig. 4 Log K_{oc} values from experimental data and predicted by pp-LFERs. The used pp-LFERs are from Endo et al. (2009) (see Table S5 in SI for details)

that previous pp-LFER models obtained at high solute concentration for K_{oc} prediction could underestimate the measured K_{oc} values by up to 1 order of magnitude. So they presented pp-LFER models generated at both low and high solute concentrations. Still, measured log K_{oc} values of four phenols deviated considerably from any one of predictions (Fig. 4). Combining two pp-LFER models can achieve a satisfactory prediction range (within 0.5 log unite). However, this seemed inconvenient. To model our data in one equation and provide more accurate prediction, activity of sorbate was introduced in the expanded pp-LFER model.

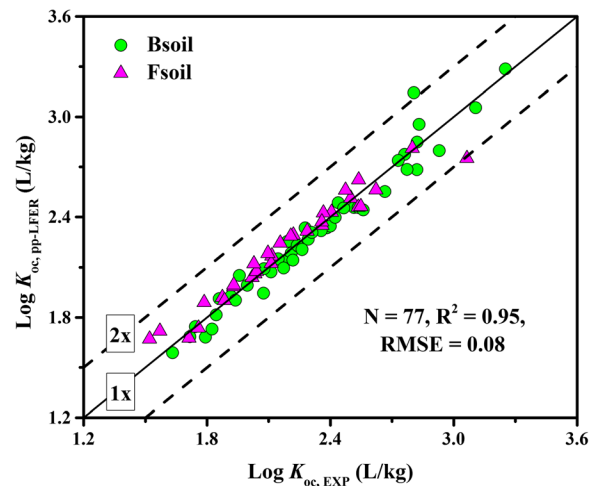


Fig. 5 Sorption data for two soils predicted by Eq. 7

4.3 Expanded pp-LFER Model

The expanded pp-LFER model (Plata et al. 2015; Shih and Gschwend 2009) depends on solute activity as shown in Eq. 6:

$$\text{Log}K_{oc} = (e_1 + e_2 \log a_i)E + (s_1 + s_2 \log a_i)S + (a_1 + a_2 \log a_i)A + (b_1 + b_2 \log a_i)B + (v_1 + v_2 \log a_i)V + c_1 + c_2 \log a_i \quad (6)$$

where a_i is the solute activity. All observed log K_{oc} values with respective a_i were used by fitting the expanded pp-LFER model. With the optimization by SPSS, the equation of the expanded pp-LFER model (Eq. 7) was obtained:

$$\begin{aligned} \text{log}K_{oc} = & [(1.829 \pm 0.488) + (3.481 \pm 0.462) \log a_i]E + [(-4.307 \pm 0.466) \log a_i]S \\ & + [(-0.876 \pm 0.138) \log a_i]A + [(-0.086 \pm 0.529) + (1.209 \pm 0.218) \log a_i]B \\ & + (6.280 \pm 0.649)V - (6.814 \pm 0.917) \end{aligned} \quad (7)$$

$$(R^2 = 0.950, N = 77, RMSE = 0.08)$$

The expanded pp-LFER model provided good prediction for our sorption data within a factor of 2 (0.3 log unit) (Fig. 5). The activity-dependency of E suggested that at lower degrees of sorbate coverage on SOM, the importance of polarizability was larger (Lu et al. 2016). The coefficient of S term was positive and became larger at lower solute coverage (Table S6). This may suggest that dipole-induced dipole or dipole-dipole interactions with SOM are stronger at lower SOM surface coverage. At higher solute activity, the dipole-induced dipole and

dipole-dipole interactions with water became stronger, and thus the effect of S term was reduced significantly (Plata et al. 2015). With increasing log a_i , the effect of A and B term gradually became insignificant (Table S6). At lower solute activity, the coefficients are positive for A term and negative for B term. It implied that loss of H-bond donating interactions between substituted phenols and water were replaced by interactions with SOM (Plata et al. 2015). However, H-bond accepting interactions showed the opposite trend. Since phenols are

bipolar and can serve as electron donors and acceptors, both of A and B terms can influence the adsorption of phenols. However, the positive coefficient of A and the negative coefficient of B suggest that substituted phenols were favored to form H-bond as electron donors with SOM. The positive coefficient of the V term showed that solute moving out from water to hydrophobic sorbents is favorable in free energy change (Apul et al. 2013; Plata et al. 2015; Shih and Gschwend 2009). The activity-independency of V demonstrates that it is a constant reward of sorbate removal from water. These results are in line with our observations that adsorption (specific interactions) was predominant at low solute concentrations, and partition (nonspecific interactions) was the main sorption mechanism at high solute concentrations.

Expanded pp-LFER models for compounds adsorption on activated carbon (Shih and Gschwend 2009), wood char (Plata et al. 2015), and diesel soot (Lu et al. 2016) were reported. In these adsorption systems, adsorption of compounds onto adsorbents was a surface process and adsorption isotherm was the Freundlich type. In contrast, partition and adsorption play roles together in the sorption of investigated phenols on two soils. As a result, the sorption isotherm was the dual-mode type. In the activated carbon-water (Shih and Gschwend 2009) and wood char-water (Plata et al. 2015) systems, the coefficients for E and A were negligible and these two terms were not involved in their models. One reason for the negligible A term was that A values for tested compounds were too small (Plata et al. 2015). In the diesel soot-water system (Lu et al. 2016), no significant dependency of S term on sorption was shown. It indicated that the lack of S term reflected a unique surface property of soot. In our expanded pp-LFER model, all the five terms were involved to describe the nonspecific interaction (partition) and specific interaction (H-bonding).

5 Conclusions

Nonlinear uptake of phenols with different substituent groups by soils was investigated. The dual-mode sorption model coupling partition and adsorption could well describe sorption behaviors. Adsorption surpassed partition at low solute activity (e.g., $a_i < 0.01$) whereas partition was dominant at high solute activity. Because of the sorption nonlinearity, measured $\log K_{oc}$ values of given solute varied by up to 1.5 orders of magnitude. In

order to have a better evaluation of varied K_{oc} for nonlinear sorption isotherms, an expanded pp-LFER model taking solute activity into consideration was established. The derived contributions from nonspecific interaction terms (E , S , and V) and specific interaction terms (A and B) to overall sorption are in agreement with the observations from sorption isotherms. The new model provides a satisfactory prediction for experimental K_{oc} values within a factor of 2 (0.3 log unit). Since the concentrations of polar organic pollutants in surface water or groundwater are pretty low (e.g., ng/L \sim μ g/L), adsorption could be dominant in their sorption processes. Therefore, specific interaction (e.g., H-bonding) should be taken into consideration when the transport of polar organic pollutants like substituted phenols is evaluated.

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