DESORPTION-RESISTANCE OF CHLOROBENZENE AND PHENANTHRENE IN WETLAND PEAT SOILS

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Abstract: Sorption/desorption study was conducted to determine desorption-resistance of organic compounds in recent deposited organic matter by studying wetland soils explicitly. Sorption/desorption characteristics for both surface marsh soil (top 0−2 cm, <5 years old) and deeper marsh soil (below 10 cm, >20 years old) were investigated to see if soil age can cause differences in sorption/desorption in wetlands. Measurements of organic matter aging were conducted using several techniques including the ratio of elemental oxygen to carbon in the organic matter. Sorption/desorption of organic compounds (chlorobenzene and phenanthrene) in recently deposited freshwater marsh soils was determined using a batch desorption procedure and compared with relatively “older” soils. Sorption was biphasic with about 30−62% (chlorobenzene) and 46.7−82.9% (phenanthrene) of the adsorbed mass residing in the desorption-resistant fraction after 7−14 desorption steps. Sorption/desorption parameters were determined for several models to explain the desorption resistance including the Tomson-Kan model, slow sorption model and dual reactive domain model (DRDM). All models indicated the presence of appreciable desorption-resistant phase in wetland peat soils and an increase in the size of the desorption-resistance in “older” organic matter. A case study of the implications of desorption-resistance in wetland remediation was presented based on the Petro Processors, Inc. Superfund site Devil’s Swamp wetland.

Key Words: sorption, desorption, desorption-resistance, wetland, biphasic sorption, slow sorption, DRDM, aging, sequestration

INTRODUCTION

Numerous studies have shown that the fate and transport of hydrophobic organic compounds (HOCs) in soil is highly dependent on sorption/desorption characteristics. Sorption of organic compounds in soils and sediments has long been considered a reversible process in assessing risk and determining remedial endpoints. However, reversible models were not able to explain the long-term persistence of contaminants at many sites. The existence of a desorption-resistant (or sequestered) fraction of HOCs in soil has been identified and the quality of organic matter is critical in determining the magnitude of the desorption-resistant effect. Desorption-resistance or “irreversible sorption” has been recognized as an important phenomenon for understanding fate of organic contaminants in soils and sediments.

While the mechanism of the desorption-resistance or “irreversible sorption” has not yet been determined, several important characteristics of this phenomenon have been identified. HOCs residing in this phase have much higher partition coefficients than would be predicted by the properties of the contaminants and the organic fraction of the soil. In fact, the partitioning of HOCs with widely different octanol: water partition coefficients (K_{ow}s) is very similar
in the desorption-resistant phase. In addition, the size of the desorption-resistant fraction appears to be predictable for sediments. An accurate estimation of this desorption-resistant phase is very important in remediation because sequestration (or aging) of contaminants is directly related to limited bioavailability. 1,12 Desorption-resistance has not been studied explicitly in the highly-organic soils found in wetlands. Several studies suggest that desorption-resistance may be less important in highly-organic peat soils. 13,14 Only a few researches regarding sorption/desorption characteristics of organic-rich peat soils have been reported. 15-19 An accurate estimation of desorption-resistance may have wide implications on the remediation of HOCs in wetlands. Our purpose of this study is to find sorption/desorption characteristics of chlorobenzene and phenanthrene in highly organic marsh soils. Model parameters of the currently proposed models (Tomson-Kan model, slow sorption model and dual reactive domain model (DRDM)) were investigated to explain the desorption resistance. Sorption/desorption characteristics for both surface soil (top 0~2 cm, <5 years old) and deeper soil (below 10~cm, >20 years old) were investigated to see whether organic matter age could cause differences in sorption/desorption in wetlands. This research was conducted as a part of a joint research project by Louisiana State University, Rice University, and Southern University. Currently, the bioavailability of organic contaminants in the desorption-resistant phase to microorganisms (bacteria and algae), benthic invertebrates (freshwater oligochates), and plant uptake is being evaluated.

### MATERIALS AND METHODS

#### Soil Sampling

Four different soils were used in this study. The soil properties were determined by Huffman Laboratories, Inc. (Golden, CO, USA) and are summarized in Table 1. Wetland peat soils (from top (0~2 cm) and deeper (10~15 cm) horizons) were obtained from a fresh marsh near Madisonville, LA, USA. Top soils were assumed to have more recently deposited organic matter than the deeper soils. Since accretion in this marsh is approximately 0.5 cm/year, the top horizon was assumed to be 0~4 years old and the deeper soil was >20 years old. The organic matter age can be inferred using the elemental ratio in the organic matter (Table 1). The H/C, O/C, and C/N ratios increased with depth while H/O ratio did not, confirming our assumptions of organic matter age. The use of H/C and O/C ratios has been proposed as measures of organic matter age related to sorption properties. 13,20-24 A second soil was removed from a bottomland hardwood wetland near the Petro Processors, Inc. Superfund site near Baton Rouge, LA. Moisture contents of the wetland soils were determined to represent all units on a dry soil weight basis.

#### Sorbate and Chemicals

Radiolabeled [14C] compounds: chlorobenzene-UL-14C (CB, Sigma, 2.7 µCi/µmol) and [9,10-14C] phenanthrene (Phen, ChemSyn Laboratories, 56.7 µCi/µmol) were used as sorbates. The [14C] compounds were further diluted with unlabeled 12C stock solutions (1000 mg/L in
methanol) to yield desired concentrations. $^{12}$C-chlorobenzene (>99.9%) and $^6$-phenanthrene (>96%) used in this study were obtained in HPLC grades from Sigma Chemical Co., Inc. 200 mg/L of NaN$_3$ was added to the solution as a bacterial inhibitor. Chemical solutions were prepared before each sorption experiment using the $^{12}$C stock solutions and an electrolyte solution containing 1mM CaCl$_2$·$2$H$_2$O, 0.5 mM MgCl$_2$, and 1mM Na$_2$B$_4$O$_{10}$·$5$H$_2$O (pH 8.0). The amount of methanol added to the vials was less than 0.2% (v/v) of the liquid so that it did not affect the cosolvent properties of the liquid significantly.

**Batch Sorption and Desorption Experiment**

Experiments were performed in batch using successive adsorption/desorption cycling. An adsorption/desorption cycle constitutes a series of 4 successive adsorptions followed by successive desorptions. The sorption/desorption experiments were conducted in glass vials with a total volume of approximately 40-mL sealed with Teflon-faced silicone septa (Wheaton). To prevent adsorption of chemicals to the glassware, either carefully cleaned or precleaned, EPA-certified vials (Fisher Scientific) were used. Control experiments were conducted to investigate sorption of chemicals on the surface of the glassware (data not shown). The adsorption of hydrophobic chemicals on the glass surfaces was minimal (<5%).

Subsamples of the homogenized soil were transferred to the vial (water to soil ratio = 10 : 1, w/w%) before the addition of chemical solutions at concentrations of 0.5 mg/L for CB and 0.1 mg/L for Phen. To obtain sorption isotherms for the slow sorption model and DRDM, 8 different concentrations of CB (100 $\mu$g/L to 30 mg/L) and Phen (10 $\mu$g/L to 1.2 mg/L) were used. After filling the vials with sediment and the spiking solution, the headspace in the vial was kept minimal. The sediment/water mixture was horizontally mixed in a shaker bath at room temperature. After 24 hours (or 21 d for slow sorption experiments), the sediment was separated from the solution by centrifugation at 2500 rpm (about 550 g) for 20 minutes and the chemical concentration in the supernatant was analyzed via liquid scintillation. Then, the sediments were re-spiked with the chemical stock solution and the adsorption experiments were repeated step-wise 4 times before the desorption experiment began.

Desorption was conducted by successively replacing approximately 75% of supernatant with contaminant-free electrolyte solution followed by shaking for 1~3 days. After the successive desorption steps, the solution was gently removed using a pipette. The actual amount removed was determined by weight. The solid phase chemical concentrations were calculated by assuming changes in solution-phase concentrations during adsorption or desorption result from changes in solid phase concentration. The solution phase chemical concentrations were determined by scintillation counting at each step.

**SORPTION MODELS**

**Biphasic Sorption Model (Tomson-Kan Model)**

The biphasic sorption model is defined as:

\[
q = q^{rev} + q^{irr}
\]

where $q$ (µg/g) = total concentration of sorbed compound in the soil phase, $q^{rev}$ (µg/g) = the concentration of sorbed compound in the labile fraction and $q^{irr}$ (µg/g) = the concentration of sorbed compound in the desorption-resistant fraction.

The sorption to the reversible (or labile) compartment is described by linear isotherm:

\[
q^{rev} = K_p C
\]

where $K_p$ (mL/g) = linear partition coefficient and $C$ (µg/mL) = solution phase concentration. If normalized to organic carbon content in soil,


\[ K_{OC} = \frac{K_f}{OC} \]  

(3)

where \( K_{OC} \) (mL/g) = organic carbon normalized partition coefficient and \( OC \) = organic carbon content.

Combining linear sorption isotherm for labile fraction and a Langmuir-type sorption isotherm for desorption-resistant fraction yields:

\[ q = K_{OC} \cdot OC \cdot C + \frac{K_{OC}^{irr} \cdot OC \cdot q_{\text{max}}^{irr} \cdot f \cdot C}{q_{\text{max}}^{irr} \cdot f + K_{OC}^{irr} \cdot OC \cdot C} \]  

(4)

where \( K_{OC}^{irr} \) (mL/g) = partition coefficient of the desorption-resistant fraction, \( f \) = fraction of compound residing in the desorption-resistant compartment, and \( q_{\text{max}}^{irr} \) (\( \mu g/g \)) = maximum capacity of desorption-resistant fraction. A semiempirical relationship was obtained to represent \( q_{\text{max}}^{irr} \):

\[ q_{\text{max}}^{irr} \approx A \cdot K_{oc}^n \]  

(5)

where \( A = \) constant, \( K_{oc} \) = octanol/water partition coefficient and \( n = \) constant.

The second term on the right-hand side of Eq. (4) can be rearranged to Langmuir isotherm:

\[ q^{irr} = \frac{bQ^f C}{1 + bC} \]  

(6)

where \( Q^f = q_{\text{max}}^{irr} f \). When the aqueous solution concentration, \( C (\mu g/mL) \) is relatively large, the second term becomes a constant, \( Q^f \). If \( C \) is small, the second term reduces to \( K_{OC}^{irr} \cdot OC \cdot C \).

**Slow Sorption Model**

Sorption can be divided into two groups, a fast fraction and a slow fraction\(^{25}\) and described using a Freundlich isotherm.

**Fast fraction:** After assuming that equilibrium is achieved for the fast fraction after 1 day, the isotherm for the fast fraction can be written as:

\[ q_f = K_f C_{f}^{N_f} = q_1 = K_1 C_1^{N_1} \]  

(7)

where \( q_f (\mu g/g) \) = the amount sorbed after 1 d in the fast fraction (= \( q_1 \)); \( K_f (\mu g/g)/(\mu g/mL) \) and \( N_f \) (dimensionless) = Freundlich parameters for the fast fraction after 1 d. \( N \) reflects the curvature in the isotherm and may represent the energy distribution of adsorption sites. A linear regression of the log transformed Freundlich isotherm expression can be used to obtain \( K_f \) and \( N_f \):

\[ \log q_f = \log K_f + N_f \log C = \log K_1 + N_1 \log C_1 \]  

(8)

**Slow fraction:** The difference between the amount sorbed after 1 d and the total amount sorbed \( (q_{s}, \mu g/g) \) after 21 d was taken to represent the slow fraction \( (q_{s}, \mu g/g) \):

\[ q_{s} = K_s C_{s}^{N_s} = q_1 - q_f = q_1 - K_1 C_1^{N_1} \]  

(9)

The log-transformed expression is:

\[ \log q_s = \log (q_1 - K_1 C_1^{N_1}) = \log K_s + N_s \log C \]  

(10)

**Dual Reactive Domain Model (DRDM)**

Huang et al.\(^{26}\) used the DRDM to fit sorption data:

\[ q_{e,T} = q_{e,L} + q_{e,NL} = K_{D,L} C_e + \frac{Q^P b C_e}{1 + b C_e} \]  

(11)

where \( q_{e,T} \), \( q_{e,L} \), and \( q_{e,NL} \) = total, linear, and nonlinear contribution to the soil phase concentration (\( \mu g/g \)) of the DRDM, respectively. \( K_{D,L} (\mu g/g)/(\mu g/mL) = \) partition coefficient of the linear component of DRDM, \( C_e (\mu g/mL) = \) the bulk solution concentration, and \( b \) (mL/\( \mu g \)) and \( Q^P (\mu g/g) \) are the Langmuir site energy and capacity factor for the nonlinear component of DRDM, respectively.

A Fortran program was written to determine the sorption model parameters through nonlinear regression using a derivative-free Levenberg-Marquadt algorithm.\(^{27 - 29}\)
RESULTS AND DISCUSSION

Biphasic Adsorption Model (Tomson-Kan Model)

The results of multiple sorption and desorption data are represented in Figure 1 (CB) and Figure 2 (Phen). The four successive sorptions for both compounds followed a linear isotherm, as expected. The log $K_{oc}$ values for CB were 2.33 for top soil and 2.52 for deeper soil which is comparable to the log $K_{ow}$ (= 2.84) of CB (Figure 1). After the desorption steps, CB concentration in the desorption-resistant compartment, $q^{irr}$, were approximately 11 µg/g (30.0% of total sorbed amount) for top soil and 28 µg/g (61.5% of total sorbed amount) for the deeper soil, respectively. Clearly, $q^{irr}$ of the deeper soil was greater than the top soil. Similar patterns were observed for phenanthrene (Figure 2). The log $K_{oc}$ values for Phen were 3.97 for top soil and 3.93 for deeper soil. Both $K_{oc}$ values were smaller than $K_{ow}$ (= 4.57) for Phen. Similar results were observed by Hamaker and Thompson. They showed that $K_{oc}$ values for soils with high organic carbon contents are usually lower than $K_{ow}$ values for soils with "normal" and very low organic carbon contents. The $q^{irr}$ value of the deeper soil (21 µg/g, 82.9% of the total sorbed amount) was significantly greater than the top soil (11 µg/g, 46.7% of the total sorbed amount). The appreciable $q^{irr}$ values of Phen even at lower spiking solution concentration (Phen: 100 µg/L and CB: 500 µg/L) indicate that Phen has a greater tendency to the desorption-resistant fraction due to its higher $K_{ow}$ value.

Results indicate that a desorption-resistant fraction does exist for highly organic peat soils. This is consistent with the finding of Chen et al. Kan et al. reported that a soil with an organic carbon content of 0.27% had a finite capacity for desorption-resistant phase. The partitioning of sorbed chemicals into desorption-resistant or "irreversible" phase was attributed to conformational changes of the organic matter.
during adsorption process or due to physical rearrangement of the organic matter phase. The characteristic term of the biphasic model to represent irreversible sorption is the irreversible sorption constant, $K'_{OC} = 10^{5.53 \pm 0.48}$ (mL/g).

$K'_{OC}$ was found to be independent of physical-chemical properties of the contaminants, however, only "normal" soils or soils with low organic carbon content (0.27 – 1.07%) were tested. Therefore, it is questionable whether this simple relationship of irreversible sorption constant, $K'_{OC} = 10^{5.53 \pm 0.48}$ (mL/g) is reasonable for highly organic wetland peat soils. Currently, a trial to determine the maximum capacity of desorption-resistant compartment, $\theta_{\text{max}}$ is under way using an iso-propanol extraction method.

Aging of the organic matter, even over the short time scales (decades) in this marsh, is a significant factor in increasing the size of the desorption-resistant compartment. Differences between the top and deeper soils are presumably due to diagenetically altered soil properties; diagenetically altered carbon appears to cause stronger bonding in the deeper soil. This has wide implications for the remediation and risk assessment of wetlands since the partitioning of a significant fraction of the contaminant would be desorption-resistant.

**Slow Sorption Model**

The isotherms of CB and Phen for wetland soils after 1 and 21 d contact time are shown in Figure 3a (CB, top soil), Figure 4a (CB, deeper soil), Figure 5a (Phen, top soil), and Figure 6a (Phen, deeper soil), respectively. The obtained slow sorption parameters are summarized and compared in Table 2. The Freundlich partition coefficients ($K$) were consistently increasing while $N$ values were decreasing during this time interval. The increase in $K$ values has been found in numerous studies of slow sorption kinetics. The decrease in $N$ values with time indicates that sorption isotherms become increasingly nonlinear with time. The plot of Equation (9) was used to calculate slow fraction sorption parameters: $K$.
and \( N_s \) as shown in Figure 3b (CB, top soil), Figure 4b (CB, deeper soil), Figure 5b (Phen, top soil), and Figure 6b (Phen, deeper soil), respectively. The results indicates that \( N_s \) is significantly smaller than \( N_f \). \( K \) values of deeper soils were greater than those of top soils. The organic carbon normalized partition coefficient, \( K_{F,OC} \) of the fast fraction of top soil was 87\% (CB) and 93\% (Phen) of the deeper soil, respectively. In all cases, \( N_s \) is significantly smaller than \( N_f \) demonstrating that the fast sorption phase is dominating over the slow sorption phase. The \( K \) values of the deeper soil were significantly greater than the top soil for both the fast and slow sorption phase. Similar results were found for the sorption of atrazine on young and aged wetland peat soils.\(^{32}\) Like the Tomson-Kan model, the results indicate that sorption capacity (both slow and fast fraction) of the deeper soil is greater than top soil. The percentage of slow sorption fraction in the deeper soil (25.4\% for CB and 1.9\% for Phen) was higher than top soil (18.9\% for CB and 1.5\% for Phen). The result of soil analysis (Table 1) shows that OC content in the deeper marsh soil (23.2\%) was lower than the top soil (27.6\%). Despite a lower organic carbon content in the deeper soil, the sorption capacity in aged deeper soil is greater than the younger top soil. This observation was also confirmed when mineral dominated PPI soil with presumably much older organic matter (higher H/C and O/C ratios) is considered; both fast and slow sorption fractions in PPI soil were greater than the marsh soils. The percentage of the slow sorption fraction in PPI soil (40\% for CB and 3.0\% for Phen) was significantly higher than two wetland soils. The "humification" concept was proposed to explain differences in atrazine sorption capacities in young and aged wetland peat soils.\(^{32,33}\) The high C/N ratios of the soils (top = 13.4, deeper = 14.0, and PPI = 22.5) used in this study indicate that these wetland soils are highly humified. Humification reduces organic matter polarity\(^{34}\) and increases organic matter uniformity. Higher organic matter capa-
Table 2. Freundlich parameters, $K_F$ and $N$, for sorption of chlorobenzene and phenanthrene in fresh marsh (top and deeper) and PPI soil ($K_{F,OC} = $ organic carbon normalized partition coefficient)

<table>
<thead>
<tr>
<th>fraction</th>
<th>$K_F^a$</th>
<th>$K_{F,OC}^b$</th>
<th>$N^c$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB Top</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fast</td>
<td>36.0±4.6</td>
<td>130.5±16.7</td>
<td>1.00±0.05</td>
<td>0.99</td>
</tr>
<tr>
<td>21 d</td>
<td>59.9±5.7</td>
<td>217.2±20.7</td>
<td>0.92±0.04</td>
<td>0.99</td>
</tr>
<tr>
<td>slow</td>
<td>15.8±4.8</td>
<td>57.3±17.4 (26.4%)d</td>
<td>0.72±0.12</td>
<td>0.85</td>
</tr>
<tr>
<td>CB Deeper</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fast</td>
<td>56.7±4.4</td>
<td>245.0±19.0</td>
<td>1.12±0.03</td>
<td>0.99</td>
</tr>
<tr>
<td>21 d</td>
<td>103.3±8.5</td>
<td>446.4±36.7</td>
<td>0.76±0.03</td>
<td>0.99</td>
</tr>
<tr>
<td>slow</td>
<td>26.2±5.8</td>
<td>113.2±25.1 (25.4%)d</td>
<td>0.49±0.09</td>
<td>0.80</td>
</tr>
<tr>
<td>CB PPI</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fast</td>
<td>4.6±0.97</td>
<td>340.7±71.9</td>
<td>0.74±0.07</td>
<td>0.94</td>
</tr>
<tr>
<td>21 d</td>
<td>9.2±1.15</td>
<td>681.5±85.2</td>
<td>0.68±0.05</td>
<td>0.97</td>
</tr>
<tr>
<td>slow</td>
<td>3.7±1.10</td>
<td>274.1±81.5 (40.2%)d</td>
<td>0.65±0.11</td>
<td>0.85</td>
</tr>
<tr>
<td>Phen Top</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fast</td>
<td>1,321.5±67.8</td>
<td>4,791.5±245.8</td>
<td>1.05±0.02</td>
<td>0.99</td>
</tr>
<tr>
<td>21 d</td>
<td>1,822.7±292.1</td>
<td>6,608.8±1,059.1</td>
<td>1.04±0.05</td>
<td>0.98</td>
</tr>
<tr>
<td>slow</td>
<td>25.2±9.4</td>
<td>91.4±34.1 (1.4%)d</td>
<td>0.92±0.11</td>
<td>0.93</td>
</tr>
<tr>
<td>Phen Deeper</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fast</td>
<td>1,244.5±188.8</td>
<td>5,710.9±293.0</td>
<td>1.09±0.05</td>
<td>0.98</td>
</tr>
<tr>
<td>21 d</td>
<td>1,874.9±178.7</td>
<td>7,876.8±1,262.3</td>
<td>1.06±0.03</td>
<td>0.99</td>
</tr>
<tr>
<td>slow</td>
<td>34.9±10.5</td>
<td>108.9±40.6 (1.9%)d</td>
<td>0.89±0.06</td>
<td>0.88</td>
</tr>
<tr>
<td>Phen PPI</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fast</td>
<td>58.9±4.4</td>
<td>4,363.0±325.9</td>
<td>0.87±0.03</td>
<td>0.99</td>
</tr>
<tr>
<td>21 d</td>
<td>76.3±11.6</td>
<td>5,652.6±859.3</td>
<td>0.82±0.06</td>
<td>0.96</td>
</tr>
<tr>
<td>slow</td>
<td>2.3±0.4</td>
<td>170.4±29.6 (3.0%)d</td>
<td>0.78±0.06</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Units: $a = (\mu g/g)/(\mu g/mL)$, $b = (\mu g/g\ OC)/(\mu g/mL)$, $c = constant$, and $d = percentage of slow sorption fraction per total sorption capacity$.

Urban areas are observed as polarity decreases with decay or greater depth.23 As shown in Table 2, the deeper (aged) soils are more humified than top (younger) soils as indicated by higher C/N ratio while PPI soils have significantly higher humification than two wetland soils. While this model considers only sorption, the slow sorption can be invoked to explain the more sequestered desorption-resistant fraction observed in these soils. The differences in the parameters between the recent and aged organic matter parallel the results observed from the Tomson-Kan model nicely.

**Dual Reactive Domain Model (DRDM)**

DRDM model parameters were determined for two wetland soils and PPI soil and the results are summarized in Table 3. The organic carbon normalized partition coefficient for the linear fraction, $K_{D,LOC}$ was consistently higher in the deeper soil. For both chemicals (CB and Phen), the Langmuir site energy factor, $b$, was higher in top soil while the Langmuir capacity factor, $Q'$, was higher in deeper soil. However, for CB, the product, $bQ'$, representing the total Langmuir sorption capacity of nonlinear term in Equation (7), was significantly greater in the deeper soil. The higher $bQ'$ value indicates higher nonlinear sorption in the deeper soil. For Phen, b values were much smaller than 1 ($b \ll 1$), the second term in the right hand side of Eq. (11) becomes $q_{e,NL} = Q'bC_e$. Then the nonlinear sorption is directly proportional to $Q'b$ at same chemical concentration. As shown in Table 3, the $Q'b$ value of the deeper soil was greater than top soil indicating that nonlinear fraction in the soil increased with soil age.

To compare the role of nonlinear sorption in DRDM, the model was calculated at two different bulk concentrations (Table 4) using the model parameters shown in Table 3. Clearly, the amounts of chemicals partitioned into the nonlinear fraction, $q_{e,NL}$ of the deeper soils were significantly greater than those of
Table 3. DRDM parameters of chlorobenzene and phenanthrene in fresh marsh (top and deeper) and PPI soil

<table>
<thead>
<tr>
<th>Model</th>
<th>$K_{OC}$</th>
<th>$K_{d,LOC}$</th>
<th>$b^c$</th>
<th>$Q^d$</th>
<th>$bQ^e$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>35.82</td>
<td>129.9</td>
<td>2.19</td>
<td>6.7</td>
<td>14.67</td>
<td>0.99</td>
</tr>
<tr>
<td>Deeper</td>
<td>52.20</td>
<td>225.6</td>
<td>0.39</td>
<td>57.5</td>
<td>22.43</td>
<td>0.99</td>
</tr>
<tr>
<td>PPI</td>
<td>1.59</td>
<td>117.8</td>
<td>0.61</td>
<td>9.7</td>
<td>5.92</td>
<td>0.94</td>
</tr>
<tr>
<td>Phen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>1,153.95</td>
<td>4,184.2</td>
<td>0.0028</td>
<td>587.6</td>
<td>1.65</td>
<td>0.99</td>
</tr>
<tr>
<td>Deeper</td>
<td>972.31</td>
<td>4,210.8</td>
<td>0.0010</td>
<td>2,419.6</td>
<td>2.42</td>
<td>0.99</td>
</tr>
<tr>
<td>PPI</td>
<td>39.97</td>
<td>29,607.4</td>
<td>0.0071</td>
<td>355.2</td>
<td>2.53</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Units: $a = (\mu g/g)/(\mu g/mL)$, $b = (\mu g/g \ OC)/(\mu g/mL)$, $c = (ML/\mu g)$, $d = (\mu g/g)$, and $e = (ML/\mu g)$

Table 4. Apportionment of DRDM in fresh marsh (top and deeper) and PPI soil

<table>
<thead>
<tr>
<th></th>
<th>$C_e$</th>
<th>$q_{LOC}$</th>
<th>$q_{NLOC}$</th>
<th>$q_{T,LOC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>0.1</td>
<td>12.99</td>
<td>4.36</td>
<td>17.35</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>1,299.49</td>
<td>23.23</td>
<td>1,322.72</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>2,255.83</td>
<td>197.78</td>
<td>2,453.61</td>
</tr>
<tr>
<td>Deeper</td>
<td>0.1</td>
<td>22.56</td>
<td>9.33</td>
<td>31.89</td>
</tr>
<tr>
<td>PPI</td>
<td>0.1</td>
<td>11.78</td>
<td>41.31</td>
<td>53.09</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>1,177.78</td>
<td>617.32</td>
<td>1,795.10</td>
</tr>
<tr>
<td>Phen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>0.1</td>
<td>41.84</td>
<td>0.06</td>
<td>41.90</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4,184.01</td>
<td>5.95</td>
<td>4,189.96</td>
</tr>
<tr>
<td>Deeper</td>
<td>0.1</td>
<td>42.02</td>
<td>0.10</td>
<td>42.12</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4,201.86</td>
<td>10.45</td>
<td>4,212.31</td>
</tr>
<tr>
<td>PPI</td>
<td>0.1</td>
<td>29.61</td>
<td>1.87</td>
<td>31.48</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2,960.74</td>
<td>185.49</td>
<td>3,146.23</td>
</tr>
</tbody>
</table>

top soils. This indicates that the role of nonlinear sorption increases with soil age. The increase of $q_{NL, LOC}$ with soil age was evident in PPI soil presumably much older than the wetland soils for both chemicals.

CONCLUSIONS

Three models, which consider different mechanistic explanations for the desorption-resistant fraction, have been used to fit sorption and sorption-desorption data from wetland soils. All models fit the data well. The results of three models consistently indicate that a desorption-resistant exists in highly organic wetland soils and that aging of the organic matter increases the size of that fraction. Desorption-resistance and the observation of increased desorption-resistance with increasing organic matter age should be considered in remediation efforts and may explain why some remediation technologies will not achieve desired results. More focused mechanistic studies on the relationships between diagenesis of recently deposited organic matter and sorption-desorption characteristics are needed. The results of this study can be used for risk analysis of remediation in wetlands.

In summary, the following conclusions are reached based on the results:

1. Biphasic adsorption model: Chemical concentration in the desorption-resistant compartment, $q^{rs}$, of the deeper soil was significantly greater than top soil for both CB and Phen. Desorption-resistant or sequestered fraction exists for highly organic wetland soils. A significant fraction of contaminants would be partitioned into desorption-resistant fraction in wetland soils.

2. Slow sorption model: $K$ values of the deeper soil were significantly greater than top soil for both fast and slow sorption phase. Both fast and slow sorption capacity of deeper peat was greater than younger peat while the sorption capacity of PPI soil was greater than wetland peat soil (PPI > Deeper > Top soil). Differences in sorption capacities with soil age were well explained by soil elemental ratios; Higher H/C and O/C ratios indicates "older" organic matter. The increase of the slow sorption fraction with soil age is further evidence that desorption-resistance
is observed in wetland soils.

3. Dual reactive domain model (DRDM): The organic matter normalized partition coefficient for linear fraction, $K_{D,LOC}$ of the deeper soil was consistently higher than top soil. For both CB and Phen, the Langmuir site energy factor, $b$ was higher in the top soil while the Langmuir capacity factor, $Q^*$ was higher in deeper soil. For CB, $Q^*b$ representing the Langmuir sorption capacity of the nonlinear sorption was significantly greater in deeper soil. For Phen ($b << 1$), $q_{e,NL} = Q^*bC_T$. The higher $Q^*b$ value of the deeper (older) soil indicates that nonlinear sorption fraction in the soil increases with soil age.

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REFERENCES


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