Sorption of polar and nonpolar aromatic compounds to four surface soils of eastern China

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In addition to the hydrophobicity of solute and the organic carbon content of soil, the solute molecular structure and the soil nature also determine the retention of organic pollutants by soils.

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Improved predictions on the fate of organic pollutants in surface environments require a better understanding of the underlying sorption mechanisms that control their uptake by soils. In this study, we monitored sorption of nine aromatic compounds with varying physicochemical properties (hydrophobicity, electron-donor/acceptor ability and polarity), including two polycyclic aromatic hydrocarbons, two chlorobenzenes, two nitroaromatic compounds, dichlobenil, carbaryl and 2,4-dichlorophenol in aqueous suspension of four surface soils of eastern China. The tested soils were characterized with respect to organic carbon (OC) content, black carbon content, mineralogy, morphology and size fraction to assess the role of the diverse soil characteristics in sorption. The results of this study show that not only the solute hydrophobicity and the OC content of soil are important to the retention of organic pollutants, but also the solute molecular structure and the soil nature.

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1. Introduction

Sorption to soil is one of the key processes controlling the fate, transport and risk of organic pollutants in surface and subsurface environments. Naturally occurring soils are heterogeneous in composition which can be broadly divided into inorganic component of soil mineral (e.g., aluminum oxides, iron oxides and smectite clays) and organic component of soil organic matter (SOM).

Soil mineral and SOM often show distinct sorptive affinities toward organic pollutants, and the relative contribution to the overall sorption depends on the content and structure of each component, as well as the physical/chemical property of solute. For nonpolar solutes (e.g., polycyclic aromatic hydrocarbons [PAHs] and chlorinated benzenes), hydrophobic partition into SOM generally dominates the sorption process. This is evidenced by observations that the uptake of a nonpolar solute by different soils generally correlates well with the content of SOM or soil organic carbon (OC) (Means et al., 1980; Chiou, 2002; Celis et al., 2006). Moreover, for sorption of different nonpolar solutes to a given soil a good linear free energy relationship is often seen between the OC-based soil-to-water distribution coefficient ($K_{OC}$) and solute n-octanol–water partition coefficient ($K_{OW}$) or water solubility ($S_W$) (Chiou, 2002). However, for highly polar solutes such as nitroaromatic compounds (NACs), polar interactions with mineral surfaces could be the predominant sorption driving force. Sheng et al. (2001) compared sorption of a series of pesticides on a unit mass basis between a reference smectite clay and SOM represented by a muck soil, and found the clay was a more effective sorbent than SOM for 4,6-dinitroresol (DNOC), dichlobenil and carbaryl. It is also well documented that smectite clays exchanged with weakly hydrated cations (e.g., $K^+$ and $Cs^+$) can strongly retain NACs and other polar compounds (e.g., dichlobenil and carbaryl) (Boyd et al., 2001; Sheng et al., 2001; De Oliveira et al., 2005). The investigators argue that direct complexation with exchangeable cations is responsible for the enhanced adsorption of these solutes on the clay surface.

Although the content of OC or SOM is a useful descriptor for quantifying sorption of organic pollutants, the measured $K_{OC}$, even for nonpolar solutes, could deviate greatly among soils due to the structural heterogeneity of SOM. In the process of humification debris of biomass originated from different sources undergo long-term, complex diagenesis reactions to form SOM varying much in geological maturity and structural heterogeneity. For example, compared with the amorphous SOM (e.g., humic acid), the condensed SOM (e.g., humin and kerogen) is more geologically mature and more enriched in cross-linked and aromatic structures,

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and often shows larger sorptive affinities and capacities toward organic pollutants. In addition, clay minerals tend to bind SOM to form stable aggregates of SOM–clay complexes (Stevenson, 1982; Schnitzer, 1986), which may also modify the structure and conformation of the bound SOM and therefore impact its sorption behavior. Wang and Xing (2005) studied sorption of phenanthrene to model humic acid–clay complexes, where the $K_{OC}$ increases with decreasing loading of the humic acid. The investigators proposed that a more condensed structure of the sorbed humic acid may develop with lower loading on the clay surface to favor sorption of the solute. Furthermore, recent studies demonstrated that naturally occurring soils and sediments often contain fairly high content of black carbon (BC), which refers soot and charcoal produced from incomplete combustion of fossil fuels and biomass (Goldberg, 1985; Schmidt and Noack, 2000). BC could play an important role in the fate of organic pollutants due to the very strong adsorption affinity, as compared to other forms of natural organic matter (e.g., humic acids) on an OC basis (Bucheli and Gustafsson, 2000; Accardi-Dey and Gschwend, 2002; Cornelissen and Gustafsson, 2004; Cornelissen et al., 2005; Lohmann et al., 2005).

Viewed from the mechanistic aspect, the rich contents of different types of functional groups (e.g., carboxyls and alcohols) and structures (e.g., aromatic rings and alkyl chains) contained in SOM may invoke various molecular-level sorptive interactions with organic pollutants, with types and intensities dependent on solute structural properties. For instance, phenols may act as H-donors and/or H-acceptors to form H-bonds with O-containing groups of SOM. However, detailed characterizations of sorption mechanisms to soils at the molecular level are technically very challenging due to the lack of thorough, comprehensive profiling of SOM structures, as well as suitable in situ microscopic observations on the relatively weak sorptive interactions. Batch sorption using a matrix of sorbates varying in physical/chemical properties (hydrophobicity, electron-donor/acceptor ability and polarity) is a ready technique to probe the underlying structural dependent sorption mechanisms.

In this study, nine polar and nonpolar aromatic compounds, including PAHs, chlorobenzenes, NACs, 2,4-dichlorophenol, dichlobenil and carbaryl were sorbed to four soils of eastern China suspended in aqueous solution, resulting in a total of 36 sorbate/sorbent combinations. The soils were collected from widely distributed locations in eastern China and represent a range of soil types. Their respective OC contents, BC contents, mineralogy, morphology and size fractions were also monitored as an integrated study to assess the role of the diverse soil characteristics in sorption.

2. Materials and methods

2.1. Materials

Four soils representing a wide range in soil properties and distributions in China were collected from the surface horizon (0–20 cm) from Shenyang, Liaoning Province, Kaifeng, Henan Province, Suzhou, Jiangsu Province and Linchuan, Jiangxi Province, respectively. A map of the sampling sites is shown in Fig. 1. The soils were air-dried, sieved (<2 mm) and stored at room temperature. Selected soil properties are given in Table 1. The ratio of clay (<2 μm size fraction) was determined based on Stokes’ law and transmission/absorption phenomenon of soil particles with a laser particle size analyzer (Mastersizer 2000) (Malvern, UK). Soil OC content was determined based on analysis of X-ray diffraction (XRD) (D/max-IIIC, Japan). Mineral composition was determined based on analysis of X-ray fluorescence (XRF) (ARL 9800XPS+, Switzerland). Scanning electron microscopy (SEM) analysis of soil samples was performed with a microscope of Hitachi S-3000N (Japan) (Fig. 2).

Sorbates include two polycyclic aromatic hydrocarbons (PAHs), phenanthrene (PHEN, Fluka) and pyrene (PYR, Fluka), two chlorinated benzenes, 1,2,4,5-tetra-chlorobenzene (TECB, Aldrich) and pentachlorobenzene (PCTB, Aldrich), two NACs, 1,3-dinitrobenzene (DNB, Aldrich) and 1,3,5-trinitrobenzene (1000 mg L–1 in acetone/tributylbenzene (TB, Supelco), 2,6-dichlorobenzonitrile (dichlobenil) (DNL, Chem Service), 1-naphthalenyldimethylcarbamate (carbaryl) (CBL, Chem Service), 1-naphthalenyl methylcarbamate (carbaryl) (CBL, Chem Service) and 2,4-dichlorophenol (DPL, Aldrich). Chemical structures of the sorbates are given in Fig. 3. The PAHs and chlorobenzenes are considered nonpolar and the rest of the compounds are considered polar. Solute aqueous solubility ($S_{aq}$), n-octanol–water partition coefficient ($K_{ow}$) and n-hexadecane-water partition coefficient ($K_{ow}$) are listed in Table 2.

2.2. Batch sorption

Sorption was carried out in PTFE-lined screw cap glass vials of capacity 15 mL or 22 mL, receiving 60–800 mg soils and sufficient volume of background solution containing 0.02 M NaCl and 200 mg L–1 NaNO3 (as the bio-inhibitor). The amount of

Table 1

<table>
<thead>
<tr>
<th>Soil</th>
<th>Classification</th>
<th>pH&lt;sup&gt;a&lt;/sup&gt;</th>
<th>OC&lt;sup&gt;c&lt;/sup&gt; (%)</th>
<th>BC&lt;sup&gt;d&lt;/sup&gt; (%)</th>
<th>BC/OC</th>
<th>CEC&lt;sup&gt;e&lt;/sup&gt; meq 100 g&lt;sup&gt;–1&lt;/sup&gt;</th>
<th>Major mineral&lt;sup&gt;f&lt;/sup&gt;</th>
<th>Al&lt;sub&gt;Ox&lt;/sub&gt;&lt;sup&gt;g&lt;/sup&gt; (%)</th>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;h&lt;/sup&gt; (%)</th>
<th>Fe&lt;sub&gt;Ox&lt;/sub&gt;&lt;sup&gt;i&lt;/sup&gt; (%)</th>
<th>Ca&lt;sub&gt;O&lt;/sub&gt;&lt;sup&gt;j&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shenyang</td>
<td>Udic Argisol</td>
<td>6.05</td>
<td>8.2</td>
<td>2.32</td>
<td>0.32</td>
<td>13.8</td>
<td>19.7</td>
<td>V, Q, M &gt; F</td>
<td>20.46</td>
<td>54.37</td>
<td>7.71</td>
</tr>
<tr>
<td>Suzhou</td>
<td>Stagnic Anthrosol</td>
<td>5.90</td>
<td>14.3</td>
<td>1.96</td>
<td>0.34</td>
<td>17.3</td>
<td>23.0</td>
<td>K, M, V &gt; Q &gt; F</td>
<td>13.63</td>
<td>65.77</td>
<td>4.78</td>
</tr>
<tr>
<td>Kaifeng</td>
<td>Aquic Cambisol</td>
<td>7.84</td>
<td>7.3</td>
<td>0.91</td>
<td>0.05</td>
<td>5.5</td>
<td>8.8</td>
<td>M, V, K &gt; Q &gt; F</td>
<td>11.89</td>
<td>63.29</td>
<td>4.31</td>
</tr>
<tr>
<td>Linchuan</td>
<td>Udic Ferroisol</td>
<td>5.34</td>
<td>17.1</td>
<td>0.55</td>
<td>0.08</td>
<td>14.5</td>
<td>9.7</td>
<td>M &gt; K &gt; Q</td>
<td>20.47</td>
<td>59.78</td>
<td>9.33</td>
</tr>
</tbody>
</table>

<sup>a</sup> Measured at 1:10 (g mL<sup>–1</sup>) soil/H<sub>2</sub>O ratio.
<sup>b</sup> Clay fraction (<2 μm) volume in whole soil.
<sup>c</sup> Organic carbon weight in whole soil.
<sup>d</sup> Black carbon weight in whole soil.
<sup>e</sup> Cation exchange capacity.
<sup>f</sup> V, vermiculite; K, kaolinite; M, mica; Q, quartz; F, feldspar. Greater than symbols indicate mineral is present in larger amount relative to other minerals identified; the absence of a symbol between minerals indicates the amounts are approximately the same; the absence of a mineral symbol indicates the amounts are below detection.
<sup>g</sup> Composition fraction in whole soil.

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soil and the volume of solution were selected for each sorbate to assure data compatibility while maintaining analytical accuracy. The pH of soil suspension was adjusted to about 6.0 by 0.1 M HCl and 0.1 M NaOH. Organic solute was added in carrier of methanol that was kept below 0.1% by volume to minimize co-solvent effects. The solutions were mixed end-over-end at 6 rpm with a tumbler at room temperature for 5–7 days.

After centrifugation, solutes of TeCB and PtCB were extracted from an aliquot of the aqueous phase with hexanes and analyzed by gas chromatography (GC) with electron-capture detection (ECD) using a 60 m × 0.25 mm DB-1 capillary column (J&W Scientific). The rest solutes were analyzed directly by high-performance liquid chromatography (HPLC) using a 4.6 × 150 mm HC-C18 column (Agilent). Isocratic elution was performed with a UV detector under the following conditions: 90% methanol/10% (v:v) water with a wavelength of 238 nm for PHEN; 60% methanol/40% water with a wavelength of 238 nm for DNB; 55% methanol/45% water with a wavelength of 266 nm for TNB; 75% methanol/25% water with a wavelength of 210 nm for DNL; 70% methanol/30% water with a wavelength of 280 nm for CBL; 80% methanol/20% water with a wavelength of 231 nm for DCP. Isocratic elution was performed with a fluorescence detector under the following conditions: 90% methanol/10% water with excitation/emission wavelengths of 334/391 nm for PYR.

Calibration curves included at least seven standards over the test concentration range. When GC/ECD was used, calibration curves were fit to a power law expression to account for the detector response nonlinearity. Adsorbed mass was assumed equal to the difference between added mass and mass in the aqueous solution phase. To take account for solute loss from processes other than sorption to the sorbent (i.e., sorption to septum and glassware and volatilization), calibration curves were obtained separately from samples receiving the same treatment as the sorption samples but no sorbent. The equilibrium pH was measured at the end of sorption experiments and was close to 6.0 (variance generally <0.2 pH units).

Another set of experiments were conducted to evaluate the role of BC in sorption. Thus far, adsorption coefficients of PAHs to BC in soils and sediments are most commonly found in the literature (Accardi-Dey and Gschwend, 2002; Cornelissen and Gustafsson, 2004; Cornelissen et al., 2005; Lohmann et al., 2005). In this study, PHEN was selected as a representative PAH in order to compare the adsorption affinity of BC in the tested soil with the reported data. Considering the detection limit of the elemental analyzer for OC is 0.03% in the present work, the low BC contents (0.05% and 0.08%, respectively, see Table 1) measured for Kaifeng and Linchuan soils might not be reliable. Therefore, the sorption experiments were limited to only the treated soils of Shenyang and Suzhou.

### 3. Results and discussion

Sorption isotherms were fit to the Freundlich model, 

\[ q = K_F C_w^n \]

by nonlinear regression weighed by \(1/q\), where \(q\) (mmol kg\(^{-1}\)) and \(C_w\) (mmol L\(^{-1}\)) are the equilibrium sorbed and solution concentrations, respectively, \(K_F\) (mmol\(^{1-n}\) L\(^n\) kg\(^{-1}\)) is the Freundlich affinity coefficient and \(n\) (unitless) is the Freundlich linearity index. The isotherms are shown in Fig. 4a–d, and the parameters are given.
Original sorption isotherms of all compounds for different soils. (a) Shenyang. (b) Suzhou. (c) Kaifeng. (d) Linchuan.

Table 2
Water solubility ($S_W$), $n$-octanol–water partition coefficient ($K_{OW}$) and $n$-hexadecane–water partition coefficient ($K_{HW}$) for sorbates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbrev.</th>
<th>$S_W$ (10^-3 mol L^-1)</th>
<th>$K_{OW}$ (L kg^-1)</th>
<th>$K_{HW}$ (L kg^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>PHEN</td>
<td>6.31</td>
<td>37200</td>
<td>55000</td>
</tr>
<tr>
<td>Pyrene</td>
<td>PYR</td>
<td>0.652</td>
<td>153000</td>
<td>350000</td>
</tr>
<tr>
<td>1,2,4,5-Tetrachlorobenzene</td>
<td>TeCB</td>
<td>5.89</td>
<td>25500</td>
<td>89000</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>PCB</td>
<td>2.63</td>
<td>151000</td>
<td>600000</td>
</tr>
<tr>
<td>1,3-Dinitrobenzene</td>
<td>DNB</td>
<td>2880</td>
<td>30.9</td>
<td>4.30</td>
</tr>
<tr>
<td>1,3,5-Trinitrobenzene</td>
<td>TNB</td>
<td>1550</td>
<td>15.1</td>
<td>1.00</td>
</tr>
<tr>
<td>2,6-Dichlorobenzonitrile</td>
<td>DNL</td>
<td>105(^{\text{a}})</td>
<td>501(^{\text{a}})</td>
<td>84 ± 3</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>CBL</td>
<td>601</td>
<td>229</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>1,3-Dichlorophenol</td>
<td>DCP</td>
<td>26900</td>
<td>1230</td>
<td>16.9 ± 0.8</td>
</tr>
</tbody>
</table>

\(^{a}\) From Schwarzenbach et al. (2003) except where noted.

\(^{b}\) Measured at 0°C from at least six replicates with ±standard deviation using the method by Zhu and Pignatello (2005a) except where noted.

\(^{c}\) From Clausen et al. (2004).

\(^{d}\) From Abraham et al. (1994).

In general the sorption data agree with the Freundlich isotherm reasonably. The different sorbate-sorbent combinations exhibit varied degrees of linearity, i.e., departures from $q_\text{m}$ versus $C_\text{W}$ for a given compound, no matter polar or nonpolar, the $K_{OC}$ is comparable among the Shenyang, Suzhou and Kaifeng soils.

Despite the primary role of hydrophobic effects, one striking observation can still be made for sorption to the Shenyang, Suzhou and Kaifeng soils that the PAHs show greater affinities than the chlorobenzenes with close hydrophobicities (PHEN vs. TeCB, PYR vs. PtCB), i.e., justified by solute $K_{OW}$ and $K_{HW}$ values (Table 2), the paired solutes have close hydrophobicities. Previous studies have reported that both solid and dissolved forms of SOM could sorb PAHs more strongly than chlorinated benzenes, biphenyls and alkanes (Gerstl, 1990; Chiou et al., 1998; Zhu et al., 2004) after taking solute hydrophobicity into account. To account for such observations, Zhu et al. (2004) proposed a mechanism of $\pi$–$\pi$ electron donor acceptor (EDA) interactions between PAHs ($\pi$-donors) and SOM $\pi$-acceptor structures (e.g., aromatic rings with electron-withdrawing substituents such as carbonyl, ketone, aldehyde, ester and amido functional groups). The enhanced sorption of the PAHs relative to the chlorobenzenes observed herein could be due to this mechanism. In addition to sorption affinities, the specific $\pi$–$\pi$ EDA interactions of the PAHs might also result in greater sorption linearity compared to the chlorobenzenes (see $n$ values in Table 3). On the contrary, chlorobenzenes are considered non-$\pi$-donors due to the chlorine substitution and cannot invoke such interactions. As a result, sorption of the chlorobenzenes is predominantly driven by hydrophobic effects and is characteristically reflected by the more linear isotherms.
It becomes more difficult to evaluate the relative contribution from the organic and inorganic components to the overall sorption of the polar solutes. It is well known that certain polar compounds (e.g., NACs, dichlobenil and carbaryl) have strong binding affinities to pure smectite clays, especially those exchanged with weakly charged cations (e.g., NACs, dichlobenil and carbaryl) have strong binding affinities from the organic and inorganic constituents to the overall sorption of the polar solutes. Consistent results were reported in an earlier study of sorption of two polar herbicides, thiazafluron and metamitron, to five soils of southern Spain (Cox et al., 1997). Thus, for sorption of polar compounds, and the effect seems to be dependent on solute structural features. For example, coadsorption of humic substance does not impact the sorption of NACs and dichlobenil to montmorillonite, possibly due to H-bonding of solutes. In adsorption by reference minerals, humic substance could be fractionated according to the type and chemistry of the underlyingly mineral surface. For example, kaolinites and montmorillonites preferentially sorb the more hydrophobic, aliphatic fractions (Wang and Xing, 2005; Feng et al., 2006; Hengpraprom et al., 2006). Alternatively, Fe and Al oxohydroxides show stronger binding affinities toward the less hydrophobic, acidic aromatic fractions via surface complexation (Kaiser et al., 1997; Zhou et al., 2001; Kaiser, 2003). Therefore, the associated SOM of the Linchuan soil could be structurally very different from that of the other three soils and overall less hydrophobic. This helps explain the lower \( K_{OC} \) observed for nearly all solutes to the Linchuan soil. The rich contents of acidic functional groups possibly contained in SOM of the Linchuan soil could also favor H-bonding of solutes (e.g., DCP and CBL) with strong H-donor/acceptor structures, resulting in greater sorption affinity and nonlinearity. Note the O=C=O (H acceptor) and NH (H acceptor or H-donor) structures of the organic solutes. In fact, previous studies have shown that removal of iron and organic matter from the clay surface increases the adsorption of thiazafenol, a polar herbicide, to montmorillonite (Celis et al., 1997).

In addition to sorption linearity, the Linchuan soil also displays different trends of sorption affinity from the other three soils. With the exception of TNB and PtCB, all compounds have much lower \( K_{OC} \) values (Table 3) to the Linchuan soil than to other soils. The lowest sorption and the highest sorption were observed for DNL and PtCB to the Linchuan soil, respectively. Lower and higher sorption were observed for CBL and PYR to other soils. Within the group of polar solutes, TNB and DCP demonstrate a trend of greater sorption than the rest compounds to the Linchuan soil, which, however, does not exist for other soils. It seems that the different sorption patterns of the Linchuan soil were due to the unique nature of SOM associated with the mineral surface. Among the four tested soils, the Linchuan soil is the only Ferrosol, appearing in the characteristic color of brown-red, and contains the highest content of iron oxides (9.33%) but no fieldspars and vermiculites (Table 1). Furthermore, the Linchuan soil is composed of finer particles with more clay fractions (17.1%, Table 1) compared to other soils. Within the group of polar solutes, the Linchuan soil sorbed less hydrophobic than the rest compounds to the Linchuan soil, which, however, does not exist for other soils. The low solubility of pyrethroids to other soils, which is also confirmed by the SEM results (Fig. 2). In adsorption by reference minerals, humic substance could be fractionated according to the type and chemistry of the underlying mineral surface. For example, kaolinites and montmorillonites preferentially sorb the more hydrophobic, aliphatic fractions (Wang and Xing, 2005; Feng et al., 2006; Hengpraprom et al., 2006). Alternatively, Fe and Al oxohydroxides show stronger binding affinities toward the less hydrophobic, acidic aromatic fractions via surface complexation (Kaiser et al., 1997; Zhou et al., 2001; Kaiser, 2003). Therefore, the associated SOM of the Linchuan soil could be structurally very different from that of the other three soils and overall less hydrophobic. This helps explain the lower \( K_{OC} \) observed for nearly all solutes to the Linchuan soil. The rich contents of acidic functional groups possibly contained in SOM of the Linchuan soil could also favor H-bonding of solutes (e.g., DCP and CBL) with strong H-donor/acceptor structures, resulting in greater sorption affinity and nonlinearity. Note the O=C=O (H acceptor) and NH (H acceptor or H-donor) structures of the organic solutes. In fact, previous studies have shown that removal of iron and organic matter from the clay surface increases the adsorption of thiazafenol, a polar herbicide, to montmorillonite (Celis et al., 1997).
with negligible potentiality for polar/polarizable, EDA interactions. This is seen by linear regression of the free energy relationship (results not shown) between $K_{OW}$ and $K_{HD}$ (values listed in Table 2), where the polar solutes and the nonpolar solutes fall into two distinct groups due to the extra polar interactions (e.g., H-bonding and dipole–dipole) with $n$-octanol. Fig. 5a–d shows the results of hydrophobicity-normalized sorption isotherms to different soils plotted as $q$ against $C_H$, (mmol L$^{-1}$), which represents the solute concentration in $n$-hexadecane that would be in equilibrium with the observed aqueous concentration ($C_W$), i.e., $q_H = C_W / K_{HD}$.

With normalization of hydrophobic effects, the sorption data can be roughly divided into two subgroups for the polar solutes and the nonpolar solutes, respectively. For all the four tested soils, the polar solutes are displaced upward relative to the nonpolar solutes by from one to more than four orders of magnitude. The results indicate that extra polar interactions and/or specific interactions contribute significantly to sorption of the polar solutes. Within the group of polar solutes, the sorption affinities show a consistent decreasing order of TNB > DNB, CBL, DCP > DNL. Having rejected soil minerals as the major contributor to the overall sorption, the sequence is believed to result from non-hydrophobic interactions with SOM, with type and intensities dependent on solute structural features. In response to the specific structure of solute, these interactions could be polar (dipole–dipole, dipole–induced dipole) interactions, H-bonding and $\pi$–$\pi$ EDA interactions. The greatest sorption affinities of TNB can be attributed to strong polar
interactions due to the high polarity of the solute and possible $\pi \cdots \pi$ EDA interactions (i.e., NACs are strong $\pi$-acceptors; Zhu and Pignatello, 2005b). The greater sorption of CBL and DCP than DNL may be due to the strong H-bonding with SOM. This also helps explain why CBL and DCP show even stronger normalized sorption to the Linchuan soil than to other soils. The associated SOM of the Linchuan soil may contain more acidic moieties due to complexation with the iron surface, therefore favoring H-bonding. Within the group of nonpolar solutes, the PAHs sorb more strongly than the chlorobenzenes by less than one order of magnitude to the Shenyang, Suzhou and Kaifeng soils, attributed to $\pi \cdots \pi$ EDA interactions of the PAHs with SOM $\pi$-acceptor structures. However, the normalized sorption data are nearly identical between these solutes for the Linchuan soil, suggesting that the mechanism of $\pi \cdots \pi$ EDA interactions is not applied due to the unique nature of the associated SOM.

Sorption isotherms of PHEN to the treated BC soils of Shenyang and Suzhou are shown in Fig. 6, along with the sorption data for the bulk soils for comparison. The Freundlich model parameters and the estimated OC-based sorption coefficients (herein noted as $K_{OC}$, in L kg$^{-1}$) for the two BC soils are also listed in Table 3. Obviously, the BC soil exhibits much higher sorption nonlinearity ($n \approx 0.6$, Table 3) than the respective bulk soil, agreeing with the mechanism of surface adsorption to the highly porous BC. The measured log$k_{BC}$ over the studied concentration range is 4.3–5.3 for the Shenyang soil and 4.1–4.8 for the Suzhou soil. These values are lower than the reported log$k_{BC}$ (5.6–6.4) (Cornelissen and Gustafsson, 2004; Cornelissen et al., 2005; Lohmann et al., 2005) by more than one order of magnitude, probably due to the different source and nature of BC in the tested soil. Nonetheless, it can be found that BC plays a key role in sorption, especially at low solute concentrations. Although BC accounts only for 14–17% (Table 1) of the total OC content, it contributes 21–95% to the overall sorption, wherein the relative importance increases with decreasing solute concentration.

Previous studies (Accardi-Dey and Gschwend, 2002; Cornelissen and Gustafsson, 2004; Lohmann et al., 2005) have proposed a dual-component model to describe the overall sorption of nonpolar solutes to BC-containing soils and sediments by summing up the nonlinear adsorption onto BC and the linear partition into humic substance. Accordingly, the relative contribution from the humic substance can be estimated by subtracting the BC adsorption from the overall sorption to soil:

$$q_{HS} = q - k_{BC}C_{W}^{n} \quad (1)$$

where $q$ and $C_{W}$ are the sorbed and solution concentrations, respectively, at sorption equilibrium to the bulk soil; $k_{BC}$ and $n$ are Freundlich parameters for sorption to the BC soil; $q_{HS}$ is the sorbed concentration to the humic substance soil without the contribution from BC. The calculated sorption isotherms for the humic substance soil are also shown in Fig. 6, along with the fitting line and parameters of linear regression. It is seen that the sorption to the humic substance soil can be well described by the linear partition model. The OC-based partitioning coefficient for pure humic substance is thus calculated to be 15,000 $\pm$ 4000 L kg$^{-1}$ (STD deviation calculated from the linear regression, see Fig. 6) for the Shenyang soil and 12,000 $\pm$ 3000 L kg$^{-1}$ for the Suzhou soil. These values are comparable with the literature data for phenanthrene sorption to soil humic acids, ranging from 11,000 to 18,000 L kg$^{-1}$ (Xing 2001; Won and Pignatello, 2005). However, recent studies (Won and Pignatello, 2005) have indicated that adsorption of organic solutes to BC in soils could be suppressed by other organic matters (e.g., humic acids). Therefore, the sorption data measured for BC with the combusted soil might be overestimated compared to the real case with the bulk soil. Furthermore, more research will still be needed to test whether the proposed additive model (Eq. (1)) is applicable to sorption of the polar solutes.

4. Conclusion

The present study demonstrated that in addition to the hydrophobicity of solute and the OC content of soil, the solute molecular structure and the soil nature also determined the retention of organic pollutants by soils. The tested soils except the Linchuan soil had comparable $K_{OC}$ for a given compound, suggesting the primary role of hydrophobic partition into SOM. The hypothesis was further confirmed by the lack of correlation between the sorption affinities and the clay fractions or the CECs of bulk soils. The different sorption pattern observed for the Linchuan soil was attributed to the unique characteristics of the associated SOM.

Upon normalization of hydrophobic effects using $K_{OC}$, the polar solutes sorbed more strongly than the nonpolar solutes (PAHs, chlorobenzenes) due to the extra polar and/or specific interactions with SOM. Both the original and the normalized sorption data displayed greater affinities of the PAHs than the chlorobenzenes with close hydrophobicities to the Shenyang, Suzhou and Kaifeng soils, attributed to $\pi \cdots \pi$ EDA interactions of the PAHs with the SOM $\pi$-acceptor structures.

The four tested soils have varied BC contents, ranging from 0.05% to 0.34%. The overall sorption of PHEN to the Shenyang soil and to the Suzhou soil was attributed to linear partition into humic substance and to adsorption onto BC. Despite the relatively low content, BC accounts for 21–95% of the overall sorption of PHEN, with the relative importance dependent on solute concentration. The $K_{OC}$ values for PHEN sorption to humic substance of the two selected soils were comparable with that for extracted soil humic acids in the literature. However, the log$k_{BC}$ values were lower than the reported data by more than one order of magnitude, likely resulting from the different source and nature of BC in the tested soil. Further studies will still be needed to determine the role of BC in sorption of the polar solutes to soils.

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