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Interaction Mechanism of Benzene and Phenanthrene in Condensed Organic Matter: Importance of Adsorption (Nanopore-Filling)

Ke Sun
Yong Ran
Yu Yang
Baoshan Xing
Jingdong Mao

Old Dominion University

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Interaction mechanism of benzene and phenanthrene in condensed organic matter: Importance of adsorption (nanopore-filling)

Ke Sun, Yong Ran, Yu Yang, Baoshan Xing, Jingdong Mao

Abstract

Although microporosity and surface area of natural organic matter (NOM) are crucial to mechanistic evaluation of the sorption process for nonpolar organic contaminants (NOCs), they have wrongly been estimated by the N₂ adsorption technique. Nuclear magnetic resonance spectroscopy (¹³C NMR), and benzene, carbon dioxide, and nitrogen adsorption techniques were used to characterize structural and surface properties for different condensed NOM samples, which were related to the sorption behavior of phenanthrene (Phen). It was found that the revised Freundlich model by taking the chemical activity into account can well describe the isotherms for benzene and Phen. The benzene and Phen adsorption volumes for the coal samples are similar to or lower than the CO₂-nanopore volumes. Adsorption volumes of both benzene and Phen are significantly related to the aliphatic carbon structure, and their correlation lines are nearly overlapped, suggesting that the nanopore filling for Phen and benzene on the investigated samples is the dominating mechanism, and also is not affected by water molecules. The entrapment of benzene and/or the pore deformation in the NOM nanopore are likely responsible for the observed hysteresis of benzene. The above results demonstrate that Phen and benzene adsorption on the condensed NOM is closely associated with the aliphatic carbon structure of the investigated samples.

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1. Introduction

Sorption and sequestration of nonpolar organic chemicals (NOCs) by natural organic matter (NOM) associated with aquifers, soils, sediments (biosorbents) control bioavailability, risk, and biodegradation of NOCs (Brusseau et al., 1991; Chefetz and Xing, 2009; Pignatello and Xing, 1996). Many investigations during the last three decades identified that the organic matter types and microporosity are important for the sorption of NOCs (Chefetz and Xing, 2009; Chen and Xing, 2005; Grathwohl, 1990; Plaza et al., 2009; Salloum et al., 2002; Senesi, 1992). However, the physicochemical mechanisms of sorption/desorption and reduced bioavailability are limited.

The chemical and structural properties of NOM strongly affect the sorption and desorption of NOCs in soils and sediments (Chefetz and Xing, 2009; Pignatello and Xing, 1996; Weber et al., 1992). Previous investigations indicated that various types of bulk SOM with high aliphatic carbon showed strong sorption for phenanthrene and pyrene (Chefetz et al., 2000; Mao et al., 2002). NOM has been characterized as comprising dual domains or components that exhibit distinctly different sorption reactivity (Grathwohl, 1990; Kleineidam et al., 2002; Ran et al., 2004; Weber et al., 1992; Xing and Pignatello, 1997). Depending on parental sources and diagenetic alteration histories, NOM may comprise different types of organic materials ranging from biopolymer, humus, kerogen and coal materials, and black carbon. Condensed organic carbons such as kerogen, coal, and black carbon can substantially contribute to NOM in soils and sediments (Cornelissen et al., 2005; Ran et al., 2002, 2007; Weber et al., 1992). It is noted that NMR spectroscopy has been increasingly used to provide a basis for inferring the molecular structure in these organic matter (Chefetz et al., 2000; Filimonova et al., 2004; Kögel-Knabner, 1997; Ran et al., 2002, 2007; Salloum et al., 2002).

Surface and geometric heterogeneity in NOM could be very important for the sorption mechanism of NOCs on NOM. The surface area of NOM is crucial to the mechanistic interpretation of sorption process. N₂ adsorption was recommended as the standard method to measure the surface area of soils/sediments (Gregg and Sing, 1982). However, large discrepancies were reported between NOM surface areas derived from CO₂ adsorption and N₂ adsorption, primarily because of the activated diffusion phenomenon (Aochi and Farmer, 2005; de Jonge and Mittelmeijer-Hazeleger, 1996; Li and Werth, 2001; Ran et al., 2013; Ravikovitch et al., 2005; Xing and Pignatello, 1997). Carbon dioxide at 273 K and benzene at 295 K have been used as alternative gases for probing the surface properties of carbonaceous materials (Corley et al., 1996;
de Jonge and Mittelmeijer-Hazeleger, 1996; Gan et al., 1972; Kwon and Pignatello, 2005; Larsen et al., 1995; Ravikovitch et al., 2005; Reucroft and Sethuraman, 1987; Walker and Kini, 1965; Xing and Pignatello, 1997). Glassy forms of NOM including humin, kerogen and coals have internal microporosity that apparently is not accessed by N2 at 77 K due to activation diffusion. Moreover, previous investigations demonstrated that the adsorption (hole-filling) mechanism is important for the sorption of hydrophobic organic contaminants by the isolated kerogen, Pahokee peat, and coals (Ran et al., 2002, 2004, 2013). However, how the microporosity measured by CO2 and benzene gas molecules is related to the structure of NOMs and the aqueous sorption capacity for NOCs on various NOMs has not yet been systematically investigated.

This study investigates how the hydrophobic nanopore volumes measured with benzene vapor and CO2 gas are related to the structure of NOM and the sorption capacity of phenanthrene (Phen) on a range of condensed NOM samples, and how the adsorption of aqueous Phen is related to that of gaseous benzene, and is affected by water molecules. We hypothesized that the hydrophobic nanopore in glassy NOM could be large enough for accommodating majority of NOCs. We used a wide range of condensed NOM ranging from nonhydrolyzable organic carbon (NHC) to black carbon (BC) and coals (Table 1) as sorbents, and Phen and benzene vapor as model sorbates to test this hypothesis.

2. Materials and methods

2.1. Sorbents and characterization

Two surface soil samples (HP04 and HP05) were collected to a depth of 20 cm in July 2002 from Hangpu district of Guangzhou city, China. Three surface sediment samples (C01, C03, and C08) (0–20 cm) were collected from the Pearl River Estuary (PRE) using a box sampler in August 2002. The water depth was 25 m for C01, 25 m for C03, and 69 m for C08. The soils and sediments were treated using an acid hydrolysis procedure. Many components of BC substrates vanish at lower temperatures, while at least portions of mineral-associated humic substances (not BC) resist to that temperature. In addition, Beulah-Zap lignite (BZ) was obtained from the American Argonne Premium coals. A lignite coal (JP), two bituminous coals (XW and XA), and an anthracite (XY), were collected from state-owned coal mines and covered a wide range of maturity with vitrinite reflectance (R0) from 0.52% to 2.50% (Chen et al., 2005).

The C, H, O, and N contents were measured using an Elementar Vario ELIII or a Heraeus CHN-O-RAPID elemental analyzer. Specific surface areas (SSA) and microporosity were measured using the N2-adsorption and CO2-sorption techniques, at the normal boiling temperature (77 K) and at 273 K in a Micromeritics ASAP 2010 instrument and Autosorb-1 gas analyzer (Quantachrome Instrument Corp., Boynton Beach, FL), respectively (Ran et al., 2013). The 13C CP/TOS (cross polarization/total sideband suppression) NMR spectra for the five coals were obtained on a Bruker Avance-400 NMR spectrometer operated at a 13C frequency range of 100 MHz and at a magic-angle-spinning (MAS) rate of 6.0 kHz. Briefly, the solid coal samples were placed in a 4-mm diameter ZrO2 rotor with a Kel-F cap. A 1.2-s recycle delay and a 1-ms contact time were used. Between 3500 and 4500 scans were collected. The physicochemical properties of the investigated samples are summarized in Table 1.

2.2. Sorption and desorption experiments

Adsorption isotherms of benzene vapor were recorded at 23 °C with an intelligent gravimetric analyzer (IGA supplied by Hidden Analytical Ltd). Benzene isotherms were obtained by setting pressure intervals relative to saturation vapor pressure (p/p0) at 298 K. Prior to the measurements, the adsorbent was outgassed in situ until constant weight was achieved at a temperature of 373 K. About 70 mg of a given sample was loaded for each run. HPLC grade benzene was used as adsorbate. Pressure steps in the range of p/p0, values 0–0.94 were used to obtain the isotherm. The equilibrium time for each point of the sorption isotherms ranged from tens of minutes to several hours.

The completely mixed batch reactor (CMBR) systems were employed for the Phen sorption isotherms at room temperature (23 °C). The equilibrium time is four weeks. Flame-sealed glass ampules (50 ml) were used as the CMBRs. The experiments consisted of preliminary tests and final equilibrium tests. The average concentrations of Phen detected in the control reactors were within 98–102% of the initial concentrations. No correction for solute loss was made during the reduction of sorption data. Solute concentrations of the initial aqueous solutions and equilibrated aqueous solutions were analyzed on a reversed-phase HPLC (Hewlett-Packard model 1100, ODS, 5 μm, 2.1 × 250 mm C-18 column) with both diode array UV

<table>
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<tr>
<th>Samples</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>O/C</th>
<th>H/C</th>
<th>N2-SSA m2/g</th>
<th>N2-Vo μg/g</th>
<th>CO2-SSA m2/g</th>
<th>CO2-Vo μg/g</th>
<th>Ash</th>
<th>R0</th>
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<td>2.49</td>
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<td>0.19</td>
<td>0.81</td>
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<td>nd</td>
<td>nd</td>
<td>50.97</td>
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<td>1.82</td>
<td>0.23</td>
<td>7.49</td>
<td>0.24</td>
<td>0.94</td>
<td>7.93</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>67.26</td>
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<tr>
<td>C08</td>
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<td>0.46</td>
<td>8.80</td>
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<td>0.94</td>
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<td>2.45</td>
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<td>13.6</td>
<td>0.20</td>
<td>0.58</td>
<td>4.28</td>
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<td>nd</td>
<td>nd</td>
<td>32.93</td>
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<td>0.24</td>
<td>0.85</td>
<td>6.71</td>
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<td>0.77</td>
<td>0.18</td>
<td>3.09</td>
<td>0.13</td>
<td>0.12</td>
<td>16.7</td>
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<td>nd</td>
<td>nd</td>
<td>78.66</td>
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<tr>
<td>BZ</td>
<td>68.1</td>
<td>4.51</td>
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<td>0.21</td>
<td>0.79</td>
<td>7.4</td>
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<td>85.0</td>
<td>6.59</td>
<td>0.50</td>
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<td>JP</td>
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<td>3.85</td>
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<td>0.16</td>
<td>0.76</td>
<td>4.91</td>
<td>10</td>
<td>169</td>
<td>73.0</td>
<td>8.10</td>
<td>0.52</td>
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<td>XA</td>
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<td>4.14</td>
<td>3.63</td>
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<td>1.61</td>
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<td>146</td>
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<td>13.91</td>
<td>1.70</td>
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<tr>
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<td>3.19</td>
<td>6.34</td>
<td>0.10</td>
<td>0.78</td>
<td>6.92</td>
<td>19</td>
<td>85.0</td>
<td>26.3</td>
<td>38.10</td>
<td>1.12</td>
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<tr>
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<td>82.5</td>
<td>3.22</td>
<td>0.53</td>
<td>1.75</td>
<td>0.02</td>
<td>0.47</td>
<td>2.57</td>
<td>10</td>
<td>253</td>
<td>84.0</td>
<td>8.93</td>
<td>2.50</td>
</tr>
</tbody>
</table>

* R0, vitrinite reflectance; N2-SSA, N2-derivived specific surface area; CO2-SSA, CO2-derivived specific surface area; N2-Vo, N2-derivived micropore volume; CO2-Vo, CO2-derivived internal hydrophobic microporosity.

a) The elemental compositions and reflectance (R0, %) were cited for the JP, XA, XW, and YX coals from Chen et al. (2005), for the BZ lignite from Larsen et al. (1995), and for the NHC (C01, C03, C08, HP04, and HP05) and BC (HP05BC) samples from Ran et al. (2007).

b) nd, not determined.
and fluorescence detector as described previously (Ran et al., 2002). The solid-phase solute concentrations were computed based on the mass balance of the solute between the two phases.

2.3. Sorption and desorption modeling

The sorption equilibrium isotherms were fitted using SYSTAT software (Version 8.0, SYSTAT Inc.) to the revised Freundlich model

\[
\log q_e = \log K_F + n \log C_r
\]

where \(q_e\) is the equilibrium solid-phase solute concentration; \(K_F\) and \(n\) are the Freundlich capacity parameter and the isotherm nonlinearity factor, respectively; \(C_r\) is the dimensionless aqueous phase concentration or gas phase pressure (\(p/p_o\)). For weakly polar and sparsely soluble compounds, \(C_r\) is related to solute activity \(a\) in water phase referenced to their respective pure liquid or supercooled liquid (scl) state at a given temperature (Carmo et al., 2000). For NOCs that are solid at the experimental temperature condition, \(C_r\) is the ratio of \(C_e\) to \(S_{\text{scl}}, S_{\text{aq}}\) for Phen is 5.18 mg/l (Ran et al., 2002). The sorption capacity parameter \(K_F\) can be normalized with OC \(K_{\text{OC}}\) (Ran et al., 2004).

3. Results and discussion

3.1. Characterization of the condensed NOM

The C contents, O/C ratios, H/C ratios of the samples range from 17.3% to 82.5%, from 0.02 to 0.24, and from 0.12 to 0.94, respectively (Table 1). The O/C and H/C atomic ratios for the NHC fractions, when plotted on the Van Krevelen diagram (Fig. 1), are similar to those of the coals (kerogen type III) derived mainly from higher plant materials, which is rich in lignin with aromatic structure. The coal samples cover a wide range of NOM maturity as vitrinite reflectance \(R_o\) varies between 0.50% and 2.50%. As dia- and catagenesis for the NOM fractions are developed, the atomic O/C and H/C ratios decrease, but the maturity index \(R_o\) increases. The O/C ratios for NHC are much lower than the average O/C ratios (0.53) for typical humic acids (HAs) extracted from soils and sediments (Ran et al., 2007; Xing and Pignatello, 1997). The BC sample (HP05BC) combusted at 375 °C from the soil sample has the lowest H/C ratio and quite low O/C, suggesting that BC has the highest degree of maturation among the investigated samples.

The measured SSA based on \(N_2\) adsorption at 77 K (\(N_2\)-SSA) for the NHC, BC, and coals ranges from 1.61 to 16.69 m²/g (Table 1). However, the surface areas of the coals based on \(C_O\) adsorption at 273 K (\(C_O\)-SSA) are much higher (85–253 m²/g) (Table 1), which are in the same order of magnitude as coals (118–207 m²/g) reported by Vorres (1990). Moreover, previous investigation showed that \(N_2\)-SSA increased as the ash content increased and organic carbon (OC) content decreased, but \(C_O\)-SSA was positively related to OC contents and inversely correlated with the ash contents (Ran et al., 2013). Hence, \(N_2\) and \(C_O\) probe different regions of the NOM matrices. \(N_2\) is adsorbed primarily on the external surface of NOM and mineral particles, while \(C_O\) additionally probes the internal porosity of NOM.

The \(^{13}C\) NMR spectra of the coals are presented in Fig. 2 and those of NHC are cited from our previous publication (Ran et al., 2007). The integration results are shown in Table S1 in the Supplemental data. Approximate band assignments are as follows: nonpolar aliphatics (0–45 ppm), methoxy (45–63 ppm), O-alkyls (63–93 ppm), aromatics (93–148 ppm), aromatic C-O (148–165 ppm), carboxylic carbon (165–187 ppm), and ketones, quinones, and aldehydes (187–220 ppm). The spectra of YX and XA are dominated by aromatic signals at around 130 ppm, and only very small aliphatic signals at 0–50 ppm are present. The spectrum of XW is also dominated by aromatic signals but its aliphatic signals are more intense than those of YX or XA. Both of the aromatic (93–165 ppm) and aliphatic signals (0–93 ppm) for the spectra of JP and BZ are significant (Fig. 2). As thermal maturity of the samples increases, their aromaticity increases while their aliphaticity is reduced. For the investigated coals, the aromaticity increases from the lignite (JP and BZ) to the bituminous coal (XW and XA), and to the anthracite coal (YX) (Table S1). For the NHC samples, the aromaticity is close to

![Fig. 1. The van Krevelen diagram for the NHC (CO1, CO3, CO8, HP04, and HP05, solid triangle), different ranks of coals (BZ, JP, XA, XW, and YX, solid circle) and BC (HP05BC, solid square) samples in Table 1. The arrow line represents the evolution pathway of chemical composition as diagenetic alteration continues for the kerogen type III. The numbers (1, 2, 3, and 4) represent different maturation stages for the investigated NOM.](image)

![Fig. 2. Cross-polarization/magic angle spinning (CP/MAS) \(^{13}C\) nuclear magnetic resonance (NMR) spectra for the investigated coals.](image)
that of the lignite except for the HP04 sample. HP04 is similar to the bituminous coal XW (Table S1). The above result is consistent with that demonstrated from the Van Krevelen diagram (Fig. 1).

3.2. Sorption and/or desorption isotherms

The sorption isotherms for Phen by the investigated samples are shown in Fig. S1 in the Supplemental data and their revised Freundlich modeling parameters are listed in Table 2. It is clear from Table 2 that the revised Freundlich equation describes the sorption isotherms for Phen quite well in the entire Ce ranges. The revised Freundlich sorption capacity $K_{\text{FOC}}$ ranges from 49.0 $\mu$/g OC to 113 $\mu$/g OC for the NHC and BC isolated from the investigated soils and sediments, and from 24.1 $\mu$/g OC to 79.0 $\mu$/g OC for the coals (Table 2). The nonlinearity factor $n$ for Phen ranges from 0.48 to 0.85.

The sorption/desorption isotherms for the benzene vapors are shown in Fig. S1. The isotherms are nonlinear and exhibit obvious hysteresis. The Freundlich sorption/desorption parameters for benzene at relative pressure from $p/p_o = 0$ to $p/p_o = 0.3$ are summarized in Table 3. At lower relative pressure ($p/p_o < 0.3$), the benzene sorption isotherms are well fitted to the nonlinear Freundlich model for the investigated samples. The isotherms for benzene are strongly nonlinear, with $n$ ranging from 0.221 to 0.598 for the sorption and 0.097 to 0.349 for the desorption (Table 3).

It is obvious that the benzene isotherms are more nonlinear than the Phen isotherms, which may be related to the fact that the benzene vapor adsorption on the minerals does not compete with the water molecule adsorption. In water solutions, the adsorption of NOCs by soil minerals is suppressed by water, and the soil uptake consists primarily of solute sorption into the organic matter (Chiou et al., 1988). Moreover, previous investigations reported the different adsorption behaviors for benzene vapor on soils and sediments. Chiou and Shoup (1985) reported that vapor sorption isotherms of benzene and other organic liquids on soil humic acid were highly linear over a wide range of $p/p_o$, which was attributed to the partitioning of organic compounds in soil humic acid. However, Lin et al. (1996) found that sorption equilibrium of benzene by a dry soil was well described by the nonlinear Freundlich isotherm ($n < 0.42$). As the relative humidity increased from zero to 33%, the isotherm gradually changed from nonlinearity to linearity, and the soil sorption capacity decreased. Farrell and Reihard (1994a,b) suggested that the existence of intragrain microporosity on micro- and mesoporous silica gels or glass beads may be responsible for the nonlinearity of gaseous NOC adsorption. In glassy polymers (1.4–1.7) (Crittenden et al., 1999) we compared the revised Freundlich model with that of the Polanyi–Dubinin–Manes model, and found that the exponent term $b$ was close to 1. Hence, we only used the Freundlich model to explain our experimental data. When $b = 1$, the revised Freundlich model is a special form of PDM model.

3.3. Sorption and desorption hysteresis of benzene vapor

The desorption hysteresis indices (HI) $(n_{\text{desorption}}/n_{\text{sorption}})$ for benzene are presented in Table 3. As HI is smaller, the desorption hysteresis is larger. It is observed that different degrees of desorption hysteresis are present for the NHC and coal samples. The most likely explanation for the hysteresis of benzene in these samples is the irreversible pore deformation and entrapment of sorbing molecules (Weber et al., 2002). As benzene enters the solid, it could be adsorbed in nanopores in the open sectors. Hydrophobic sorbate molecules may also expand or penetrate condensed NOM matrices at high $q_e$ values, generating “tenant pores” in which they then reside (Braidaitis et al., 2001; Huang and Weber, 1997). This matrix expansion process is highly dependent on the compatibility (similarity of solubility parameters) of the sorbate and the NOM matrices and is likely rate-controlled by diffusion process (Huang and Weber, 1997; Pignatello and Xing, 1996). In the desorption stage, the aqueous-phase solute concentration decreases abruptly, and the NOM configuration may be changed. In addition, Fig. 3 shows that the HI values are inversely related to the OC contents and are positively correlated with the ash contents ($p < 0.01$), suggesting that the organic matter is the major factor for the hysteresis of benzene. This pore deformation mechanism could in part explain the observed desorption hysteresis of benzene at high benzene pressure ($p/p_o > 0.3$).

Entrapment of benzene in the nanopore is also important for the investigated samples. XA and YX are high-rank coals with $R_o$ of 1.7% and 2.5%, respectively (Table 1). It is noted that their glassy-transition temperatures are higher than 600 K (Pignatello and Xing, 1996). Hence,

<table>
<thead>
<tr>
<th>Samples</th>
<th>$K_{\text{F}(\text{OC})}$</th>
<th>$K_{\text{FOC}(\text{OC})}$</th>
<th>$S^e$</th>
<th>$n$</th>
<th>$SE^s$</th>
<th>$R^2$</th>
<th>$N^s$</th>
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<td>31.1</td>
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<td>0.044</td>
<td>0.97</td>
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$^a$ OC normalized Freundlich $K_o$.

$^b$ Standard error of $K_o$.

$^c$ Standard error of $n$.

$^d$ Number of observations.
their NOM structures are the most rigid, and should be the least expanded by benzene among the investigated samples. However, they showed the highest hysteresis (Table 3). For HP05BC, it also shows the higher NOM maturation degree (Fig. 1), and the higher rigid NOM structure, although its O/C atomic ratio is slightly higher than that of XA or YX. However, it also exhibits one of the lowest hysteresis among the samples (Table 3). The above phenomenon may be related to the NOM structure and nanopore size distribution. Transmission electron microscopy illustrated that pore diameters in exinite and inertinite of coals ranged from 20 to 100 nm, with most of the pores varying from 2 to 50 nm, but those in vitrinite were smaller than 2 nm (Harris and Yust, 1976). In kerogen samples at low and medium

<table>
<thead>
<tr>
<th>Samples</th>
<th>$K_F(\mu l/g)$</th>
<th>SEa</th>
<th>$n_{sorption}$</th>
<th>SEb</th>
<th>$R^2$</th>
<th>N</th>
<th>$K_F(\mu l/g)$</th>
<th>SE</th>
<th>$n_{desorption}$</th>
<th>SE</th>
<th>$R^2$</th>
<th>N</th>
<th>$R_{\text{desorption}}/R_{\text{sorption}}$</th>
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<tr>
<td>C01</td>
<td>43.4</td>
<td>0.95</td>
<td>0.60</td>
<td>0.017</td>
<td>1.00</td>
<td>9</td>
<td>39.1</td>
<td>0.24</td>
<td>0.23</td>
<td>0.006</td>
<td>0.99</td>
<td>9</td>
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<td>C03</td>
<td>20.5</td>
<td>0.39</td>
<td>0.47</td>
<td>0.014</td>
<td>1.00</td>
<td>9</td>
<td>25.1</td>
<td>0.66</td>
<td>0.31</td>
<td>0.010</td>
<td>0.99</td>
<td>9</td>
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<td>2.16</td>
<td>0.49</td>
<td>0.011</td>
<td>1.00</td>
<td>9</td>
<td>52.6</td>
<td>2.00</td>
<td>0.35</td>
<td>0.016</td>
<td>0.99</td>
<td>9</td>
<td>0.615</td>
</tr>
<tr>
<td>HP04</td>
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<td>0.64</td>
<td>0.59</td>
<td>0.026</td>
<td>0.99</td>
<td>9</td>
<td>24.4</td>
<td>0.59</td>
<td>0.21</td>
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<td>0.23</td>
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<td>1.68</td>
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<tr>
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<td>1.00</td>
<td>9</td>
<td>25.0</td>
<td>1.02</td>
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<td>9</td>
<td>0.496</td>
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<td>38.2</td>
<td>0.41</td>
<td>0.10</td>
<td>0.003</td>
<td>0.99</td>
<td>9</td>
<td>0.198</td>
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</tbody>
</table>

- Standard error of $K_F$.
- Standard error of $n$.
- Number of observations.

Fig. 3. Correlations between hysteresis index of benzene and the aromatic C (a), volume obtained from CO$_2$ adsorption isotherm (a), ratios of O/C (c) and H/C (d), organic carbon (OC) (e), and ash contents (%) (f) on the investigated samples.
degrees of catagenesis, the interlayer spacings are widely spread (0.34–
more than 0.8 nm), probably due to the fixation of non-aromatic groups
on the graphitic layer which prevent them from getting closer. As
catagenesis progresses, the non-aromatic groups begin to disappear
and the interlayer spacing spreading decreases (Durand, 1980). Moreover,
the correlation analysis shows that the HI values are significantly
related to the aromaticity and H/C, and marginally significantly to
nano particle volume and O/C and H/C ratios for the samples (Fig. 3). As
the aromaticity is elevated, and O/C and H/C ratios are reduced, the
NOM maturation is elevated, and the benzene hysteresis increases. As
the nanoparticle volume derived from the CO2 sorption is the higher, the
more benzene is trapped in the NOM matrix. In addition, previous in-
vestigation demonstrated that aromatic NOCs can form the specific
π–π bonds with the aromatic rings of the condensed NOM (Zhu et al.,
2004). Huang and Weber (1997) also observed that the desorption hys-
teresis of Phen was closely associated with the aromatic C of the peat,
shale, and kerogen samples. The above result suggests that the entrap-
ment of benzene in NOM nanopore and aromatic graphitic interlayers is
likely responsible for the observed hysteresis of benzene.

3.4. Relationship of adsorption with sorbent properties

The KFOC values for Phen and benzene are related to some of the
physicochemical properties for the condensed NOM (Fig. 4). They are
significantly related to the aliphatic carbons ($p<0.01$) and inversely
correlated with the aromatic carbons of the NOM ($p<0.01$). Moreover,
the positive correlations between KFOC and H/C or O/C ratios for Phen
on the investigated samples are significant (Fig. 4). The observed signifi-
cant correlations are generally consistent with prior studies except for
that between KFOC and aliphatic carbon for Phen (Ran et al.,
2007). This investigation suggested that even the coal samples with different NOM maturation degrees also showed the similar phenomenon. In addition, the nearly overlapped correlations between KFOC and aliphatic carbon for Phen and benzene (Fig. 4) suggest that water molecules could not affect the nanopore filling of NOM on the condensed NOM. Hence, the above results further suggest that the NOM structures and nanoparticles are responsible for the ob-
served difference in the adsorption capacity for the gaseous benzene and
the aqueous Phen.

As the NHC fractions and the low maturation coals contain high polyethylene, they exhibit high sorption capacity for benzene and Phen. The glassy and resistant aliphatic carbon might be more non-
polar than the corresponding aromatic carbon with oxygen-containing
functional groups. Moreover, as the OM maturation for YX is the
highest, the spacings between aromatic interlayers are the smallest.
The Phen and benzene molecules could not enter a portion of the aromat-
ic interlayers, but the CO2 molecules could enter all of the aromatic inter-
layers. Hence, the Phen or benzene adsorption volume is much lower
than the CO2 adsorption volume on the YX anthracite (Tables 1–3). This
study further suggests that the NOM nanopore size has an important in-
fluence on the NOC adsorption.

Two possible types of adsorption sites had been proposed for car-
bonaceous geosorbents (Cornelissen et al., 2005): (i) sorption on the external surface, and (ii) adsorption in nanopores inside the sorb-
ents. In this study, the N2-SSA of the condensed NOM is a measure of
the outer surface on the minerals and organic matter. But, the
CO2-SSA of coals were found to be one to two orders of magnitude
higher than the N2-SSA, and the adsorption volume CO2–V0 is close
to the benzene and Phen adsorption volume estimated by the revised
Freundlich model. These results further provide the direct evidence to
support our hypothesis that the adsorption in nanopores is the dom-
inant mechanism for the sorption of Phen and benzene on the con-
densed NOM. Furthermore, this study shows that the condensed
NOMs rich in aliphatic carbons have higher adsorption volumes for
benzene and Phen.

Fig. 4. Correlation of the phenanthrene (Phen) and benzene capacity parameters with physicochemical properties of the samples. Aliphaticity% = 100 − Aromaticity%, which is listed in Table S1 in the Supplemental data.
4. Conclusions
The above results provide important implications for the interpretation of sorption mechanisms of organic contaminants in SOM. Our data support the concept of “adsorption” of NOCs in the internal nanopores of NOM. Moreover, quantitative estimates of nanopore and surface area derived from the CO₂ or benzene adsorption allow for a more specific formulation of this concept. The majority of total surface area is formed by nanometer scale pores. Finally, the findings suggest a possible mechanism for sequestration of chemicals.

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Appendix A. Supplementary data
One table containing the integral results of ¹³C NMR spectra, one figure illustrating the sorption and desorption isotherms of benzene and Phen sorption isotherms, and one figure showing the correlation between the adsorption volumes of benzene and Phen. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.geoderma.2013.04.008.

References
Chiou, C.T., Shoup, T.D., 1985. Soil sorption of organic vapors and effects of humidity on sorption (CBET-0853950). This is contribution No. IS-1630 from GIGCAS.