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# Sorption of polycyclic aromatic hydrocarbons to soils enhanced by heavy metals: perspective of molecular interactions

Xiao Liang[1,2] · Lizhong Zhu[1,2] · Shulin Zhuang[1]

**Abstract**

*Purpose* Combined pollution by polycyclic aromatic hydrocarbons (PAHs) and heavy metals are commonly found in industrial soils. This study aims to investigate the effect of the coexistence of heavy metals on the sorption of PAHs to soils. We focused specifically on the relationship of the sorption capacity with the estimation of the binding energy between PAHs and heavy metals.

*Materials and methods* The sorption of typical PAHs (naphthalene, phenanthrene, and pyrene) to soils coexisting with heavy metals (Cu(II), Pb(II), and Cr(III)) was characterized in batch sorption experiments. The binding energy between PAHs and heavy metals in aqueous solution was estimated by quantum mechanical (QM) method using density functional theory (DFT) at the M06-2x/def2svp level of theory.

*Results and discussion* Sorption capacity and nonlinearity of the PAHs to the soils were enhanced by the coexisting heavy metals. The extent of increment was positively associated with the hydrophobicity of the PAHs and the electronegativity and radius of the metal cations: $Cr(II) > Pb(II) > Cu(II)$. The cation-$\pi$ interaction was revealed as an important noncovalent binding force. There was a high correlation between the binding energies of the PAHs and $K_f'$ ($K_f$ adjusted after normalizing the equilibrium concentration ($C_e$) by the aqueous solubility ($C_s$)) ($R^2 > 0.906$), indicating the significant role of the cation-$\pi$ interactions to the improved PAH sorption to soils.

*Conclusions* In the presence of heavy metals, the sorption capacities of naphthalene, phenanthrene, and pyrene to soils were enhanced by 21.1–107 %. The improved sorption capacity was largely contributed from the potent interactions between PAHs and heavy metals.

**Keywords** Heavy metals · PAHs · Molecular interactions · Soil · Sorption

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## 1 Introduction

Hydrophobic organic contaminants (HOCs), such as polycyclic aromatic hydrocarbons (PAHs), often coexist with heavy metals in industrial soils, including e-waste dismantling sites, gas works, and coking plants (Abel et al. 2015; Vácha et al. 2015; Zhang et al. 2012; Zhong and Zhu 2013). The combined pollution poses risks to the environment and human health (Alternatives 1994; Khan and Cao 2012; Lin et al. 2005; Zheng et al. 2014). For assuring food security and implementing remediation strategies, it is critical to understand the mechanism on the transport and fate of HOCs in the presence of heavy metals in soils.

Sorption behavior of PAHs to soils may be influenced by coexisting heavy metals. For instance, the sorption capacity of phenanthrene to soils was increased after being polluted by heavy metals, which was due to parts of rubbery organic carbon which became condensed on soil

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surfaces and the sorbed organic carbon which had a larger sorption affinity to PAHs (Gao et al. 2006; Luo et al. 2008, 2010). Different structure and composition of heavy metals could have distinct influence on PAH sorption. The hard metal cations formed shells of dense water by surface complexation, inhibiting the sorption of PAHs, while softer metal cations increased the hydrophobic of the local region, enhancing the sorption affinity of PAHs to materials (Xiao et al. 2007; Liu et al. 2012; Zhang et al. 2015). Additionally, acidic conditions were shown to be more favorable for phenanthrene sorption, probably via lowering the polarity of humic materials (Zhu et al. 2004a; Ping et al. 2006).

While most studies focused on the effects of soil organic matter (SOM), the cation-π interaction between PAHs and heavy metal cations also contributed to PAH sorption (Keiluweit and Kleber 2009). Furthermore, ^{1}H nuclear magnetic resonance (NMR) spectroscopy and batch experiments indicated that saturated minerals with metal cations generally increased the sorption capacity of PAHs by forming cation-π bonding between PAHs and exchangeable metal cations accumulated on mineral surfaces (Qu et al. 2008; Zhu et al. 2004b). Zhang et al. (2011) found a stronger enhancement of phenanthrene sorption by Pb(II) after removing a portion of organic matter, which was caused by the cation-π bonding between the sorbed metal cations and the aromatic ring of phenanthrene in solution.

However, the cation-π interaction was usually estimated or speculated on surface of minerals or biogenic lipids (Qu et al. 2007; Zhang et al. 2011), but rarely in natural soils. The magnitude of the cation-π binding energy was about five times higher than those of a hydrogen bond and an inner-/outer-sphere complex formation (Keiluweit and Kleber 2009), which could be competitive with the expected strongest noncovalent binding forces. As heavy metal cations may accumulate at the soil-water interface, the formation of cation-π bonding may influence the sorption behavior of PAHs. The cation-π interaction energies are not directly related to the sorption capacity of PAHs to soils. Thus, quantum mechanics is needed to calculate the binding energy.

This study aims to (1) quantify the sorption properties of PAHs to soils in the presence of heavy metal cations; (2) estimate the bonding energy between heavy metal cations and PAH molecules; and (3) investigate the relationship between the sorption capacity and the binding energy. Batch sorption experiments and quantum mechanical calculation were conducted to investigate the effects of common heavy metals on sorption of typical PAHs to soils. The obtained results were expected to facilitate the understanding of the mechanisms on the transformation and migration of PAHs coexisting with heavy metals in soils.

## 2 Materials and methods

### 2.1 Soils and chemicals

Two typical soils in China were included in this study. Soil 1 (paddy soil) was collected from Zhejiang Province, and soil 2 (black soil) was collected from Heilongjiang Province. The soil samples were taken from the surface layer (0–20 cm depth), air-dried, and sieved through a 100-nylon-fiber mesh. The soil organic carbon (SOC) was determined by the Shimadzu SSM-5000A. The pH values of the soils were measured with a glass electrode in a 1:2.5 soil/water (w/v) suspension. The cation exchange capacity (CEC) was measured by the $NH_4Ac$ exchange method (Lu 2000). The content of metal was determined by flame atomic absorption spectrophotometry (FAAS) (Tokalioğlu et al. 2000). The properties of the soils are listed in Table 1. None of the soil samples were contaminated with PAHs or heavy metals.

Naphthalene, phenanthrene, and pyrene, which commonly exist in contaminated soils, were purchased from Acros Organics, with physicochemical properties listed in Table 2. Heavy metal nitrates, $Cu(NO_3)_2$, $Pb(NO_3)_2$, and $Cr(NO_3)_3$, obtained from Aladdin Industrial Corporation, were selected as the coexisting heavy metals, as Cu(II), Pb(II), and Cr(III) are usually present together with PAHs. All PAHs and heavy metals were of A.R. grade.

### 2.2 Batch sorption experiments

Batch sorption experiments were performed in polytetrafluoroethylene (PTFE) screw cap vials at 25 °C. PAH compounds were dissolved in methanol to prepare stock solution. Background solution (pH = 6.0) containing

**Table 1** Soil properties

| Soil | Location | OC (%) | CEC (cmol kg$^{-1}$) | Clay (%) | Slit (%) | Sand (%) | pH[a] |
|------|----------|--------|----------------------|----------|----------|----------|-----|
| 1 | Zhejiang | 0.55 | 11.2 | 10.4 | 88.1 | 1.48 | 7.00 |
| 2 | Heilongjiang | 3.60 | 33.1 | 38.1 | 52.5 | 9.44 | 7.03 |

CEC cation exchange capacity

[a] pH, 1:2.5 (soil/H$_2$O)

**Table 2** Properties of naphthalene, phenanthrene, and pyrene

| PAH | MW (g mol$^{-1}$) | $C_s$ (mg L$^{-1}$) | log$K_{ow}$ |
|---|---|---|---|
| Naphthalene | 128.2 | 31.7 | 3.33 |
| Phenanthrene | 178.2 | 1.29 | 4.55 |
| Pyrene | 202.3 | 0.135 | 4.81 |

*MW* molecular weight, $C_s$ aqueous solubility at room temperature, $K_{ow}$ octanol-water partition coefficient

0.01 mol L$^{-1}$ NaNO$_3$ in deionized water with 200 mg L$^{-1}$ NaN$_3$ as a bio-inhibitor was used. PAH stock solutions were diluted to various concentrations by background solution, which contains 0.01 mol L$^{-1}$ heavy metal cations (Cu(II), Pb(II), or Cr(III) in nitrate). Then, the mixed solution was added in PTFE vials (8 or 22 mL) placed with soil 1 and soil 2. The solid-to-water ratios for naphthalene, phenanthrene, and pyrene were 0.8 g/8 mL, 0.4 g/22 mL, and 0.05 g/20 mL, respectively. Different solid-to-water ratios were chosen to ensure 20–90 % of the sorbate to be sorbed at equilibrium. The volume of methanol in working solution was regulated to less than 0.1 % to refrain from cosolvent effect. Each concentration point of the isotherm including blank and calibration control was run in duplicate. To exclude the effect of hydrolytic acidification caused by metal cations, the pH value of the solution was adjusted to $6 \pm 0.1$ by 0.1 mol L$^{-1}$ HNO$_3$ and NaOH solution. The pH was set to 6.0, where most of the heavy metals exit in free cation form (Rafatullah et al. 2009; Pei et al. 2014). All vials were placed on a shaker and agitated in the dark at 170 rpm for 72 h (according to preliminary experiments) to reach equilibrium.

## 2.3 Analytical methods

After centrifugation, the supernatants were passed through a 0.45-μm membrane filter. The PAH concentrations were analyzed by Agilent 1200 HPLC (XDB-C 18 column, 4.6 mm × 250 mm × 5 μm) with a fluorescence detector. Isocratic elution was performed at a flow rate of 1.0 mL min$^{-1}$ using the methanol/water (90:10) mobile phase. The wavelengths for measurements of naphthalene, phenanthrene, and pyrene were at excitation wavelengths of 225, 244, and 237 nm while at emission wavelengths of 335, 360, and 385 nm, respectively. Chromatography was performed at 30 °C. Heavy metal cation concentrations in solution were determined by



**Fig. 1** Sorption of **a** naphthalene, **b** phenanthrene, and **c** pyrene to soil 1 and soil 2 (*dots*) and best fit Freundlich isotherm equation (*lines*). The equilibrium concentration ($C_e$) is normalized by the water solubility ($C_s$), and the Freundlich parameters are listed in Table 3
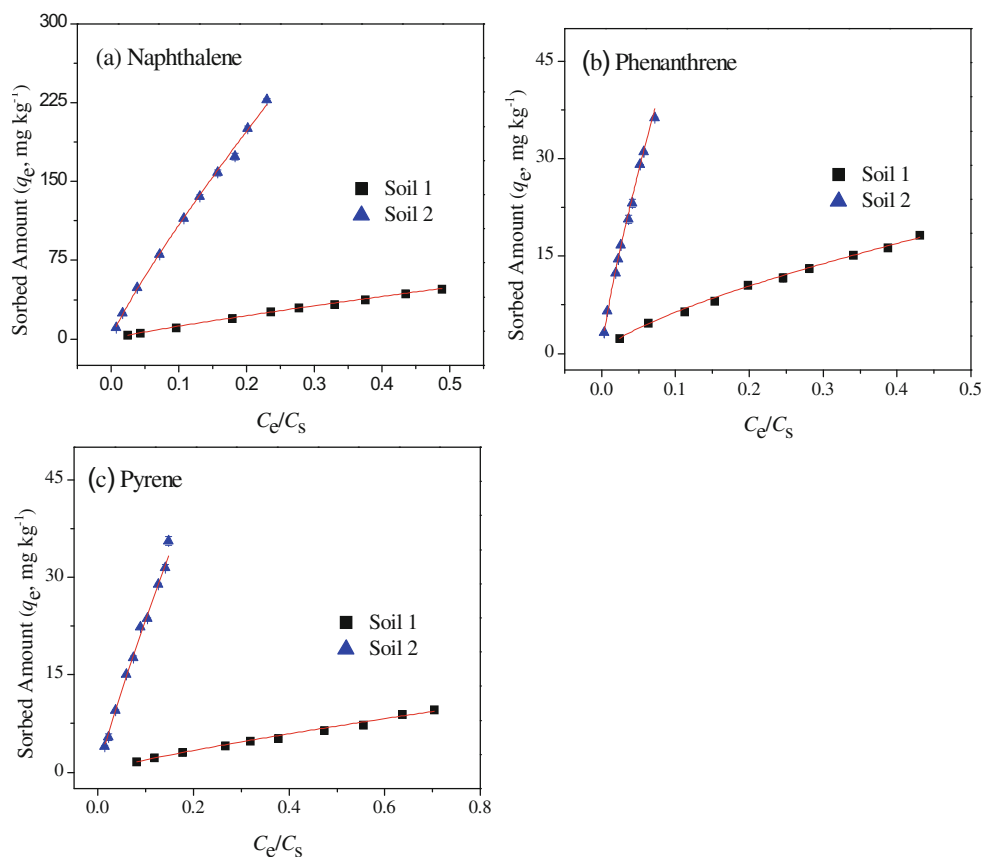
**Table 3** Freundlich parameters for the sorption of naphthalene, phenanthrene, and pyrene to soil 1 and soil 2

| PAH | Soil | Control | | | Cu(II) | | | Pb(II) | | | Cr(III) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $K_f'$ | $n$ | $R^2$ | $K_f'$ | $n$ | $R^2$ | $K_f'$ | $n$ | $R^2$ | $K_f'$ | $n$ | $R^2$ |
| Naphthalene | 1 | 96.5 (1.02)[d] | 0.86 (0.0078) | 0.998 | 101 (2.70) | 0.82 (0.017) | 0.998 | 116 (1.08) | 0.76 (0.0073) | 0.996 | 123 (4.19) | 0.71 (0.017) | 0.997 |
| | 2 | 799 (12.5) | 0.87 (0.0066) | 0.999 | 846 (7.07) | 0.82 (0.0040) | 0.999 | 877 (16.4) | 0.76 (0.010) | 0.999 | 896 (10.6) | 0.69 (0.0029) | 0.999 |
| Phenanthrene | 1 | 33.7 (0.993) | 0.73 (0.021) | 0.995 | 35.1 (0.215) | 0.68 (0.0038) | 0.995 | 40.7 (0.781) | 0.65 (0.0088) | 0.999 | 41.5 (0.372) | 0.55 (0.0046) | 0.999 |
| | 2 | 246 (16.0) | 0.74 (0.021) | 0.997 | 251 (12.4) | 0.70 (0.015) | 0.997 | 270 (7.36) | 0.67 (0.0074) | 0.997 | 307 (19.0) | 0.66 (0.015) | 0.996 |
| Pyrene | 1 | 12.6 (0.192) | 0.82 (0.0088) | 0.999 | 15.6 (0.415) | 0.78 (0.014) | 0.999 | 19.5 (0.243) | 0.74 (0.012) | 0.994 | 26.1 (2.01) | 0.72 (0.034) | 0.966 |
| | 2 | 178 (9.12) | 0.88 (0.022) | 0.997 | 186 (2.18) | 0.84 (0.0047) | 0.997 | 215 (4.38) | 0.81 (0.0070) | 0.999 | 236 (5.62) | 0.72 (0.0082) | 0.998 |

Data in parentheses are standard errors

$K_f'$ adjusted Freundlich affinity coefficient ($K_f$) after normalizing the equilibrium concentration ($C_e$) by the aqueous solubility ($C_s$), $n$ the exponential coefficient indicating isotherms nonlinearity, $R^2$ adjusted coefficient of determination

FAAS. The amount of PAH and metal cation sorption to soils was calculated as the difference between the initial and equilibrium concentrations.

## 2.4 Zeta (ζ) potential measurements

The soil suspensions for zeta potential measurements contained 0.1 % solid in 0.01 mol L$^{-1}$ NaNO$_3$ in the absence or presence of Cu(II), Pb(II), or Cr(III) (1.0 mmol L$^{-1}$) (Luo et al. 2006). Before measurement, the suspension was exposed to ultrasonic dispersion for 20 min. After stabilization, the pH value was registered to various pH by 0.1 mol L$^{-1}$ HNO$_3$ and NaOH. Then, the zeta (ζ) potentials were measured ($N = 5$) on the basis of microelectrophoresis measurements using Zetasizer (Nano ZS90, Malvern Instruments).

## 2.5 Data analysis

The distribution sorption coefficient of solute between soil and water is calculated by Eq. (1). The Freundlich model was employed to describe the sorption of PAHs as in Eq. (2):

$$K_d = q_e / C_e \tag{1}$$
$$q_e = K_f C_e^n \tag{2}$$

where $q_e$ (mg kg$^{-1}$) is the sorbed amounts of PAHs to soil, $C_e$ (mg L$^{-1}$) is the equilibrium concentration, $K_f$ (mg$^{1-n}$ L$^{-n}$ kg$^{-1}$) is the Freundlich affinity coefficient, and $n$ is the exponential coefficient which indicates isotherm nonlinearity. To compare different isotherms directly, a modified Freundlich parameter, $K_f'$ (mg kg$^{-1}$) was adjusted after normalizing $C_e$ by the aqueous solubility value ($C_s$) (Carmo et al. 2000; Feng et al. 2006):

$$C_r = C_e / C_s \tag{3}$$
$$q_e = K_f' C_r^n, \tag{4}$$

The values of $K_f'$ and $n$ for all sorption isotherms were calculated by the Freundlich equation fitted using Origin 8.0.

## 2.6 Gibbs free energy calculation

The geometries of PAHs and their complexes were optimized using the density functional theory (DFT) by the Gaussian 09 program (Frisch et al. 2009). The single-point energies were calculated at the M06-2x/def2svp level of theory (Zhao and Truhlar 2008). The calculations were performed in aqueous environment, and the effect of solvent was treated using the polarized continuum model (PCM) (Barone and Cossi 1998). The binding energies were calculated as the difference between Gibbs free energies of the PAH-metal complex and the total energy of individual PAHs and metals.

**Fig. 2** Sorption of naphthalene, phenanthrene, and pyrene to soil 1 and soil 2 affected by Cu(II), Pb(II), and Cr(III) (1.0 mmol L$^{-1}$) (*dots*) and best fit Freundlich isotherm equation (*lines*). The equilibrium concentration ($C_e$) is normalized by the water solubility ($C_s$), and the Freundlich parameters are listed in Table 3
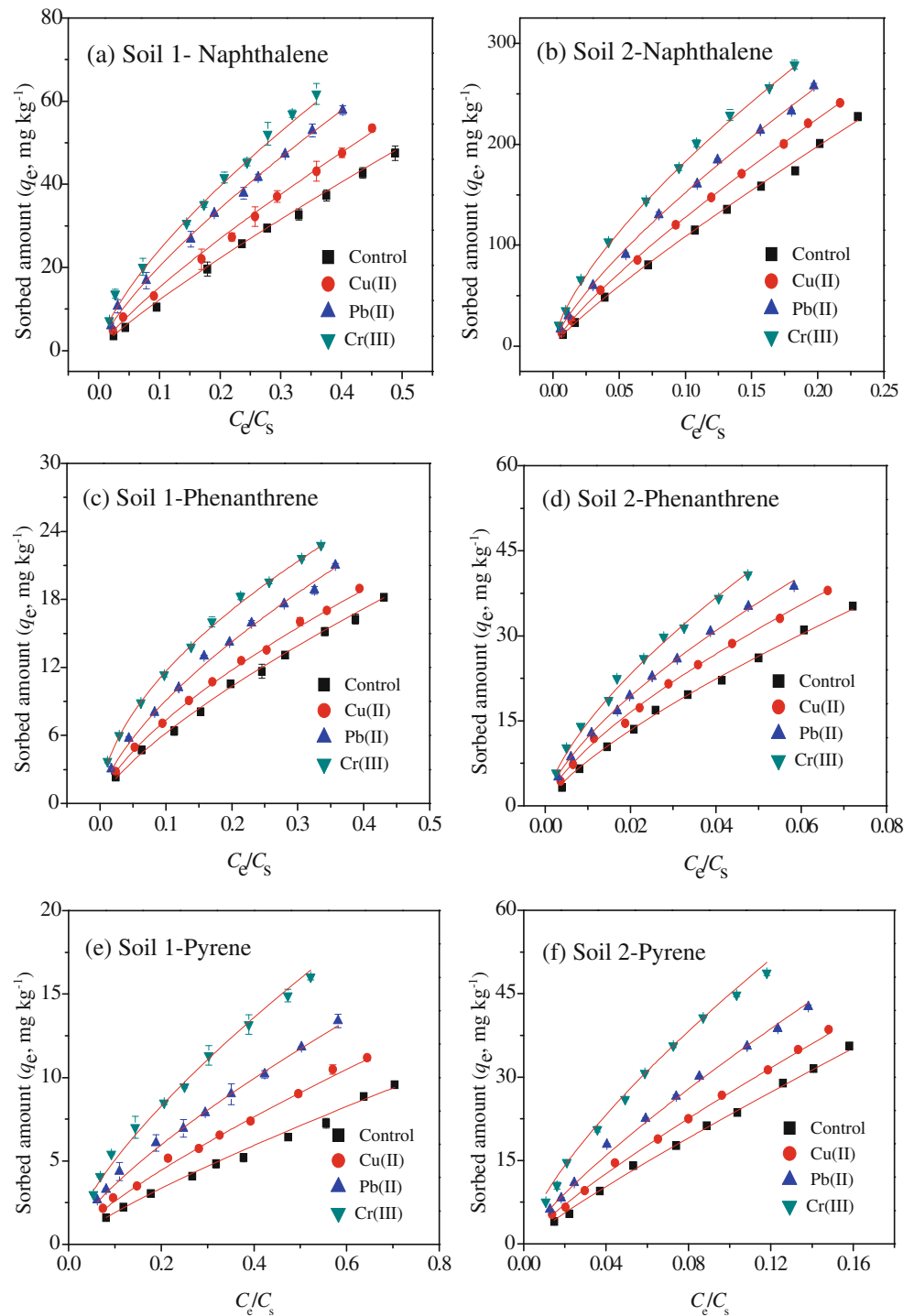
# 3 Results and discussion

## 3.1 Sorption of PAHs to two soils

The sorption isotherms of naphthalene, phenanthrene, and pyrene to the two soils are shown in Fig. 1. The sorption characteristics were adequately captured by the Freundlich model, with adjusted coefficients of determination ($R^2$) larger than 0.995 (Table 3). The sorption capacity of PAHs was different in the two soils. For naphthalene, $K_f'$ for the two soils was 96.5–799 mg kg$^{-1}$. Soil 2 (with higher SOC) had higher $K_f'$ (Fig. 1a), indicating the important effect of organic carbon on PAH sorption (Chiou et al. 1983). Similar results were found for phenanthrene ($K_f'$, 33.7–246 mg kg$^{-1}$) (Fig. 1b)

**Fig. 3** The relationship between the distribution sorption coefficient ($K_d$) and the equilibrium concentration ($C_e$) of naphthalene, phenanthrene, and pyrene
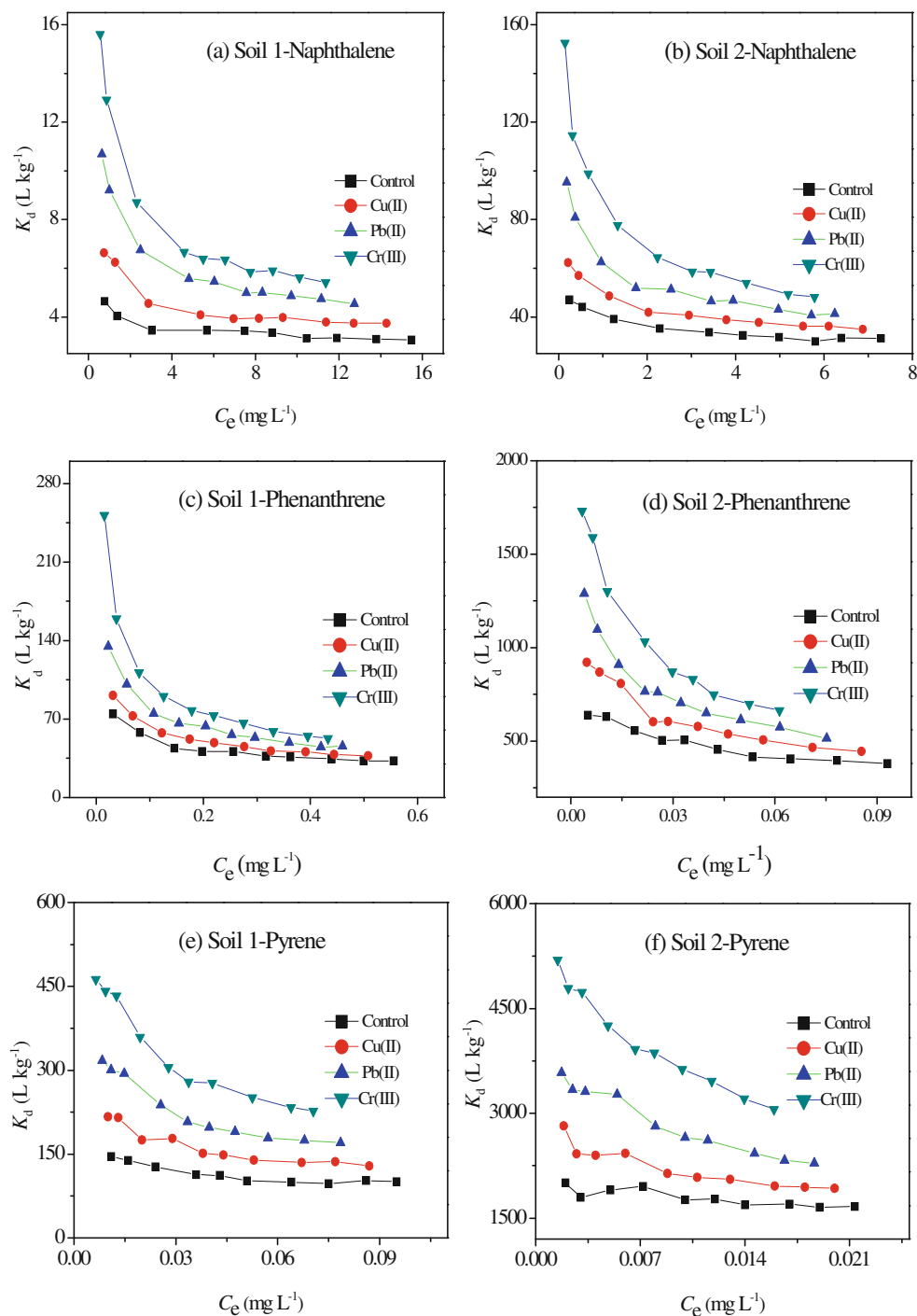


and pyrene ($K_f'$, 12.6–178 mg kg$^{-1}$) (Fig. 1c). As opposed to the empirical pattern that the sorption capacities of PAHs are positively associated with their hydrophobic properties ($K_{ow}$) (Chiou et al. 1979), the order of $K_f'$ was in a reverse order to the $K_{ow}$ of the three PAHs (Table 2). It could be mainly due to that the aqueous solubility values ($C_s$) of naphthalene were larger than those of phenanthrene and pyrene (Table 2). On the basis of Eq. (4) and the sorption isotherms, $K_f'$ was negatively correlated with $K_{ow}$.

All the sorption isotherms exhibited nonlinearity with the values of $n$ below 0.88 (Table 3). The nonlinear sorption phenomenon of PAHs to soils could be explained by a dual reactive domain model (Huang et al. 1997; Huang and Weber 1997; Wang et al. 2005). The nonlinearity of PAH sorption depended on the rigidity of SOC (Xing and Pignatello 1997; Xing 2001; Yuan and Xing 2001). Humic acids were considered to be soft (rubbery) organic carbon (OC) and yet humin was hard (glassy) OC, which had been verified by the NMR

results (Xing and Chen 1999). Partitioning happened in both rubbery and glassy domains, whereas nonlinear sorption only occurred in glassy domains (Xing 2001). In general, $K_d$ values should be a constant in the partitioning process, but the $K_d$ values decreased rapidly at lower equilibrium concentrations and stabilized at higher concentrations (Fig. 4). It seemed that nonlinear sorption of PAHs to soils took place at relatively low concentrations, and the partitioning became the dominant process at high concentrations.

## 3.2 Sorption of PAHs to soils enhanced by heavy metal cations

The effects of heavy metal cations on the sorption of naphthalene, phenanthrene, and pyrene are presented in Fig. 2. The Freundlich model almost perfectly fitted the isotherms, with adjusted coefficients of determination ($R^2$) larger than 0.986 (Table 3). A large difference in the sorption as reflected by $K_f'$ capacity was observed between the two soils. Comparing $K_f'$ of the sorption isotherms, we could deduce that the presence of heavy metal cations indeed enhanced the PAH sorption to soils.

As seen in Fig. 2a, b, the sorption isotherms of naphthalene in the two soils slightly shifted up with the addition of 1.0 mmol L$^{-1}$ Cu(II), Pb(II), or Cr(III). $K_f'$ of naphthalene increased from 96.5 to 123 mg kg$^{-1}$ in soil 1 and increased from 799 to 896 mg kg$^{-1}$ in soil 2 (Table 3). The increment of sorption capacity was in the following order: Cu(II) < Pb(II) < Cr(III) (Fig. 2a). In particular, higher effects of Cr(III) than the other two heavy metal cations were clearly observed for both soils, probably due to their being more charged by 1 valence of Cr(III) and its greater sorption capacity in the two soils (Fig. S1, Electronic Supplementary Material). The sorption isotherms of phenanthrene and pyrene affected by heavy metal cations were similar to that of naphthalene (Fig. 2c–f). When Cr(III) presented in solution, the sorption affinity of naphthalene to soil 1 and soil 2 was

enhanced by 27.5 and 12.1 %, respectively. In addition, $K_f'$ of phenanthrene and pyrene for soil 1 was enhanced by 29.1, and 107 %, respectively, and by 24.8 and 32.6 % for soil 2 (Table 3).

The enhanced sorption capacity by the heavy meal cations was in the same order with that of the PAH hydrophobicity ($K_{ow}$) (Table 2). The nonlinearity of naphthalene sorption to the two soils was also enhanced by the metal cations, since the exponential coefficients ($n$) decreased from 0.86 to 0.71 for soil 1 and decreased from 0.87 to 0.69 for soil 2 (Table 3). A lower $n$ indicated higher heterogeneity of a sorption site (Carmo et al. 2000; Delle Site 2001). In other words, the apparent diversity of energy sites was increased by the heavy metal cations, resulting in more sorption sites for PAHs. Thus, the nonlinearity of PAH sorption to soils was enhanced (Luo et al. 2008, 2010).

Higher SOC content caused stronger enhancement of sorption affinities modified by the metal cations. The absolute increment of sorption capacity of naphthalene in soil 2 (97 mg kg$^{-1}$) was higher than that in soil 1 (26.5 mg kg$^{-1}$). The sorption affinities of the PAHs enhanced by the heavy metal cations were higher in soil 1 than in soil 2 (Table 2). Parts of the flexible SOC may be coordinated with the heavy metal cations and tended to be condensed on the soil surfaces (Yang et al. 2001; Lu and Pignatello 2004). Thus, with the complexation between flexible SOC and heavy metal cations, the soil surface tended to be more rigid as the calculated glass transition temperature ($T_g$) was higher (Luo et al. 2010). Consequently, the affinity and nonlinearity of PAH sorption to soils were enhanced according to the dual reactive domain model (LeBoeuf and Weber 1997; Xing and Pignatello 1997).

To directly compare the sorption affinities of phenanthrene, naphthalene, and pyrene to the soils, the distribution sorption coefficient ($K_d$) was chosen. The $K_d$ values of PAHs at different equilibrium concentrations in the absence or presence of Cu(II), Pb(II), and Cr(III) (1.0 mmol L$^{-1}$) were described in Fig. 3. The $K_d$ values of PAHs increased in the presence of the heavy metal cations especially at lower



Fig. 4 Zeta potentials of **a** soil 1 and **b** soil 2 in the absence or presence of 1.0 mmol L$^{-1}$ Cu(II), Pb(II), or Cr(III)
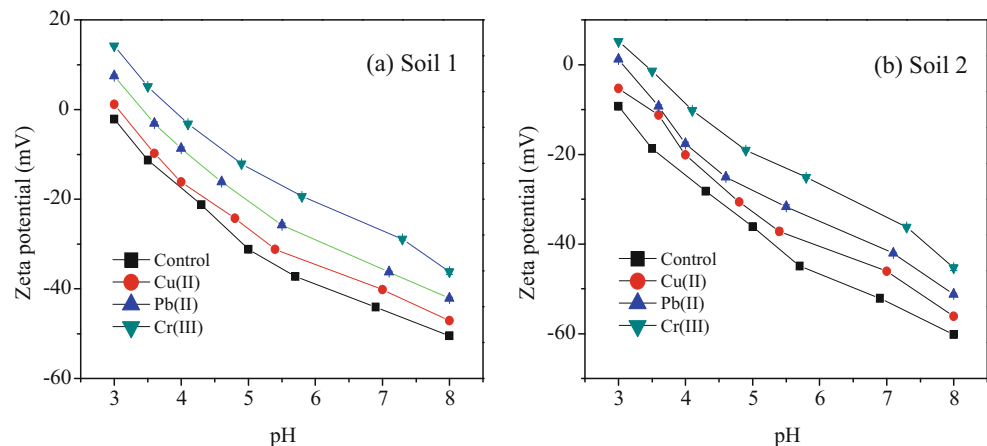
**Table 4** Bond length ($r$) and interaction energy ($G$) between PAHs and heavy metal cations

| PAH | Metal | $r$ (Å)[a] | $G$ (kcal mol$^{-1}$)[a] |
|---|---|---|---|
| Naphthalene | Cu(II) | 2.25 | −10.49 |
|  | Pb(II) | 2.80 | −64.55 |
|  | Cr(III) | 3.76 | −106.4 |
| Phenanthrene | Cu(II) | 2.21 | −13.09 |
|  | Pb(II) | 2.83 | −69.26 |
|  | Cr(III) | 3.74 | −106.9 |
| Pyrene | Cu(II) | 2.23 | −13.34 |
|  | Pb(II) | 2.84 | −76.75 |
|  | Cr(III) | 3.69 | −127.5 |

[a] The bond length and interaction energy in aqueous solution were calculated with the polarized continuum model PCM at the theoretical M06-2x/def2svp level, where the geometry optimization of the complex was performed using the Gaussian 09 program

concentrations. It should be noted that slight differences occurred in the facilitating effects to the three PAH compounds in the two soils, with the following order: pyrene > phenanthrene > naphthalene. This was generally consistent with the order of their $K_{ow}$ (Table 2). $K_{ow}$ was an important parameter to compare the sorption affinities of PAHs among soils; the extent of solute insolubility in water was the primary factor affecting the sorption affinity coefficients (Chiou et al. 1979, 1983). Hydrophobicity of PAHs was positively correlated with the numbers of aromatic ring. Therefore, the sorption affinity of pyrene to soils was higher than those of both phenanthrene and naphthalene, and the former could be more easily enhanced by heavy metals.

The sorption of Cu(II), Pb(II), and Cr(III) increased the zeta ($\zeta$) potentials of soil surfaces (Fig. 4). An increased zeta ($\zeta$) potential indicated that the soil surfaces became neutralized and more hydrophobic by sorbed heavy metal cations. Therefore, the formation of surface complexes of Cu(II), Pb(II), and Cr(III) increased the affinity of soil surfaces for

the PAH sorption. The $\zeta$ potentials of soils followed this order: Cu(II) < Pb(II) < Cr(III). Compared with Cu(II) and Pb(II), Cr(III) had higher positive charge and could neutralize more negative charge from soils. As a result, Cr(III) enhanced more PAH sorption than Cu(II) and Pb(II) did (Fig. 2). Meanwhile, the polarity of humic materials was probably decreased in the presence of heavy metals and hence improved the partitioning of PAHs into SOM through π-π electron donor-acceptor interactions (Zhu et al. 2004a; Ping et al. 2006), resulting in an enhanced hydrophobic partitioning (Zhou et al. 2004; Xiao et al. 2007).

### 3.3 Quantum mechanical calculation of cation-π bonding between heavy metal cations and PAHs

The optimized structures of the PAH complex with heavy metal cations were illustrated in Fig. S2 (Electronic Supplementary Material). The binding energies were calculated by DFT method at the M06-2x/def2svp level of theory (Table 4). The calculations were also validated by B2LYP basis sets (Grimme 2006); the obtained energies were close, and the ranking of the binding energies remained the same (Table S2, Electronic Supplementary Material), showing the reliability of the applied computational methods. The measured bond length ($r$) ranks as Cr(III) > Pb(II) > Cu(II) (Table 4). The bond length was mainly determined by the characteristics of the heavy metal cations. For Cu(II), Pb(II), and Cr(III) coexisting with different PAHs, the bond lengths changed little. The interaction energy ($G$) between the metal cation and the PAH molecules ranges from −127.5 to −10.49 kcal mol$^{-1}$ (Table 4), showing that the interaction was a strong force (Table S1, Electronic Supplementary Material), which may have high influence on the sorption of PAHs (Zhu et al. 2004b ; Keiluweit and Kleber 2009).

Figure 5 shows that $G$ was linearly correlated with $K_f'$ of PAHs ($R^2 > 0.906$). Thus, the sorbed metal cations in soil appeared to be positively correlated with the capacity and



**Fig. 5** The relationship between the cation-π interaction energy $G$ and $K_f'$ (adjusted Freundlich affinity coefficient ($K_f$) after normalizing the equilibrium concentration ($C_e$) by the aqueous solubility ($C_s$)) in soil 1 and soil 2
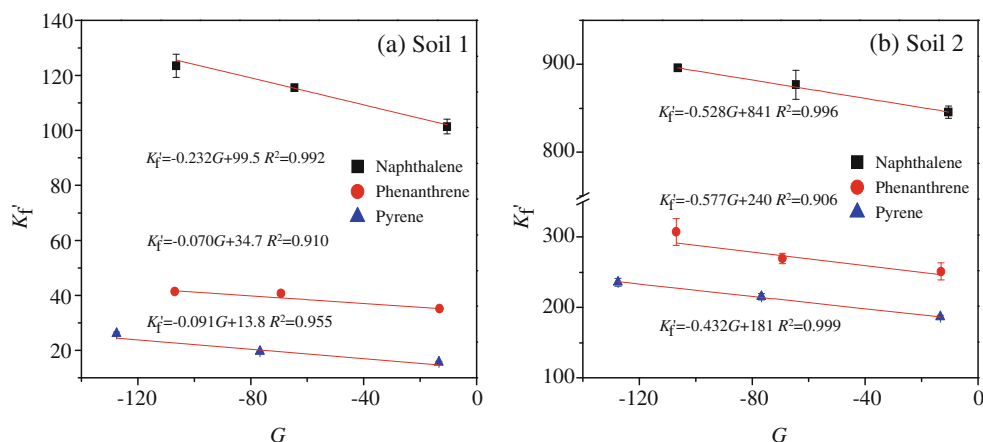
nonlinearity of PAH sorption. The cation-π interaction played an important role in enhancing the sorption of PAHs to soils. Cation-π bonding between electron-rich aromatic structures and free or complexed metal ions toward molecular recognition and selection has been well acknowledged (Ma and Dougherty 1997; Mahadevi and Sastry 2013). The cation-π bonding between aromatic π-donors (PAHs) and metal cations (Cu(II), Pb(II), Cr(III)) on the mineral surface was proposed to enhance the sorption affinities of PAHs (Zhu et al. 2004b; Qu et al. 2008). In aqueous solution, heavy metal cations, especially softer cations, had a "salting out" effect on PAHs; that is, the solubility of PAH would decrease with increasing metal cation concentration, suggesting no formation of heavy metal cation-PAH complexes in aqueous solution (Chen et al. 2007). This was likely due to the "desolvation penalty" induced by strong metal cation hydration, and the cation-π bonding between heavy metal cations and PAHs was prohibited in aqueous solution (Qu et al. 2007). Therefore, binding of heavy metal cations to soils was expected to create hydrophobic microenvironments surrounding the metal cations, thus facilitating cation-π interactions.

Cation-π interactions are also important in environmental toxicity and bioavailability studies (Ma and Dougherty 1997; Mahadevi and Sastry 2013). Cation-π interactions between PAHs and heavy metal cations at mineral/soil surfaces are sufficiently strong to drive PAH sorption to mineral/soils through the free binding energy of the reaction (Keiluweit and Kleber 2009). Some heavy metal cations (transition metals) are expected to have even higher cation-π interaction energy compared to base cations. Therefore, quantum mechanical calculation of the binding energy between heavy metal cations and the PAHs would help to reveal the mechanisms on sorption of PAHs to soils. Our QM calculation of the binding energies considers only the interactions between PAHs and heavy metals. The SOM and some other soil components with ligand groups and aromatic structures can also interact with heavy metal cations (Cabaniss 2009, 2011). In the future, more realistic soil conditions should be considered (Braida et al. 2001; Zhao et al. 2001).

## 4 Conclusions

The sorption mechanisms of PAHs to soils in the presence of heavy metals were extensively investigated in this study. We found that coexisting heavy metals consistently enhanced the capacity and nonlinearity of PAH sorption to soils. The results of quantum mechanical calculations indicated that the cation-π interaction between PAHs and heavy metal cations played an important role in increasing the sorption of PAHs, as the binding energy was linearly related to the sorption affinity coefficients. This study advances the understanding of the mechanisms on the interaction between PAHs and heavy

metals in soils. In the future, spectroscopic studies are required to estimate more direct interaction energy between PAHs and heavy metals in soils.

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