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New Insights into the Influence of Heavy Metals on Phenanthrene Sorption in Soils

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Soil contamination by combinations of heavy metals and organic contaminants has become an increasingly important environmental issue. Effects of heavy metal cations (Cu^{2+} , Ni^{2+} , and Pb^{2+}) on phenanthrene sorption were systematically investigated using two soils with contrasting physicochemical properties. Spectral and microscopic analyses provide direct evidence for the modification of composition and conformation of dissolved organic carbon (DOC) and hydrophobicity of the interfaces in the presence of metal cations. Parts of rubbery organic carbon (including flexible DOC and humic acids) became condensed on solid surfaces in the presence of heavy metals as evidenced by an increase in the glass transition temperature of the soils. These modifications led to a significant increase in the capacity and nonlinearity of phenanthrene sorption in the soils. As the added metal cations aged for 70 days, the soil solution gradually recovered its original physicochemical properties, and the facilitating effects of the heavy metals on phenanthrene sorption were significantly attenuated. This work highlights the important implications of DOC properties and aging processes of metals in the sorption of hydrophobic organic compounds (HOCs) such as phenanthrene in soils and provides compelling evidence for the facilitating effects of heavy metals on HOC sorption in soils.

Introduction

It is widely known that sorption of hydrophobic organic compounds (HOCs) is governed mainly by the chemical composition and conformation of organic carbon (OC) in the soil environment (1–3) and can be modified by environmental conditions including coexisting materials (4–6). For example, several workers have suggested that heavy metals can enhance or inhibit the sorption of HOCs to carbonaceous materials depending on the composition and structure of the sorbents (7, 8). Combined contamination by heavy metals and organic contaminants often occurs in the soil environment (9, 10). However, little information is

available regarding effects of heavy metals on the sorption of HOCs in natural soils.

The contact time between field soils and contaminants such as heavy metals is referred to as the aging process (11). During the aging process, heavy metals in soils show a slow redistribution or change in speciation. For example, the proportions of heavy metals associated with the weakly bound fraction tend to decline with a corresponding increase in the strongly bound fraction over time (12). At the same time, the presence of heavy metals can result in a series of changes in composition and conformation of dissolved organic carbon (DOC) and hydrophobicity of interfaces (8, 13, 14). It is therefore to be expected that the influence of heavy metals on these properties will be affected by their aging processes, which may consequently influence HOC sorption in soils. However, as far as we know there is little information available on the changing characterization of soil solution chemistry as affected by aging of heavy metals (15). Moreover, the impacts of aging of heavy metals on HOC sorption in soils have not been explored to date, and the mechanisms involved have not been elucidated.

Accurately exploring HOC sorption mechanisms in intact soils is still challenging because soils are highly heterogeneous with respect to mineralogy and composition. In particular, OC has defied molecular-level characterization for nearly a century (16). Direct characterization of the composition and conformation of OC will no doubt greatly improve our understanding of the sorption mechanisms of HOCs in soils. Recent developments in analytical techniques open up possibilities for advancing such investigations. A combination of multiple analytical techniques should provide comprehensive information on both organic carbon and interface properties in soils and is therefore highly desirable.

The aim of the present work was to investigate the influence of heavy metals and their aging processes on soil solution chemistry and subsequently on HOC sorption in soils. Phenanthrene and Cu, Ni, and Pb were chosen as our model HOC and heavy metal contaminants. Attempts were made to explore the mechanisms involved by examining the changes in soil interface characteristics and solution chemistry using a combination of liquid state NMR spectroscopy, atomic force microscopy (AFM), high-pressure size exclusion chromatography (HPSEC), and glass transition temperature (T_g) analyses. This study for the first time points to the important effect of aging of heavy metals on soil interfacial processes and provides direct microscopic and chromatographic evidence for the mechanisms involved.

Materials and Methods

Materials. Two contrasting Chinese soils from very different environments were used, namely a black soil (a clay loam Mollisol) and a red soil (a clay Ultisol). The original soils had pH values (soil: water, 1:5 (w/v)) of 6.8 and 5.0, OC contents of 3.82% and 0.61% (0–25 cm depth), and cation exchange capacities of 33.6 and 8.3 cmol(+)/kg, and the main clay minerals were smectite and kaolinite in the black soil and the red soil, respectively. In addition to the original soils, samples with DOC removed were also used as the sorbents. In brief, the soils were extracted with 0.005 mol/L NaCl (soil: solution, 1:50 (w/v)) for 6 h at least 4 consecutive times to remove DOC and then centrifuged at $7200 \times g$ for 30 min. The residues were collected and freeze-dried.

In order to evaluate the effects of metal cations on the characteristics of the soils, the original soils were incubated with 1.0 mmol/L Cu^{2+} , Ni^{2+} , or Pb^{2+} as chloride (soil: solution, 1:100 (w/v)) for 48 h and centrifuged, the supernatant

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TABLE 1. DOC Contents, SUVA, Thermodynamic Properties, and ζ Potentials of the Soil Samples as Affected by Metal Cations and Aging Process^a

| soil sample | DOC | | T_g (°C) | ζ potential (mV) |
|--------------------------|---------|------|----------------|------------------------|
| | (mg/kg) | SUVA | | |
| black soil - original | 1885 | 2.03 | 65.3 | -12.2 ^f |
| + Cu ²⁺ | 759 | 1.03 | 69.8 | -4.7 |
| + Cu ²⁺ aging | 1630 | 1.83 | - ^b | -9.1 |
| + Ni ²⁺ | 836 | 1.26 | 68.7 | -1.2 |
| + Ni ²⁺ aging | 1568 | 2.02 | - | -7.3 |
| + Pb ²⁺ | 563 | 0.72 | 69.4 | -3.6 |
| + Pb ²⁺ aging | 1427 | 1.78 | - | -10.2 |
| red soil - original | 471 | 0.36 | 59.3 | -8.9 |
| + Cu ²⁺ | 282 | 0.16 | 63.9 | 3.9 |
| + Cu ²⁺ aging | 406 | 0.27 | - | -5.3 |
| + Ni ²⁺ | 319 | 0.25 | 63.1 | 2.2 |
| + Ni ²⁺ aging | 412 | 0.29 | - | -4.0 |
| + Pb ²⁺ | 262 | 0.05 | 63.2 | 4.8 |
| + Pb ²⁺ aging | 393 | 0.26 | - | -5.6 |

^a Cation (Cu²⁺, Ni²⁺, Pb²⁺) concentration used was 1.0 mmol/L. The aging process indicates that the heavy metal-spiked soils were equilibrated for about 10 weeks and subjected to at least three wet-dry cycles during this period. DOC in the soil samples under various treatments was extracted with 0.005 mol/L NaCl and a soil/solution ratio of 1/100. SUVA is the specific ultraviolet absorbance at 254 nm (UV₂₅₄ × 100/DOC). T_g is the calculated glass transition temperature. ζ potential is determined at pH 6.0. ^b - indicates not detected.

solutions were used for DOC characterization, and the solids were freeze-dried for physicochemical characterization. In addition, heavy metals were added to the soils as chloride salts in aqueous solution (50 mmol/L) and then mixed thoroughly. The application rate of the heavy metals was equivalent to the above treatments. After spiking, the soils were equilibrated for 10 weeks and subjected to at least three dry-wet cycles during the period for aging treatment to simulate the natural aging process of heavy metals under field conditions (17). After aging, the soils were air-dried and homogenized. All samples were freeze-dried and stored in a desiccator for physicochemical characterization and for sorption experiments.

The original soils and the treated soil samples obtained were characterized in terms of their T_g , ζ potentials, and DOC properties comprising DOC contents, chemical group distribution, specific UV absorbance at 254 nm (SUVA = UV_{254 nm} × 100/DOC) (18), molecular weight distribution, and microtopography. DOC content and its functional group composition (¹H liquid-state NMR spectral analysis), T_g analysis, and ζ potential analysis were performed as described previously (6). UV absorbance was measured with a 752-UV/vis spectrophotometer at 254 nm using a quartz cell with a 1-cm path length. Relative size and apparent molecular weight distribution of DOC were estimated using HPSEC because it is rapid and nondestructive. The mobile phase was 0.01 mol/L NaCl and 100 mg/L NaN₃. Further technical details are provided in Zhou et al. (19). Microtopography of DOC was characterized by AFM as described below. The results, based on triplicate analyses unless otherwise indicated, are listed in Table 1.

Each DOC sample for AFM imaging was prepared by placing a 10- μ L droplet of soil supernatant from one of the 0.25 mm sieved soil samples onto a microscope slide. The images were performed at different zones of a sample and of different samples prepared in the same conditions to evaluate their reproducibility. Imaging with the tapping mode was conducted simultaneously in the height mode and phase mode using a NanoMan VS scanning probe microscope

(Veeco Instrument Inc., Plainview, N.Y.). Further technical details are provided in the Supporting Information (SI).

Sorption Experiments. Phenanthrene (>98%) was purchased from Acros Organics and used as received. Each sorbent sample (0.4000 g) from the original soils, soils incubated with heavy metals, and soils with DOC removed was placed into a PTFE-lined cap glass centrifuge vial of 45 mL capacity, and a 40-mL aliquot of phenanthrene solution of varying concentration (0.02–0.8 mg/L) was added as previously described (6). The solid-to-liquid ratios allowed 30–95% of the sorbate be sorbed at equilibrium. An aqueous stock solution of metal cation (in chloride) solutions was added to the suspension for dilution to a cation concentration of 1.0 mmol/L with 100 mg/L NaN₃ to evaluate their effects on phenanthrene sorption. The solutions were shaken on an orbital shaker incubated in the dark at 20 ± 2 °C for 72 h based on earlier studies (6). After centrifugation, phenanthrene in the supernatant solution was analyzed by HPLC as described previously (6). The sorption experiments and zero sorbent blank assays were all conducted in triplicate. Results of zero sorbent blanks indicated that the loss of phenanthrene other than through sorption by the sorbents was negligible. Phenanthrene sorption was therefore calculated by mass balance. The amounts of the cations sorbed by the sorbents were also measured by inductively coupled plasma - optical emission spectroscopy (ICP-OES).

Data Analysis. Sorption of phenanthrene was described by the modified Freundlich model, that is, $S = K_f(C_e/S_s)^n$ (20), where S is the amount of sorbate sorbed per unit mass of sorbent (mg/kg), C_e is the concentration of sorbate in equilibrium solution (mg/L), and S_s is the supercooled liquid-state solubility of phenanthrene (5.902 mg/L). The parameter K_f is the Freundlich sorption coefficient (mg/kg), and n is the isotherm nonlinearity parameter, an indicator of site energy heterogeneity (i.e., the smaller n is, the more heterogeneous the sorption site). The modified model makes it possible to compare different isotherms directly. The values of K_f and n for all sorption isotherms were calculated by the Freundlich equation fitted using Origin 7.5 software at the 95% confidence level. Statistical analysis of the results was performed using SPSS for Windows (version 10.0, SPSS Inc.) using ANOVA (Tukey test, $p < 0.05$).

Results

Characterization of the Sorbents. Table 1 shows that both the contents and SUVA values of DOC in the two soils decreased significantly in the presence of the three heavy metal cations. Simultaneously, the T_g of the samples tended to be enhanced, and the ζ potential became more positive in the presence of the metal cations. After the added heavy metals had aged for 70 days the properties of the soil samples tended to recover their original state (Table 1).

The functional group distributions of DOC from the soils were examined by ¹H liquid state NMR spectra. Here Cu²⁺ is used as an example to demonstrate the influence of heavy metal cations and their aging processes on the functional group composition of the DOC as shown in Figure 1. It is clear that aliphatic carbon dominated the functional group composition of the DOC, and a significantly higher proportion of the alkyl chains (at 1.9–2.8 ppm regions) was observed in the black soil. Although poor signal-to-noise ratio occurred in the soils, it is clear that both the signals of aliphatic moieties (0.5–2.8 ppm regions), particularly of alkyl moieties, and a combination of sugars, amino acids, aromatic methoxyl, and CH₂ units adjacent to ether and ester groups (3–5.5 ppm regions) of the DOC declined significantly in the presence of Cu²⁺. It should be noted that the signal at 4.79 ppm came from the depressed water peak. Furthermore, the signals from aromatic and conjugated double-bond groups (at 6.0–8.6 ppm regions) were limited since the hydrophobic aromatic carbons are not easily water accessible. Interestingly, the NMR spectra of the DOC in the presence of Cu²⁺ tended to recover their original

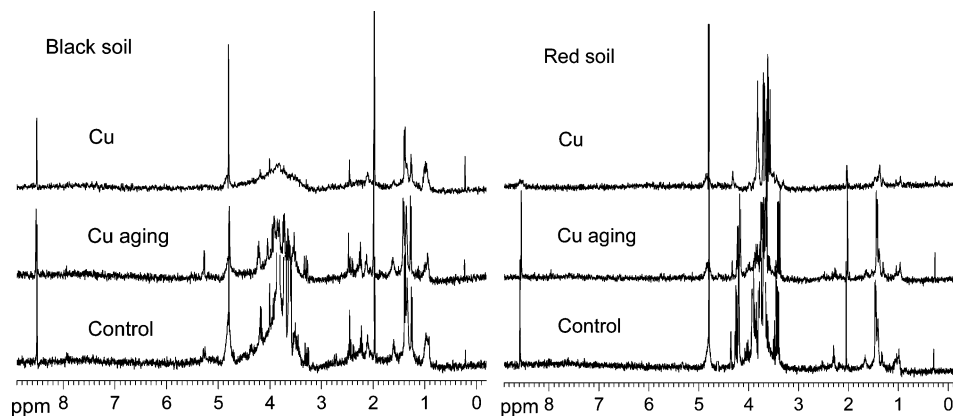


FIGURE 1. ^1H liquid state NMR spectra (given in arbitrary units) of DOC from two soils affected by Cu^{2+} and its aging process.

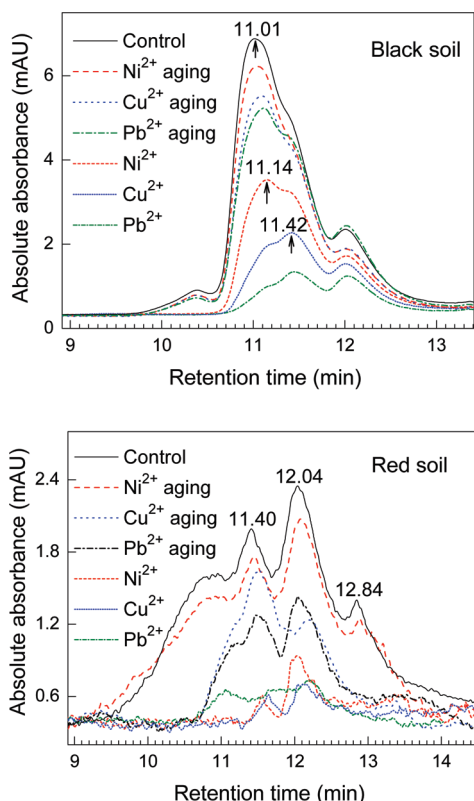


FIGURE 2. HPSEC elution curves (absorbance at 254 nm) of the DOC of two soils as affected by heavy metals and their aging processes.

composition after the 70-day aging process (Figure 1). Similar results were also obtained from the soils in the presence of the other two metal cations (data not shown).

The molecular weight distributions of DOC from the two soils in the presence of the metal cations are shown in Figure 2. The measured absorbance was proportional to the concentration of DOC. This clearly demonstrates that the release of higher-molecular-weight DOC was inhibited by the presence of the metal cations since a shorter retention time is related to the larger size fraction with higher molecular weight, and a longer retention time corresponds to the small size fraction with lower molecular weight (21). Lower SUVA values were also obtained in the presence of the metal cations (Table 1), indicating that higher-molecular-weight DOC molecules were preferentially complexed and flocculated from the solutions (18), which is consistent with the HPSEC analysis. After the 70-day aging process of the added heavy metals in the soils, the proportion of higher-molecular-weight DOC was clearly enhanced, and the molecular weight

distributions of the DOC tended to recover their original pattern (Figure 2).

The microtopography of DOC from the two soils in the presence of Cu^{2+} was observed by tapping mode AFM (Figure 3). Some of the nanoparticles in the original DOC were aggregated into regularly ringed microaggregates with lateral diameter from 38 to 89 nm and height from 0.9 to 4.6 nm. The loosely ringed structure of DOC was disrupted into a small single spherical structure by the presence of Cu^{2+} (Figure 3), which involved significant intramolecular rearrangement, i.e., changes in the conformation of the DOC molecules (5, 14, 22). As a result, the single DOC particle sizes tended to decrease significantly in contrast to the original microaggregates of DOC in the soils. After the 70-day aging process, the single spherical structures tended to aggregate into larger micelle microaggregates in the soils, which was more apparent for the organic carbon-rich black soil and even the ringed structure tended to reform in the DOC aggregates (Figure 3C). Similar changes in the conformation of the DOC in the presence of the other two metal cations were also observed in the two soils (data not shown).

Phenanthrene Sorption Isotherms. Phenanthrene sorption isotherms for the two soils in the presence of the metal cations are shown in Figure 4, together with the corresponding values of the Freundlich parameters (K_f and n). The sorption data fit well with the Freundlich models ($r^2 > 0.993$). All the samples exhibited nonlinear sorption for phenanthrene with values of n below 0.89. Sorption affinity tended to increase ($p < 0.01$), and the nonlinearity of sorption also tended to be enhanced ($p < 0.05$) when Cu^{2+} , Ni^{2+} , or Pb^{2+} was present at a cation concentration of 1.0 mmol/L compared to the controls. The three cations differed slightly in the degree to which they enhanced the nonlinearity of sorption according to the following sequence: $\text{Ni}^{2+} < \text{Cu}^{2+} < \text{Pb}^{2+}$; however, the differences were smaller in the red soil as shown in Figure 4 ($p > 0.05$).

Interestingly, the facilitating effects on phenanthrene sorption in soils by the metal cations were markedly attenuated in the aging spiked soils. Although the facilitating effects of the metal cations on phenanthrene sorption were still significant for the black soil ($p < 0.05$), no significant differences in phenanthrene sorption were observed among the metal cations (Figure 5).

Discussion

Previous work has demonstrated that the affinity and nonlinearity of HOC sorption are controlled mainly by the composition and conformation of OC in soils. It is proposed that OC in soils is envisaged as comprising rubbery (including flexible DOC and humic acids) and glassy (for example, humin) phases, both of which contain sorption domains according to a well accepted dual reactive domain model

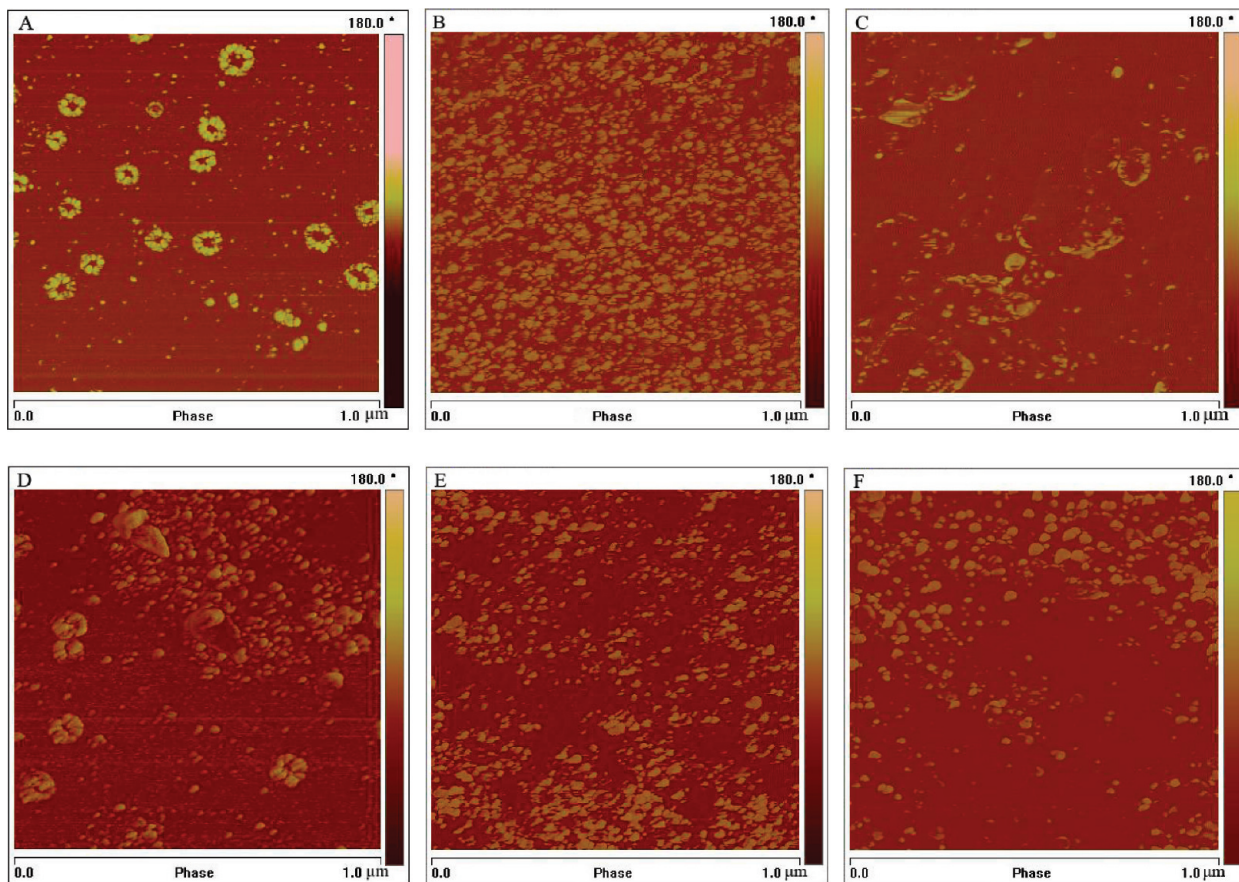


FIGURE 3. AFM phase images ($1 \mu\text{m} \times 1 \mu\text{m}$) of DOC from two soils as affected by Cu^{2+} and aging treatment (A, black soil; B, with Cu^{2+} ; C, with Cu^{2+} aging; D, red soil; E, with Cu^{2+} ; and F, with Cu^{2+} aging).

(1–3), among which DOC can bind phenanthrene through hydrophobic interactions and inhibit the accumulation of phenanthrene on solid surfaces (23–27). In fact, DOC is also a highly heterogeneous mixture of compounds varying in size, shape, composition, and physicochemical properties (14, 21, 24) although the exact structure of DOC still remains unclear. In the presence of metal cations, both aliphatic and aromatic moieties of DOC were significantly flocculated from the soil solution as evidenced by the changes in DOC contents and NMR spectra. In particular, parts of the relatively high-molecular-weight DOC were preferentially fractionated from the soil solutions in the presence of the added metal cations as indicated by the HPSEC results (13, 14). Consequently, the binding affinity of the remaining DOC to phenanthrene was greatly impeded. Simultaneously, the aromaticity in the DOC also decreased significantly as reflected by the SUVA values since higher molecular weights are positively correlated with the aromaticity of DOC (21, 22), which is also expected to inhibit the binding of phenanthrene in solutions (23, 26, 28) and thus facilitate the sorption of phenanthrene in the solid interfaces. In addition, the hydrophobic interactions in the ringed aggregates were disrupted in the presence of the metal cations and the DOC exhibited single spherical nanoparticles (29, 30), which also foiled the binding of phenanthrene with the nanoparticles in the soil solutions.

The flocculated higher-molecular-weight DOC as a result of complexation with the metal cations are expected to form intramolecular hydrophobic domains in solid surfaces where metal cations act as bridges between the hydrophilic carboxyl functional groups of DOC (3–5, 14). As a result, parts of the hydrophilic functional groups were enwrapped in the inner parts of the complexes, and the negative charges in the soil surfaces were neutralized by the complexed heavy metals

as reflected by the increased ζ potential. Thus, the interfaces exhibited less hydrophilicity, resulting in a facilitated hydrophobic sorption of phenanthrene on the solid surfaces of the soils (8, 31).

Apart from DOC, parts of flexible HAs on soil surfaces may also have complexed or coordinated with the metal cations and tended to be condensed on soil surfaces in their presence (3, 5, 25). Therefore, soils from which the DOC had been removed still exhibited facilitating sorption affinity for phenanthrene in the presence of the metal cations ($p < 0.05$) (Figure S1 in the SI). In addition, with the complexation or coordination between flexible OC and metal cations, the soil matrix tended to be more rigid or harder as reflected in the T_g analysis. Consequently, the affinity and nonlinearity of phenanthrene sorption were enhanced according to the dual reactive domain model (1–3).

It should be noted that slight differences occurred in the facilitating effects to the three cations with $p < 0.05$ in the black soil, exhibiting the following order: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$. This is generally consistent with their effects on the contents and molecular distribution of the DOC and on sorption affinity in the soils (Figure S2 in the SI). The differences in the effects of the metal cations on phenanthrene sorption are in accordance with the ionic radius ranking of the metals: Pb^{2+} (0.119 nm) $>$ Cu^{2+} (0.073 nm) $>$ Ni^{2+} (0.069 nm). In particular, greater effects of Pb^{2+} over the other two cations were clearly observed for both the soils, probably due to the greater Misono softness parameter of Pb and/or its greater first hydrolysis constant (32). However, no significant difference in the nonlinearity of sorption was observed among the metal cations, probably due to their having the same valence.

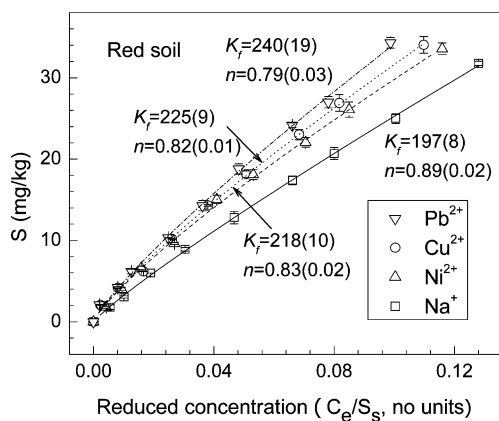
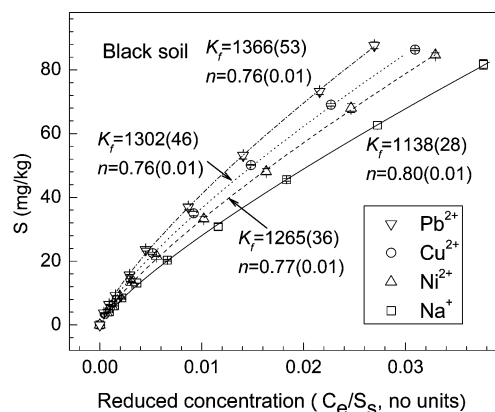


FIGURE 4. Effects of Cu^{2+} , Ni^{2+} , and Pb^{2+} (1.0 mM) on phenanthrene sorption by two soils (dots) and best fit Freundlich isotherm equation (lines).

Once in soils, metal cations may move into microvoids and/or nanopores of soil clay minerals and organic carbon with time and a redistribution of the weakly bound fraction to a more strongly bound fraction occurred during the aging process (12). Our analytical results also confirm that the dissolved metal cations decreased significantly after the 70-day aging process (Figure S2 in the SI). There is evidence that the release of DOC in soils is adapted to changes in environmental conditions and can also be affected by the aging process (13, 33). During the aging of the metal cations, DOC in soil also suffered a corresponding “aging process”, and its content and composition gradually recovered their original states in the control soils through a process of homeostasis of soil solution chemistry. For example, the higher-molecular-weight DOC was released and exhibited larger micelle aggregates in soil solutions in the aged soils. Consequently, sorption of phenanthrene in the soils was less affected by the presence of the aged metal cations (Figure 5). In addition, the soil interfaces tended to be less hydrophobic since the ζ potentials of the aged soils were approaching the status of the original soils during the aging process, which further confirms that the physical and chemical properties of the soils after the aging process gradually recovered their original state as in the control soils. Therefore, the facilitating effects of metal cations were gradually attenuated, and no significant difference was observed in the nonlinearity of phenanthrene sorption in the soils between the controls and aged soils. Nevertheless, clear facilitating effects of the metal cations on phenanthrene sorption were still obtained ($p < 0.05$) in the aged black soil which contained a higher content of OC. It should be noted that the aging process

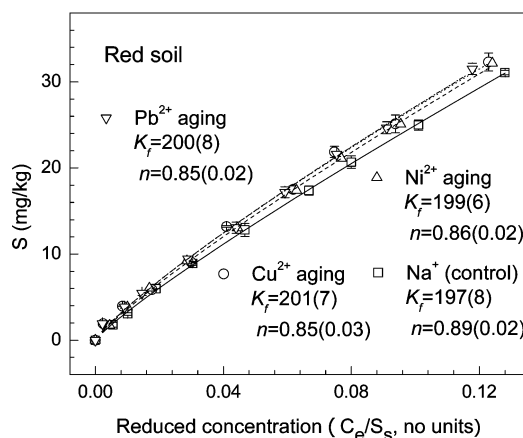
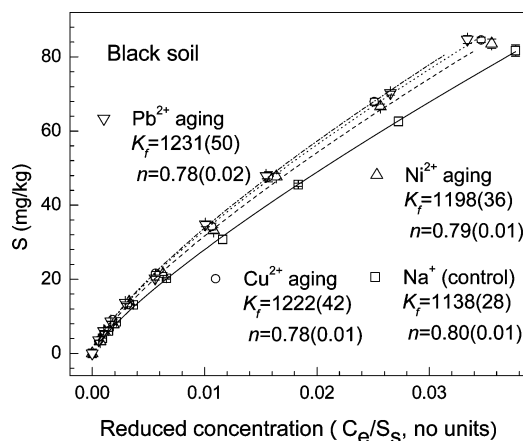


FIGURE 5. Aging effects of heavy metal cations on phenanthrene sorption by soils and best fit Freundlich isotherm equation (lines).

of heavy metals is very slow and usually takes hundreds of days or even longer to reach equilibrium (15). Therefore, one would expect the effects to be further attenuated and even disappear in the aged soils if they were incubated for very long periods.

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Supporting Information Available

Two figures and details of atomic force microscopy analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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