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Effect of phosphate on phenanthrene sorption in soils

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ABSTRACT
Phosphate is ubiquitous in the environment. However, its impact on sorption of hydrophobic organic compounds in soils has received little attention. Some effects of phosphate on phenanthrene sorption were investigated in this study using two Chinese soils with contrasting properties. The presence of phosphate significantly decreased the capacity and increased the nonlinearity of phenanthrene sorption in the soils, and this sorption-inhibiting effect was more significant at high phosphate concentration. The influence of phosphate on phenanthrene sorption in the soils was governed by the release of dissolved organic carbon (DOC), particularly higher-molecular-weight and highly aromatic DOC, which tended to be enhanced in the presence of phosphate (p < 0.01) as evidenced by size exclusion chromatography and specific UV absorbance analysis. Atomic force microscopy and zeta potential analysis reveal that the ringed microaggregates of DOC were disrupted into larger condensed microaggregates and the solid interfaces tended to be more hydrophilic in the presence of phosphate which also inhibited the accumulation of phenanthrene in the soils. This study for the first time points to an important role of phosphate in the sorption of phenanthrene in soils and provides substantial evidence for the mechanisms involved using a combination of microscopic and chromatographic techniques.

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1. Introduction
Sorption of hydrophobic organic compounds (HOCs) is of great concern because it significantly affects the behavior and fate of organic contaminants in the environment. Previous studies have demonstrated that soil physicochemical properties, particularly of organic carbon (OC), play a dominant role in the sorption reaction [1–4]. The properties of OC can be readily affected by various coexisting substances [5–7] which subsequently influence the sorption characteristics of the compounds in the environment [8–10]. For example, Xiao et al. [11] observed that coexisting heavy metals modified the hydrophobicity of OC and thus exerted pronounced effects on the sorption of HOCs. Yuan and Xing [8] suggested that metal cations could coagulate humic acids from solution and facilitate HOC sorption in humic acids. However, the effects of coexisting substances on the sorption of HOCs in soils have received less attention to date and the exact mechanisms involved still remain obscure [6,12].

Phosphorus is a ubiquitous nutrient element in the environment and it can induce and facilitate the biodegradation of HOCs in soils by providing the nutrient for the biological systems [13,14]. At the same time, the presence of phosphate can definitely affect the characteristics of environmental microinterfaces through non-biological reactions. For example, it has been demonstrated that phosphate can be specifically adsorbed by soil minerals [15], strongly competing with dissolved organic carbon (DOC) for sorption sites [7,16] and effectively changing the composition and aggregation of dissolved humic acid on mineral surfaces [5]. On the other hand, due to its colloidal properties, DOC can enhance the apparent solubility of HOC and reduce their sorption to solid matrixes in environmental interfaces [3,17–19]. It is therefore reasonable to expect that the presence of phosphate may exert significant effects on the interfacial processes of HOCs in the environment. However, no information is available on the influence of phosphate on sorption of any HOC by soils in spite of its important role in the environment.

Soils are matrices with complicated structure and composition. Research on interactions between coexisting substances such as phosphate and OC in soils is still not sufficiently advanced to allow quantitative description and understanding of HOC sorption in soils in their presence [7]. Recent developments in microscopic and chromatographic techniques open up possibilities for advancing such investigations. For example, atomic force microscopy (AFM) allows both the imaging of the surface structure and microtopography of environmental particles and the determination of the changes in microtopography during environmental interfacial reactions at the nanometer scale [20,21]. A combination of AFM,
NMR, high performance size exclusion chromatography (HPSEC) and surface analysis enables a good attempt to be made to provide comprehensive information on the structure and composition of DOC and the interfacial properties in soils and subsequent direct evidence for the mechanisms involved in the influence of phosphate on the sorption of HOCs in soils.

The aim of the present study was therefore to elucidate the effects of phosphate on the sorption of the model HOC phenanthrene in two contrasting Chinese soils. Attempts were made to explore the mechanisms involved by examining the changes in soil solution chemistry, particularly the compositional and morphological properties of DOC in the soils in the presence of phosphate in relation to the interactions between HOCs and the soil matrix.

2. Materials and methods

2.1. Materials

Two Chinese soils with contrasting properties were collected from Heilongjiang Province and Jiangxi Province, 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, and OC contents of 3.82% and 0.61% (0–25 cm depth), 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 the DOC removed were also used as sorbents. In brief, the soils were extracted with 0.005 mol/L NaCl (soil:solution, 1:50 (w/v)) for 6 h at least four consecutive times to remove DOC and then centrifuged at 7200 rpm for 30 min. The residues were collected and freeze-dried. In order to evaluate the effect of phosphate on the characteristics of the soils, the original soils were incubated with 1.0 mmol/L phosphate buffer at pH 6.5 (soil:solution, 1:100 (w/v)) for 48 h, centrifuged, and the supernatant solutions were used for DOC characterization and the solids were freeze-dried for physicochemical characterization. All samples were freeze-dried and stored in a desiccator.

Phenanthrene (98%, Acros Organics) in electrolyte solution (NaCl at pH 6.5) was used as previously described [6]. An aqueous stock solution of phosphate buffer (pH 6.5) was prepared at 30 mmol/L and used for analytical grade NaH2PO4 and Na2HPO4.

2.2. Soil characterization

To determine the effect of phosphate on soil physical and chemical properties, the original soils and the treated soil samples were characterized in terms of their N2 surface areas (N2 SA), ζ potentials, and DOC properties including DOC contents, molecular weight distribution, chemical group distribution, and specific UV absorbance at 254 nm (SUVA = UV254nm × 100/DOC) which can be used as an index of relative aromaticity of DOC [22]. Surface analysis, ζ potential analysis, and DOC contents and functional group composition (1H liquid-state NMR 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. Number-average apparent molecular weight distribution of DOC was estimated using HPSEC because it is a rapid and nondestructive analytical method. Further technical details are provided in the Supplementary Data (SD). In addition, the microporography of the soil samples was characterized by AFM as described below. The results, based on triplicate analyses unless otherwise indicated, are listed in Table 1.

Air-dry samples for AFM imaging were prepared by placing a 10-μL droplet of soil supernatant and suspension from each 0.25 mm sieve soil sample onto a microscope slide. The images were acquired at different zones of a sample and of different samples prepared under the same conditions to evaluate their reproducibility. Imaging with the tapping mode was conducted simultaneously in the height mode and phase mode using a Nano-Man VS scanning probe microscope (Veeco Instrument Inc., USA). Further technical details are provided in the SI.

2.3. Sorption experiments

Triplicate sorbent samples (0.4000 g) were placed in PTFE-lined cap glass centrifuge vials of 45 mL capacity and a 40-μL aliquot of phenanthrene solution of varying concentration (0.02–0.8 mg/L) was added. The solid-to-liquid ratio allowed 30–95% of the sorbate to be sorbed at equilibrium. Aqueous stock solution of phosphate buffer (pH 6.5) was added to each suspension for dilution to a phosphate concentration of 1.0 mmol/L with 100 mg/L NaN3. A higher concentration (3.0 mmol/L) of phosphate with 100 mg/L NaN3 was also used to examine the effect of phosphate concentration on phenanthrene sorption by the original soils. The solutions were shaken in 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 phosphate sorbed by the sorbents were also measured by ICP-OES.

2.4. Data analysis

Sorption of phenanthrene was described by the modified Freundlich model [23]

Table 1

<table>
<thead>
<tr>
<th>Soil sample</th>
<th>DOC (mg/kg)</th>
<th>SUVA</th>
<th>ζ potential (mV)</th>
<th>N2 BET SA (m2/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black soil</td>
<td>1885a</td>
<td>2.03</td>
<td>−23.5b</td>
<td>37.4c</td>
<td>5.1</td>
</tr>
<tr>
<td>+P low</td>
<td>3531</td>
<td>2.58</td>
<td>−29.1</td>
<td>36.7</td>
<td>5.3</td>
</tr>
<tr>
<td>+P high</td>
<td>3822</td>
<td>2.83</td>
<td>−29.8</td>
<td>36.1</td>
<td>5.4</td>
</tr>
<tr>
<td>Red soil</td>
<td>471</td>
<td>0.36</td>
<td>−17.1</td>
<td>42.0</td>
<td>12.6</td>
</tr>
<tr>
<td>+P low</td>
<td>810</td>
<td>1.23</td>
<td>−21.4</td>
<td>38.5</td>
<td>14.3</td>
</tr>
<tr>
<td>+P high</td>
<td>997</td>
<td>1.30</td>
<td>−23.7</td>
<td>37.9</td>
<td>14.6</td>
</tr>
</tbody>
</table>

a Phosphate concentrations used were 1.0 mmol/L and 3.0 mmol/L representing low and high concentrations, respectively.
b DOC in the soil samples was extracted with 5 mmol/L NaCl for 6 h and a soil/solution ratio of 1/100.
c SUVA is the specific ultraviolet absorbance at 254 nm (UV254 × 100/DOC).
d ζ Potential was determined at pH 6.5.
e N2 BET SA is the cumulative surface area of pores between 1.7 nm and 300 nm in diameter determined with N2 at 77 K using the BET equation. Average pore diameter was estimated from pore volume, V, and surface area, A: diameter = 4V/A.
$S = K_f (C_e/S)= n$ (1)

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 $S_n$ 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 at the 95% confidence level. Statistical analysis of the results was performed with SPSS for Windows (version 10.0, SPSS Inc.) using ANOVA (with the Tukey test, $p < 0.05$).

3. Results and discussion

3.1. Physicochemical characterization of sorbents

The quantities of DOC released from the two soils increased significantly and the $\zeta$ potential became more negative in the presence of added phosphate as shown in Table 1. The $N_2$ surface areas of the soils tended to decrease in the presence of phosphate probably due to the occupancy of micropores in soil minerals by the sorption of phosphate [15] and, consequently, the average pore diameter tended to enlarge (Table 1). At higher loadings the influence of phosphate on these parameters became more pronounced.

$^1$H liquid-state NMR spectra of DOC from the soils are presented in Fig. 1. It is clear that aliphatic moieties (0.5–2.8 ppm regions) and a combination of sugars, amino acids, aromatic methoxyl and CH$_2$ units adjacent to ether and ester groups (3–5.5 ppm regions) were the dominant fractions in the soil extracts [24], while the strong signal at 4.79 can be attributed to H$_2$O in the soil samples. Distinct functional group compositions occurred in the two soils and significantly higher contents of the alkyl chains (at 1.9–2.8 ppm regions) were observed in the black soil. Signals from aromatic groups (at 6.0–8.6 ppm regions) were limited since the hydrophobic aromatic carbons were not readily water and/or phosphate accessible. Although poor signal to noise ratios occurred, the signals were generally proportional to the DOC contents in the extracting solutions, and the presence of phosphate significantly enhanced the amounts of both aliphatic and aromatic moieties released from the soils (Fig. 1).

The chromatograms of the DOC from the two soils are shown in Fig. 2. The measured absorbance was proportional to the concentration of DOC (Fig. S1) and the number-averaged molecular weight of the DOC for the red soil (2485 Dalton) was slightly lower than that for the black soil (3042 Dalton). Fig. 2 demonstrates more DOC molecules with higher molecular weights being released in the presence of phosphate since shorter retention time relates to the larger size fraction with higher molecular weight and longer retention time corresponds to the small size fraction with lower molecular weight [5]. Higher SUVA values in the presence of phosphate were also obtained (Table 1), indicating that higher–molecular-weight DOC molecules with hydrophobic and aromatic characters were preferentially released by phosphate [22], which is consistent with the HPSEC analysis. It is important to note that the SUVA values for the red soil increased much more in the presence of phosphate than those for the black soil, probably due to the higher content of iron ions in the solutions from the formation of the dissolved DOC–iron–phosphate complexes [22,25].

The microtopography of the soil particles was observed by tapping mode AFM (Fig. 3 and S2). Fig. 3 shows examples of the nanoparticles from the soil supernatants. Some of the nanoparticles in the original soil supernatants are aggregated into regularly ringed microaggregates with lateral diameter from 38 to 89 nm and height from 0.9 to 4.6 nm (Fig. S3A) and these are believed to be the DOC particles from the soils since dissolved inorganic ions cannot form such aggregates in the supernatants [21,26]. Furthermore, the ringed shape can lower the overall energy when hydrophilic groups of the DOC end on a molecule bend and join together, presenting a hydrophobic domain [21,26]. The loosely ringed structure of the microaggregates was compressed into larger condensed microaggregates by phosphate (Fig. 3 and S3B). The ringed structure of the nanoparticles in red soil was less obvious due to its lower OC content. However, the effect of phosphate was still noticeable (Fig. 3D). For bulk soil particles, no ringed structure was observed in the surfaces while the surface tended to be rougher in the presence of phosphate probably due to the partial release of OC once coated on the solid surfaces (Fig. S2).
3.2. Phenanthrene sorption isotherms

Phenanthrene sorption isotherms for the two soils are shown in Fig. 4, together with the corresponding values of the Freundlich parameters ($K_f$ and $n$). The sorption data fitted well with the Freundlich models ($r^2 > 0.995$). All the samples exhibited nonlinear sorption for phenanthrene with values of $n$ below 0.89. A large difference in phenanthrene sorption capacity was observed between the two soils as reflected by $K_f$, in spite of the presence of phosphate.

The sorption affinity for phenanthrene for the two soils decreased significantly ($p < 0.05$) and the nonlinearity of sorption tended to increase in the presence of phosphate ($p < 0.05$). The efficiency of phosphate in decreasing the affinity of phenanthrene sorption tended to increase at the higher concentration of phosphate ($p < 0.05$), while the nonlinearity of the sorption was less affected by the increasing concentration of phosphate (Fig. 4).

3.3. Analysis of mechanisms

It is well known that sorption characterization including affinity and nonlinearity of HOCs is controlled mainly by the chemical and physical properties of OC in soils [1,8,10]. As a heterogeneous mixture, OC is proposed to be divided into two sorption domains: a rubbery or soft domain (including DOC and flexible humic acids, particularly fulvic acid) and a glassy or hard domain (for example, humin) depending on its structure and molecular weight [12,27,28]. Previous studies have demonstrated that the inherent DOC can attenuate the affinity and the nonlinearity of HOC sorption in soils [6,29]. It has been proposed that DOC can bind phenanthrene through hydrophobic interactions and enhance the proportion of phenanthrene in soil solutions [17–19,30]. In the presence of phosphate the amount of OC released into solutions was significantly increased as evidenced by the results of DOC content and NMR spectra, which facilitated the mobility of phenanthrene by forming dissolved complexes with the OC in solutions.
and consequently inhibited the sorption accumulation of phenanthrene in soils [19,30]. This assumption was further confirmed by the decreased sorption of phenanthrene in the soils at higher phosphate loadings (i.e. 3.0 mmol/L) (Fig. 4) where the DOC released increased substantially compared with the lower phosphate loadings (Table 1).

As the amounts of DOC released increased in the presence of phosphate, the proportion of higher-molecular-weight DOC also increased as indicated by the HPSEC results, suggesting that phosphate could preferentially desorb the relatively higher molecular weight fraction of DOC due to the competitive sorption of phosphate on soil minerals [5]. Higher-molecular-weight DOC, characterized as structurally more complicated and with more functional groups, bound phenanthrene more efficiently in soil solutions, thus suppressing phenanthrene sorption in the soils [17,18,31,32]. In addition, the increased proportion of aromatic moieties in the DOC confirmed by the SUVA results also facilitated the complexation of phenanthrene with DOC. Although the role of aliphatic and aromatic moieties as sorption domains for organic compounds is still a matter of debate, the preferential affinity of aromatic moieties for binding hydrophobic molecules is well accepted, particularly in the relatively homogeneous and chemically similar OC [4,31,33].

It is noteworthy that the inhibitory effect of phosphate on phenanthrene sorption capacity was also evident in the soils from which the DOC had been removed (Fig. 5) when compared with the anthrene sorption capacity was also evident in the soils from similar OC [4,31,33].

Consequently, the conformation of DOC also makes an important contribution to the sorption of phenanthrene in soils [2,8,34]. The presence of phosphate compressed the weak intermolecular hydrophobic interactions between the nanoparticles and thus drove the loosely ringed aggregates into larger condensed microaggregates such as pseudomicelles in the equilibrium solutions (Fig. 3) [21,26,34] and this is believed to facilitate the binding of phenanthrene in the inner sorption domains of the DOC microaggregates [6,12,19]. At the same time, with increasing release of the rubbery OC from the soil surfaces by phosphate as stated above, the proportion of rigid or condensed OC remaining in the solid matrices increased accordingly, which would enhance the nonlinearity of phenanthrene sorption according to the well-accepted dual reactive domain model [8,27,28]. Moreover, the specifically adsorbed phosphate occluded the micropores in the clay minerals [15] and made the solid surfaces more hydrophilic as indicated by the lower ζ potential values, resulting in a decreased hydrophobic partitioning of nonpolar organic compounds such as phenanthrene on soil surfaces [11].

4. Conclusions

The present study for the first time demonstrates the effect of phosphate on the sorption of HOCs (phenanthrene as a model compound) in soils. Phosphate can significantly change soil solution chemistry, particularly the compositional and morphological properties of DOC in the soils, and consequently exert effects on the sorption of phenanthrene in soils. The results of this study will improve our understanding of the role of solution chemistry in sorption mechanisms of organic compounds. A combination of microscopic and chromatographic techniques was used to provide direct evidence for the influence of phosphate on soil microinterfaces, which will be useful for exploring other complicated...
microinterface processes in the environment. In addition, the inhibitory effect of phosphate on HOC sorption is expected to have profound implications for the final fate, including bioavailability and degradation, of HOCs in the environment and this merits further investigation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2010.09.037.

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