

Impact of exotic and inherent dissolved organic matter on sorption of phenanthrene by soils

Yanzheng Gao^a, Wei Xiong^a, Wanting Ling^{a,*}, Xiaorong Wang^{b,**}, Qiuling Li^a

^a College of Resource and Environmental Sciences, Nanjing Agricultural University, Nanjing 210095, PR China

^b State Key Laboratory of Pollution Control and Resources Reuse, School of Environment, Nanjing University, Nanjing 210093, PR China

Received 12 November 2005; received in revised form 6 May 2006; accepted 19 June 2006

Available online 21 June 2006

Abstract

The impacts of exotic and inherent dissolved organic matter (DOM) on phenanthrene sorption by six zonal soils of China, chosen so as to have different soil organic carbon (SOC) contents, were investigated using a batch technique. The exotic DOM was extracted from straw waste. In all cases, the sorption of phenanthrene by soils could be well described by the linear equation. The presence of inherent DOM in soils was found to impede phenanthrene sorption, since the apparent distribution coefficients (K_d^*) for phenanthrene sorption by deionized water-eluted soils were 3.13–21.5% larger than the distribution coefficients (K_d) by control soils. Moreover, the enhanced sorption of phenanthrene by eluted versus control soils was in positive correlation with SOC contents. On the other hand, it was observed that the influence of exotic DOM on phenanthrene sorption was related to DOM concentrations. The K_d^* values for sorption of phenanthrene in the presence of exotic DOM increased first and decreased thereafter with increasing the added DOM concentrations (0–106 mg DOC/L). The K_d^* values at a low exotic DOM concentration (≤ 28 mg DOC/L) were 14.7–48.4% larger than their control K_d values. In contrast, higher concentrations (≥ 52 mg DOC/L) of added exotic DOM clearly impeded the distribution of phenanthrene between soil and water. The effects of exotic and inherent DOM on phenanthrene sorption by soils may primarily be described as ‘cumulative sorption’, association of phenanthrene with DOM in solution, and modified surface nature of soil solids due to DOM binding.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Dissolved organic matter (DOM); Polycyclic aromatic hydrocarbons (PAHs); Sorption; Soil

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are by-products from the incomplete combustion or pyrolysis of organic materials. Several of these compounds are carcinogenic and/or mutagenic, posing great threats to human health [1–3]. The contamination of soils by PAHs as well as other nonionic organic contaminants (NOCs) is a worldwide environmental problem [4–9]. Understanding of the transport and fate of NOCs in soil environment is paramount to determinations of the NOC risks to human health and the environment and of remediation strategies for soil contamination.

The distribution of NOCs including PAHs in soil environment involves complex phenomena which are influenced by many pro-

cesses, among which sorption to soil solids is a most important process that has a decisive effects on their transport, bioavailability, and fate in natural environments [7,10–14]. Extensive research has shown that the sorption of NOCs in a soil–water system is governed by a mechanism where the NOC molecules partitions into the soil organic matter (SOM) phase [15–17]. It is well documented that the NOC sorption increases with increasing SOM content. Soils with high organic matter serve as huge sinks of these compounds, and limit their bioavailability in environments [7,18–20]. In addition, the NOC sorption is known to be dependent on the characteristics of SOM such as polarity and aromaticity [1,21–23].

In recent years, growing attention has been given to the influence of dissolved organic matter (DOM) on sorption of NOCs by soil. Some studies revealed that the presence of DOM promoted sorption of NOCs such as nonionic pesticides [21,24]. By contrast, in other cases the sorption of NOCs was obviously inhibited in the presence of DOM [4,5,17,25]. Cox et al. [18] reported that DOM reduced sorption of herbicide due to DOM–herbicide

* Corresponding author. Tel.: +86 25 84396208; fax: +86 25 84395210.

** Corresponding author.

E-mail addresses: gaoyanzheng@njau.edu.cn (Y. Gao),
lingwanting@njau.edu.cn (W. Ling), ekxr@nju.edu.cn (X. Wang).

interactions and/or competition for sorption sites on soil particles. Spark and Swift [26] observed that the presence of DOM had little effect on sorption of atrazine, isoproturon and paraquat by soils. Similarly, Seol and Lee [27] found that DOM (up to 150 mg DOC/L) did not significantly suppress the sorption of either atrazine or prometryne by soil solids. Clearly, results on sorption of NOCs by soils in the presence of DOM are not identical. But the mechanisms involved still need to be well defined.

The influence of DOM on sorption of NOCs by soil up-to-date mostly focused on nonionic pesticides. Only very limited information is available on the influence of DOM on sorption of PAHs by soils. In addition, the experimented DOMs in literatures are generally exotic, particularly deriving from organic composts, sediments, sewage sludges, and water from waste disposal sites [4,17,28]. In fact, total soil organic matter includes both the soluble and insoluble fractions of organic matter, although the proportion of soluble fraction in a soil is relatively very small [26]. However, to our best knowledge, the impacts of this soluble organic matter, i.e., the soil inherent DOM, on distribution of NOCs in three phase system including soil, water and DOM are heretofore still under elucidation.

Thus, in the present study, we seek to determine the effects of exotic and inherent DOM on sorption of PAHs, as representatives of NOCs, by a series of soils differing in organic matter contents. The mechanisms involved were evaluated, based on the observed distribution of DOM between soil and water. Results of this work would provide insight into the environmental behaviors of NOCs in three phase system with DOM.

2. Materials and methods

2.1. Chemicals

Phenanthrene, as a representative of PAHs, was provided by Aldrich Chemical Co. with a purity >98%. The molecular weight, solubility in water at 25 °C, log K_{ow} of phenanthrene were 178.23 g/mol, 1.18 mg/L, and 4.46, respectively [29].

2.2. Soils

Six natural surface soil samples, as representatives of major zonal soils in China, were collected and experimented in this

Table 1
Some characteristics of the experimented soils

Soil no.	Location (city, province)	pH values	f_{oc} (g/kg)
Soil 1	Jinxian, Jiangxi	4.43	4.90
Soil 2	Nanjing, Jiangsu	5.19	13.9
Soil 3	Hangzhou, Zhejiang	6.00	13.5
Soil 4	Changchun, Jilin	6.18	19.1
Soil 5	Shengzhou, Zhejiang	6.32	22.9
Soil 6	Haerbin, Heilongjiang	5.50	41.7

study. Samples were taken from the A horizons, air-dried, and sieved through a 100 mesh. A summary of the characteristics of these soil samples is shown in Table 1. The soil organic carbon contents (f_{oc}) were determined using LECO CS-344 type carbon-sulfate analyzer at the condition of 50% relative humidity and 25 °C. From soil 1 to soil 6, the f_{oc} of tested soils increased from 4.90 to 41.7 g/kg.

To evaluate the impact of soil inherent DOM on sorption of phenanthrene by soils, the deionized water-eluted soil samples were used. Soil samples were divided into two groups. One group is the control soils. That is, after being collected, samples were air-dried and sieved through a 100 mesh, and no other treatment was adopted. The second group is the deionized water-eluted soils. Certain amounts of control soils were placed into 100 mL glass tubes with 60 mL deionized water. The tubes were shaken on a rotating shaker for 4 h, and centrifuged at $4000 \times g$ for 30 min. Then the supernatant was decanted, and the soils were replenished with fresh deionized water. This process was repeated four times. Then soil samples were dried, grounded, and sieved through a 100 mesh. Thus the deionized water-eluted soils were obtained. The total organic carbon in effluent, i.e., the inherent DOM eluted off from soils (T_{doc}), were detected and listed in Table 2. The soil organic carbon contents of these eluted soils (f_{oc}^*) were calculated and also shown in this table.

2.3. DOM

The exotic DOM was extracted from the straw waste by shaking in the dark for 4 h with deionized water (solid:water = 1:15) at 250 rpm. The suspensions were centrifuged for 30 min at $10,000 \times g$ and filtered through a 0.45 μm cellulose acetate filter. The filtered solution, containing DOM, was analyzed for pH

Table 2
Regression data for phenanthrene sorption by deionized water-eluted and control soils using linear-type sorption isotherms

Soil no.	Control soil			Eluted soil			R^2	K_d^* (L/kg)	K_{oc}^* (L/kg)
	R^2	K_d (L/kg)	K_{oc} (L/kg)	T_{doc} (g/kg)	f_{oc}^* (g/kg)				
Soil 1	0.9863	46.05	9398	0.390	4.51	0.9831	47.49*	10530*	
Soil 2	0.9959	70.49	5071	0.555	13.4	0.9696	75.48*	5656*	
Soil 3	0.9987	112.9	8365	0.660	12.8	0.9925	119.6	9311	
Soil 4	0.9987	122.7	6425	0.495	18.6	0.9887	136.2	7319	
Soil 5	0.9878	185.5	8101	0.795	22.1	0.9979	211.1	9552	
Soil 6	0.9279	310.5	7456	0.840	40.8	0.9698	377.1	9241	

T_{doc} is the amounts of inherent DOM eluted off from soils, f_{oc}^* the calculated soil organic matter contents in eluted soils, and R^2 is the simulated correlation constants for phenanthrene sorption by linear equation.

* K_d^* or K_{oc}^* value was not significantly different from its corresponding K_d or K_{oc} values for the same soil ($p < 0.05$).

(5.92) and conductivity (0.85 mS/cm). The dissolved organic carbon (DOC), representing the amount of DOM in solution, was determined by a total organic carbon (TOC) analyzer (Shimadzu TOC-5000). DOM solution was acidified and sparged with nitrogen prior to injection to remove carbonates. The content of DOM (in the filtered solution) was 212 mg DOC/L.

2.4. Sorption experiments

Batch experiments were conducted to determine phenanthrene sorption by treated soils including the control and eluted ones [4,11,13,14,30]. A series of quantities of phenanthrene were added to 25 mL glass centrifuge tubes sealed with screw caps, containing 1 g of soil in 15 mL of 0.02 mol/L KCl solutions with 0.05% NaN₃ and a given exotic DOM concentrations. The tubes were shaken in the dark for 24 h at 250 rpm on a gyratory shaker to reach the equilibrium state. The solution and soil were separated by centrifugation at 3000 × g for 20 min. An amount of supernatant was removed and analyzed for phenanthrene concentrations. Control tubes were prepared at each concentration level with no soil present to monitor the loss of phenanthrene. The losses of phenanthrene by photochemical decomposition, volatilization, and sorption to tubes were found to be negligible.

2.5. Phenanthrene analysis

Three millilitres aliquots of the supernatant were loaded into 10 mL glass tube and then diluted by 7 mL methanol (HPLC grade). After being filtered through 0.22 μm filter units, diluted solution was analyzed with a high-performance liquid chromatograph (HPLC; Waters, USA) fitted with a reverse phase C₁₈ column (3.9 mm × 150 mm, 5 μm particle size) using methanol as the mobile phase at a flow rate of 0.8 mL/min [31]. The detection wavelength of phenanthrene was 245 nm, and its detection limit was 44.1 pg.

3. Results and discussions

3.1. Sorption isotherms of phenanthrene by soils

In this work, over the range of concentrations the sorption isotherms of phenanthrene by six tested soils could be well described using linear distribution-type model [17] with the correlation constants (R^2) greater than 0.93 (Fig. 1 and Table 2). The distribution coefficient (K_d , L/kg) of solute between soil and water according to the linear sorption model is expressed as:

$$K_d = \frac{Q}{C_e} \quad (1)$$

here Q denotes the amount of NOC sorbed by soil solids (mg/kg). C_e is the equilibrium concentration of NOC in aqueous phase (mg/L). In this study, the values of K_d for phenanthrene sorption by tested soils were 46.05–310.5 L/kg, and were in the order of soil 6 > soil 5 > soil 4 > soil 3 > soil 2 > soil 1 (Table 2). This order significantly correlated to the order of relative contents of soil organic carbon (SOC) with a statistical R^2 value for fit

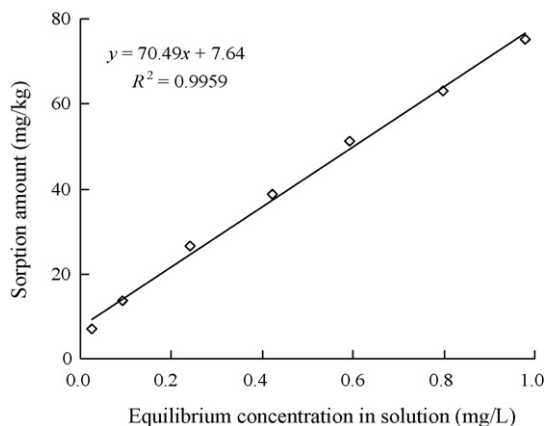


Fig. 1. Linear isotherm for phenanthrene sorption by soil 2.

of 0.96 (Fig. 2), indicating that the soil organic matter (SOM) dominates phenanthrene sorption by soils [13].

The values of the corresponding carbon-normalized distribution constant (K_{oc} , L/kg) were also given in Table 2. K_{oc} , i.e., the ratio of the K_d value to the SOC content, can be expressed as:

$$K_{oc} = \frac{K_d}{f_{oc}} \quad (2)$$

where f_{oc} is the fractional organic carbon content of soil (%). Clearly, the calculated K_{oc} values for six soils were dramatically closer than their corresponding K_d values. The averaged K_{oc} values were 7469 ± 1929 L/kg (representing 26% variation). However, soil 1 (9398 L/kg) gave the highest K_{oc} value, which was still 85.3% larger than that for soil 2 (5071 L/kg) with the lowest K_{oc} . This suggests that except for SOM contents, the nature of SOM may also play a key role in NOC sorption [7,14].

The large variation of K_{oc} values of a single hydrophobic organic compound for different soils has also been reported in literatures [20,26]. Such variations may be the reason that the total organic carbon content of a soil does not account for the nature, location, and composition of the organic matter, which will affect the effective levels of active organic matter to sorb NOCs

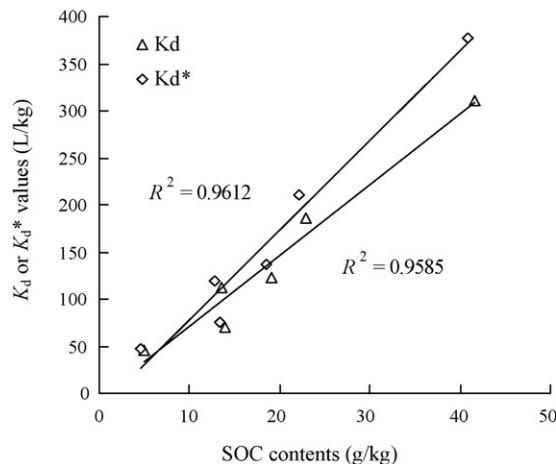


Fig. 2. Correlation between K_d or K_d^* values and soil organic carbon (SOC) contents.

[21,23,32]. There is evidence that some of soil organic matter may be inaccessible to NOC if it associates within solid-state humic particles or clay aggregates, reducing the effectiveness of active organic matter in soil [14,26]. Similarly, some soils may have a lower proportion of strong sorptive to less sorptive organic matter present [22]. In this work, the larger value of K_{oc} for soil 6 suggests that this soil may have higher proportions of strong sorptive organic matter than other soils.

3.2. Effect of inherent DOM on phenanthrene sorption by soils

DOM has been the subject of considerable interest in recent years because its interaction with organic pollutants and thus affecting the fate of these pollutants in soils and other environment. However, the reported DOMs associated with NOC sorption are mostly exotic, as stated previously. And the impacts of soil inherent DOM on NOC sorption by soil is by far less understood. Thus, in this part, the deionized water-eluted soil samples, in which the inherent DOM was removed from soils, were experimented to evaluate the influence of soil inherent DOM on phenanthrene sorption by soil.

Over the range of tested concentrations, the sorption isotherms of phenanthrene by eluted soils were also fit well to linear distribution-type model ($R^2 > 0.97$). The apparent distribution constant (K_d^*) of phenanthrene simulated from linear equation were 47.49–377.1 L/kg, as shown in Table 2. Although some of the soil inherent DOM were eluted off from the soil solids, and the SOC contents of eluted soils were relatively a little (2.01–7.96%) lower than those of the corresponding control soils (Tables 1 and 2), the K_d^* values were still significantly correlated to the SOC contents (Fig. 1). This indicates that partitioning into SOM is still the dominant mechanism of phenanthrene sorption by these soils, and the SOM serves as the primary sorbent for phenanthrene sorption.

It was notable that the decrease of SOC contents due to the elution of soil inherent DOM resulted in the enhanced sorption of phenanthrene by tested soils. Table 2 shows that the K_d^* values were 3.13–21.5% larger than their corresponding K_d values for the same soil. This means that the presence of the soil inherent DOM impedes phenanthrene sorption by soil solids.

Similarly, the calculated apparent carbon-normalized distribution constants (K_{oc}^*) for phenanthrene sorption by eluted soils were accordingly greater than the K_{oc} values by control soils, indicating that the SOM would be strong sorptive in phenanthrene sorption when soil inherent DOM was eluted off. These results suggest that including the total SOM content, the nature of the inherent DOM in soil also plays an important role in NOC sorption, although the soils may have very small proportions of inherent DOM.

A further investigation reveals that the enhanced sorption of phenanthrene by the deionized water-eluted soils versus control soils was obviously in positive correlation with their SOC contents (f_{oc}), as shown in Fig. 3. For instance, K_d^* value for soil 6 with the highest SOC content was 66.6 L/kg and 21.5% larger than its K_d value. By contrast, the K_d^* values for soil 1 and soil 2 were only equal to or a little larger than their respective K_d values (Fig. 3).

NOC sorption between soil and water is dependent on its distribution between three phases: the aqueous solution, DOM, and soil solids [4]. The association of DOM with NOCs such as nonionic pesticides in solution phase is well documented, and has been proposed as an important process that results in solubility enhancement and reduced the sorption of these compounds by soil sorbents [13,14,17,24,25]. There is also much evidence of the interaction of DOM with PAHs in aqueous solution. It has been suggested that the interactions of PAHs with DOM are more pronounced with its hydrophobic fractions, and the affinity of DOM to PAHs was controlled by the molecular properties of PAHs [24,28]. The reported partition coefficients (K_{doc}) of benzo(e)pyrene and benzo(k)fluoranthene with DOM in solution were 19,953–79,432 L/kg [28], and K_{doc} of phenanthrene with DOM was 8317.6 L/kg [33]. Clearly, K_{doc} values of PAHs were generally much larger than their distribution constants (K_d or K_d^*) between soil solids and water (Table 2). This indicates that the strong binding affinity of PAHs with DOM in solution would impede the sorption of PAHs by soils. The higher DOM concentration in solution leads to the stronger inhibition of PAH sorption by soil solids. In this work, the enhanced sorption of phenanthrene by eluted versus control soils may also primarily be the reason that DOM concentrations (C_{doc}) in solution for the former were far lower than C_{doc} for the latter (Fig. 4).

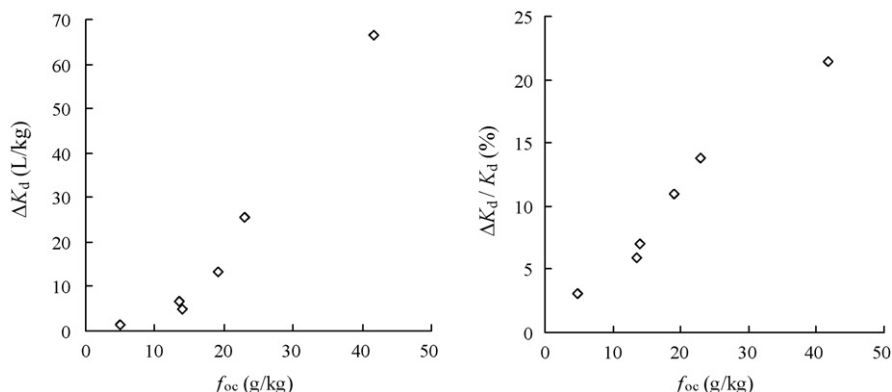


Fig. 3. Correlations of the enhanced sorption of phenanthrene with soil organic carbon contents; $\Delta K_d = K_d^* - K_d$.

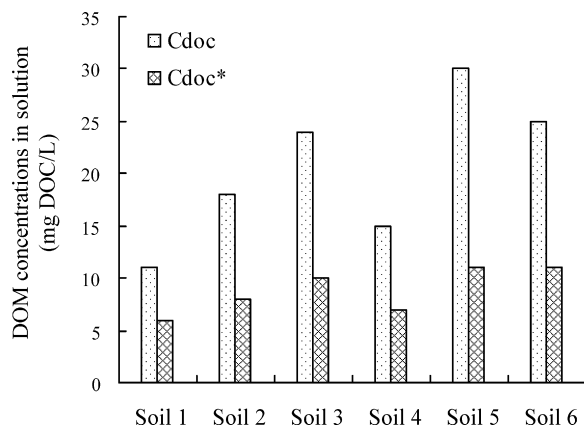


Fig. 4. DOM concentrations in aqueous solution for phenanthrene sorption by deionized water-eluted soils (C_{doc}^*) and control soils (C_{doc}).

In addition, the modified surface characteristics of solids due to the bond of inherent DOM with soil solids such as soil insoluble organic matter may also account for the enhanced sorption of phenanthrene by eluted soils. For instance, binding of inherent DOM to soil solids could take place through hydrophobic regions of DOM with hydrophilic and ionizable groups oriented to the aqueous solution, which may make the soil–water interface more hydrophilic resulting in preferential sorption of water molecules instead of PAHs [17,20,30]. As such, the presence of the inherent DOM in control soils would make the surface of soil solid more hydrophilic and impede phenanthrene sorption. As to the positive correlation of the enhancement of phenanthrene sorption by eluted versus control soils with SOC contents, the involved mechanisms still needs to be further investigated.

3.3. Effect of exotic DOM on phenanthrene sorption by soils

The sorption of phenanthrene by tested soils was determined in the presence of exotic DOM at added concentrations ≤ 106 mg DOC/L. In all cases, sorption could be well described by the linear isotherm with $R^2 > 0.94$. In the presence of exotic DOM, the apparent distribution coefficient, K_d^* , for phenanthrene sorption by soils, taking soil 5 as an example, increased first and decreased thereafter with the increase of the added DOM concentrations (0–106 mg DOC/L) (Fig. 5). That is, the presence of exotic DOM at a low concentration (≤ 28 mg DOC/L) promoted the sorption of tested PAH. In contrast, higher exotic DOM concentrations (≥ 52 mg DOC/L) added in soil–water system clearly impeded the distribution of phenanthrene into soil solids. For instance, the maximum K_d^* value of 221.6 L/kg at DOM concentration of 28 mg DOC/L was 16.3% higher than its corresponding control K_d value (185.5 L/kg). Whereas the tested minimum K_d^* value at DOM concentration of 106 mg DOC/L was 15.6% lower than the control one, as shown in Fig. 5.

In addition, the enhanced sorption of phenanthrene by other soils with present exotic DOM of low concentrations was also observed in this work. As shown in Fig. 6, the respective K_d^* values for phenanthrene sorption by soil 2, soil 3, and soil 4 in the presence of 28 mg DOC/L DOM were 104.6, 129.5,

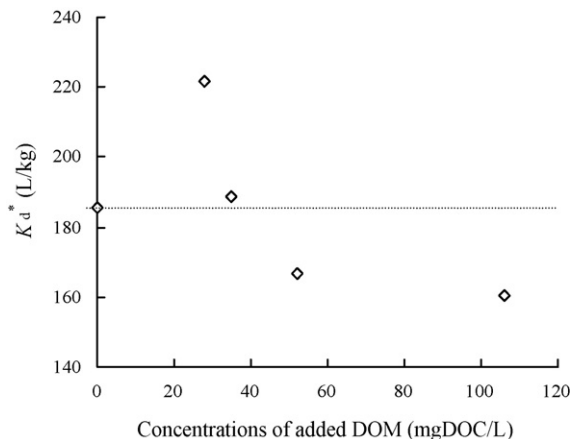


Fig. 5. The apparent distribution constant (K_d^*) for phenanthrene sorption by soil 5 as function of the added exotic DOM concentrations.

and 145.0 L/kg, which were 14.7–48.4% larger than their corresponding K_d values. By contrast, significant impediment of phenanthrene sorption was observed when high exotic DOM present. For example, the K_d^* values for soil 4 and soil 6 in the presence of 106 mg DOC/L were 11.9 and 50.3 L/kg lower than their control K_d values, respectively (Fig. 6).

Results above were somewhat different from previous findings on sorption of NOCs by soils in the presence of exotic DOM. Celis et al. [17] reported that the added DOM from sewage sludge decreased atrazine sorption by soils, and similar results were reported in literatures [4,5,25]. By contrast, the enhanced sorption of NOCs was also well documented [24]. Others observed that the presence of DOM had little effects on NOC sorption [26,27]. In this work, we found that the impacts of exotic DOM on phenanthrene sorption by tested soils actually were DOM concentration-dependant (Figs. 5 and 6).

The influence of exotic DOM on NOC sorption may be ascribed to their interaction in solution, competition for sorption sites, co-sorption, and cumulative sorption [13,14,17,24,25]. As discussed previously, the association of DOM with NOC in solution may decrease the NOC sorption by soil solids. In addition, the competition of DOM with relatively polar NOC such as some pesticides for sorption sites also tended to reduce its

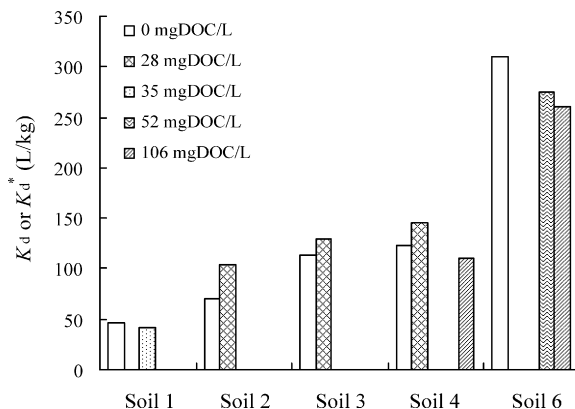


Fig. 6. The K_d^* and K_d values for phenanthrene sorption by soils at various exotic DOM concentrations.

Table 3

Some parameters for phenanthrene sorption by soil 5 in the presence of exotic DOM at various concentrations

Added DOM concentrations (mg DOC/L)	K_d^* (L/kg)	C_{doc}^* (mg DOC/L)	Q_{doc} (mg DOC/kg)	$K_{ph/soc}$ (L/kg)
0	185.5	30		
28	221.6	48	150	461848
35	188.6	60	75	668813
52	166.6	69	195	180219
106	160.4	109	405	198265

C_{doc}^* is the equilibrium concentrations of DOM in aqueous solution for phenanthrene sorption by soil 5.

sorption by soil [4,17,26]. However, as a highly hydrophobic organic compound with a $\log K_{ow}$ of 4.46 [29], phenanthrene sorption was closely related to SOC content irrespective of the presence of DOM, i.e., organic matter dominates phenanthrene sorption by soil. While the clay mineral surface generally contributes to the sorption of DOM [13,34]. As such, competition of phenanthrene with DOM for sorption sites seems to be a minor mechanism of the impacts of exotic DOM on phenanthrene sorption. Additionally, the DOM-mediated sorption (co-sorption), i.e., the formation of a DOM–NOC complex and its sorption by soil which is suggested to increase NOC sorption, did not seem to be a major factor controlling phenanthrene sorption, since sorption in the presence of DOM could be well described by the linear model [20].

The sorption of DOM in soil–water system was observed, and its sorption amounts (Q_{doc}) were calculated and shown in Table 3. The DOM sorption to soil solids may increase the bulk SOC contents, and hence provide new sorption sites. As a result, such ‘cumulative sorption’ would increase the soil’s capacity of taking up phenanthrene and promote its sorption. In this work, the added exotic DOM at low concentrations (≤ 28 mg DOC/L) was primarily sorbed to soil solids. The initial rise in K_d^* values for phenanthrene sorption by tested soils in the range of tested DOM concentrations, as showed in Figs. 5 and 6, was consistent with the above suggestion.

On the other hand, the increased SOM (expressed as Q_{doc} , as shown in Table 3) due to the DOM sorption may not have the same capacity of phenanthrene uptake as the original SOM in soils, since the enhanced SOC contents (Q_{doc}) were less than 1.77% of the soil f_{oc} , taking soil 5 as an example. We further evaluated the capacity of the sorbed DOM for phenanthrene uptake, based on the equation [17,20,30] as follows:

$$K_d^* = \frac{K_d + K_{ph/soc} Q_{doc}}{1 + K_{ph/doc} \times \Delta C_{doc}} \quad (3)$$

This equation could also be expressed as:

$$K_{ph/doc} = \frac{K_d^*(1 + K_{ph/doc} \times \Delta C_{doc}) - K_d}{Q_{doc}} \quad (4)$$

where $K_{ph/soc}$ is the distribution coefficient of phenanthrene between water and the sorbed DOM on soil solids, $K_{ph/doc}$ the association coefficient of phenanthrene with DOM in water, and its value was 8317.6 L/kg [33], and ΔC_{doc} is the difference of DOM concentration in aqueous solution in the presence versus absence of exotic DOM. According to Eq. (4), the $K_{ph/soc}$ values of phenanthrene were calculated and displayed in Table 3. Obvi-

ously, $K_{ph/soc}$ values were about three magnitudes larger than their corresponding K_d values. As stated previously, the nature or location of organic matter in soil will affect the effective level of active organic matter to sorb NOCs [21,23,26,32]. The large values of $K_{ph/soc}$ compared to K_d suggest that the sorbed DOM on soil solids are much stronger sorptive and do have far stronger capacity of phenanthrene uptake than the original SOM, which may also be a major mechanism of the enhanced sorption of phenanthrene by tested soils in the presence of exotic DOM at lower concentrations.

However, in the range of tested concentrations, the K_d^* values turned to decrease after an initial increase with the extensive increase of the added exotic DOM concentrations (Figs. 5 and 6). The decreased sorption may be the result of the enhancement of phenanthrene association with DOM in solution since C_{doc}^* increases straightly with increasing the added DOM concentrations (Table 3), as mentioned previously. On the whole, the influence of exotic DOM on phenanthrene sorption could be approximately considered as the net effect of the ‘cumulative sorption’ and the association of phenanthrene with DOM in solution. While the co-sorption and competition between DOM and phenanthrene for sorption sites would have minor effects on phenanthrene sorption by soil solids.

4. Conclusions

The influence of exotic and inherent DOM on phenanthrene sorption by six zonal soils of China was evaluated using a batch equilibrium technique. In all cases, phenanthrene sorption by various treated soils could be well described by a linear-type sorption model irrespective of the presence of DOM. The apparent distribution coefficients (K_d^*) for phenanthrene sorption by deionized water-eluted soils were larger than the K_d values by the corresponding control soils. The enhancement of phenanthrene sorption by eluted versus control soils was positively correlated to SOC contents. These results indicate that the presence of inherent DOM in soils impedes the distribution of phenanthrene between soil and water.

The impacts of exotic DOM on phenanthrene sorption were DOM concentration-dependant. The K_d^* values for phenanthrene sorption by soils increased first and decreased thereafter with the increase of the added exotic DOM concentrations (0–106 mg DOC/L). The presence of exotic DOM at a low concentration (≤ 28 mg DOC/L) promoted the sorption of tested PAH. In contrast, higher exotic DOM concentrations

(≤ 52 mg DOC/L) clearly impeded the distribution of phenanthrene into soil solids.

The mechanisms involved in the effects of exotic and inherent DOM on phenanthrene sorption may be primarily described as ‘cumulative sorption’, the association of phenanthrene with DOM in solution, and the modified surface characteristics of soil solids due to DOM binding. Results of this work would provide insight into the NOC distribution in three phase systems including soil, water and DOM.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (20507009), the Natural Science Foundation of Jiangsu Province, China (BK2006518), the International Foundation for Science (IFS; C/3958-1), the Foundation of State Key Laboratory of Pollution Control and Resources Reuse (PCRRF05004), the Foundation of Ministry of Education Key Lab of Environment Remediation and Ecological Health (050302), and the Young Scientist Innovation Science Foundation of Nanjing Agricultural University (KJ05009).

References

- [1] J.C. White, J.W. Kelsey, P.B. Hatzinger, M. Alexander, Factors affecting sequestration and bioavailability of phenanthrene in soils, *Environ. Toxicol. Chem.* 16 (1997) 2040–2045.
- [2] K.D. Jones, C.L. Tiller, Effect of solution chemistry on the extent of binding of phenanthrene by a soil humic acid: a comparison of dissolved and clay bound humic acids, *Environ. Sci. Technol.* 33 (1999) 580–587.
- [3] Y.Z. Gao, L.Z. Zhu, Plant uptake, accumulation and translocation of phenanthrene and pyrene in soils, *Chemosphere* 55 (2004) 1169–1178.
- [4] J.P. Gao, J. Maguhn, P. Spitzauer, A. Kettrup, Sorption of pesticides in the sediment of the Teufelsweiher pond (southern Germany). 2. Competitive adsorption, desorption of aged residues and effect of dissolved organic carbon, *Water Res.* 32 (1998) 2089–2094.
- [5] S.D. Nelson, J. Letey, W.J. Farmer, C.F. Williams, M. Ben-Hur, Facilitated transport of napropamide by dissolved organic matter in sewage sludge-amended soil, *J. Environ. Qual.* 27 (1998) 1194–1200.
- [6] I. Kögel-Knabner, K.U. Totsche, B. Raber, Desorption of polycyclic aromatic hydrocarbons from soil in the presence of dissolved organic matter: effect of solution composition and aging, *J. Environ. Qual.* 29 (2000) 908–916.
- [7] L. Nemeth-Konda, Gy. Füleky, Gy. Morovjan, P. Csokan, Sorption behaviour of acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon on Hungarian agricultural soil, *Chemosphere* 48 (2002) 545–552.
- [8] C.M. Cooke, G. Shaw, C.D. Collins, Determination of solid–liquid partition coefficients (K_d) for the herbicides isoproturon and trifluralin in five UK agricultural soils, *Environ. Pollut.* 132 (2004) 541–552.
- [9] Y.Z. Gao, L.Z. Zhu, Phytoremediation for phenanthrene and pyrene contaminated soils, *J. Environ. Sci.* 16 (2005) 12–18.
- [10] J. Walter, W.J. Weber Jr., Distributed reactivity model for sorption by soils and sediments. 15. High-concentration co-contaminant effects on phenanthrene sorption and desorption, *Environ. Sci. Technol.* 36 (2002) 3625–3634.
- [11] H. Li, B.J. Teppen, C.T. Johnston, S.A. Boyd, Thermodynamics of nitroaromatic compound adsorption from water by smectite clay, *Environ. Sci. Technol.* 38 (2004) 5433–5442.
- [12] M. Krauss, W. Wilcke, Persistent organic pollutants in soil density fractions: distribution and sorption strength, *Chemosphere* 59 (2005) 1507–1515.
- [13] P.M. McGinley, L.E. Katz, W.J. Weber Jr., A distributed reactivity model for sorption by soils and sediments. 2. Multicomponent systems and competitive effects, *Environ. Sci. Technol.* 27 (1993) 1524–1532.
- [14] W.T. Ling, J.M. Xu, Y.Z. Gao, Effects of dissolved organic matter from sewage sludge on the atrazine sorption by soils, *Sci. China* 16 (2005) 478–482.
- [15] C.T. Chiou, L.J. Peters, V.H. Freed, A physical concept of soil–water equilibria for nonionic organic compounds, *Science* 206 (1979) 831.
- [16] S.W. Karickhoff, D.S. Brown, T.A. Scott, Sorption of hydrophobic pollutants on natural sediments, *Water Res.* 13 (1979) 241–248.
- [17] R. Celis, E. Barriuso, S. Houot, Effect of liquid sewage addition on atrazine sorption and desorption by soil, *Chemosphere* 37 (1998) 1091–1107.
- [18] L. Cox, R. Celis, M.C. Hermosin, J. Cornejo, A. Zsolnay, K. Zeller, Effect of organic amendments on herbicide sorption as related to the nature of the dissolved organic matter, *Environ. Sci. Technol.* 34 (2000) 4600–4605.
- [19] S. Hwang, T.J. Cutright, Preliminary evaluation of PAH sorptive changes in soil by Soxhlet extraction, *Environ. Int.* 30 (2004) 151–158.
- [20] W.T. Ling, J.M. Xu, Y.Z. Gao, Dissolved organic matter-enhanced sorption of atrazine by soil in three-phase system, *Biol. Fert. Soils* 42 (2006) 418–425.
- [21] E.M. Murphy, J.M. Zachara, The role of sorbed humic substances on the distribution of organic and inorganic contaminants in groundwater, *Geoderma* 67 (1995) 103–124.
- [22] B. Xing, J.J. Pignatello, Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter, *Environ. Sci. Technol.* 31 (1997) 792–799.
- [23] D. Brion, E. Pelletier, Modeling PAHs adsorption and sequestration in freshwater and marine sediments, *Chemosphere* 61 (2005) 867–876.
- [24] K.U. Totsche, J. Danzer, I. Kögel-Knabner, Dissolved organic matter-enhanced retention of polycyclic aromatic hydrocarbons in soil miscible displacement experiments, *J. Environ. Qual.* 26 (1997) 1090–1100.
- [25] D.Y. Lee, W.J. Farmer, Y. Aochi, Sorption of napropamide on clay and soil in the presence of dissolved organic matter, *J. Environ. Qual.* 19 (1990) 567–573.
- [26] K.M. Spark, R.S. Swift, Effect of soil composition and dissolved organic matter on pesticide sorption, *Sci. Total Environ.* 298 (2002) 147–151.
- [27] Y.K. Seol, L.S. Lee, Effect of dissolved organic matter in treated effluents on sorption of atrazine and prometryn by soils, *Soil Sci. Soc. Am. J.* 64 (2000) 1976–1983.
- [28] B. Raber, I. Kögel-Knabner, Influence of origin and properties of dissolved organic matter on the partition of polycyclic aromatic hydrocarbons, *Eur. J. Soil Sci.* 48 (1997) 443–455.
- [29] C.L. Yaws, *Chemical Properties Handbook*, McGraw-Hill Book Co., New York, 1999, pp. 340–389.
- [30] Y.Z. Gao, W. Xiong, W.T. Ling, J.M. Xu, Sorption of phenanthrene by contaminated soils with heavy metals, *Chemosphere* (2006), in press.
- [31] Y.Z. Gao, L.Z. Zhu, W.T. Ling, Application of the partition-limited model for plant uptake of organic chemicals from soil and water, *Sci. Total Environ.* 336 (2005) 171–182.
- [32] C.T. Chiou, R.L. Malcolm, T.I. Brinton, D.E. Kile, Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids, *Environ. Sci. Technol.* 20 (1986) 502–508.
- [33] H.V. Mott, Association of hydrophobic organic contaminants with soluble organic matter: evaluation of the database of K_{doc} values, *Adv. Environ. Res.* 6 (2002) 577–593.
- [34] J. Satterberg, T.S. Amerson, E.J. Lessard, R.G. Keil, Sorption of organic matter from four phytoplankton species to montmorillonite, chlorite and kaolinite in seawater, *Mar. Chem.* 81 (2003) 11–18.