Sorption of pyrene on two paddy soils and their particle-size fractions

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Abstract: In the present study, the sorption of pyrene on two kinds of bulk paddy soils, Gleyic Stagnic Anthrosols, and Ferric accumulic Stagnic Anthrosols as well as their particle-size fractions was investigated. The sorption isotherms fitted well with Freundlich equation. For both soils, the clay fraction(< 2 μm) and coarse sand fraction(2000—250 μm) had higher sorption capacity than fine sand fraction(250—20 μm) and silt fraction(20—2 μm). The log K_{oc} values obtained of each soil and its particle-size fractions were similar, proving that SOM content was a key factor affecting pyrene sorption. The K_d values showed a significant correlation with contents of dithionite-extractable Fe in both paddy soils and a good relationship with CEC in Gleyic Stagnic Anthrosols, indicating possible effects of surface properties of particle-size fractions on the sorption of pyrene.

Keywords: paddy soil; particle-size fraction; PAHs; sorption

Introduction

Polycyclic aromatic hydrocarbons(PAHs) are ubiquitous persistent organic contaminants present in environment, and have aroused much concern due to their toxic, mutagenic and carcinogenic effects on human health and toxic impacts on terrestrial ecosystems. Once PAHs are released, they can reach the soil via various pathways, such as deposition from the atmosphere, and the contaminants are very hard to be completely removed from the soil. Wild and Jones(Wild, 1995) estimated that at least 90% of the environmental PAH burden in Great Britain is stored in soil.

Particle-size separates have been widely used to distinguish pools of different soil organic matter (SOM) quality and turnover rates(Christensen, 1992). Distribution of PAHs in different particle-size fractions is important concern in research on the physical movement of these pollutants and their redistribution in the environment. Resuspension and inhalation as direct pathways for exposure to humans also strongly depend on particle size(Livens, 1988). Sorption to and partitioning into SOM have been considered to be the primary processes controlling the bioavailability of hydrophobic organic contaminants (Pignatello, 1996; Nieman, 1999). The extent of sorption of an organic contaminant to soil has a major influence on its transport and fate in the environment.

As a special kind of anthropogenic soil, paddy soils are in active exchange of materials with water and air. Understanding mobility and bioavailability of PAHs in paddy soils requires knowledge of their association with soil particle-size fractions of the paddy soils. In an attempt to elucidate the PAHs behavior in paddy soils and to clarify environmental risks of PAHs accumulation in these soils, an experiment on pyrene, sorption on bulk soil and their particle-size fractions was conducted and reported in the paper.

1 Materials and methods

1.1 Soil samples

Samples of two different types of paddy soil types, Gleyic Stagnic Anthrosols (Soil W) and Ferric accumulic Stagnic Anthrosols(Soil H) were collected from depth of 0—15 cm soil layer of paddy fields in Kunshan City(120°30′E, 31°35′N) and Wujiang City(120°46′E, 31°05′N) in the Taihu Lake area, China. The samples were air-dried and size fractions of coarse sand(2000—250 μm), fine sand(250—

20 μm), silt(20—2 μm), and clay(< 2 μm) were separated with the method described by Amelung *et al*. (Amelung, 1998). The bulk samples for experiment were ground to pass 2 mm sieve prior to sorption experiment.

Soil organic carbon and humic carbon were determined with wet digestion method, the cation exchange capacity (CEC) was determined with extraction with buffered 1 mol/L ammonium acetate, and dithionite-extractable Fe (Fe_d) was extracted with dithionite-citrate-bicarbonate and determined according to the procedures described by Lu (Lu, 1999) respectively. Properties of the bulk soils and separates of particle-size fractions were presented in Table 1.

Table 1   Selected properties of the paddy soils and their particle-size fractions

Samples	Percen-tage, %	Organic C	Humic C	Fe_d	CEC, cmol$_c$/kg
			g/kg		
Soil W					
Bulk soil		15.5	3.5	20.4	20.5
Coarse sand	2.3	20.0	4.5	34.6	22.7
Fine sand	36.6	12.2	3.3	14.4	14.0
Silt	33.2	13.7	4.6	19.6	17.5
Clay	26.9	23.7	4.8	40.9	42.1
Soil H					
Bulk soil		17.3	3.6	25.3	19.5
Coarse sand	5.2	26.2	2.9	43.9	20.8
Fine sand	28.3	15.0	3.1	20.9	13.0
Silt	37.5	14.4	5.7	23.0	16.3
Clay	30.0	20.8	3.8	44.7	22.5

1.2 Chemicals and sorption experiments

Standard pyrene(PYR) was purchased with a purity of over 98% from the Aldrich Chemical Company, Inc. PYR stock solution (2 g/L) was prepared in the HPLC-grade methanol obtained from the Tedia Company, Inc. Sodium azide(NaN₃) was purchased in reagent grade, and dissolved in distilled water to prevent any microbial activity during the study.

Sorption experiments were carried out according to the procedure described by Chiou *et al*.(Chiou, 1998), briefly described as follow: 0.5 g sample each from the bulk soil and their particle-size fractions was placed into glass centrifuge tube with aluminum-liner cap separately, 10 ml of 200 mg/L NaN₃ solution and a desired amount of PYR stock solution was added to each sample to give initial concentration

of 2, 4, 6, 8, 10, 12, and 14 mg/L. The tubes were horizontally placed in a rotation shaker (25 ± 2°C, 150 r/min) in darkness for 24 h. After equilibrium, the tubes were centrifuged at the rate of 4000 r/min for 15 min, and the supernatant solutions were filtrated through 0.45 μm glass-fiber filter paper. Three replicates were used for each concentration.

1.3 Analytical methods

Pyrene was quantified with a high performance liquid chromatograph(HPLC, Waters 1525, Waters, Milford, MA) equipped with a fluorescence detector(Waters 474 scanning fluorescence detector) and a reverse-phase precolumn and a LC-PAH column (15 cm × 5 mm, 5 μm, Supelcosil LC-PAH, Supelco, Bellefone, PA). Acetonitrile-water(80:20) was the mobile phase at a rate of 1.0 ml/min. The excitation and emission wavelengths determined were λ_{ex} = 245 nm and λ_{em} = 390 nm respectively. Concentrations of pyrene in solution were analyzed by direct injection of 20 μl supernatants into the HPLC system. Pyrene sorption capacity of each sample was calculated based on the difference between the pyrene concentration in the solution and the total

amounts of pyrene added to the solution.

1.4 Statistical analysis

Experimental results were statistically analyzed using SPSS 11.5 for Windows.

2 Results

Sorption isotherms are usually described by either linear, Freundlich, or Langmuir sorption models. In this study, the amount of PYR sorbed on paddy soils and their particle-size fractions was plotted against the equilibrium PAH concentration, the isotherms were in S shapes(Fig.1), and all adsorption data were well fitted by the Freundlich sorption model base on a sum of least square analysis. The Freundlich model is depicted as follows:

$$q = K_d C_e^N,$$

where q is the amount of compound sorbed (mg/kg), C_e is the concentration in the liquid phase (mg/L). K_d is the Freundlich distribution coefficient (L/kg), and N is the Freundlich exponent.
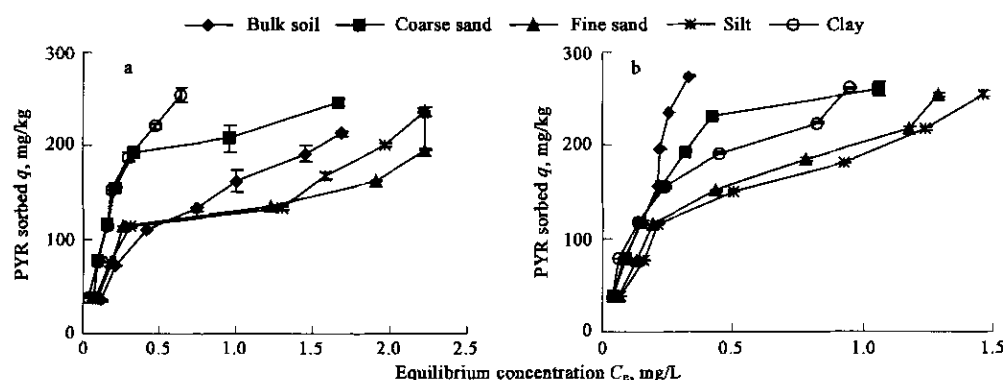

Fig.1 Sorption isotherms of PYR on Soil W(a), Soil H(b) and their particle-size fractions

Some parameters of the Freundlich equation were given in Table 2. K_{oc} was calculated from the K_d being normalized to the C level of each sample($K_{oc} = K_d / C_{org}$).

Table 2 Parameters of pyrene sorption on samples of bulk soils and separates of particle-size fractions

Samples	K_d	N	R^2	$\log K_{oc}$	$\log K_{HC}$ *
Soil W					
Bulk soil	171.61	0.549	0.865	4.04	4.69
Coarse sand	218.08	0.432	0.726	4.04	4.69
Fine sand	137.17	0.404	0.858	4.05	4.61
Silt	147.81	0.447	0.912	4.03	4.51
Clay	405.05	0.698	0.932	4.23	4.87
Soil H					
Bulk soil	781.52	0.952	0.953	4.65	5.28
Coarse sand	351.85	0.634	0.911	4.13	5.08
Fine sand	221.14	0.548	0.916	4.17	4.85
Silt	205.63	0.551	0.941	4.16	4.56
Clay	282.21	0.519	0.941	4.13	4.87

Note: * $K_{HC} = K_d / C_{Humic}$

The Freundlich exponents (N) ranged from 0.404 to 0.698, far less than 1.0 except for that of the bulk soil of Soil H (N = 0.952). For Soil W and its particle-size fractions, the K_d values decreased in the order: clay(405) > coarse sand(218) > bulk soil(172) > silt(148) > fine sand (137), while for the Soil H and its particle-size fractions, the K_d values decreased in an order of: bulk soil(781) > coarse sand (352) > clay (282) > fine sand (221) > silt (205).

The cluster analysis revealed that the K_d values of

particle-size fractions of each paddy soil could be divided into three major groups(Fig.2). The first group consists fine sand and silt, and the second and third groups are mainly composed of coarse sand or clay. The coarse sand and clay fractions of the both paddy soils showed greater K_d values than fine sand and silt fractions of them.
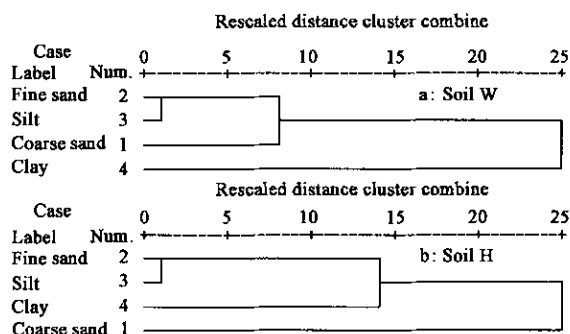

Fig. 2 Dendrogram for particle-size fractions of two paddy soils using between-groups linkage and Euclidean distance

3 Discussion

3.1 Effects of SOM on pyrene sorption

Pyrene equilibrium concentrations were higher than its solubility in water at 25°C, this may result from the dissolved organic matters and the colloids of soil in the supernatant. The results of Mackay and Gschwend(Mackay, 2001) showed

that excess pyrene could associate with colloids that passed an ultrafilter, and given an over purely dissolved concentration. This suggested the association of pyrene with humic acids.

K_d values of Soil W were in significant correlation with soil organic carbon(SOC) contents ($R^2 = 0.831$), previous studies also reported that polycyclic aromatic hydrocarbons were unevenly distributed among particle-size fractions in close relation to the contents of organic carbon (Wilcke, 1996; Krauss, 2002). However, the $\log K_{oc}$ values of all the particle size fractions were similar after the K_d values being normalized to the C level of each sample, indicating a determining role of soil organic carbon in sorption of PAHs both in bulk soil and in particle-size fractions.

The dual peak sorption capacity of PAHs in the coarse sand and clay fractions of the both soils were similar to the distribution of heavy metals in particle-size fractions of these soils(Li, 2001). Wang *et al* . (Wang, 2001) investigated the distribution of PAHs in particle-size fractions of sediment from Boston harbor, and found that the highest PAH concentrations were associated with the large size(> 250 μm) fractions. These suggested that coarse sand fraction acted as bigger sinks for both heavy metals and organic pollutants.

The SOM of the coarse sand fraction were identified dominantly as fresh or slightly decomposed plant debris with a high content of carbohydrates (Guggenberger, 1994; Amelung, 1998), which can sharply sorb the organic compounds in a short time. In contrast, the SOM in clay-size fractions represents a more highly decomposed pool consisting mainly of aromatic and aliphatic structures (Guggenberger, 1995), which could be highly affinitive for PAHs. The SOM of the coarse sand fraction is easily degradable and the organic pollutants sorbed on it would be released into environment and redistributed, while the SOM of clay-size fraction is more resistant to microbial degradation (Baldock, 1992). As SOM is believed to be one of the most important sorbents of PAHs (Wilcke, 2000) and components and its characteristics varies with the size fractions of particles, the binding mechanism might differ from coarse to fine size fractions as being implicated by the different N values. Nevertheless, the binding of PAHs to clay-sized fraction is of stronger environmental significance than to coarse sand ones as the later account for a small proportion of the bulk of both soils.

For Soil H, the K_{oc} value of the PAHs in a given particle-size fraction was significantly lower than that in bulk soil. This was probably due to the disaggregation or stretching of organic aggregates by ultra-sonic dispersion and freeze-drying of the particle-size fractions, which increased extractability of the compounds. In this case, the K_{oc} values of silt and clay fractions could have been underestimated. However, a certain amount of PAHs might be lost with floating particles during fractionation. Müller *et al* . (Müller, 2000) distinguished a floatable fraction consisting mainly of plant debris and soot-like material, which showed high PAH and PCB concentrations although the mass contribution to total soil was low. The loss of this fraction could explain the difference in K_{oc} values between bulk soil and particle-size fractions, because PAHs sorbed to soot show high K_{oc} values (Jonker, 2000).

The K_{oc} values of PAHs can often be estimated from their related physical parameters, such as the octanol-water partition coefficients K_{ow} or the solute water solubilities(S_w). As originally obtained considering the partition of organic compounds in sediment particles, the correlation between K_{oc} and K_{ow} can be expressed as follows:

$$\log K_{oc} = a + b \log K_{ow},$$

K_{oc} values calculated were higher than those measured in present study, which could be attributed to the tested sorbents. Chiou *et al* . (Chiou, 1998) concluded the mean K_{oc} values on the sediments were about twice the values on the soils for the organic carbon in sediments has a lower polarity than that in soil. The results of Zhou *et al* .(Zhou, 2004) also showed that sediment exhibited much higher sorption capacities than soil. The aromatic component of SOM could make a considerable contributes to the sorption of nonpolar pollutants, and the sorption coefficient (K_{oc}) of organic contaminants can not be accurately predicted from their K_{ow} without some consideration of SOM quality such as polarity and degree of aromaticity(Xing, 1997).

The aromatic component of SOM can be used as a good predictor of a soil's ability to bind nonionic contaminants (Ahmad, 2001). In this study, the effects of aromaticity of the SOM on the sorption were showed with the content of humic carbon, but no significant relationship were observed between K_d values and humic carbon contents of both bulk soils and their different particle-size fractions, which was not in agreement with previous work(Xing 1997; Chefez, 2000). In those researches, pure materials were employed and there were significant difference of pyrene sorption on various type of natural organic matter varing in chemical composition or the different composition of SOM. In fact, in natural soil texture, the SOM will combine with minerals to form organ-mineral complex, then soil aggregates, which would take part in soil processes as a whole (Pan, 2000) and result in differences from the pure SOM or its individual components. Nam *et al* .(Nam, 2003) found that aggregation may reduce the biodegradation of aged phenanthrene compared with other samples with similar organic carbon content. And other earlier studies also suggested that soil aggregates may play a key role in the sequestration of organic contaminants probably by providing tortuous sorptive and/or desorptive pathways (Steinberg, 1987; Pignatello, 1990; Ball, 1991). Data here may reflect the interaction of organic carbon and particle-size fraction aggregation.

3.2 Effects of dithionite-extractable Fe and CEC on pyrene sorption

Besides the SOM contents and SOM quality, the surface characteristics of particle-size fractions may also affect pyrene sorption. The effects of dithionite-extractable Fe on pyrene sorption are showed in Fig. 3. For Soil W, the K_d values were very well correlated with the dithionite-extractable Fe contents in particle-size fractions and the bulk soil. Hydro-oxyhydrates of iron were believed to be active and mobile solid phase affecting the surface charge or the sorbents. The above mentioned correlation suggested that the sorption of pyrene on paddy soils and their particle-size fractions may be affected by the surface characteristics. Moreover, under field conditions, paddy soils is subject to alternation of drying and re-wetting, which would induce cyclic change in redox

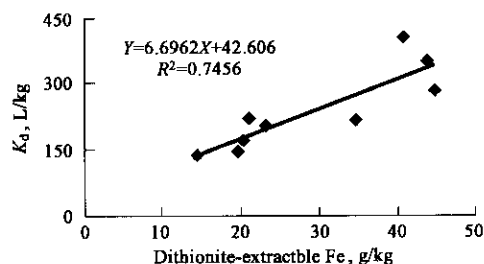$Y=6.6962X+42.606$
$R^2=0.7456$

Fig.3   Relationship between K_d and dithionite-extractable Fe

potential. Ferric oxides coating could be formed on particle surface imbedding sorption sites for apolar compounds binding to organic matter. Thus, the K_d values of bulk soils and the particle-size fractions could be lower than those of sediments.

The effects of CEC on the pyrene sorption were different in different paddy soil and its particle-size fractions(Fig.4). For Soil W, the CEC values showed a good correlation with K_d values in bulk soil and separates of all particle-size fractions, while for soil H and its particle-size fractions, there was no significant relationship observed between CEC contents and K_d values. A study by de Jonge et al. (de

Jonge, 2000) showed that the K_d values of polar compounds such as prochloraz were in close correlation with the CEC values in bulk soil and soil separates. The sorption of pyrene, an apolar contaminant, related to CEC contents in Soil W may result from the cation components. There were much more exchangeable calcium and magnesium in Soil W, and the high affinity between Ca^{2+} or Mg^{2+} and sorption sites in humic acid (Lee, 2003) can affect pyrene binding to SOM, and may result in the lower K_d values, while the ferric hydroxyhydrates commonly found in Soil H may form tightly associated domains with SOM not accessible to pyrene.
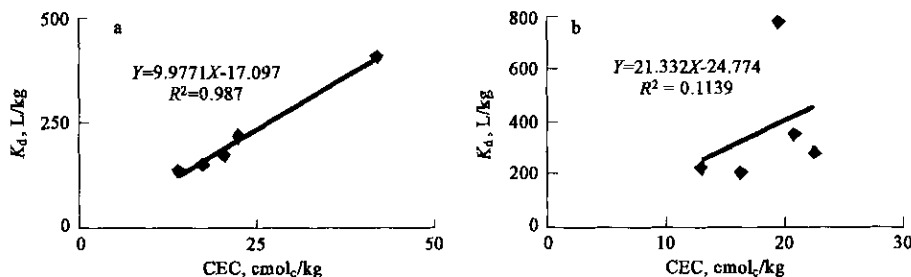

Fig.4   Correlations between K_d and CEC of Soil W(a), Soil H(b) and their particle-size fractions

4 Conclusions

The sorption of pyrene on particle-size fractions varies with the size of the particle fractions of the paddy soil, which was, in turn, controlled by the amount and the structural properties of the SOM associated, supporting that SOM is the most important sorbent for hydrophobic compounds in the soils. The measured $\log K_{oc}$ values were lower than those in sediments, which could be attributed to the lability of organic matters in sediments. However, the soil CEC and peodgenic oxyhydrates may also affect the capacity and mechanism of PAHs binding to soil particles. Further studies should be conducted on SOM chemistry and binding behaviors in different size fractions of the paddy soils.

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