

Determination of Retardation Effect of SOM on Aqueous Leaching of Polycyclic Aromatic Hydrocarbons Using Confocal Laser Scanning Microscope

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ABSTRACT: Influence of soil organic matter (SOM) on the adsorption, desorption and transport of polycyclic aromatic hydrocarbons (PAHs) has already been given full investigation in soils. In this paper, confocal laser scanning microscope (CLSM) was used to elucidate aqueous leaching of PAHs in different types of soil with soil columns, which enhanced understanding on transport of PAHs appreciably. Four typical soils in China including fluvo-aquic soil (FAS), aquic brown soil (ABS), red soil (RS) and black soil (BS) were selected in the experiment. Target pollutants of phenanthrene and pyrene were extracted from the leachate by solid phase extraction (SPE) and then determined by high performance liquid chromatography (HPLC). The experimental results showed that the retardation ability of pollutants to the four selected types of soil increased in the order: FAS > ABS < RS < BS. To better expatiate the dissimilar ability of the PAHs transported in the four typical soils, the retardation factor (R), distribution constant (K_d) and partition coefficient (K_{oc}) were evaluated based on the observed breakthrough curves (BTCs). Furthermore, CLSM was used to visualize the effects of SOM on the transport ability of PAHs in different types of soil. All the results provided vivid understanding with mathematical and especially optical measures that SOM was considered the single most important factor limiting the availability and mobility of PAHs in soil over the duration of the experiment.

Key words: PAHs, BTCs, Soil column, SOM, CLSM

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants of natural or anthropogenic origin. Industrial processing, petroleum spills, and incomplete combustion of organic material from both natural and anthropogenic processes, such as volcanic eruption, coal pyrolysis and oil cracking, are all significant events which contribute to the high level of PAHs in the environment (Sanders, 1995, Gong, 2006). Presently, PAHs contamination becomes more and more serious in soils, groundwater, even rice roots (Tang *et al.*, 2005, Jiao *et al.*, 2007). The transport of PAHs in the subsurface environment poses a serious threat to groundwater resources, even at minor concentrations (Danzer and Grathwohl, 1998). Therefore, it is of significant importance to investigate the transport and fate of PAHs in soils. Evidently, column-based experiments are advantageous in this area of study as they provide a controlled, simplified environment and facilitate the collection of well-resolved

spatial and temporal data (Amos and Mayer, 2006). PAHs are transported horizontally over long distances in soils and can be found in both wet and dry depositions (Knopp *et al.*, 2000). Annekatriin et al studied the long-term change of PAH deposition from the year of 1850 to 2000 and concluded that increasing PAH depositions are caused by rapid industrialization accompanied by extensive use of fossil fuels; decreasing PAH depositions are caused by the substitution of fossil fuels for other energy sources and the movement of PAH-emitting industries to different regions (Dreyer *et al.*, 2005). As far as the vertical transport of PAHs in soils is concerned, innumerable field and laboratory experiments have been conducted in order to understand the various interactions that take place among contaminants, colloids, and porous media (Danzer, 1998, Bouchard, 1998, Enell *et al.*, 2004). As an example, the column experiments of Chi and Amy focused on determining the transport characteristics of anthracene and

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benz(a)anthracene through iron-quartz and three aquifer materials in laboratory columns. (Chi and Amy, 2004). They found that the sorption capacity of SOM for PAHs determined from column experiments was related to the SOM fraction observed on mineral surfaces and to the properties of the PAHs. In addition, transport can be facilitated by changes in the chemical composition of the carrier solution, such as higher pH, lower ionic strength, and the presence of surfactants, soil organic matter or natural organic matter (Chi and Amy, 2004, Andrew and Breitenbeck, 1994, Johnson and Logan, 1996).

Dissolved organic matter (DOM) is considered to have hydrophobic as well as hydrophilic moieties and was sometimes conceptualized as a separate phase able to retain hydrophobic organic contaminants (Sabbah *et al.*, 2004). However, more attention is now being paid to the ability of DOM to bind contaminants and thus accelerate their transport through porous media (McCarthy and Zachara, 1989). Knabner *et al.* (1996) showed the effect of DOM as a contaminant-retarding agent, and reported that anthracene breaks through the media after 50 pore volumes in the absence of DOM, whereas in the presence of DOM, breakthrough occurred after 140 pore volumes (Knabner *et al.*, 1996). On the other hand, colloidal matter inherent in the subsurface may provide a favorable phase for contaminant partitioning and furthermore act as agents for facilitated contaminant transport (Villholth, 1999, Ranville *et al.*, 2005). The mobility of strongly sorbing pesticides in soils may be higher than formerly assumed, due to facilitated transport along with mobilized colloids (Jonge *et al.*, 1998).

Recently, CLSM are applied in lots of research areas such as iatrology, agrology, physics, biology, and chemistry (Jung *et al.*, 2008, Kevin *et al.*, 2003). Lu Yan *et al.* (2007) engaged in biological analysis, ie. organic – inorganic microporous membranes observation with confocal laser scanning microscope and founded that CLSM is an effective tool for investigating microporous membrane characteristics (Lu *et al.*, 2007). Zenji Kato *et al.* observed the granule packing structure using a confocal laser scanning microscope and the internal structure of alumina granule compact was clearly expressed (Zenji *et al.*, 2006). Schmidt and Bottlinger determined the 3-dimensional shape of fiber aggregates using confocal laser scanning microscope and discovered the results from investigations in resolving power and the ability to reconstruct complex three-dimensional structures (Schmidt *et al.*, 1996).

Our previous work focused on the vertical transport of PAHs in different particle-size fractions of sandy soils, and it was concluded that clay fractions

of soil would retain more pollutants in the soil columns (Zhang *et al.*, 2008). However, it is not certain that if CLSM can be applied in determination of SOM effect on the progress of aqueous leaching of PAHs. In response to these cases, a series of transport experiments were conducted in order to investigate the correlation of SOM with the transport of selected PAHs through a mobile phase saturated soil column. The primary objectives of this study were (1) to delineate the breakthrough curves (BTC) of the selected PAHs of phenanthrene and pyrene in the four typical types of soil; (2) to elucidate the vertical distribution of phenanthrene and pyrene in soil columns after the end of the leaching procedure; (3) to expatiate the effect of SOM on the transport of selected PAHs with schematic and optical graphs originated from LSCM.

MATERIALS & METHODS

The collected soil samples included fluvo-aquic soil (FAS) from Changping County (Beijing), aquic brown soil (ABS) from Qinyuan County (Liaoning Province), red soil (RS) from Jinxian County (Jiangxi Province) and black soil (BS) from the suburb of Harbin (Heilongjiang Province)(Fig. 1). These soil samples were air dried and sieved to 2 mm, and then their physico-chemical properties were analyzed and the results listed in Table 1. Pure water and ultrapure water were prepared using a Millipore water purification system. PAH standard samples of phenanthrene and pyrene were provided by Supelco Co. (Bellefonte, PA, USA). Acetonitrile, cyclohexane, hexane, pentane, acetone, methanol and methylene chloride (99.99%, HPLC grade) were obtained from J. T. Baker Co. (Germany). Silica gel (activated at 130 °C for 16 hours) (USEPA, 2003) and anhydrous sodium sulfate (activated at 400 °C for 4 hours) (USEPA, 2003) were purchased from Beijing Chemical Reagent Co. (Beijing, China). Simulation experiments with soil columns were performed at 22±0.5 °C in glass columns of 25 cm length and 5 cm diameter. To support the soil, a sand lining (0.5 cm) was applied and held in place above the bottom of the column. A layer of arenaceous quartz (2 cm) was placed on the sand lining to prevent soil washout. Soil layers (16 cm) were placed into the columns according to its volumetric weight (Table 1). Then, a layer of arenaceous quartz and several glass beads were placed on top of the soil layer to prevent splashing. (Fortner *et al.*, 2003) Sodium azide was added to the influent water to prevent biodegradation of the studied organic compounds. A high performance liquid chromatography (HPLC) pump (LC10 AT) was used to control the flow rate. The operational conditions in the column experiments were: pH 6.8, a flow rate of 0.2 ml/min and room temperature (22±0.5 °C). Initially, the

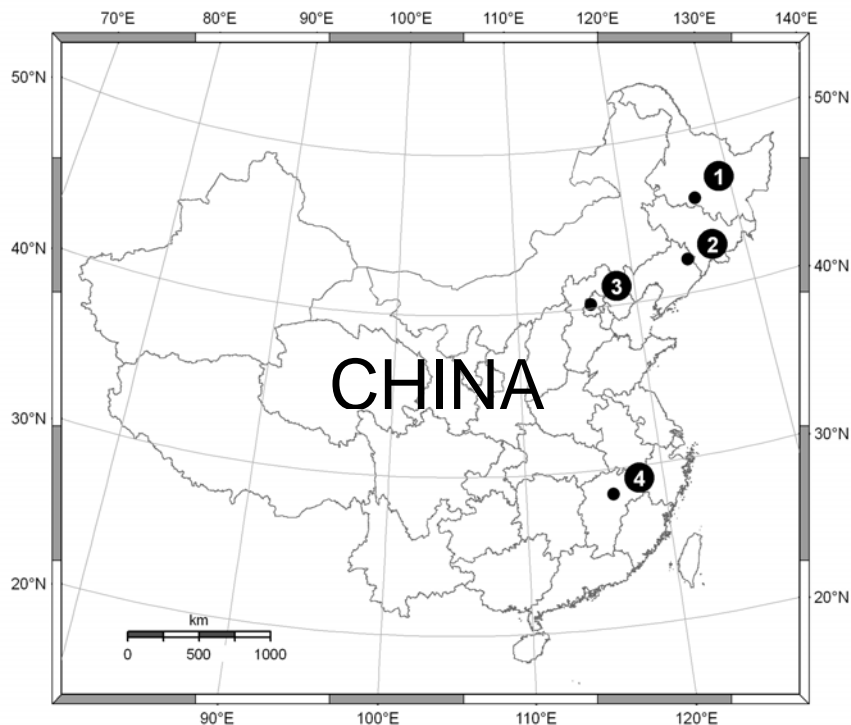


Fig. 1. Location of sampling sites in China. Soil samples of (1) is black soil (BS) from Harbin suburb of Heilongjiang province, (2) is aquic brown soil (ABS) from Qinyuan county of Liaoning province, (3) is fluvo-aquic soil (FAS) from Changping county of Beijing city and (4) is red soil (RS) from Jinxian county of Jiangxi province

Table 1. Physico-chemical properties of the four selected soils

| Sample | pH ^a | Volumetric weight ^b (g/cm ³) | SOM ^c (%) | CEC ^d (cmol/kg) | Size analysis ^e (%) | | | |
|------------------|-----------------|---|----------------------|----------------------------|--------------------------------|-----------------|---------------|-------------|
| | | | | | Coarse Sand (>200µm) | Sand (20-200µm) | Silt (2-20µm) | Clay (<2µm) |
| fluvo-aquic soil | 7.40 | 1.52 | 0.54 | 84.0 | 11.42 | 74.03 | 13.41 | 1.14 |
| aquic brown soil | 5.15 | 1.42 | 0.60 | 894.1 | 23.33 | 63.44 | 11.49 | 1.74 |
| red earth | 4.85 | 1.59 | 0.95 | 187.5 | 22.31 | 58.47 | 17.59 | 1.63 |
| black soil | 6.31 | 1.31 | 1.81 | 1294.2 | 7.16 | 71.17 | 20.50 | 1.17 |

^a measured in water suspension (soil/water ratio, 1:2.5 w/w) with a glass pH electrode, Horiba pH/10N meter F-23. [29]

^b measured by the method of Liu *et al.*, (1996).

^c SOM: soil organic matter, measured by a colorimetric method using chromic acid. [29]

^d CEC, cation exchange capacity, determined following the procedure reported by Hendershot and Duquette. [29]

^e evaluated with MasterSizer X Ver. 1.1a.

column was wetted slowly from the bottom with a solution of 0.01 M CaCl₂ until the system was completely saturated. The column was then prepared by passing a minimum of 50 pore volumes of the experimental mobile phase (methanol: water 3: 7) through the column. It is obviously that research

conclusion will be influenced by accession of organic solvent. In order to save dozens of years in getting the breakthrough curves (BTCs) and in view of the purpose of the experiment is to elucidate the effect of SOM on distribution of PAHs on soil particles, the organic phase of methanol was applied to accelerate the

breakthrough progress. Standard sample of phenanthrene and pyrene were added into the mobile phase and the initial concentration (C_0) of them are 20 mg/L. Breakthrough curves (BTCs) were then conducted by introducing the mobile phase into the column and monitoring the column effluent until the solute effluent concentration, C (mg/L), approached the influent concentration, C_0 (mg/L), i.e., $C/C_0=1$. In certain cases, it was considered acceptable that the value of C/C_0 was essentially constant because some physico-chemical progress such as volatilization and degradation existed in the experiment (Bekhit *et al.*, 2006). According to the EPA method, two different methods were performed for the extraction and purification of PAHs from the soil and water samples, respectively (USEPA, 2003, 1996b, 1996d). Solid phase extraction (SPE) was applied for the extraction of PAHs from water samples collected from the soil column (USEPA, 1996b). 500 mL of water sample were pumped through the C_{18} column that was activated by 5 mL methylene, in sequence of 5 mL deionized water. PAHs were adsorbed to the column and then were eluted with 15 mL methylene chloride, the extractant was concentrated to 1 mL for HPLC analysis. The determination of PAHs was performed using a HPLC (20 AT, provided by Shimadzu Co. Japan) instrument equipped with an ultraviolet detector operating at a 254 nm wavelength and a column temperature of 30°C. The separation of PAH-compounds was obtained with a PAHs- C_{18} (5 μ m) column (4.0 mm i.d. \times 20 cm) using a mobile phase of acetonitrile-water (60/40, v/v) at a flow rate of 1 ml/min. The sample injection volume was 10 μ l and the total analysis time was 66 min. Target compounds recovery of this extraction method have been measured and they are 79 \pm 2% of phenanthrene and 68 \pm 4% of pyrene (Zhang *et al.*, 2008). The retardation factor is a parameter obtained from the integration above the breakthrough curve according to Eq. (1). (Chi and Amy, 2004) The distribution constant (K_d) is the ratio of PAH equilibrium concentrations in the sorbed phase to that in the solution phase as shown in Eq. (2).

$$R = \int_0^{T_{\max}} \left(1 - \frac{C}{C_0}\right) dt \quad \text{Eq.(1)}$$

$$K_d \left(\frac{l}{kg}\right) = \frac{C_s}{C_i} \quad \text{Eq.(2)}$$

where T_{\max} is the maximum pore volume in the adsorption limb, C_0 is the influent concentration, C_s is the amount of PAHs sorbed onto the solid phase per unit of mass, and C_i is the influent concentration of

PAHs in continuous-flow column experiments. In the presence of organic matter on solid surfaces, the sorption of nonpolar organic contaminants is dominated by the sorption to organic carbon. The distribution constant (K_d) can be normalized by f_{oc} to yield the partition coefficient, K_{oc} , (Eq. (3))

$$K_{oc} \left(\frac{l}{kg}\right) = \frac{K_d}{f_{oc}} \quad \text{Eq.(3)}$$

Soils were taken out from the columns when the progress of simulation experiment ended, then they were fractionated into three degrades as sand (>200 μ m), silt (200-20 μ m) and clay (<20 μ m) according to the method established before. (Zhang *et al.*, 2008) 0.2g silt and clay samples were placed on the microscope slides of LSCM (Olympus FV500, provided by Olympus Co. Japan) equably and dispartate optical grapes were displayed as Fig. 5 and Fig. 6.

RESULTS & DISCUSSION

The breakthrough curves of phenanthrene and pyrene for four typical soils took more than 60 pore volumes (Fig. 2). From these curves, it was found that phenanthrene, a representative pollutant of 3 rings PAHs, penetrates the soil and reaches equilibrium more rapidly than pyrene, a representative compound of 4 rings PAHs. The contents of phenanthrene and pyrene in BS were undetectable until the leaching volumes reached 41 and 44 pore volumes, while 14, 17 pore volumes in FAS, 14, 17 pore volumes in ABS, and 22, 26 pore volumes in RS, respectively. Furthermore, the equilibrium concentration of phenanthrene in the leachate is lower than that of pyrene. The primary properties of the two selected PAHs are most probably the reasons that resulted in this trend. Firstly, according to the result of the chromatogram effect, the pollutants with low molecular weights were eluted more rapidly than those with higher molecular weights. Secondly, the solubility of phenanthrene in the influent is about 8 times higher than that of pyrene, which is another explainable reason for the fast breakthrough of phenanthrene in the column experiments. Thirdly, in view of the value and property of K_{ow} and K_{oc} reported previously, the higher the value of K_{oc} , the more PAHs may be adsorbed (Villholth, 1999).

As far as the effect of the soil physico-chemical properties of the four selected soils are concerned, the soil organic matter (SOM) is perhaps the most important reason that contributes to the different trend of the BTCs. It is well known that the transport of PAHs can be influenced in the presence and absence of dissolved natural organic matter (NOM) or soil

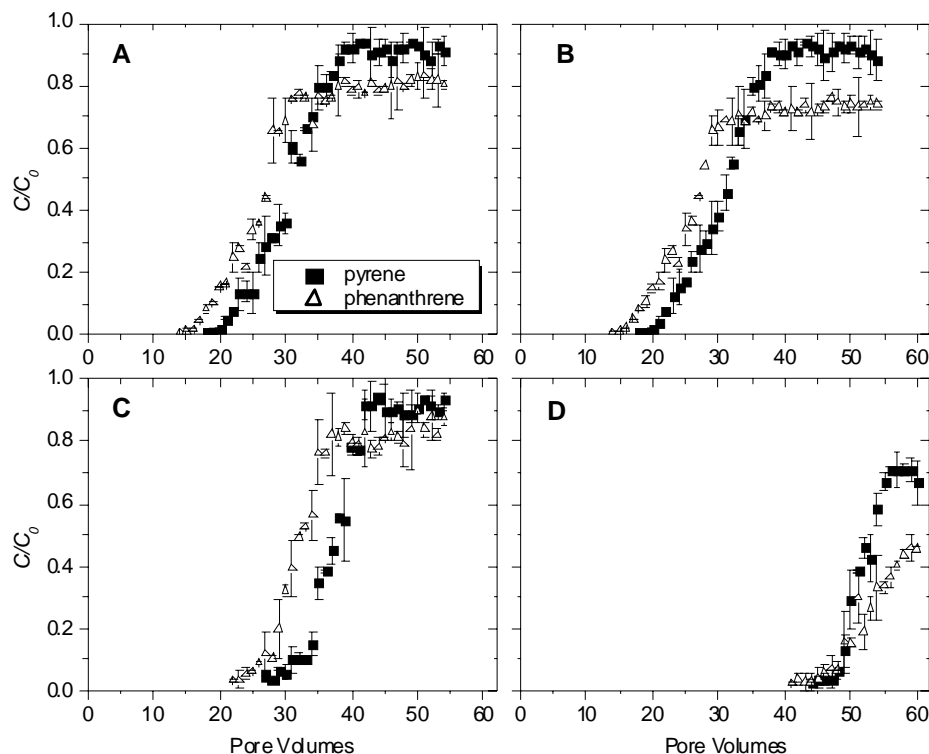


Fig. 2. Comparison of BTCs of phenanthrene and pyrene in four typical soils in a 0.3 volume of methanol (f_c): (A) fluvo-aquic soil (FAS); (B) aquic brown soil (ABS); (C) red soil (RS); (D) black soil (BS). C_0 is the influent concentration and C_i is the concentration of PAHs in the leachate. The error bar represents the standard deviation ($n=3$)

organic matter (SOM). The adsorption and partitioning of PAHs onto SOM or micropores are considered as their primary mechanisms. These associations involve noncovalent and covalent interactions between the pollutants and hydrophobic regions of humic materials (USEPA, 1996a). Table 1 indicates that the amount of SOM content in BS reaches 1.81%, which is significantly higher than that in either the FAS, ABS and RS (0.54, 0.60 and 0.95% respectively) soils. Hence, it is reasonable that: (1) the amounts of phenanthrene and pyrene adsorbed in the soil decrease in the order: BS > RS > ABS > FAS; (2) the transport ability of the pollutants decreased with the enhancement of SOM, and: (3) the transport equilibria of phenanthrene and pyrene through BS are slower than through the other three types of soil. It is in accordance with the conclusion obtained by Northcott and Jones (2003). The partition coefficients of phenanthrene and pyrene transport through the four selected types of soils (FAS, ABS, RS and BS) are calculated from the BTCs using Eqs. (1), Eqs. (2) and Eqs. (3), and the results presented in Table 2. All the results are consistent with the $\log K_{ow}$ values of phenanthrene and pyrene. The difference between the K_{ow} values for phenanthrene and pyrene in the four selected types of soils indicates the

dissimilar characteristics of the soil organic matter. It has been noted that the structure of organic matter varies due to the origin and geological history, strongly influencing the sorption affinity for nonionic organic compounds. From Table 2, it is clear that the retardation factor of phenanthrene on FAS (6.7) is close to the retardation factors on ABS and RS (6.7, 7.6 respectively), but it is comparatively higher on BS (29.0). Interestingly, if f_{oc} is considered correlatively with the retardation factors, the correlation is significant at the 0.05 level. As far as pyrene is concerned, the results are obviously similar in every parameter except that the correlation between f_{oc} and the retardation factor is significant at the 0.01 level. The detailed parameters of K_{oc} and $\log K_{oc}$ are calculated according to Eq. (3) and presented in Table 2 (Luthy *et al.*, 1997). Fig. 3 illustrates the concentrations of phenanthrene and pyrene retained in the soil columns after ending the leaching procedure. Three distinct trends are revealed as follows: (1) Contents of phenanthrene and pyrene retained in the soil layers extracted from each of the columns decrease with increasing of soil column depth. (2) Average concentration of phenanthrene in each of the layers are lower than pyrene, e.g. 8.81, 9.94 mg/kg in FAS,

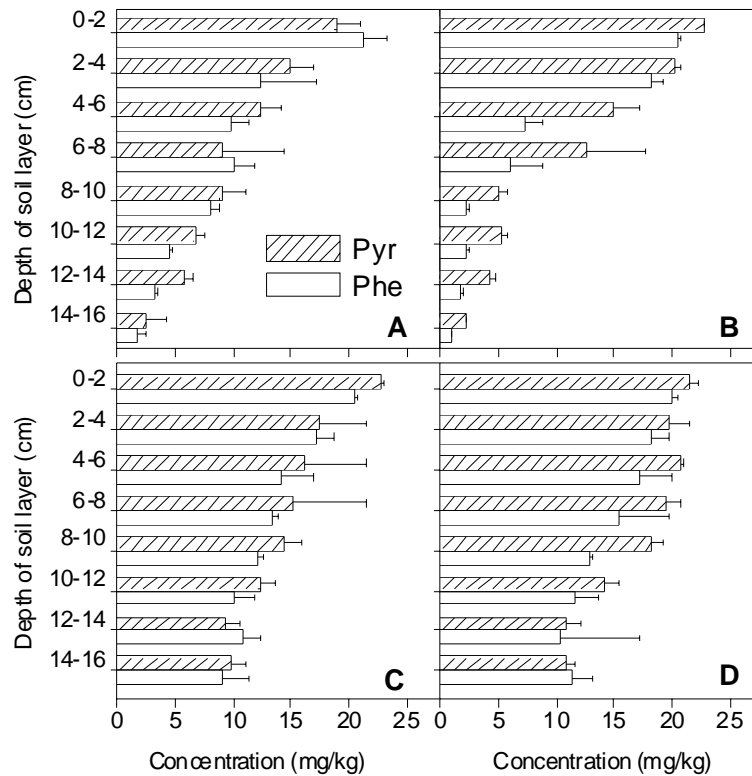


Fig. 3. Individual PAH levels of phenanthrene and pyrene which remained in the columns filled with four typical soils of FAS (A), ABS (B), RS (C) and BS (D). This study was conducted according to the following procedure: after ending the leaching procedure, 2cm slices of soil samples were taken from each soil column for HPLC analysis of PAHs. The error bar represents the standard deviation (n=3)

Table 2. Partition coefficients of phenanthrene and pyrene calculated from the BTCs through four typical soils of FAS, ABS, RS and BS

| | FAS | ABS | RS | BS | FAS | ABS | RS | BS |
|-----------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| | Phenanthrene | | | | Pyrene | | | |
| f_{oc} (%) | 0.54 | 0.6 | 0.95 | 1.81 | 0.54 | 0.6 | 0.95 | 1.81 |
| R | 6.7 | 6.7 | 7.6 | 29.0 | 4 | 3.7 | 4.4 | 16.8 |
| K_d (l/kg) | 76 | 86 | 144 | 300 | 187 | 212 | 361 | 720 |
| K_{oc} (l/kg) | 1.41×10^4 | 1.45×10^4 | 1.51×10^4 | 1.66×10^4 | 3.47×10^4 | 3.55×10^4 | 3.80×10^4 | 3.98×10^4 |
| Log K_{oc} | 4.15 | 4.16 | 4.18 | 4.22 | 4.54 | 4.55 | 4.58 | 4.60 |

f_{oc} , fraction of organic contents; R , retardation factor; K_d , distribution constant; K_{oc} , partition coefficient

7.37, 10.90 mg/kg in ABS, 13.40, 14.66 mg/kg in RS and 14.62, 17.02 mg/kg in BS. (3) Both average concentrations of phenanthrene and pyrene sequestered in the soil layer increased according to the order: FAS < ABS < RS < BS. The properties as calculated herein (Table 2) may be useful to predict this sequestration, especially of soil organic matter (SOM). It indicated that the rate and extent of

sequestration vary among the different soils because of similarities and differences of organic compounds, extractability, bioavailability and other properties. Interesting, it is extraordinary accordant with the research conclusion of some researchers (Chung, 1998, Pignatello and Xing, 1996, Brusseau *et al.*, 1991). Afterward, embedded discussion about soil particle size are carried out to some extent. It is obvious that

the amounts of silt and clay fractions increase in the order: FAS < ABS < RS < BS, which is similar to the order of retardation factor (R), distribution constant (K_d), f_{oc} and $\log K_{oc}$ of the PAHs. Interestingly, this result was in accordance with the conclusion reported by Doick and Amellal. [Doick *et al.*, 2005] They revealed that the ^{14}C -PCB and ^{14}C -PAH associated activities are primarily located in the humin fraction of the 20-2 and < 2 μm particle-size fractions of the soil. Furthermore, Amellal *et al.* investigated the role of aggregate sizes on the PAHs bioavailability in soils employing particle-size fractionation, and concluded that limited (or zero) degradation may further explain the accumulation of hydrophobic organic contaminants (HOCs) in these aggregate fractions (Amellal *et al.*, 2001).

In order to elucidate correlation of SOM and retardation factor (R), mathematical and optical methods were used jointly and conclusions were presented as in Fig. 4-6. Firstly, Fig. 4 convey us the meaning that the retardation factors of phenanthrene and pyrene increase in the order: FAS < ABS < RS < BS, which is accordant with the concentration of soil organic matter (SOM) of the soil. The squared correlation coefficients (R^2) of phenanthrene were 0.802, 0, 0.784 and 0.962, respectively. That of pyrene was

0.807, 0, 0.787 and 0.962. Secondly, intuitionistic understandings were achieved from schematic graphs of both silt and clay fractions of the soil originated from CLSM. As it is well known that PAHs adsorbed in soils could radiate green light while minerals couldn't when the soil samples were excited by laser, hence the density of green light was representative value of adsorbed PAHs. It is deductive that PAHs were adsorbed much more on clay fraction (Fig. 6) than those on silt fraction (Fig. 5). Given solely analysis to the clay fraction as illustrated in Fig. 6, BS soil sample radiated dense green light, namely a mass of PAHs were adsorbed on the surface of BS simultaneously, our previous work had revealed that majority of SOM consist in clay fraction of soil (Zhang *et al.*, 2008). Hence, it can be induced indirectly that the density is representative of SOM contents. sample. So CLSM provided extraordinary intuitionistic graphs to elucidate the SOM effect on adsorption and aqueous leaching of PAHs. All of the above results provide significant insight into the parameters controlling the transport of PAHs in soil columns and show that, over the duration of the experiment, SOM was considered the single most important factor limiting the availability and mobility of PAHs in soil.

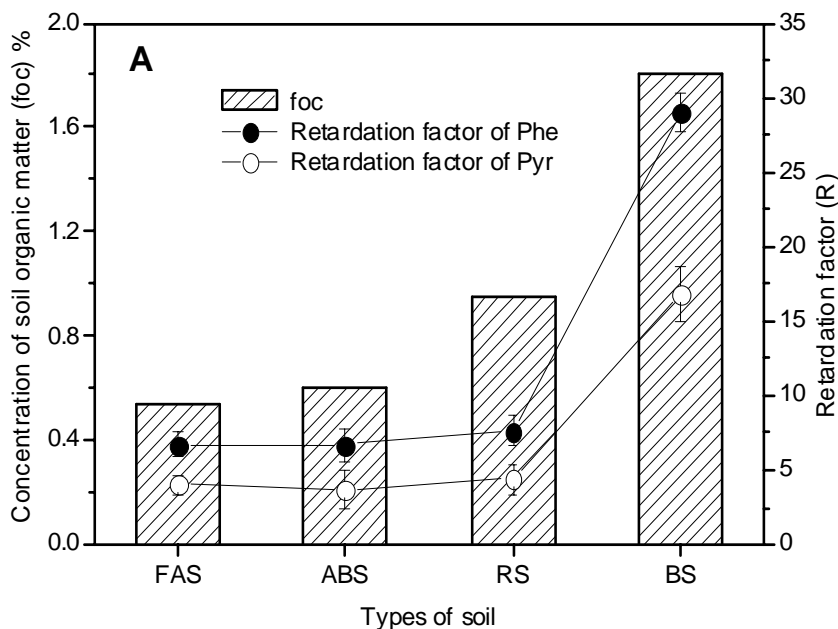


Fig. 4. Correlation of soil organic matter (*foc*) with retardation factor, $R_1^2=0.962$, $R_2^2=0.962$, $P < 0.05$. R_1^2 and R_2^2 is the squared correlation coefficients of Phe and Pyr, respectively. FAS: fluvo-aquic soil, ABS: aquatic brown soil, Rs: red soil, BS: black soil. The error bar represents the standard deviation (n=3)

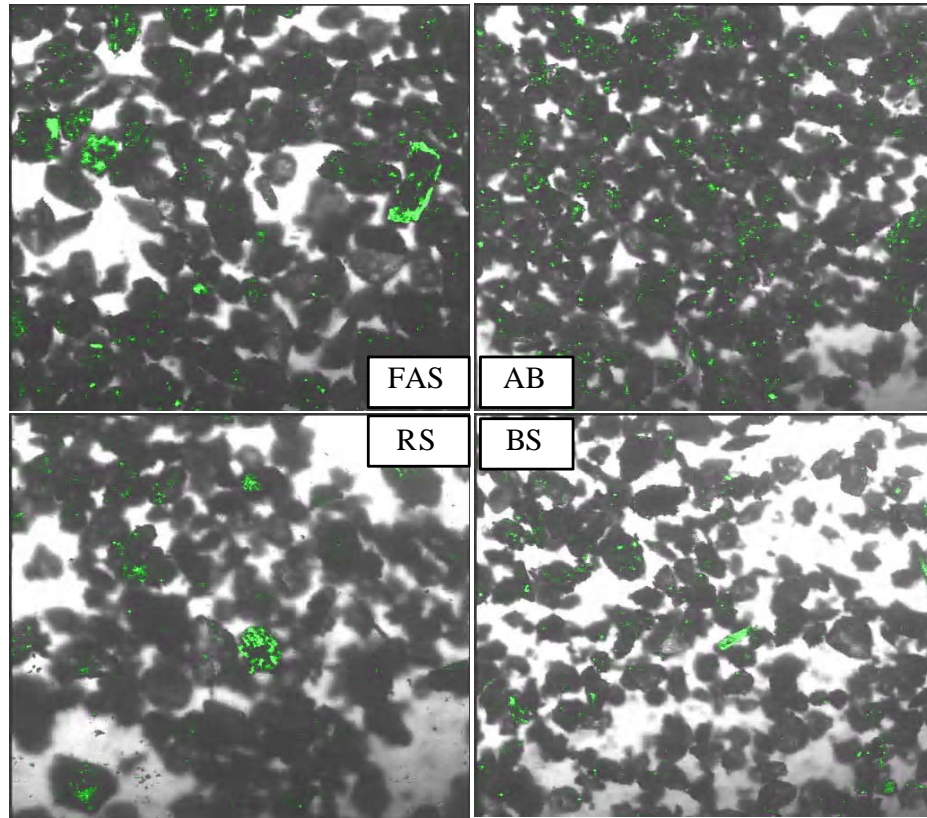


Fig. 5. CLSM graphs of silt fraction of four selected types soils. Meaning of FAS, ABS, RS and BS is the same as before

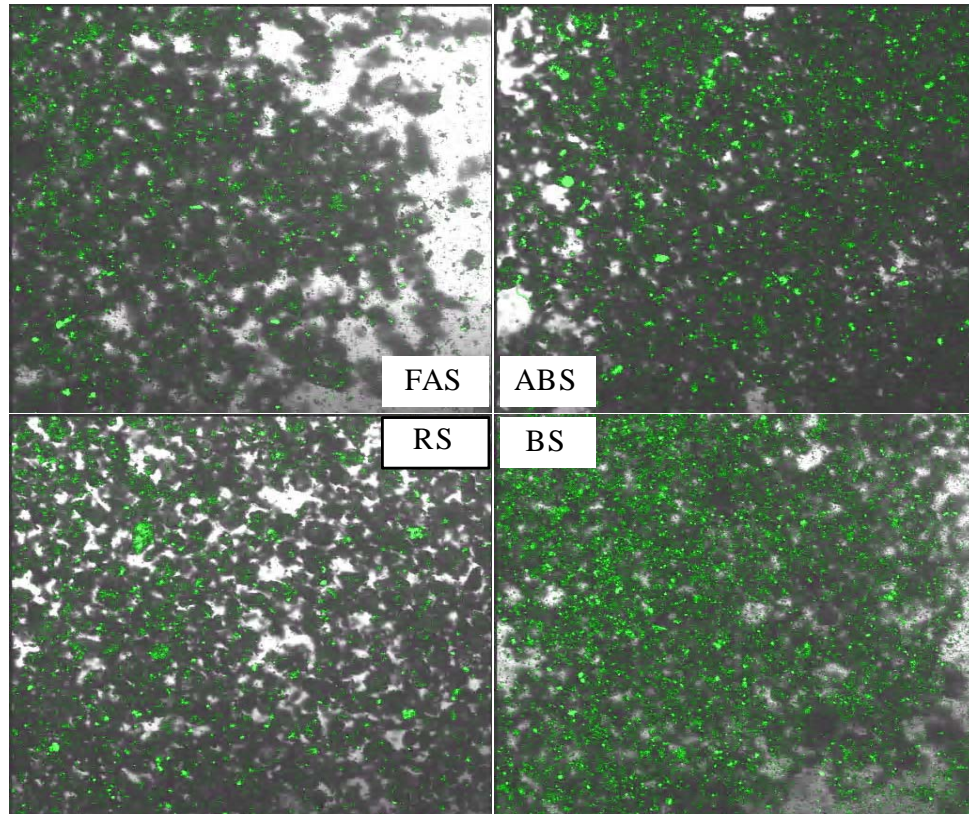


Fig. 6. CLSM graphs of clay fraction of four selected types soils. Meaning of FAS, ABS, RS and BS is the same as before

CONCLUSION

The retardation factors of selected PAHs on four typical types of soils in China named FAS, ABS, RS and BS were calculated from simulation column experiment. It revealed direct proportion between contents of SOM and retardation factor, and the squared correlation coefficients (R^2) of phenanthrene and pyrene revealed in this paper were 0.802, 0, 0.784, 0.962 and 0.807, 0, 0.787, 0.962, respectively. CLSM graphs provided schematic and optical understanding about the SOM effect on both progresses of adsorption and aqueous leaching of PAHs. All the results showed that effect of SOM contributed much more on the transport of PAHs in soils. The investigation results highlighted in this paper will help to understand the fate of organic pollutants in the soils of different regions and provide a intuitionistic means to study environmental progress of persistent organic pollutants.

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