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Mobility of TX100 suspended multiwalled carbon nanotubes (MWCNTs) and the facilitated transport of phenanthrene in real soil columns

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ABSTRACT

The transport behavior of TX100 suspended multiwalled carbon nanotubes (MWCNTs) through different soil columns as well as their effects on the mobility of phenanthrene was systematically studied. Results showed that the mobility of MWCNTs varied with soils, which was found to be correlated positively to the average soil particle diameters and soil sand contents, while correlated negatively to soil clay contents. The retention of MWCNTs on soil columns is most likely due to surface deposition and physical straining. Co-transport of phenanthrene with MWCNTs was tested in three selected soils (soil HB, DX and BJ), where MWCNTs could act as carriers of phenanthrene and enhance the mobility of phenanthrene in soils. However, during passing through the soil columns phenanthrene initially adsorbed onto MWCNTs could be partially "stripped" off. In soil with the lowest phenanthrene sorption affinity and highest water velocity (soil HB), only 8.5% phenanthrene was desorbed during transport, suggesting that a strong MWCNT-associated phenanthrene mobile may occur in this soil. More than 80% of phenanthrene was stripped off in soils with higher sorption affinity (soil DX and BJ), indicating the limitation of the co-transport of phenanthrene and MWCNTs in such soils.

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1. Introduction

Carbon nanotubes (CNTs) including single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) are considered as one of the most promising materials in nanotechnology, with attractive properties for many applications, such as optical activity and electrical conductivity. Recently, the mass production of CNTs is rapidly growing. World production capacity for MWCNTs exceeded 390 tons in 2008, reached 1500 tons in 2009, and is expected to reach more than 9400 tons by 2015 (Zhang and Huang, 2012). Given the widespread application and production of CNTs, their large-scale release to the environment is inevitable. The release of CNTs may cause undesired/unforeseen risks to the environment and human/wildlife health (Dinesh et al., 2012; Nowack and Bucheli, 2007; Wiesner et al., 2006; Zhang and Huang, 2012). A thorough understanding of the environmental behavior of CNTs, such as their stability in aqueous media and transport through porous media, is a prerequisite to better evaluate their migration potential in the environment.

The mobility of CNTs in porous media has been reported (Jaisi et al., 2008; Lecoanet et al., 2004; Liu et al., 2009; Tian et al., 2011). Lecoanet et al. (2004) found that surfactant-modified SWCNTs exhibited high mobility, with calculated migration potential to be more than 10 m in unfractured sand aquifers. Increasing solution ionic strength or addition of calcium ions resulted in an increased deposition of SWCNTs (Jaisi et al., 2008). Filtration played an important role in SWCNT transport in a well-defined porous media (Tian et al., 2011). Liu et al. (2009) found that MWCNTs were more mobile in the glass bead-packed columns than in quartz sand-packed columns. It is worthy to note that most previous studies of CNT mobility in porous media were conducted using model solid medium (quartz sand or glass beads). However, the relevance of the results from model media to real soil environment is unknown, considering the more complex nature of soil (e.g. diverse mineral surface types, surface charge heterogeneity, roughness of granular media and organic matters) (Zhang and Huang, 2012). Up to now, information regarding the transport behavior of CNTs in soils is quite limited. Only few studies reported that the retention of SWCNTs in columns packed with a natural soil or sediment was mainly influenced by the shape and aggregation of SWCNTs, as well as the heterogeneity in soil (sediment) particle size, porosity and permeability (Bouchard et al., 2012; Jaisi and Elimelech, 2009).

The transport of CNTs in soils generally leads to another question: How do CNTs affect the mobility of contaminants in soils during transportation? Hofmann and von der Kammer (2009) theoretically analyzed the probability of facilitated transport of hydrophobic organic

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contaminants (HOCs) in porous media by carbonaceous engineered nanoparticles (ENPs). Their results indicated that carbonaceous ENPs may act as carriers for contaminants. They pointed out that ENPs meeting the following conditions would facilitate the contaminant transport in porous media: 1) ENPs must be present in a sufficiently high concentration; 2) ENPs must be mobile; and 3) contaminant must be strongly adsorbed to ENPs and slowly desorbed relative to the transport time scale. When it comes to CNTs, factor 1 refers to the amount of CNTs in the environment. Although the average concentration of CNTs in real environment is expected to be at μg L^{-1} levels, high concentration of CNTs may exist in certain special regions, especially in the case of the leaking accident of CNT production factory (Gottschalk et al., 2010). Regarding to their mobility, CNTs are usually kept disperse by surfactants or polymers in their manufacture and applications (Fu and Sun, 2003), and can also be stabilized by natural organic matters (Hyung et al., 2007). Factor 3 concerns the sorption of contaminants to CNTs. In the past decades, numerous studies showed that CNTs were excellent sorbents with a high sorption capacity for organic pollutants, especially for HOCs (Wang et al., 2008; Yang et al., 2006). However, there is no experimental study so far on the effects of CNT on the transport of HOCs in natural soil media.

Therefore, the aims of this study were i) to investigate the transport behavior of MWCNTs in various soil columns; and ii) to explore how MWCNTs affected the mobility of phenanthrene in soils, in order to determine whether MWCNTs associated with contaminants like phenanthrene posed any threat to soils and groundwater via enhanced contaminant migration.

2. Theory

Particle transport in porous media can be described by three mechanisms: 1) direct interception of the particles with the media, 2) sedimentation due to gravity, and 3) diffusion due to Brownian motion (Yao et al., 1971). Under steady saturated flow conditions the transport of particles through porous media can be described by a convective–dispersive transport equation including a term for first-order particle deposition (Kretzschmar et al., 1997):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_p\frac{\partial C}{\partial x} - kC \tag{1}$$

where C is the particle concentration in solution, t is the elapsed time, x is the travel distance, D is the dispersion coefficient of particles, v_p is the average travel velocity of particles, and k is the particle deposition rate coefficient.

Based on the assumption of first-order deposition kinetics, particle breakthrough curves resulting from step-inputs are often evaluated by a clean-bed filter coefficient given by (Lecoanet et al., 2004):

$$\lambda_0 = -\frac{1}{L}\ln\left(\frac{C_f}{C_0}\right) \tag{2}$$

where λ_0 is a clean-bed filter coefficient, L is the column length, C_0 is the initial effluent particle concentration, and C_f is the final effluent particle concentration after the breakthrough curve has reached a plateau. The particle deposition rate coefficient k can then be estimated using the following equations (Lecoanet et al., 2004):

$$k = \lambda_0 v_p = \lambda_0 L/t_p \tag{3}$$

$$k = -\frac{1}{t_p}\ln\left(\frac{C_f}{C_0}\right) \tag{4}$$

where t_p is the average travel time of particles through column. Here k represents a time- and distance-averaged parameter. The term C_f/C_0 corresponds to fraction of particles recovered at the column outlet after the breakthrough curve has reached a plateau. The maximum travel distance, defined by the distance at which 99.9% of particles have been removed from solution, which can be expressed by (Lecoanet et al., 2004):

$$L_{max} = -\frac{v_p}{k}\ln\left(\frac{C_f}{C_0}\right) \tag{5}$$

where $C_f/C_0 = 0.001$.

3. Materials and methods

3.1. Soils

14 surface soils (0–20 cm) were collected from 12 Chinese provinces. Soils were air dried, and passed through a 1 mm sieve prior to use. Soil organic matter (SOM) was determined using the Walkley–Black procedure (Nelson and Sommers, 1982). Soil pH was measured at soil to deionized distilled water (DDW) ratio of 1:5 (1 g soil:5 mL water) using an Orion (Model 250A+) pH meter. Cation-exchange capacity (CEC) of soils with soil pH < 7 was determined by BaCl$_2$ method while soils with soil pH > 7 were determined by CH$_3$COONa method (Rhoades, 1982). Zeta potential of soils was measured using a Zetasizer Nano Series Instrument (Malvern Instrument Ltd. UK). Soil texture (sand, silt and clay contents) was measured using a pipette method (Konert and Vandenberghe, 1997). For calculating soil collector diameter, the sand particle diameter (0.175 mm), silt particle diameter (0.02 mm) and clay particle diameter (0.0015 mm) were multiplied by their respective percentage, and average particle diameters were obtained by adding the resultant numbers (Ley et al., 1994). Selected soil properties are given in Table 1.

3.2. MWCNT suspension preparation

MWCNTs with an average outer diameter of 28 nm and length of 1–2 μm were purchased from Shenzhen Nanotech Co., China. It was synthesized from a CH$_4$/H$_2$ mixture at 700 °C using a chemical vapor deposition method with Ni as catalyst, and purified by a mixed HNO$_3$ and H$_2$SO$_4$ solution to remove catalyst and amorphous carbon. MWCNT suspension was prepared using surfactant Triton X-100 (TX100) solution according to Han's method (Han et al., 2008). A portion of 50 mg L^{-1} MWCNTs was added to 1 L 40 mg L^{-1} TX100 solution, and subsequently sonicated for 1.5 h. After that, samples were transferred into beakers which were allowed to settle down for 48 h. The supernatant that contained unsettled MWCNT suspensions was collected and used for sorption and leaching experiments. The absorbance of MWCNT suspensions was measured using a UV–visible spectrophotometer at 800 nm, and the sample concentration was calculated from a calibration curve. The suspended MWCNTs obtained from the above experiments were about 37 mg L^{-1} with pH 6.58. The surface charge of suspended MWCNTs is negative with zeta potential of −33 mV. TEM observations showed that the suspended MWCNTs were well dispersed and most existed as single MWCNT (Fig. 1).

3.3. Phenanthrene

Phenanthrene was purchased from Sigma-Aldrich Co., and used without further purification. The concentrations of phenanthrene were determined using a Hewlett-Packard model 1100 gradient HPLC system with a UV–vis detector. The absorption wavelength was 247 nm. The mobile phase was 90:10 methanol:water (v/v), and the flow rate was 1.0 mL min^{-1}.

3.4. Column transport experiments

Column breakthrough experiments of MWCNTs in various soil columns were performed under saturated flow conditions. The

Table 1
Selected properties of soils used in this experiment.

Soil	Sample address (province)	pH	CEC (cmol kg^{-1})	SOM (%)	Zeta potential (mv)	Texture % (v/v)			Taxonomy[a]
						clay	silt	sand	
						(<2 μm)	(2–20 μm)	(20–1000 μm)	
HB	Hebei	8.89	25.4	0.24	−20.3	1.1	5.0	93.9	Sand
BJ	Beijing	7.26	12.5	2.96	−18.7	19.4	47.8	32.8	Silt-sandy-loam
DX	Beijing	8.64	65.8	0.25	−19.4	5.7	14.3	80.0	Sandy-loam
ZJ	Zhejiang	7.01	6.9	2.87	−21.9	23.6	23.5	53.5	Silt-sandy-loam
JS	Jiangsu	7.57	7.6	1.74	−18.2	6.7	19.4	73.9	Sandy-loam
GZ	Guangdong	7.32	8.3	2.03	−23.9	21	21.4	57.6	Silt-sandy-loam
SD	Shandong	7.68	11.1	0.46	−21.8	9.8	23.5	66.7	Sandy-loam
QHD	Hebei	7.23	16.2	2.18	−20.9	9.8	16.3	73.9	Sandy-loam
HLJ	Heilongjiang	6.16	20.2	6.86	−21.5	13.1	30.0	56.9	Loam
NMG	Neimenggu	8.25	24.9	3.81	−19.5	13.3	23.1	63.6	Sandy-loam
LN	Liaoning	7.96	18.4	0.89	−18.4	23.1	29.6	47.4	Loam
YN	Xinjiang	8.68	26.3	1.10	−21.4	17.4	40.0	42.6	Silt-sandy-loam
JL	Jilin	6.93	19.9	3.32	−20.7	28.2	24.5	47.4	Loam
HN	Hainan	5.26	8.7	2.59	−19.1	52.7	24.5	22.9	Clay-loam

column system used in this study was the same as that reported previously (Fang et al., 2009). Briefly, a glass column (20 cm long with an inner diameter of 25 mm) was depolished in the inner wall to make it rough to avoid the preferential flow. The column was uniformly packed to a height of 10 cm with air-dried soil and the column was initially saturated with DDW. DDW was added from the bottom of the column and gradually moved upwards through the entire column to remove any air pockets, and then the saturated soil columns were leached with 100 mL DDW. After that the absorbance of outflow at 800 nm was measured, and it was found that the absorbance was less than 0.02, suggesting soil colloid in the outflow has been significantly reduced. Following the leaching step, MWCNT suspensions were pumped onto the top of soil columns and the gravity flow was used for leaching. A 9 cm constant water head was maintained throughout the experiment using a peristaltic pump and the effluent was collected at certain leaching time intervals for the measurement of MWCNT concentrations. Additionally, a saturated soil column leached with 40 mg L^{-1} TX100 solution was used as the control. The control column effluent absorbance was also measured to monitor the soil colloid release. The effluent absorbance subtracted by the control absorbance was used to determine the concentration of MWCNTs in the outflow. Detailed physical parameters of various soil columns are given in Table 2. During the course of the experiment, the MWCNT concentration of inflow, C_0, and outflow, C_f, was monitored to obtain breakthrough curves of C_f/C_0 as a function of the number of pore volumes passing through the soil columns. A steady plateau value of C_f/C_0 was then interpreted using

Eq. (4) to obtain an estimated deposition rate coefficient. All experiments were conducted at room temperature (20 ± 1 °C).

To investigate the effect of MWCNTs on the transport of phenanthrene, three soils (soil HB, BJ and HLJ) were selected in this study. Column breakthrough experiments of phenanthrene in the presence or absence of MWCNTs were performed under saturated flow conditions and the column systems were similar to those described above. Phenanthrene-associated MWCNT suspensions were obtained by equilibrating MWCNT suspensions with 100 μg L^{-1} phenanthrene. The preliminary experiment found that the concentration of MWCNT suspensions in the presence of phenanthrene was the same as that in the absence of phenanthrene, suggesting that the addition of phenanthrene did not lead to MWCNT aggregation. Total concentrations of phenanthrene and MWCNTs in both inflow and outflow were determined. A saturated soil column leaching with solutions consisted of 100 μg L^{-1} phenanthrene and 40 mg L^{-1} TX100 was used as a control. The concentration of eluted MWCNT suspensions was also measured by a UV–visible spectrophotometer at 800 nm. Our previous experiment showed that there was almost no absorbance of phenanthrene and TX100 at 800 nm. So the contribution of phenanthrene and TX100 to the absorbance could be neglected when measuring MWCNT concentration. Eluted phenanthrene leached by phenanthrene-associated MWCNT suspensions was separated into dissolved and MWCNT-associated fractions by splitting column effluent into two portions. One portion of the effluent was centrifuged at 15,000 ×g for 1 h in PTEF tubes, and the concentration of phenanthrene in supernatant
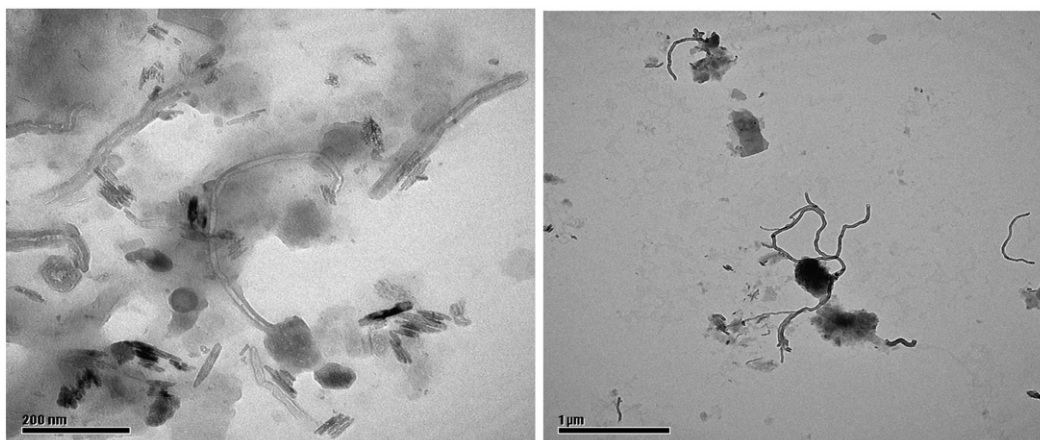

Fig. 1. TEM image of MWCNT suspension.

Table 2
Physical conditions of soil columns experienced during breakthrough experiments.

Soil columns	Average soil collector diameter (μm)	Darcy velocity (cm h^{-1})	Pore volume of columns V_0 (mL)
HB	165.3	58.24	21.5
BJ	76.1	10.16	23.3
DX	142.9	17.93	25.2
ZJ	98.7	9.80	24.4
JS	133.3	5.93	26.2
GZ	105.4	1.77	24.1
SD	121.6	7.20	25.8
QHD	132.7	6.60	25.9
HLJ	105.8	4.07	26.6
NMG	116.1	4.90	24.8
LN	89.2	7.64	25.0
YN	82.8	3.39	21.6
JL	88.3	4.52	24.9
HN	45.8	8.13	28.9

was defined as dissolved fraction. The turbidity of supernatant solution was also examined by UV–vis spectrophotometry and the results showed that the turbidity detected by UV–vis spectrophotometric measurements was below the detection limit of 0.09 ± 0.02 mg L^{-1} for colloids, indicating that after centrifugation the concentration of particles remaining in suspension was negligible. While the other effluent portion, which was not centrifuged, was defined as total phenanthrene concentration. The determination of total phenanthrene concentration in the effluent samples was in accordance with the extraction methods of Fang et al. (2008). 5 mL effluent samples were added to 15 mL methanol in 20 mL lined capped polytetrafluoroethene (PTFE) tubes and then vibrated on a horizontal motion shaker for 24 h at 20 ± 1 °C. After extraction, the samples were centrifuged at 15,000 ×g for 1 h and the concentration of phenanthrene in supernatant aqueous phase was calculated as total phenanthrene concentration. The recovery of phenanthrene in MWCNT suspensions by methanol extraction was 97–102%. MWCNT-associated phenanthrene fraction was obtained by subtracting dissolved phenanthrene from total phenanthrene.

3.5. Sorption of phenanthrene on soils and MWCNT suspensions

Sorption of phenanthrene on three soils (soil HB, DX and BJ) was conducted in 36 mL lined capped glass bottles by mixing soil (0.2 g) with 0.01 M NaNO$_3$ solution (20 mL) plus 100 mg L^{-1} NaN$_3$ and 40 mg L^{-1} TX100 with varying concentrations of phenanthrene on a horizontal motion shaker for 48 h at 20 ± 1 °C (preliminary experiments had shown that all solid–solution mixture reached apparent equilibrium before 48 h). After a 48 h equilibration, the suspension was centrifuged at 5000 ×g for 20 min and phenanthrene concentration in equilibrium aqueous phase was determined using HPLC. For sorption of phenanthrene on MWCNT suspensions, MWCNT suspensions (37 mg L^{-1}, 20 mL) containing various concentrations of phenanthrene (0–800 μg L^{-1}) were rotated end-over-end for 24 h. Then the suspension was centrifuged at 15,000 ×g for 1 h and phenanthrene concentration in equilibrium aqueous phase was determined. All sorption experiments were conducted in triplicate. Concentrated phenanthrene stock solutions were prepared in methanol and added to the batch vials as needed. Final methanol concentrations in the aqueous phase were less than 0.5%, which has no measurable effect on sorption (Wang et al., 2007).

Sorption isotherms were fit to the Freundlich equations:

$$Q = K_f C_e^n \qquad (6)$$

where Q (mg kg^{-1}) and C$_e$ (mg L^{-1}) are respectively the apparent solid-phase and solution-phase equilibrium concentrations, K_f [(mg kg^{-1}) (mg L^{-1})$^{-n}$] is the Freundlich affinity coefficient, and n is the linearity parameter.

4. Results and discussion

4.1. Transport of MWCNTs through soil columns

Breakthrough curves were used to indicate the mobility of MWCNTs in soil columns (Fig. 2). Transport behaviors of MWCNTs varied with soils. In soil columns of HB, BJ, DX, QHD, ZJ and JS, MWCNTs passed through rapidly and their contents in the first pore volume were more than 30% of inflow concentrations. MWCNT concentrations in final plateau value were 83.5%, 73.4%, 57.7%, 74.5%, 48.5% and 40.9% of inflow concentration for soils HB, BJ, DX, QHD, ZJ and JS, respectively. In other tested soil columns (soils GZ, SD, NMG, HLJ, LN, YN and JL), the passage of MWCNTs tended to increase slowly with leaching time and reached their plateau values (C_f/C_0) ranging 7.6–31.6%. For soil HN, the passage of MWCNTs was completely prevented and no MWCNTs were detected in the outflow after leaching for 15 pore volumes. Meanwhile, precipitated MWCNTs were clearly visible on the soil surface of HN soil column, which suggests that deposition of MWCNTs on soil grain surface may contribute to the retention of MWCNTs. Zeta potential of both the MWCNTs and the soil grains was negative, thus attachment between them is unfavorable according to the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. However, deposition under unfavorable condition is still likely, as pointed out by Yi and Chen (2011). The soil grain surfaces are usually heterogeneous with both negative and positive sites (Bouchard et al., 2012). These positive or less negative sites will be locally favorable for MWCNT deposition.

Correlation analysis between plateau concentration of MWCNTs (C_f/C_0) and selected soil properties showed that the breakthrough of MWCNTs is significantly positively correlated to the average soil collector diameter (r = 0.56, p < 0.05) and soil sand content (r = 0.51, p < 0.1), while it is negatively correlated with soil clay content (r = −0.58, p < 0.05). No significant correlation between soil pH (r = 0.38, p = 0.17), soil zeta potential (r = 0.09, p = 0.75), SOM (r = −0.24, p = 0.41), or CEC (r = 0.25, p = 0.39) and C_f/C_0 was found. The highest retention of MWCNTs in soil HN is probably due to its highest soil clay content (52.7%, Table 1). Larger soil particle diameters resulting from their high sand content are ready to create big pores and shadow zones, where particle deposition would be significantly hindered (Ko and Elimelech, 2000). Increases of the TiO$_2$ nanoparticle retention in soil columns with higher soil clay content were also found in our previous work (Fang et al., 2009). Current knowledge believes that soil clay can lead to more physical straining during transportation and is responsible for the removal of particles (Bradford et al., 2002; Harvey et al., 1993). Physical straining occurs within pore water passages that are too narrow to permit particles to pass. Straining could be important when the ratio of the particle to median grain
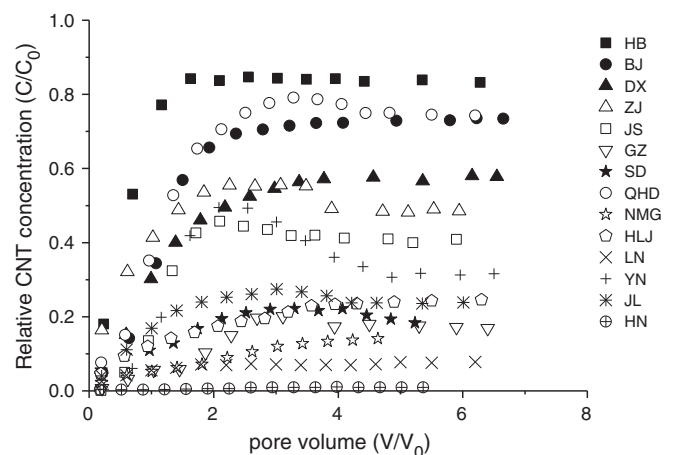

Fig. 2. Breakthrough curves of MWCNTs in various soil columns.

diameter was higher than 0.002 (Bradford et al., 2003). In our study, if the trapping of MWCNTs was controlled by their lengths, the retention of MWCNTs in soils was expected to be observed. When MWCNTs oriented parallel to streamlines, the physical straining was reduced. In soil columns of YN, QHD and ZJ, a breakthrough maximum was reached at pore volumes of 3 or 2 and then the MWCNT concentrations were gradually decreased with further increasing pore volumes until reaching their final concentration plateaus (Fig. 2). We interpret this phenomenon as "ripening deposition", which occurred when MWCNTs stick to deposited MWCNT sites. This "ripening deposition" did not continue in the above three soils, and was not observed in the other columns. This finding suggested that there are some unexplained processes affecting the MWCNT deposition. Further studies on the transport mechanisms in soil media are of great importance for better understanding the behavior and fate of MWCNTs in the natural environment.

Estimates of particle deposition rate coefficient (k) and transport distance L_{max} provide measures of a particles' mobility (Table 3). Experimental k values of MWCNTs in the tested soil columns ranged from 0.19 to 1.97. The mobility indices L_{max} of the tested 14 soil columns are 26.8–383.1 cm, except for HN soil which completely retained MWCNTs. The estimated transport distances of MWCNTs in soil columns of HB, QHD and BJ were found to be 383.1, 234.7 and 223.4 cm, which is farther from a typical surface soil depth of 30 cm, indicating severe risks to deeper soil layers or even groundwater.

4.2. Phenanthrene sorption onto soils and onto MWCNTs

The sorption isotherms of phenanthrene on soils and MWCNTs fitted well with Freundlich model (Fig. 3, Table 4). A direct comparison between the K_f values of these samples cannot be made because of their different units as a result of nonlinearity. The concentration-dependent sorption coefficient K_d at selected concentrations was used to compare the sorption capacity (Wen et al., 2007). The K_d values followed the order soil BJ > DX > HB at two selected concentrations ($C_e = 0.05$ and 0.40 mg L^{-1}). It was reported that SOM plays a key role in the sorption of phenanthrene to soils and high SOM always resulted in high sorption affinity for HOCs (Chiou et al., 1979; Xing and Pignatello, 1997). Therefore, it is not hard to understand that soil BJ with relatively higher SOM content has high phenanthrene sorption capacity. However, SOM may also exhibit different sorption features for HOCs depending on its origin (Bonin and Simpson, 2007; Wang and Xing, 2005). For soils containing only a very small amount of SOM, adsorption of HOCs onto clay surfaces is the dominant mechanism (Su et al., 2006). Soils DX and HB have similar SOM content, but the sorption affinity for phenanthrene differs greatly. Such difference was probably due to their different properties of SOM and mineral composition. The K_d values of phenanthrene on MWCNTs were 5484, 274 and 186 times higher than that of soil HB, DX and BJ at $C_e = 0.05$ mg L^{-1}, respectively (Table 4), indicating that MWCNTs had potential for preferential sorption of phenanthrene and
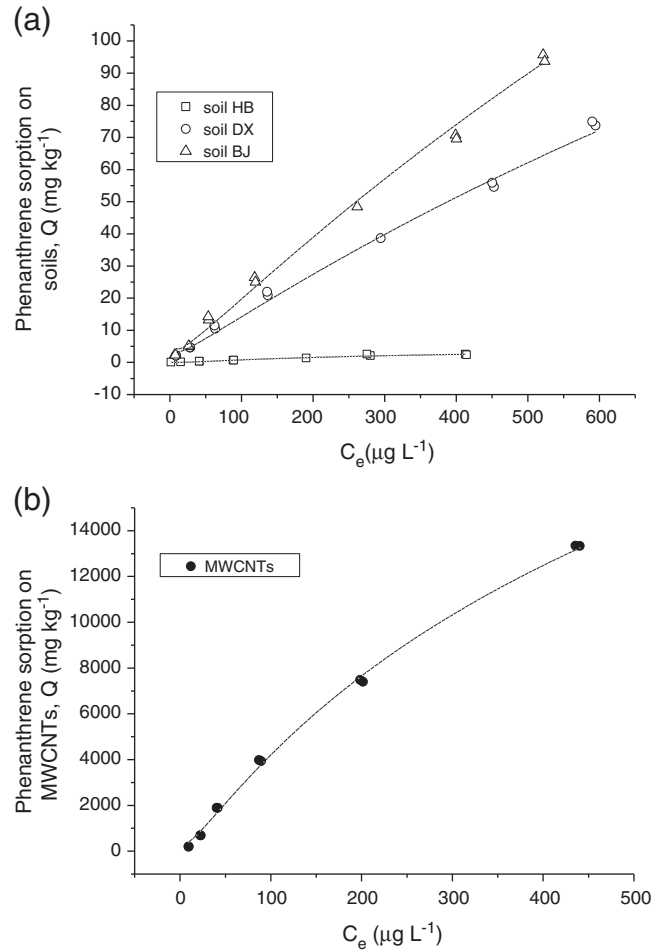

Fig. 3. Measured (dots) and Freundlich model fitted (lines) sorption isotherms of phenanthrene on soils (a) and MWCNTs (b).

consequentially increased transport of phenanthrene through soil pores. Karathanasis (1999) suggested that when the sorption capacity of colloid for pollutants was larger than that of soil, colloid-associated transport might be likely.

4.3. Transport of MWCNTs associated with phenanthrene through soil columns

Total concentration of phenanthrene was 100 μg L^{-1} in the inflow MWCNT suspension and the content of phenanthrene sorbed on MWCNTs was 1.61 mg g^{-1} (Table 5). As shown in Fig. 4, the breakthrough of phenanthrene with and without MWCNTs varied with soils. In soil HB which had the lowest sorption capacity of phenanthrene, the passage of phenanthrene increased gradually with pore volumes both in the presence and in the absence of MWCNTs (Fig. 4a). At pore volume of 18, 78% of inflow phenanthrene was

Table 3
Transport experimental results.

Soil column	Transported (%)	k (1/h)	L_{max} (cm)
HB	83.5	1.05	383.1
BJ	73.4	0.31	223.4
DX	57.7	0.98	125.6
ZJ	48.5	0.71	95.5
JS	40.9	0.53	77.3
GZ	16.9	0.31	38.9
SD	18.3	1.22	40.7
QHD	74.5	0.19	234.7
HLJ	23.5	0.58	47.7
NMG	13.7	0.97	34.8
LN	7.6	1.97	26.8
YN	31.6	0.39	60.0
JL	23.8	0.65	48.1
HN	0.0	5.7	–

Table 4
Freundlich equation parameters for phenanthrene sorption by soils HB, DX and BJ and MWCNTs.

Materials	K_f (mg kg^{-1}) (mg L^{-1})$^{-n}$	n	R^2	[a]Concentration-dependent K_d (L kg^{-1})	
				$C_e = 0.05$ mg L^{-1}	$C_e = 0.4$ mg L^{-1}
Soil HB	5.4800	0.815	0.991	8.26	6.21
Soil DX	114.21	0.882	0.998	165.4	120.6
Soil BJ	169.82	0.915	0.997	243.5	177.3
MWCNTs	26,200	0.810	0.994	45,300	30,300

[a] K_d is the partition coefficient; C_e is the liquid-phase equilibrium concentration (mg L^{-1}).

Table 5
Sorption and desorption of phenanthrene (PHE) on MWCNTs in inflow and outflow samples.

Soil columns	Inflow			Outflow		
	Total PHE in MWCNT suspensions ($\mu g\ L^{-1}$)	PHE sorbed on MWCNTs (PHE/MWCNTs, mg g^{-1})	Dissolved PHE in the solution ($\mu g\ L^{-1}$)	PHE sorbed on MWCNTs (PHE/MWCNTs, mg g^{-1})	Dissolved PHE in the solution ($\mu g\ L^{-1}$)	PHE desorbed from MWCNTs (%)[a]
HB	100	1.61	51.7	1.47	27.0	8.5
DX	100	1.61	51.7	0.26	<0.2	83.8
BJ	100	1.61	51.7	0.21	<0.2	87.1

[a] Amount of phenanthrene desorbed from MWCNTs in outflow compared to phenanthrene on MWCNTs in inflow.

obtained in the outflow in the presence of MWCNTs, which was significantly higher than 54% of inflow phenanthrene in the absence of MWCNTs. This demonstrated that MWCNTs enhanced the mobility of phenanthrene in soil HB. Additionally, 1.47 mg g^{-1} phenanthrene was still associated with MWCNTs in the outflow (Table 5), which indicated that MWCNTs acted mainly as phenanthrene carrier in the transport process.

Sorption capacities of phenanthrene on soils DX and BJ were higher than that of soil HB. Phenanthrene was completely retained by these soils in the absence of MWCNTs (Fig. 4b, c). Studies found that soil dissolved organic carbon (DOC) could act as carriers for organic pollutants and significantly enhanced the mobility of pollutants in porous media (Magee et al., 1991; Seta and Karathanasis, 1997). In the absence of MWCNTs, no phenanthrene in the outflow suggested that DOC facilitated phenanthrene transport could be neglected for soils DX and BJ. In the presence of MWCNTs, ratio of plateau phenanthrene concentration in outflow to phenanthrene concentration in inflow was 4.8% and 4.6% for soil DX and soil BJ at pore volume of 18, respectively (Fig. 4b, c). Additionally, MWCNT-associated phenanthrene in the outflow was 0.26 and 0.21 mg g^{-1} for soil DX and soil BJ, respectively, and little amount of dissolved phenanthrene was observed (Table 5). These results revealed that MWCNT-associated phenanthrene was the only fraction that transports through soil columns DX and BJ, and MWCNTs served as a co-transport carrier for phenanthrene in these soils.

Some researchers found that during the transport of colloids in soils, the pre-sorbed pollutants could be partially or completely "stripped" off from colloids and subsequently sorbed by soil components, and the "strip" rate was mainly depended on the sorption affinity of soils (Fang et al., 2011; Zhuang et al., 2003). The amount of phenanthrene desorbed from MWCNTs during transport was calculated based on the difference between phenanthrene sorbed on MWCNTs in the inflow and those in the outflow (Table 5). The desorption contents of phenanthrene varied with soils. A portion of 8.5% phenanthrene was desorbed during transport through soil HB which had relative low sorption capacity of phenanthrene. While the desorption ratio of phenanthrene raised to 83.8% and 87.1% in soils DX and BJ, respectively, which had much higher sorption capacity, indicating that co-transport of phenanthrene with MWCNTs in these soils was limited. Moreover, desorption of pollutant from colloids was a nonequilibrium process during transport in soils, which was partially residence-time-dependent (Chen et al., 2005). In soil HB with high sand content, the transport pore water velocity was the highest (58.24 cm h^{-1}, Table 2), and desorption kinetic of phenanthrene from MWCNTs was far from equilibrium state in the tested length of soil column, which led to the low phenanthrene desorption rate from MWCNTs. This result suggests that MWCNT-associated transport of phenanthrene could reach far distance, hence pose potential harm to soil and even groundwater in soil HB.

5. Conclusions

The present study demonstrated that MWCNTs could transport efficiently through most soil columns. The mobility of MWCNTs through soils was positively correlated with average soil diameters and soil sand contents, while it was inversely related to soil clay contents. The calculated maximum travel distances L_{max} of soils HB, BJ and QHD under saturated homogeneous conditions exceeded 30 cm, a typical surface soil depth, indicating the severe risks to deeper soil layers or even groundwater would potentially occur in these soils. MWCNTs were observed to act as carriers for phenanthrene transport. However, phenanthrene was partially desorbed from MWCNTs during transport, and the desorption degree increased with an increase of sorption affinity of phenanthrene on soils. Although caution should be taken in extrapolating our laboratory results into actual field situations, it is noteworthy that the rapid breakthrough behaviors of MWCNTs and low phenanthrene desorption rate from MWCNTs in some soils (i.e. soil HB with high sand content) create favorable conditions for the MWCNTs co-transport of phenanthrene. The enhanced risk of phenanthrene to some soils and even groundwater by MWCNTs should be paid attention in the future.
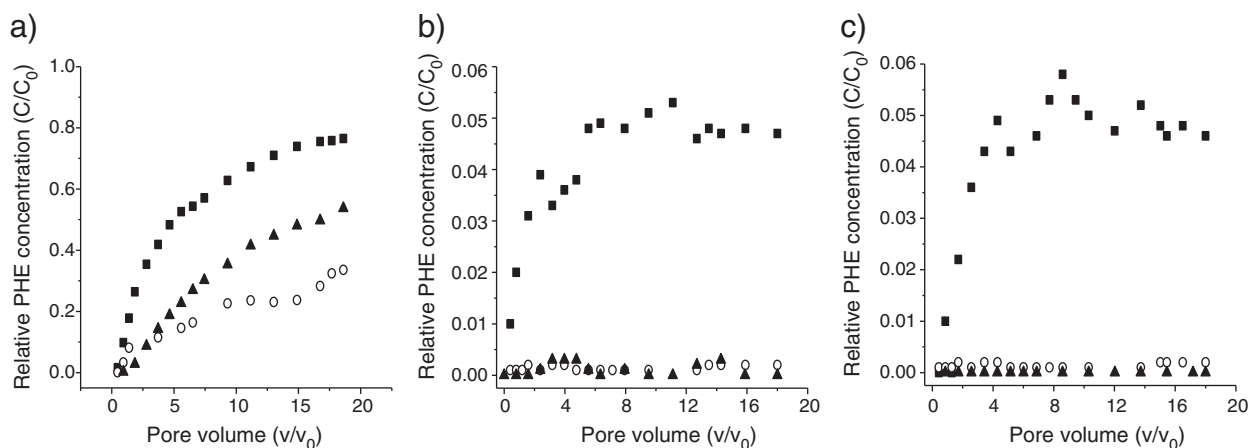

Fig. 4. Breakthrough curves of phenanthrene in the presence or absence of MWCNTs. (a: soil HB; b: soil DX; c: soil BJ). Total phenanthrene in the presence of MWCNTs (■), dissolved phenanthrene in the presence of MWCNTs (○), total phenanthrene in the absence of MWCNTs (▲).

Acknowledgments

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