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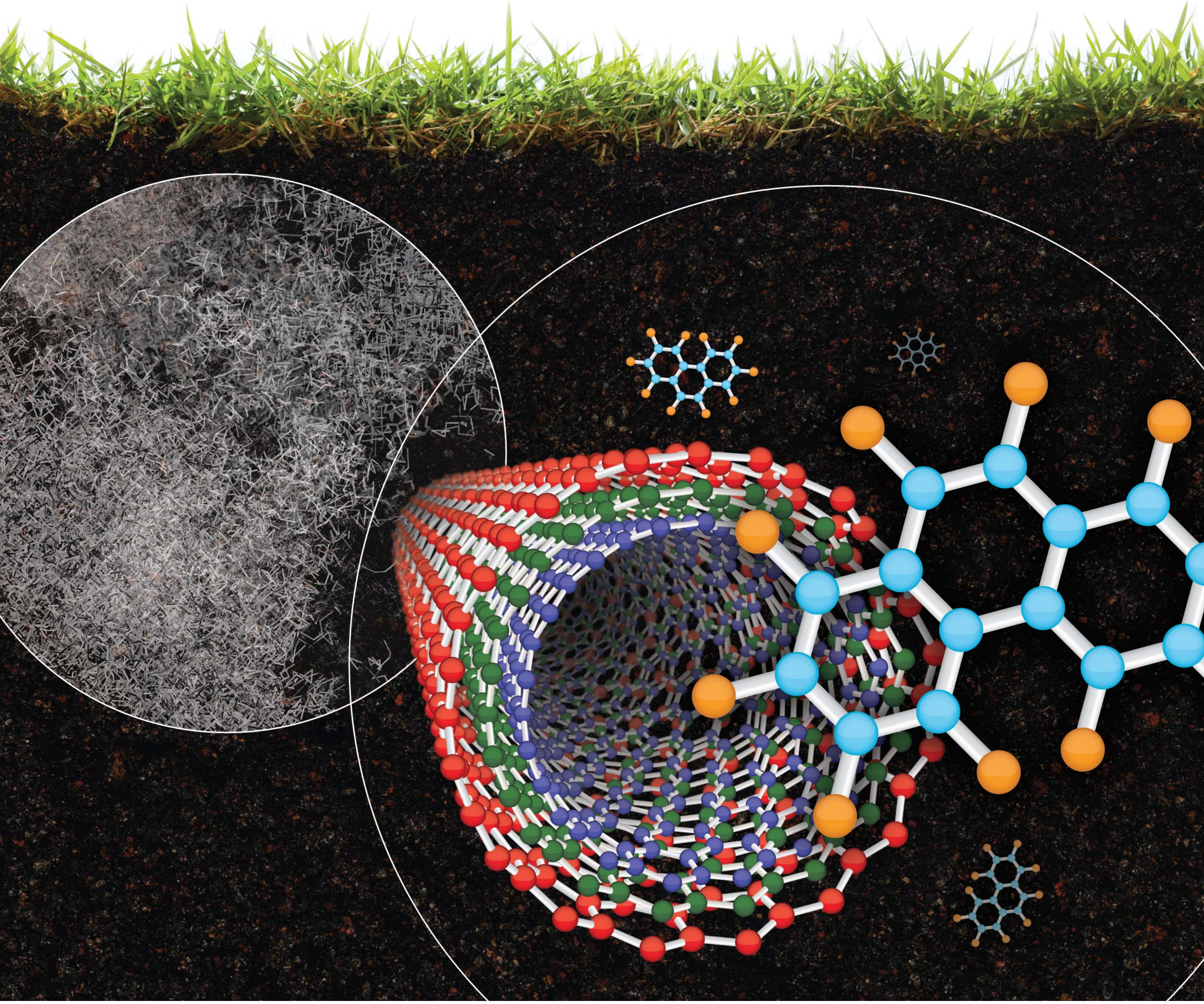

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Polyaromatic hydrocarbons (PAHs) sorption behavior unaffected by the presence of multi-walled carbon nanotubes (MWNTs) in a natural soil system†

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The batch equilibrium approach was used to examine the influence of multi-walled carbon nanotubes (MWNTs) on the sorption behaviors of polyaromatic hydrocarbons (PAHs) in soil. To the knowledge of the authors, this is the first study of PAH sorption to MWNTs in real natural soil systems. The sorption behavior of three PAHs (naphthalene, fluorene, and phenanthrene) in the presence of commercially available MWNTs in two natural soils (a sandy loam and a silt loam) and Ottawa sand was evaluated. Adsorption of PAHs by MWNTs in this study was three orders of magnitude higher than that of natural soils. Sorption coefficients of PAHs (K_d and K_{oc}) were unchanged in the presence of 2 mg g^{-1} MWNTs in soil ($p > 0.05$). A micro-mechanics approach, termed 'the rule of mixtures' was used for predicting PAH sorption behaviors in mixtures based on sorption coefficients derived from single sorbents. The equation, $K_T = K_M\alpha + K_N(1 - \alpha)$ (K, sorption coefficients, K_d or K_{oc}), predicted sorption coefficients in a mixture based on mixture component sorption coefficients and mass fractions. Data presented in this study could be used to fill data gaps related to the environmental fate of carbon nanotubes in soil.

Environmental impact

With rapid commercial development, there is an increased chance of CNTs being released into the environment during their production, application, and disposal. However, there is still limited knowledge of their fate, especially their interaction with other conventional contaminants in the environment. With high and strong sorption capacity, CNTs has the potential to disturb the bio-availability and bio-reactivity of other contaminants. This study explored the influence of CNTs on sorption behaviors of polyaromatic hydrocarbons (PAHs) in a terrestrial soil system. In this study, at a concentration of 2 mg g^{-1} in soil, multi-walled carbon nanotubes (MWNTs) did not change PAH sorption capacities. Data presented in this study are useful for future CNT risk assessment and regulations.

Introduction

Because of their unique and remarkable chemical, physical, and electrical properties, carbon nanotubes (CNTs) have received much attention in areas such as material science, electronics, pharmaceuticals, and environmental science.[1–4] However, studies of CNT toxicity to the environment and humans have raised attention to the potential risks associated with these materials.[5] Also, with rapid commercial development, there is an increased chance of release of CNTs into the environment during production, application, and disposal. To better inform future risk assessments, it has been proposed that in addition to assessing CNT toxicity, fate and the associated impact of such materials in a real environment should also be understood.[6]

It has been reported that CNTs have a strong sorption capacity for various hydrophobic organic compounds (HOCs).[7–11] Such strong sorption capacity may pose risks or impacts in various ways, such as an alteration in the uptake, bioaccumulation, bioavailability, and toxicity of HOCs. Supported by decades of research regarding sorption behavior of carbon-based sorbents,[12–14] numerous sorption studies with CNTs have been conducted. These studies suggest that compared with traditional sorbents, CNTs have rapid equilibrium rates, high adsorption capacity, and consistency with Brunauer, Emmett and Teller (BET), Langmuir, or Freundlich isotherms.[10,15–18] Most current studies have focused on sorption behaviors of HOCs to CNTs in an aqueous phase.[10,11,19–21] One study on the competition between HOCs and humic acid (a major organic component of soil) for sorption to MWNTs provided useful information regarding the interactions between

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MWNTs, HOCs, and humic acid in an aqueous system.[22] However, it is well accepted that humic acid is not the only portion of soil responsible for sorption of HOCs. Many other components, such as humin, soot, and char, are also responsible for the sorption behaviors of HOCs in a soil system.[23,24] The complexity of interactions between CNTs, various soil components, and contaminants of interest make it difficult to draw definite conclusions from previous related sorption studies of what really happens in natural soils. Also, modeling based on probabilistic material flow analysis suggests that CNT concentration in soils would be a factor of 20 higher than that in water.[25] Hence, a study of the interactions of CNTs and HOCs in real terrestrial soils is urgently needed.

This study explored the influence of MWNTs on the sorption behaviors of PAHs in a natural terrestrial soil system. A MWNT concentration (2 mg g^{-1}) that is higher than what has been estimated to be in most environment compartments was used in this study. However, if the influence of MWNTs on the fate of PAHs in soil is concentration dependent, no or minimal influence observed at high concentrations would also be relevant at lower environmentally relevant concentrations. In addition, at this time MWNT concentrations in natural soils are still largely unknown. The batch equilibrium method was used to study sorption behavior of PAHs in MWNT-contaminated soil systems. This study involved three PAHs (naphthalene, fluorene, and phenanthrene), one type of commercially available MWNTs, two natural soils (sandy loam soil and silt loam soil), and Ottawa sand as a reference sorbent.

Materials and methods

Chemical and supplies

Naphthalene (purity > 99%), fluorene (purity > 98%), and phenanthrene (purity > 98%) were purchased from Sigma-Aldrich (St. Louis, MO). High performance liquid chromatography (HPLC)-grade acetonitrile was obtained from Fisher Scientific (Pittsburgh, PA). Standard solutions of PAHs were prepared in acetonitrile.

Commercially available pristine MWNTs (>95 wt% purity, <1.5 wt% ash content, and specific surface area of 60 m^2 g^{-1}) were purchased from Cheap Tubes Inc (Brattleboro, VT). A Hitachi H-8100 Transmission Electron Microscope (TEM) was used to characterize MWNTs following the method reported in Li *et al.* (2013).[26] Several characteristics of the MWNTs (length of 1–3 μm, relatively little bundling, and an outer diameter of 11 nm) indicate a fairly high surface area for interaction.

Sandy loam (Terry County, TX) and silt loam (Harlan County, NE) soils were used in this study. Prior to use in any experiments, soils were analyzed to determine background PAH concentrations; no PAHs were detected. All soils were passed through a 2 mm sieve to remove large debris. The physicochemical properties of soils were determined by A&L Midwest Laboratories (Omaha, NE) using standard techniques as described in Karnjanapiboonwong *et al.* (2010).[27] As mentioned in Karnjanapiboonwong *et al.* (2010),[27] soil characteristics were: (a) sandy loam soil (pH = 8.3, organic carbon content = 1.3%) consisted of 74% sand, 10% silt, and 16% clay and (b) silt loam soil (pH = 7.0, organic carbon content = 2.5%) consisted of 34% sand, 54% silt, and 12% clay. Previous analysis of reference sorbent – Ottawa sand (20–30 mesh; Fisher Scientific) indicated 98.8% sand, 1.2% silt, 0% clay, and 0% organic carbon.[28] Organic carbon content of the sand was assumed to be 0.1% for calculation purposes. After the addition of 2 mg g^{-1} MWNTs, the calculated organic carbon contents for sand, sandy loam soil and silt loam soil were 0.3%, 1.5%, and 2.7%, respectively.

Batch equilibrium sorption–desorption experiments

Batch equilibrium experiments were conducted at room temperature (20–22 °C) to determine sorption isotherms. Preliminary experiments showed that for each PAH, each sorbent–sorbate pair could reach apparent equilibrium at each initial concentration within 5 days. This was consistent with previous studies on sorption of PAHs to sediments, soils, or various MWNTs.[10,29,30] All batch sorption experiments were conducted in amber vials with Teflon-backed silicon septa in the dark for 5 days. The pH of aqueous solutions was kept at 7.0 and acetonitrile concentration was kept at less than 0.2% (v/v) to avoid a co-solvent effect. Mercuric chloride (0.01 mM) and calcium (0.01 M) chloride in ultrapure water was added to each vial. A single PAH, rather than a mixture of PAHs was used in each sorption test. Various initial concentrations of naphthalene (0.18, 0.51, 0.85, 3, 5.09 and 7.94 mg L^{-1}), fluorene (0.16, 0.33, 0.7, 1.02, 1.38 and 1.62 mg L^{-1}), and phenanthrene (0.10, 0.18, 0.44, 0.77 and 0.91 mg L^{-1}) were used to expand equilibrium concentration ranges as large as possible without losing quantification capability of PAHs in solution after sorption. All initial concentrations for each PAH were kept under the solubility. Dispersed MWNT aqueous solutions were added to soil and pre-equilibrated for 2 days before the addition of PAHs. The ratio of sorbent mass to solution volume varied among both PAHs and initial concentrations, but MWNT concentrations in sand and soils were maintained at 2 mg g^{-1} for comparison purposes.

Various sorbents were used in this experiment: MWNTs, sand, sandy loam soil, silt loam soil, sand mixed with 2 mg g^{-1} MWNTs (sand + MWNTs), sandy loam soil mixed with 2 mg g^{-1} MWNTs (sandy loam soil + MWNTs), and silt loam soil mixed with 2 mg g^{-1} MWNTs (silt loam soil + MWNTs).

After equilibrium, tubes were centrifuged for 40 min at 3000*g*. This long centrifuge time ensured separation of solid and liquid phases to minimize natural dispersant effects on CNTs. Desorption studies were performed for only one initial sorption concentration (0.85 mg L^{-1} of naphthalene, 0.7 mg L^{-1} of fluorene, and 0.91 mg L^{-1} of phenanthrene) for each PAH. Briefly, after sorption tests, the remaining supernatant was removed and replaced with fresh background solution, then tubes were further agitated for 24 h, under the same conditions. For both sorption and desorption studies, 0.5 mL of supernatant was placed into a 1.5 mL amber borosilicate glass HPLC autosampler vial for HPLC analysis.

All experiments were conducted in triplicate. Blank samples and control samples (no sand or soil) were included in each treatment to account for losses of PAHs caused either by sorption to container or volatilization. After each treatment, pH value was measured and no change was observed. Sorption and desorption were calculated by mass differences since less than 3% of loss of PAHs was detected in all treatments.

Determination of PAHs

An Agilent 1100 HPLC with a fluorescence detector was used for the determination of PAHs. An Agilent ZORBAX Eclipse PAH column (4.6 mm × 50 mm, 1.8 μm) was used for separation. Naphthalene and fluorene were determined using a mobile phase containing acetonitrile : water (isocratic: 60 : 40 v/v; flow rate = 1.0 mL min^{-1}). Phenanthrene was detected using a mobile phase containing acetonitrile : water (isocratic: 70 : 30 v/v; flow rate = 1.0 mL min^{-1}). The following excitation and emission wavelengths were used: 220 nm (ex) and 330 nm (em) for naphthalene, 289 nm (ex) and 321 nm (em) for fluorene, and 244 nm (ex) and 360 nm (em) for phenanthrene. All PAHs were quantified using external standards based on response factors.

Data analysis

Freundlich parameters (K_f and n) were calculated from the nonlinear form of the Freundlich equation: $S = K_f C^{1/n}$, where S (μg g^{-1}) is the concentration of chemical on the sorbent; C is the solution-phase concentration (μg mL^{-1}); K_f ($\mu\text{g}^{1-1/n}$ $\text{mL}^{1/n}$) is the Freundlich affinity coefficient and $1/n$ is the non-linearity factor. $S = K_d C$ is a simple linear Freundlich equation when $1/n = 1$, where K_d is the sorption coefficient (μg g^{-1}). After normalizing K_d based on organic carbon content, the K_{oc} value was derived from the equation: $K_{oc} = (K_d/\%$ organic carbon) × 100.

Statistical analysis was performed with SPSS16.0 for Windows (SPSS Inc.). Means were compared with analysis of variance (ANOVA). Multiple comparisons were conducted with the Tukey's honestly significant difference (HSD) test. Significant differences were analyzed by applying the least significant difference of means at a 5% confidence level ($p \leq 0.05$).

Results and discussion

Sorption

Sorption isotherms for each compound are shown in Fig. 1 (phenanthrene), Fig. S1† (naphthalene), and Fig. S2† (fluorene). In general, sorption behaviors of each PAH followed these two orders: (1) MWNTs > silt loam soil > sandy loam soil > sand and (2) MWNTs > silt loam soil + MWNTs > sandy loam soil + MWNTs > sand + MWNTs. Compared with other sorbents, MWNTs had nearly three orders of magnitude more sorption ability (μg mg^{-1} *vs.* μg g^{-1}). The sorption order of other pure sorbents (without adding MWNTs) suggests that sorption

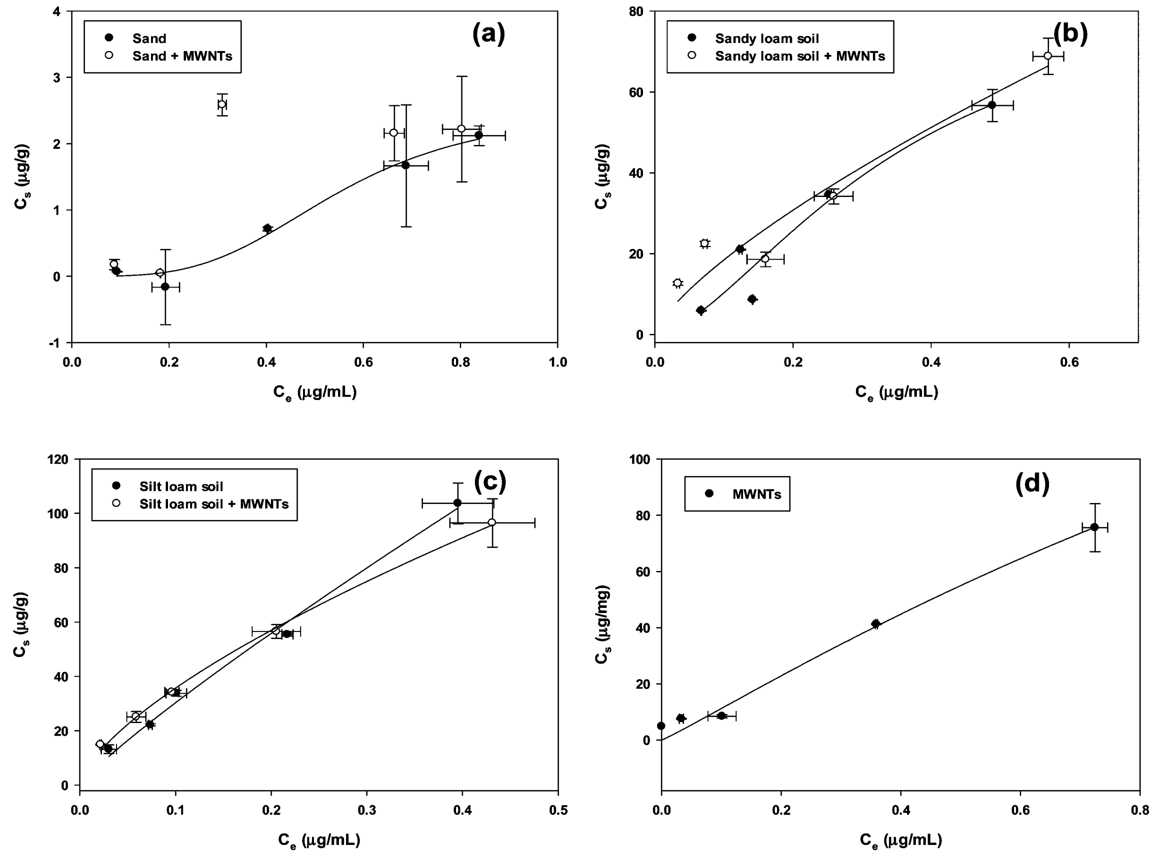

Fig. 1 Sorption of phenanthrene in (a) sand with or without addition of MWNTs, (b) sandy loam soil with or without addition of MWNTs, (c) silt loam soil with or without addition of MWNTs and (d) MWNTs. Data points represent means ($n = 3$) and error bars for both solution and sorbent concentration indicate ±1 standard deviation of the mean. The y axis unit is μg g^{-1} (except for MWNTs which is μg mg^{-1}). Solid lines are the isotherms fitted by Freundlich equation. Data for sand + MWNTs are not fitted due to the low r^2 value.

affinities in these sorbents are directly related to organic carbon content in these sorbents. This fits the assumption that overall transport and binding reactions are dominated by sorbent organic carbon content when organic carbon content is present above 0.2%, especially for nonionic hydrophobic chemicals.[31–33] Similar clay content (12% *vs.* 16%) in the two types of soils used further supports this observed pattern. By comparing isotherms of natural sorbents with corresponding sorbent mixtures with MWNTs, the addition of MWNTs did not seem to have an obvious influence on natural sorbent sorption. This indicates that even in soil contaminated with high concentrations of MWNTs (2 mg g^{-1}), soil organic carbon content still determines PAH sorption behavior in soil.

There is still a lot of controversy regarding which isotherm model to use for estimating PAH sorption to MWNTs. In this study, the various interactions between PAH, MWNTs, and various components of complex natural soil led to difficulty in fitting all sorption test data with just one model. The Freundlich model, which majority of the data (except for sand loam + MWNTs) fit best, was used to make more careful and detailed observations of PAH sorption behavior on various sorbents. Freundlich constants (K_f and n), sorption coefficients (K_d and log K_{oc}), and regression coefficients (r^2) are reported in Table 1 (phenanthrene), Table S1† (naphthalene), and Table S2† (fluorene). Generally, all the parameters, except those for sand or sand + MWNTs, had small standard deviations. In general, high regression coefficients for both Freundlich and linear equations supported overall linearity (except for sand loam + MWNTs, $r^2 = 0.45$). The large deviations in regression coefficients observed in sand or sand + MWNTs would be expected given the low sorption capacity of sand and sand + MWNTs. Given the overall good linearity of the majority of the isotherms, sorption behaviors of different PAHs in various sorbents were compared based on sorption coefficients (K_d and log K_{oc}).

Sorption behaviors of different PAHs on various sorbents

Sorption of PAHs on natural sorbents, like sands, sandy loam soils, and silt loam soils has been intensely studied. It is well recognized that in the same natural sorbent with a relatively large amount of organic carbon, PAHs with higher K_{ow} values sorb more on the sorbent since hydrophobic interactions are the main force for partition and sorption to occur. In general, different PAH sorption coefficients derived from each sorbent followed this trend in this study; the addition of MWNTs to each natural sorbent did not disturb this trend. The same trend was found for log K_{oc} values for different PAHs. This demonstrates that organic carbon content is the driving component for sorption in this study. Given the chemical composition and structure of MWNTs, and the fact that MWNTs did not alter this trend, MWNTs could serve as another kind of hard carbon once released to the environment.

It has been stated that the amorphous carbon phase is the primary reason for partitioning of HOCs, while the condensed carbon phase might serve more as adsorption medium.[34] The ratio of amorphous carbon to condensed carbon indicates sorption linearity. It is interesting that the addition of MWNTs altered linear sorption behaviors of PAHs in natural sorbents. For naphthalene and fluorene, the addition of MWNTs in sand, sandy loam, and silt loam generally led to a decreased $1/n$ value. However, for phenanthrene, the addition of MWNTs to all sorbents led to an increased $1/n$ value. Hence, further characterization might be helpful to explore any structural change of soil organic carbon following the addition of MWNTs by techniques such as ^{13}C nuclear magnetic resonance (NMR) spectroscopy. One important thing to note is that the majority of the changes in $1/n$ values were not significantly different ($p > 0.05$). It is not clear if the lack in significant differences were caused by the MWNT concentrations. Therefore, future studies need to be conducted with more MWNT concentrations in soil. However, these data suggest that hydrophobic interactions in MWNT-contaminated soil systems are still the dominant force governing the sorption capacity of PAHs tested. The change in linear sorption behavior is complicated by the potential competition between types of contaminants, various components of soils, types and related properties of MWNTs, and MWNT concentrations in soil.

Adsorption of PAHs by MWNTs in this study was three orders of magnitude higher than that of natural soils, which is consistent with previous studies.[10] Based on the linear sorption behavior, the overall energy of these interactions was uniform with increasing concentrations, which is in agreement with previous studies[35,36] PAH sorption on MWNTs followed the trend, naphthalene < fluorene < phenanthrene, which follows the same trend of their increasing hydrophobicity (K_{ow}) (Table S3†). A similar trend in aqueous solution has also been reported by Yang *et al.* (2006).

Table 1 Freundlich parameters and sorption coefficients for phenanthrene in various sorbents. Data are presented as average ± standard deviation

	Freundlich equation			Linear equation		
Sorbent	K_f[a]	$1/n$	r^2	K_d[b]	log K_{oc}	r^2
MWNTs	74 929 ± 5276	0.66 ± 0.02	0.93 ± 0.01	1×10^5 ± 10 079	7.01 ± 0.04	0.96 ± 0.04
Sand	2.77 ± 1.12	1.58 ± 0.27	0.94 ± 0.04	2.55 ± 1.20	3.37 ± 0.24	0.92 ± 0.06
Sand + MWNTs	4.58 ± 2.44	1.81 ± 0.61	0.64 ± 0.04	2.88 ± 0.75	2.97 ± 0.11	0.58 ± 0.17
Sandy loam	74.91 ± 7.86	0.54 ± 0.04	0.83 ± 0.07	102.02 ± 14.89	3.83 ± 0.06	0.95 ± 0.02
Sandy loam + MWNTs	130.70 ± 8.64	1.28 ± 0.35	0.94 ± 0.01	125.43 ± 33.12	3.98 ± 0.11	0.94 ± 0.05
Silt loam	161.4 ± 14.95	0.64 ± 0.04	0.97 ± 0.01	240.79 ± 53.68	3.94 ± 0.10	0.99 ± 0.00
Silt loam + MWNTs	199.1 ± 23.31	0.80 ± 0.09	0.96 ± 0.05	245.22 ± 36.12	3.99 ± 0.07	0.98 ± 0.02

[a] $\mu g^{1-1/n}$ $mL^{1/n}$ g^{-1}. [b] mL g^{-1}.

Sorption behaviors of the same PAH on different sorbents

Generally, for each individual PAH (naphthalene, fluorene or phenanthrene), the sorption coefficients (K_d, log K_{oc}) only changed when the natural sorbent type changed ($p < 0.05$). Sorbent type had a significant effect on K_d values, reflected by the following K_d order: K_d-MWNTs > K_d-silt loam soils > K_d-sandy loam soils > K_d-sand ($p < 0.05$). As mentioned before, the differences in organic carbon content among different sorbents might account for this since hydrophobic interactions are the main driving force in this case. In addition, the K_d value of each PAH in each sorbent did not change when 2 mg g^{-1} MWNTs was added ($p > 0.05$). In general, log K_{oc} values for each PAH remained constant in a reasonable range with a few exceptions. Specifically, the difference in log K_{oc} of each PAH between sand and sand + MWNTs was caused by the assumption of organic carbon content (0.1%) of sand for calculation purposes. The differences between sandy loam and sandy loam + MWNTs (or silt loam and silt loam + MWNTs) were in an expected range of variances of K_{oc} that occur in nature as there are numerous variations of organic carbon components and clay.

Desorption

Desorption of PAHs over 24 h was minimal in various sorbents. Results are presented in Table S3.† Naphthalene was not detected in the majority of sorbents. This might be due to the low initial concentration used for desorption tests and relatively lower adsorbed amounts. Future studies with either a higher initial concentration which would result in an increase in the amount adsorbed, or with more sensitive detection methods for naphthalene might overcome this problem. Generally, for fluorene and phenanthrene, the addition of MWNTs in various sorbents decreased the percent desorbed, although such changes were not statistically significant ($p < 0.05$). This might further support that MWNTs might act as another kind of hard carbon, which can adsorb PAHs strongly. Future studies of the influence of MWNTs on PAH sorption and desorption isotherms, with more initial concentrations and a longer testing period are needed. Such studies could provide information on both sorbate–sorbent interaction and structural properties of sorbents.

All of these results might indicate that even with a much higher concentration (2 mg g^{-1}) than what is environmentally relevant, the MWNTs used in this study still did not exhibit a significant influence on the overall sorption behavior of PAHs in soil. In addition, despite the strong sorption capability of MWNTs for PAHs, MWNTs still did not significantly influence the fate of PAHs in soil.

Estimation of the influence of MWNTs on sorption behaviors of PAHs in soils

As a method with low costs, batch equilibrium methods have been one of the most, if not the most, widely used method for studying sorption behaviors and obtaining sorption coefficients of various organic chemicals.[27,37,38] Batch equilibrium methods are conceptually simple but are subject to a variety of operational difficulties. Extensive work needs to be done to avoid experimental artifacts related to the separation of phases, agitation speed, insufficient time for equilibration and exposure of new sorptive surfaces during agitation.[39] When using a mixture of sorbents in a batch equilibrium method, the situation will become even more complex. Thus, a method to estimate HOC sorption behavior in a mixture of sorbents would save time and expenses for such studies and related applications in risk assessment.

A straightforward rule of mixtures was used to predict PAH sorption behaviors in mixtures based on sorption coefficients derived from single sorbents. The rule of mixtures is widely used to predict properties of mixtures, such as composite mechanical properties.[40,41] A similar modeling approach has also been used in the evaluation of the impact of black carbon and CNTs on sorption of PAHs in aquatic sediments and their impact on PAH bioavailability in earthworms.[42–44] This study explored whether sorption coefficients (K_d and log K_{oc}) of the composite (MWNTs + terrestrial soils) could be estimated based on those of its individual components.

As mentioned before, sorption coefficients (K_d and log K_{oc}) were calculated from a simple linear Freundlich equation: $S = K_dC$. Three separate linear equations were derived from the mixture system:

$$S_T = K_{dT}C,\ S_M = K_{dM}C,\ S_N = K_{dN}C$$

S_T, S_M, S_N represent the concentration (μg g^{-1}) of chemical on the total sorbent, MWNTs, and natural sorbent, respectively; C (μg mL^{-1}) is the solution-phase concentration; K_{dT}, K_{dM}, K_{dN} (μg g^{-1}) represent the sorption coefficient of total sorbent, MWNTs, and natural sorbent, respectively.

An equation can be derived from $S_T = S_M\alpha + S_N(1 - \alpha)$, where α is the mass fraction of MWNTs in the total sorbent and $(1 - \alpha)$ is the mass fraction of natural sorbent in the total sorbent, $K_{dT}C = K_{dM}C\alpha + K_{dN}C(1 - \alpha)$.

$$K_{dT} = K_{dM}\alpha + K_{dN}(1 - \alpha) \qquad (1)$$

Eqn (1) is well known as a parallel combination rule of mixtures. For another sorption coefficient (K_{oc}), a similar eqn (2) can also be derived.

$$K_{ocT} = K_{ocM}\alpha + K_{ocN}(1 - \alpha) \qquad (2)$$

To test whether these equation are reliable in predicting mixture sorption coefficients, theoretically predicted data and experimentally gained data were compared with a one way ANOVA, as shown in Fig. 2. For most sorption coefficients, there were no significant differences between the predicted values and real values ($p > 0.05$). For naphthalene and fluorene in sandy loam soil, there were significant differences ($p < 0.05$) between predicted and real values while these values were close. Various unavoidable experimental artifacts, as those mentioned above, might contribute to these differences. Overall, rule of mixtures could serve as a reliable prediction tool for K_d value of mixtures, as long as each sorbent sorption coefficient and mass fraction in the mixture is known.

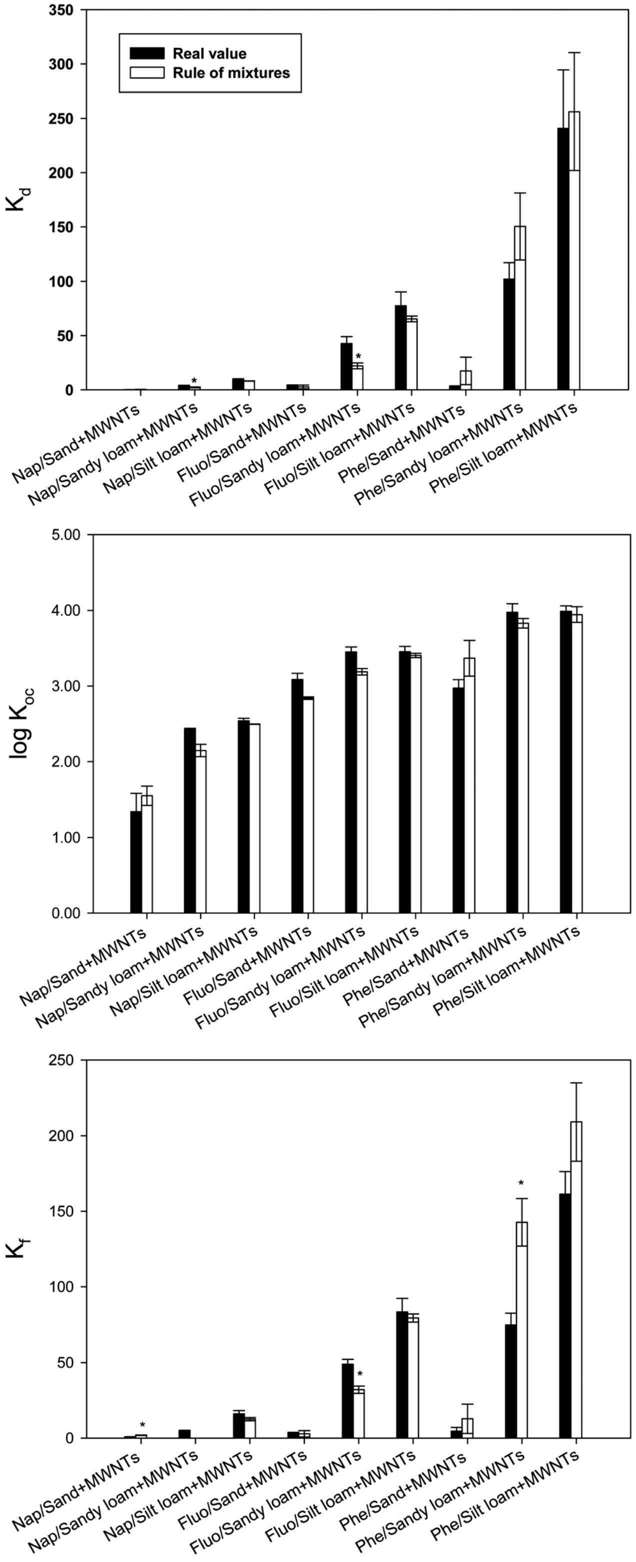

Fig. 2 Comparison of theoretically predicted and experimentally gained K_d, log K_{oc}, and K_f values. Asterisks (*) indicate significant differences from corresponding experimental values ($p < 0.05$). Naphthalene, fluorene and phenanthrene are represented by Nap, Fluo, and Phe.

However, caution should be taken when the sorption of a mixture is not linear. In this situation, a different equation can be derived:

$$K_{fT}C^E = K_{fM}C^F + K_{fN}C^G \qquad (3)$$

C is the solution-phase concentration (μg mL^{-1}); K_{fT}, K_{fM}, K_{fN} (μg$^{1-1/n}$ mL$^{1/n}$) are the Freundlich affinity coefficients for total sorbent, MWNTs, and natural sorbent, respectively; and E, F, G are the non-linearity factors for total sorbent, MWNTs, and natural sorbent, respectively. Compared with eqn (1) or (2), eqn (3) is complicated by the differences among linearity terms, E, F, and G. Also note that rule of mixtures assumes that there is no void space in the mixture. Inaccuracy might be expected since natural soils normally have void spaces, which might be filled with air or water.

Future studies to explore the effect of MWNT concentration on natural sorbent sorption behavior, especially linearity, should be conducted. Also, additional work involving a systematic study of the interactions between MWNTs and natural sorbents (especially those that do not sorb linearly in the first place) and related structural changes would be helpful in fully understanding mixture sorption behavior.

This study serves as a novel and necessary step forward in understanding the behavior of CNTs in the environment. The major findings of this study were: (1) sorption behavior of PAHs was still predictable by traditional equilibrium models in the presence of MWNTs in soil; (2) although adsorption of PAHs by MWNTs in this study was three orders of magnitude higher than that of natural soils, sorption coefficients (K_d and K_{oc}) of PAHs remained unchanged after the addition of 2 mg g^{-1} MWNTs (which is much higher than possible environmentally relevant concentrations in soil); (3) the 'rule of mixtures' could be used for predicting PAH sorption behavior in soil contaminated with MWNTs, at least for PAHs with linear sorption behaviors.

A previous study reported MWNTs could adsorb onto soil and different MWNTs have different adsorption affinities and linearities.[36] Also, various soil components, such as humic acid, could compete with PAHs for adsorption sites on MWNTs.[22] While all these interactions happen simultaneously in the complex MWNT-contaminated soil system, whether or not these interactions would affect PAH fate in soil with or without MWNTs would be the ultimate concern for regulatory agencies. In this MWNT-contaminated soil system, hydrophobic interactions dominate the overall sorption behaviors among MWNTs, PAHs, humic acid, fulvic acid, and other soil components, although π–π interactions have extensively been recognized as another major driving force in a simple PAH–MWNT aqueous solution.[7,16] Hydrophobicity of hydrophobic organic compounds is still a good indicator of sorption capacity in non-functionalized MWNT-contaminated soil.

Conclusions

This study explored the influence of MWNTs on sorption behaviors of polyaromatic hydrocarbons (PAHs) in a terrestrial soil system. Fate of PAHs in soil was not affected by non-functionalized MWNTs even at a concentration higher than environmentally relevant ones. For future 'hotspots' in the environment with higher MWNT concentration than that applied in present study, a 'rule of mixture' approach could be used to predict the influence of MWNTs on the fate of hydrophobic chemicals. Data presented in this study are useful for future MWNT risk assessment and regulations.

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