

Phase Distribution of ^{14}C -Labeled Multiwalled Carbon Nanotubes in Aqueous Systems Containing Model Solids: Peat

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 Supporting Information

ABSTRACT: Understanding the phase distribution of nanoparticles between soils or sediments and water is a critical factor in determining their fate in environmental systems. As such, we examined the interactions of ^{14}C -labeled multiwalled carbon nanotubes (MWNTs) in aqueous systems with peat as a model solid organic material. MWNTs that had been treated with strong oxidative acids possessed negative charges on their surfaces and were relatively stable in deionized water. In the absence of peat, MWNTs aggregated when the concentration of sodium cations was above 4.0 mM or at a solution pH of 4.0. Dissolved organic matter (DOM) from peat effectively stabilized MWNTs in solution by making the suspended nanotubes less sensitive to changes in sodium concentration or solution pH. Direct sorption interactions between MWNTs and solid peat were not observed in the absence of sodium cations, whereas they became apparent when the ionic strength was sufficiently high to reduce electrostatic repulsion between peat and MWNTs.

INTRODUCTION

Carbon nanotubes (CNTs) are long (often micrometer scale), thin (nanometer scale), hollow cylinders comprising single or multiple coaxial tube(s) of hexagonal graphitic sheet(s). Those composed of a single cylinder are known as single-walled carbon nanotubes (SWNT), while multiple-layered nanotubes are called multiwalled carbon nanotubes (MWNTs). CNTs possess exceptional physicochemical, optical, and mechanical properties,^{1,2} which enable numerous applications such as reinforced composites, conductive materials, sensors, drug delivery vessels, hydrogen storage media, and sorbents.^{1,3} The total mass of CNTs synthesized worldwide during the 2007/2008 year was estimated to be 350 tons,⁴ and the global market for CNTs is expected to grow exponentially at an annual rate of 73.8%,⁵ indicating substantial CNT production and rapid predicted growth. This gives rise to concerns about the potential environmental impacts of CNTs after incidental release during manufacturing, transportation of raw CNTs, or via product use and disposal.

One important component of understanding the risks CNTs may pose in ecosystems is the extent to which they are accumulated by organisms. Earlier studies have shown that organisms in the water column accumulate substantially higher masses of CNTs compared to those in soils or sediments.^{6–12} For example, bioaccumulation of CNTs by terrestrial and benthic organisms was minimal in spiked soils or sediments,^{6–10} while *Daphnia magna* had nanotube body burdens of up to 6.3% on a dry mass basis after being exposed to MWNTs suspended in water.^{11,12} As such, information on the phase distribution of CNTs between water and sediments is essential to assessing their environmental risks in natural aquatic systems, but the interactions between nanotubes and soils or sediments are currently not well understood.

Aggregation appears to be an important process governing the phase distribution of CNTs in aqueous systems. It is generally accepted that pristine CNTs have a strong tendency to aggregate as a result of attractive van der Waals forces acting across their large surface areas. However, in practice, defects typically occur during CNT synthesis and subsequent purification processes, which usually impart the CNTs with hydroxyl or carboxyl surface functional groups.^{13,14} In addition, it is often necessary to modify CNT surfaces to increase aqueous solubility and biocompatibility for various applications.^{15,16} While the introduction of hydrophilic surface functional groups tends to mitigate CNT aggregation, the effects of these functional groups are highly sensitive to solution ionic strength. Cations present in the solution facilitate CNT aggregation, seemingly via compression of the electric double layers surrounding CNTs.^{17,18} In contrast, dissolved organic matter (DOM) can effectively stabilize CNTs in solution, likely through surface adsorption of amphiphilic DOM molecules.^{19,20} When DOM and cations are both present, such as in natural aquatic systems, the impact of different concentrations of DOM and cations on CNT aggregation is unclear.

Potential sorption of CNTs on sediments is another process expected to govern the phase distribution of CNTs in natural aquatic systems. One indirect mechanism through which sediments may influence surfactant-stabilized MWNTs is through competitively absorbing those surfactants, as was previously found with clay particles.²¹ However, there are no studies yet to our knowledge on direct interactions between CNTs and soil or sediment particles. Interactions between CNTs and sediments

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may be highly complex because, in addition to direct sorption to the solid matter itself, sediments may also release cations or DOM, which may themselves affect CNT phase distributions.

The lack of previous studies on CNT sorption to soils and sediments is likely due, in large part, to the challenges related to quantification of CNTs in samples containing solid materials. In the present study, we used carbon-14-labeled CNTs to overcome this difficulty and investigated the phase distribution of MWNTs in aquatic systems containing peat as a model soil component. Our objectives were to quantify and compare the influences of the solid and dissolved components of peat on the phase distribution of MWNTs under various conditions (i.e., ionic strength and pH) and to probe the interactions between MWNTs and solid peat. This paper marks the first study to our knowledge of the phase distribution of CNTs between water and soil or sediment materials.

MATERIALS AND METHODS

Multiwalled Carbon Nanotube Synthesis and Suspension Preparation. Carbon-14-labeled carbon nanotubes were synthesized by a modified chemical vapor deposition technique,⁷ purified, and treated with a 3:1 mixture of sulfuric to nitric acid⁶ as described in the Supporting Information. These surface-modified MWNTs have a specific radioactivity of 0.1 mCi/g as determined by liquid scintillation counting after biological oxidation (OX 500; R. J. Harvey Instrument Co., Tappan, NY). The surface area of the acid-treated MWNTs is 111 m²/g as measured by the standard Brunauer–Emmett–Teller (BET) method via nitrogen adsorption at 77 K (Micromeritics Gemini 2375, Norcross, GA), which accords with a previous result of 118 m²/g for purified but not acid-treated MWNTs synthesized by the same method.²²

To prepare a stable stock solution, 100 mg of MWNTs was dispersed in 1 L of deionized water by ultrasonication (200 W, Cole-Parmer CV33) for 6 h, and then the mixture was left at room temperature for 6 h. The stable supernatant with a concentration measured as 74 mg/L was collected and kept at room temperature as a stock solution for all subsequent experiments. Before experiments, a sample of the stock solution was centrifuged at 3500g for 5 min, and the supernatant was collected and diluted to predetermined concentrations. To assess the extent to which the ultrasonication process damaged the MWNTs, the initial MWNT powder and the stock solution of suspended MWNTs were examined by thermal gravimetric analysis (TGA) (Pyris 1 TGA, Perkin-Elmer) and X-ray photoelectron spectroscopy (XPS) (Kratos Analytical Axis Ultra X-ray photoelectron spectrometer).

Model Solid Phase: Canadian Peat. Peat, an organic component frequently present in soil and sediments, was used as a model organic material in this study. Peat is usually composed of recently deposited plant organic materials and is thus a diagenetically young organic material.²³ Canadian peat (Quebec, Canada) that had been sieved to obtain a particle size fraction of less than 2 mm was used in our experiments. The total organic carbon fraction of this material was previously determined to be 47.5%.²³ Its specific surface area is 1.8 m²/g as determined by the BET method described above.

Multiwalled Carbon Nanotube and Peat Characterization. Microscopic investigations of MWNTs and peat were performed with a FEI Inspect F50 FEG scanning electron microscope (SEM) operating at an accelerating voltage of 10.00 kV. Zeta (ζ)

potentials of MWNTs were measured on a Malvern Zetasizer Nano ZS instrument. Point of zero charge (PZC) of the MWNT stock solution was determined by use of 10 points from pH 1.00 to 5.83. Concentrations of metal ions released by peat were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000, Perkin-Elmer, MA).

Multiwalled Carbon Nanotube Phase Distribution. Experiments were conducted to examine the distribution of MWNTs between solid and aqueous phases in 150-mL flasks as batch reactors. MWNT concentrations were quantified by radioactivity via a Beckman LS 5801 liquid scintillation counter (Brea) after a 3-mL sample was mixed with 3 mL of scintillation cocktail (Insta-Gel Plus, Perkin-Elmer). The detection limit for the radioactivity quantification method was 0.04 mg/L; this value was determined by mixing 3 mL of deionized water with 3 mL of scintillation cocktail ($n = 6$), measuring the radioactivity, and defining the detection limit as 3 times the standard deviation of these measurements.

Peat can be divided into two components: one that readily dissolves in water and one that remains as a solid phase, both of which may have different effects on the phase distribution of MWNTs. To separate the effects of these two components, three types of treatments were examined. In the blank (control) treatment, the solution was prepared in deionized water without peat; in the peat treatment, the solution was prepared in deionized water with 50 mg of peat added to the reactor; and in the DOM treatment, the solution contained DOM extracted from 50 mg of peat but not the solid peat itself (see the Supporting Information for additional details about DOM solution preparation). This DOM treatment was designed to imitate the effect of DOM released by peat in the reactor. Thus, differences between DOM and blank treatments can be attributed to effects from DOM, while differences between peat and DOM treatments stem from the presence of solid peat. For each system, two sets of varying solution conditions were examined. One set involved three different Na⁺ concentrations (0, 4, and 40 mM) that were prepared by addition of NaCl. The other set was prepared at three different pHs (4.0, 6.0, and 8.0). The pH 4.0 solution was prepared with a 1 mM sodium acetate buffer and the pH 6.0 and 8.0 solutions with a 1 mM sodium phosphate buffer. The actual pH values for various conditions are listed in Table S1a in Supporting Information. To maintain a constant ionic strength at different pH values, an appropriate mass of NaCl was added to each buffer solution to adjust the final Na⁺ concentration to 4 mM. For each condition tested, reactors containing 10 mL of solution were prepared with 10 different initial concentrations of MWNTs from 0.15 to 67 mg/L (see Table S1b in Supporting Information for exact concentrations).

Experiments were performed at least twice to ensure that the patterns observed were reproducible. The reactors were hand-shaken for mixing when all components were added and then were left without shaking in the dark at room temperature for 7 days. We selected this period on the basis of our preliminary time-course tests, which showed that most of the change for the solid-phase distribution pattern occurred within the first 7 days, thus indicating that a pseudo-steady state had been reached (Figure S1, Supporting Information). After 7 days, 5 mL of the supernatant in each reactor was transferred to a centrifuge tube and centrifuged at 3500g for 3 min to ensure the separation of solid and liquid phases. Preliminary tests showed that sedimentation for 6 h was not sufficient to achieve good separation. A 3-mL liquid phase sample was taken for radioactivity measurements as

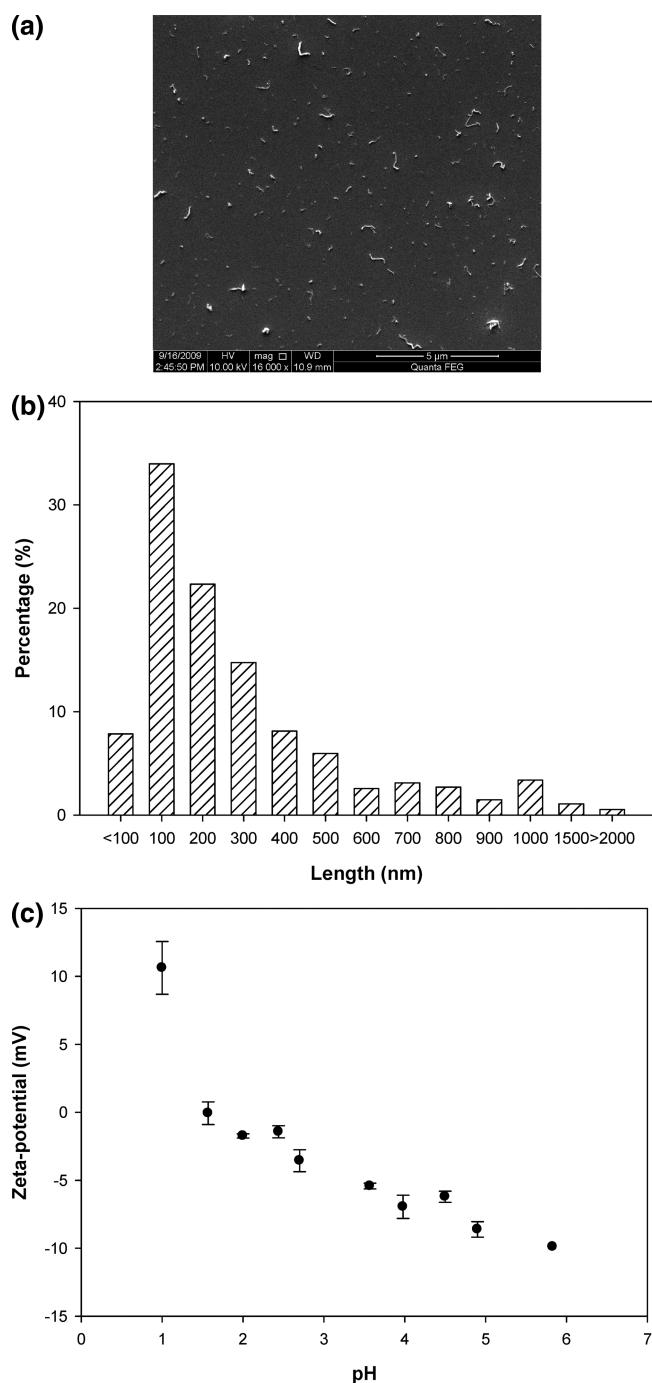


Figure 1. (a) Scanning electron microscopy (SEM) images showing the morphology of suspended MWNTs at 16000 \times magnification, (b) initial length distribution of MWNT suspension measured by SEM ($n = 797$), and (c) ζ potentials of suspended MWNTs after ultrasonication at pHs varying from 1.00 to 5.83. Error bars represent the standard deviation from two measurements made of the same sample at each pH value; each run consisted of 50–100 subruns. The pH was adjusted by HCl, and the cation concentration was kept constant at 0.1 mol/L by addition of NaCl.

described above. The total mass of MWNTs that had distributed into the solid phase in each treatment, M_s (milligrams), was then obtained by

$$M_s = (C_0 - C_{aq})V \quad (1)$$

where C_0 (milligrams per liter) and C_{aq} (milligrams per liter) are the initial and final concentrations of MWNTs, respectively, and V is the sample volume (10 mL). While M_s resulted primarily from aggregative settling in the blank and DOM treatments, both sorption and aggregation may contribute to M_s in a system containing solid peat.

We also calculated an apparent solid-phase MWNT concentration q_a (milligrams per gram of peat) for systems containing solid peat (peat treatment)

$$q_a = \frac{M_s^P - M_s^D}{D} \quad (2)$$

where M_s^P and M_s^D are the total mass of MWNTs in solid phase for peat treatment and DOM treatment, respectively, and D is the peat dosage of 0.050 g. The apparent solid-phase concentration thus obtained approximates the solid-phase partitioning of MWNTs directly attributable to the presence of solid peat by excluding the mass of settled MWNTs. For certain discussions, we also estimated the total solid-phase MWNT concentration, q_t (milligrams per gram of peat), by eq 3, in which the contribution of MWNT settling was not excluded:

$$q_t = \frac{M_s^P}{D} \quad (3)$$

RESULTS AND DISCUSSION

We experimentally examined the phase distribution of MWNTs in three types of systems, under a series of identical pH and ionic strength conditions, including (1) systems without organic matter present, (2) systems containing DOM extracted from peat but not the peat particles themselves, and (3) systems with peat particles present. Our goal was, through the comparison of systems 1 and 2, to identify the effect of DOM on MWNT aggregation and to probe the direct interaction between solid peat and MWNTs by comparing systems 2 and 3. We present below the results of MWNT characterization followed by data collected respectively for each of the three systems, in sequence, along with quantitative comparison and analysis.

Multiwalled Carbon Nanotube Characterization. MWNTs were thoroughly characterized and the effects of sonication were investigated. Given that amorphous carbon impurities generally burn at lower temperatures than carbon nanotubes, peaks of the derivative of the mass change with respect to temperature at lower temperatures than the principal MWNT peak represent the oxidation of carbon impurities in TGA analyses. As shown in the TGA graphs in Figure S2 (Supporting Information), the amount of metal catalyst remaining in the nanotube samples was nearly identical before and after sonication, and an amorphous carbon peak was not observed. This indicates that sonication did not produce a detectable increase in the fraction of amorphous carbon, a result that corresponds to the high purity of the MWNT samples as determined by scanning electron microscopy (SEM) (Figure 1a; Figure S3 in Supporting Information). XPS high-resolution C (1s) spectra for the powder and the sonicated MWNTs suggests that the total fraction of carbon atoms associated with oxygenated functional groups increased slightly from roughly 7.4% to 8.6% after sonication and that the total oxygen percentage increased from 7.5% to 8.6%. The MWNT length distribution is provided in Figure 1b.

Effect of Cation Concentrations on Multiwalled Carbon Nanotube Settling. MWNT settling in solutions prepared using deionized water in the absence of peat is shown in Figure 2a.

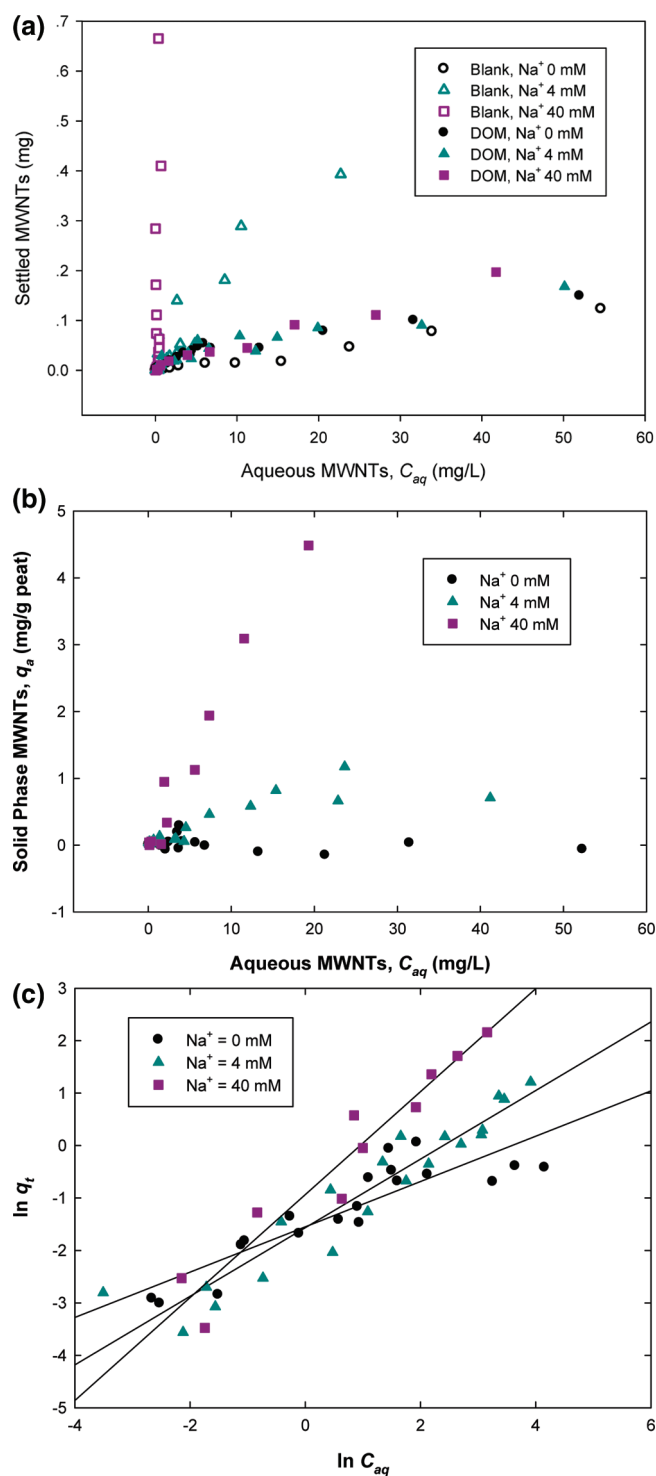


Figure 2. MWNT phase distributions in different solutions with varying sodium concentrations (0, 4, and 40 mM). (a) MWNT settling in DOM solutions (solid symbols) or water (labeled blank; open symbols). (b) Apparent solid-phase concentration (q_s) of MWNTs in peat-containing solutions. The apparent solid-phase concentration was calculated by eq 2, whereby the contribution of MWNT settling was subtracted. (c) Overall phase distribution of MWNTs between peat and water modeled with the parameters from Table 1.

In the absence of sodium cations, $22.1\% \pm 8.6\%$ ($n = 20$; uncertainties always represent standard deviations) of MWNTs

Table 1. Parameters Obtained by Data Fitting to the Equation $q_t = KC_{aq}^n$

sodium concn (mM)	N^a	K (mg/g of peat) $^{(1-n)}$	n (dimensionless)	R^2
0	20	0.207 (0.196, 0.219) b	0.395 (0.369, 0.421)	0.729
4	20	0.209 (0.198, 0.221)	0.654 (0.630, 0.678)	0.929
40	10	0.393 (0.348, 0.982)	0.981 (0.914, 1.0493)	0.929

a Number of data points used in data fitting. b Values in parentheses are 95% confidence intervals.

settled after the 7-day experiments and centrifugation, indicating that the acid-treated MWNTs were relatively stable in aqueous phase. If the sodium concentration is increased to 4 mM, an environmentally relevant cation concentration in fresh water, the percentage of deposited MWNTs ranged from 60.4% to 90.6% ($71.2\% \pm 9.9\%$, $n = 20$) for the tests with different initial MWNT dosages, whereas with 40 mM sodium, MWNTs were almost entirely eliminated from the aqueous phase for all cases. This trend is consistent with earlier observations that cations such as sodium, potassium, calcium, and magnesium can induce MWNT aggregation by reducing the MWNT surface electrostatic potential, indicated by ζ potential. 2,17,18 Aggregated MWNTs are larger and thus are more easily removed by settling or centrifugation. Our measurements indicated the ζ potentials of MWNTs were -29.7 ± 0.9 , -20.3 ± 3.1 , and -12.0 ± 0.8 mV under sodium concentrations of 0, 4, and 40 mM, respectively. Figure 1c shows the point of zero charge value for the MWNTs is near pH 1.57 given that the ζ potential at this pH value was -0.068 ± 0.83 mV.

Effects of Peat Dissolved Organic Matter on Multiwalled Carbon Nanotube Settling. The presence of DOM dramatically decreased MWNT settling at sodium concentrations of 4 and 40 mM as shown in Figure 2a, a result consistent with past research on DOM interactions with CNTs. 24 The total organic carbon (TOC) values of DOM solution released for the 0, 4, and 40 mM sodium experiments were 73, 70, and 66 $\mu\text{g/mL}$, respectively. The enhanced MWNT stabilization in DOM solutions occurred despite the fact that the DOM solutions also contained additional cations that peat released (see Table S2, Supporting Information). These findings support previous research indicating that DOM can stabilize MWNTs in a manner similar to surfactants. 24 Molecular DOM are adsorbed by their aromatic rings or aliphatic chains binding to MWNTs' surface carbon rings via π - π or CH- π interactions, while their hydrophilic moieties are exposed to water. 25,26 TEM images have indicated adsorption of Suwanee River natural organic matter (NOM) by CNTs. 19,20 We also conducted an experiment to verify the sorption of DOM on MWNTs by TOC analysis (Supporting Information). DOM sorption by MWNTs was 0.26 ± 0.13 , 0.41 ± 0.12 , or 0.49 ± 0.13 mg of C DOM/mg of MWNT ($n = 4$) when there was 0, 4, or 40 mM sodium added, respectively. DOM adsorption changed MWNT surfaces from being dominated by a hydrophobic aromatic-like structure to possessing an extended surface of hydrophilic organic functional groups in DOM. The sorbed DOM thus helped inhibit aggregation between the CNTs through steric hindrance as well as electrostatic repulsion. Increasing cation concentrations are expected to significantly reduce electrostatic repulsion by double layer compression. However, more NOM was adsorbed by MWNTs with increasing ionic strength, a result that accords with previous studies. 19,20 As such, the net result of higher ionic strengths in the presence of DOM may be that the steric hindrance from NOM still maintains

a significant effect although electrostatic repulsion is impaired by cations. Therefore, these DOM–MWNT composites are much less susceptible to the effects of higher cation concentrations, as shown in our data (Figure 2a).

Effects of Solid Peat. Sorption of MWNTs to solid peat was also investigated (Figure 2b). The apparent solid-phase MWNT concentration (defined in eq 2) was calculated with MWNT settling subtracted, thus approximating the direct effect from the solid peat on the MWNTs. Solid peat did not appear to adsorb MWNTs in the absence of sodium ions, indicating that the DOM–MWNT composites exhibit a greater affinity toward water than the solid phase. The pH for this unbuffered peat–water system was 5.17, indicating the acidic nature of peat. The solid peat and DOM were thus likely charged negatively as a result of deprotonation. Electrostatic repulsion between the DOM–MWNT composites and peat surfaces, in combination with the hydrophilic nature of the functional groups extending from the DOM wrapped on the nanotubes, may have led to the greater affinity of DOM–MWNT composites with water than with peat.

However, solid peat sorbed MWNTs when sodium cations were added, as shown in Figure 2b, and this effect became more pronounced with increasing sodium concentrations. This result indicates that the presence of sodium cations increased the relative affinity between solid peat and DOM–MWNT composites. Cations such as sodium can decrease the charge potential of solid peat surfaces as well as of DOM–MWNT composites, a change expected to facilitate interactions between the solid peat and DOM–MWNTs through van der Waals attractions and/or hydrophobic interactions.

Phase Distribution Modeling. While the above discussion focuses on the direct interaction between MWNTs and solid peat by examining the apparent solid-phase concentration q_a , we have also calculated the total solid-phase MWNT concentrations, q_t , using eq 3 to investigate the overall solid-phase distribution of MWNTs effected by both settling and peat sorption (Figure 2c). In an attempt to quantify the relationship between q_t and the MWNT concentration remaining in aqueous phase (C_{aq}), we fit the data to the equation $q_t = KC_{aq}^n$. Simulation parameters thus obtained (K , n) were used to compare the phase distribution behaviors among systems having different sodium concentrations. The simulation parameter n reflects to what extent the solid-phase MWNT concentration is linearly correlated to its aqueous-phase concentration, while the parameter K denotes the tendency of MWNTs to enter the solid phase. This modeling is not intended to indicate that these are equilibrium constants, because equilibrium was not reached under our experimental conditions. Instead, these parameters were used to allow for comparison of sorption behaviors under various conditions after 7 days of incubation, a period in which the sorption approached pseudo-steady state (Figure S1, Supporting Information).

Table 1 shows the simulation parameters, K and n , obtained by data fitting, along with their 95% confidence intervals and coefficients of determination, R^2 . The data were fitted quite well to the equation, as indicated by high R^2 values. The higher sodium concentrations increased not only the amount of solid-phase MWNTs, as evidenced by increasing K , but also the linearity of the phase distribution equation, as shown by n becoming closer to 1. A linear relationship indicates the overall forces that drive the solid-phase distribution of MWNTs—that is, aggregation and peat sorption—are uniform with varying MWNT concentrations.²⁷ This can result from the electric

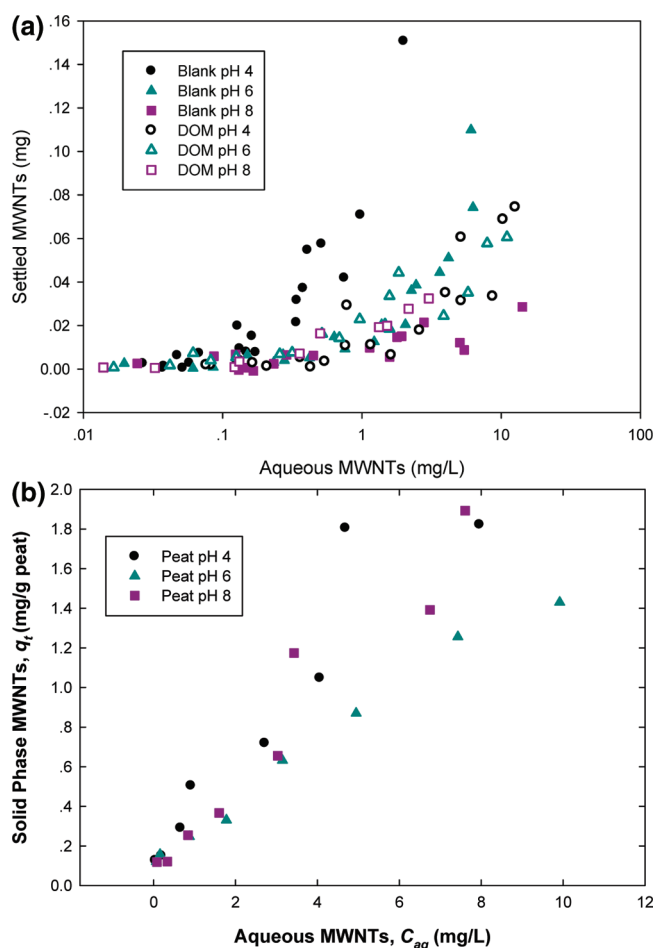


Figure 3. Phase distribution of MWNTs across a range of pH values. (a) Control treatments are denoted as blank, and those with DOM extracted under various pHs are denoted as DOM. (b) Phase distribution of MWNTs with peat at different pHs.

screening effect at higher ionic strengths that effectively reduces the heterogeneity in charge potential distribution on the surfaces of both MWNTs and peat particles. When the repulsive electrostatic forces are reduced, van der Waals attraction and/or hydrophobic interactions become dominant and thus cause greater MWNT solid-phase distribution. We also similarly analyzed the apparent solid-phase concentration, q_a (Figure 2b), by fitting the data to $q_a = KC_{aq}^n$, and the same trend was obtained that higher sodium concentration leads to greater linearity of the equation (Table S3, Supporting Information).

Effects of pH. MWNTs are negatively charged across the solution pH range from 4.0 to 8.0. At a sodium concentration of 4 mM, the ζ potential did not change substantially, with -11.9 ± 1.3 , -18.0 ± 1.4 , and -19.3 ± 0.2 mV at pH values of 4.0, 6.0, and 8.0, respectively.

The effect of pH on CNT aggregation has been previously investigated, and it was clear that decreasing pH from 10 to 3 enhanced aggregation.^{17,18} Our data for the systems without DOM present showed that a change in the pH from 8.0 to 6.0 did not substantially impact the final aqueous concentration of MWNTs, but more settling occurred at a pH of 4.0 (see Figure 3a).

In the presence of DOM, increasing the pH from 4 to 8 did not significantly influence the phase distribution of MWNTs

(Figure 3a). This occurred despite an increase in TOC from the released peat DOM with increasing pH: 80.1, 86.5, and 95.4 $\mu\text{g/mL}$ at pHs of 4, 6, and 8, respectively. We also conducted additional experiments in which the pH was adjusted after extraction of the DOM by water to yield a consistent DOM concentration in solutions across the pH range, and there was no significant difference in the phase distribution observed, as shown in Figure S4 (Supporting Information). When experiments were conducted in the presence of solid peat, a difference was still not evident across this pH range (Figure 3b). These results suggest that the surface charge of solid peat and DOM–MWNT composites does not change significantly within the pH range investigated here.

Environmental Implications. The phase distribution behaviors observed in this study reveal the complex interactions between MWNTs and peat across a range of environmentally relevant aqueous-phase conditions. The dissolved fraction of peat can assist MWNT dispersion by preventing their aggregation even with a high sodium concentration (40 mM), a concentration beyond those relevant to fresh water systems. Therefore, the presence of DOM in natural water is expected to increase the duration that MWNTs remain in suspension, consequently increasing their exposure risk for human and ecological receptors in the water column. Solid peat can have the opposite effect by sorbing MWNTs under environmentally relevant ionic strength conditions. Although the impact of ionic strength on MWNT aggregation is significantly reduced by DOM, sorption is enhanced by increasing ionic strength. These results suggest that solid soil organic matter has the potential to sorb MWNTs during their contact with soil and sediment particles.

The overall effect of increasing ionic strength is that more MWNTs will transfer out of the aqueous phase. The environmental consequence of this result is that MWNTs are unlikely to transport long distances in seawater or hard freshwater. Changes in pH are unlikely to have a major effect on MWNT suspensions, especially when the relatively steady pH in most natural water systems is considered.

Understanding the phase distribution of MWNTs in a peat–water system provides useful information toward elucidating the environmental fate of MWNTs in real soil– or sediment–water ecosystems. This work also helps identify important factors in conducting such sorption experiments and provides a method for future investigations. Additional work is needed to investigate sorption of CNTs to other components of soils and sediments and thus eventually yield a comprehensive understanding of the behaviors and fate of CNTs in the natural environment.

■ ASSOCIATED CONTENT

S Supporting Information. Additional text describing chemicals used in the experiments; detailed experimental methods for MWNT synthesis, purification, and acid treatment procedures; DOM-only solution preparation; and sorption of DOM on MWNTs; and four figures and three tables illustrating MWNT phase distribution at certain conditions and periods, TGA analysis, SEM images of the peat particles, solution conditions of certain experimental systems, and certain parameters obtained by data fitting. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ REFERENCES

- (1) Mauter, M. S.; Elimelech, M. Environmental applications of carbon-based nanomaterials. *Environ. Sci. Technol.* **2008**, *42* (16), 5843–5859.
- (2) Kennedy, A. J.; Hull, M. S.; Steevens, J. A.; Dontsova, K. M.; Chappell, M. A.; Gunter, J. C.; Weiss, C. A. Factors influencing the partitioning and toxicity of nanotubes in the aquatic environment. *Environ. Toxicol. Chem.* **2008**, *27* (9), 1932–1941.
- (3) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. Carbon nanotubes - the route toward applications. *Science* **2002**, *297* (5582), 787–792.
- (4) Mueller, N. C.; Nowack, B. Exposure modeling of engineered nanoparticles in the environment. *Environ. Sci. Technol.* **2008**, *42* (12), 4447–4453.
- (5) Carbon nanotubes: Technologies and commercial prospects 2007. Available at <http://www.bccresearch.com/report/NAN024C.html>.
- (6) Petersen, E. J.; Huang, Q.; Weber, W. J. Relevance of octanol-water distribution measurements to the potential ecological uptake of multi-walled carbon nanotubes. *Environ. Toxicol. Chem.* **2010**, *29* (5), 1106–1112.
- (7) Petersen, E. J.; Huang, Q. G.; Weber, W. J. Ecological uptake and depuration of carbon nanotubes by *Lumbriculus variegatus*. *Environ. Health Perspect.* **2008**, *116* (4), 496–500.
- (8) Petersen, E. J.; Huang, Q. G.; Weber, W. J. Bioaccumulation of radio-labeled carbon nanotubes by *Eisenia foetida*. *Environ. Sci. Technol.* **2008**, *42* (8), 3090–3095.
- (9) Ferguson, P. L.; Chandler, G. T.; Templeton, R. C.; Demarco, A.; Scrivens, W. A.; Englehart, B. A. Influence of sediment-amendment with single-walled carbon nanotubes and diesel soot on bioaccumulation of hydrophobic organic contaminants by benthic invertebrates. *Environ. Sci. Technol.* **2008**, *42* (10), 3879–3885.
- (10) Galloway, T.; Lewis, C.; Dolciotti, I.; Johnston, B. D.; Moger, J.; Regoli, F. Sublethal toxicity of nano-titanium dioxide and carbon nanotubes in a sediment dwelling marine polychaete. *Environ. Pollut.* **2010**, *158* (5), 1748–1755.
- (11) Petersen, E. J.; Akkanen, J.; Kukkonen, J. V. K.; Weber, W. J. Biological uptake and depuration of carbon nano-tubes by *Daphnia magna*. *Environ. Sci. Technol.* **2009**, *43* (8), 2969–2975.
- (12) Petersen, E. J.; Pinto, R. A.; Mai, D. J.; Landrum, P. F.; Weber, W. J. Influence of polyethyleneimine graftings of multi-walled carbon

nanotubes on their accumulation and elimination by and toxicity to *Daphnia magna*. *Environ. Sci. Technol.* **2011**, in press.

(13) Banerjee, S.; Hemraj-Benny, T.; Wong, S. S. Covalent surface chemistry of single-walled carbon nanotubes. *Adv. Mater.* **2005**, *17* (1), 17–29.

(14) Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen, R.; Itkis, M. E.; Haddon, R. C. Chemistry of single-walled carbon nanotubes. *Acc. Chem. Res.* **2002**, *35* (12), 1105–1113.

(15) Shen, M. W.; Wang, S. H.; Shi, X. Y.; Chen, X. S.; Huang, Q. G.; Petersen, E. J.; Pinto, R. A.; Baker, J. R.; Weber, W. J. Polyethyleneimine-mediated functionalization of multiwalled carbon nanotubes: Synthesis, characterization, and in vitro toxicity assay. *J. Phys. Chem. C* **2009**, *113* (8), 3150–3156.

(16) Vaisman, L.; Marom, G.; Wagner, H. D. Dispersions of surface-modified carbon nanotubes in water-soluble and water-insoluble polymers. *Adv. Funct. Mater.* **2006**, *16* (3), 357–363.

(17) Saleh, N. B.; Pfefferle, L. D.; Elimelech, M. Aggregation kinetics of multiwalled carbon nanotubes in aquatic systems: Measurements and environmental implications. *Environ. Sci. Technol.* **2008**, *42* (21), 7963–7969.

(18) Smith, B.; Wepasnick, K.; Schrote, K. E.; Bertele, A. H.; Ball, W. P.; O'Melia, C.; Fairbrother, D. H. Colloidal properties of aqueous suspensions of acid-treated, multi-walled carbon nanotubes. *Environ. Sci. Technol.* **2009**, *43* (3), 819–825.

(19) Hyung, H.; Kim, J. H. Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: Effect of NOM characteristics and water quality parameters. *Environ. Sci. Technol.* **2008**, *42* (12), 4416–4421.

(20) Hyung, H.; Fortner, J. D.; Hughes, J. B.; Kim, J. H. Natural organic matter stabilizes carbon nanotubes in the aqueous phase. *Environ. Sci. Technol.* **2007**, *41* (1), 179–184.

(21) Han, Z. T.; Zhang, F. W.; Lin, D. H.; Xing, B. S. Clay minerals affect the stability of surfactant-facilitated carbon nanotube suspensions. *Environ. Sci. Technol.* **2008**, *42* (18), 6869–6875.

(22) Petersen, E. J.; Pinto, R. A.; Landrum, P. F.; Weber, W. J. Influence of carbon nanotubes on pyrene bioaccumulation from contaminated soils by earthworms. *Environ. Sci. Technol.* **2009**, *43* (11), 4181–4187.

(23) Huang, W. L.; Weber, W. J. A distributed reactivity model for sorption by soils and sediments. 10. Relationships between desorption, hysteresis, and the chemical characteristics of organic domains. *Environ. Sci. Technol.* **1997**, *31* (9), 2562–2569.

(24) Chappell, M. A.; George, A. J.; Dontsova, K. M.; Porter, B. E.; Price, C. L.; Zhou, P. H.; Morikawa, E.; Kennedy, A. J.; Steevens, J. A. Surfactive stabilization of multi-walled carbon nanotube dispersions with dissolved humic substances. *Environ. Pollut.* **2009**, *157* (4), 1081–1087.

(25) Piao, L. Y.; Liu, Q. R.; Li, Y. D.; Wang, C. The adsorption of L-phenylalanine on oxidized single-walled carbon nanotubes. *J. Nanosci. Nanotechnol.* **2009**, *9* (2), 1394–1399.

(26) Lin, D. H.; Xing, B. S. Tannic acid adsorption and its role for stabilizing carbon nanotube suspensions. *Environ. Sci. Technol.* **2008**, *42* (16), 5917–5923.

(27) Weber, W. J.; Digiano, F. A. *Process dynamics in environmental systems*; John Wiley and Sons: New York, 1996.

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