Limited transport of functionalized multi-walled carbon nanotubes in two natural soils

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ABSTRACT

Column experiments were conducted in undisturbed and in repacked soil columns at water contents close to saturation (85–96%) to investigate the transport and retention of functionalized ^{14}C-labeled multi-walled carbon nanotubes (MWCNT) in two natural soils. Additionally, a field lysimeter experiment was performed to provide long-term information at a larger scale. In all experiments, no breakthrough of MWCNTs was detectable and more than 85% of the applied radioactivity was recovered in the soil profiles. The retention profiles exhibited a hyper-exponential shape with greater retention near the column or lysimeter inlet and were successfully simulated using a numerical model that accounted for depth-dependent retention. In conclusion, results indicated that the soils acted as a strong sink for MWCNTs. Little transport of MWCNTs is therefore likely to occur in the vadose zone, and this implies limited potential for groundwater contamination in the investigated soils.

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1. Introduction

Carbon nanotubes (CNT) are tubular nanoparticles with nano-scale diameters and micro-scale lengths composed of aligned benzene rings (Iijima, 1991; Mauter and Elimelech, 2008; Petersen et al., 2011). Two types of CNT are most commonly distinguished and produced: single-walled carbon nanotubes (SWCNT) are individual graphene tubes, and multi-walled carbon nanotubes (MWCNT) are tubes within tubes consisting of more than two carbon walls (Sinnott, 2002). Due to their exceptional electrical, chemical, and physical properties, CNT are used in numerous applications (Jaisi and Elimelech, 2009; Mattison et al., 2011). This widespread use will result in their release to the environment through point sources (e.g., production facilities, landfills, or wastewater treatment plants), nonpoint sources (e.g., abrasion of materials containing CNT), accidental release (e.g., during transport), or intentional release (e.g., for groundwater remediation) (Jaisi and Elimelech, 2009; Köhler et al., 2008; Nowack and Bucheli, 2007; Pan and Xing, 2012).

To date, there is still a lack of knowledge on the fate and effects of CNT in the environment (Saleh et al., 2008). Ecotoxicological studies on CNT have revealed potential for bioaccumulation (e.g., daphnia magna) (Petersen et al., 2009a), health risks to different organisms (e.g., rainbow trout and rats) (Farré et al., 2009; Handy et al., 2008; Lam et al., 2006; Ma-Hock et al., 2009), and growth inhibition of algae due to shading and agglomeration of cells with CNT (Schwab et al., 2011). Furthermore, CNT act as strong adsorbents for organic pollutants (Chen et al., 2007; Li et al., 2012; Lu et al., 2005; Peng et al., 2003) and may therefore affect the fate and mobility of these chemicals in natural environments. A CNT facilitated transport (co-transport) of organic pollutants could lead to enhanced migration of contaminants (Cheng et al., 2005) but adsorption of organic pollutants onto CNT may also decrease bioavailability (Petersen et al., 2009b). To assess potential risks to humans and other organisms, it is important to gain knowledge on the environmental fate of CNT. Thus, information on CNT transport and deposition in natural soils is needed.

In general, CNT can be released as agglomerates or as individual particles. Recently, the release of free-standing individual CNTs from CNT-embedded nanocomposites was demonstrated (Schlagenhauf et al., 2012). The environmental behavior of nano-particles is frequently controlled by their colloidal stability. Functionalized CNT are of special interest because the modification will

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not only increase their stability in aqueous suspensions but also increase their mobility in the environment (Mattison et al., 2011).

Several studies have reported on the transport of CNT in water-saturated sand columns (Jaisi et al., 2008; Liu et al., 2009; Mattison et al., 2011; Tian et al., 2010, 2012). Most of these studies have been conducted in repacked, homogeneous, coarse textured porous media in order to understand mechanisms and factors influencing CNT retention. Results indicate that CNT transport is sensitive to a diversity of experimental conditions including ionic strength (IS), pore water velocity, and collector grain size. However, mechanisms influencing the transport and deposition of MWCNT are still not completely understood even in these highly idealized systems (Mattison et al., 2011). Information on MWCNT retention profiles is still very scarce (Kasel et al., 2013; Wang et al., 2012). Determination of retention profiles provides mass balance information and gives useful insight on mechanisms controlling retention (Bradford and Bettahar, 2005).

The transport of CNT in field soils has received very limited attention (Jaisi and Elimelech, 2009). In general, soil is expected to be a more important sink for nanoparticles than sand because its chemical composition and pore size distribution are more heterogeneous (Pan and Xing, 2012). However, preferential flow paths in soils (e.g., root or earthworm channels) may enhance transport through the vadoze zone (Camobreco et al., 1996). Undisturbed soil cores and lysimeters are much closer to environmental conditions than packed sand columns because they allow consideration of preferential flow paths. To our knowledge, there is no study available on the transport and retention of MWCNT in undisturbed soil cores or lysimeters. Furthermore, there are only a few studies on CNT transport under unsaturated flow conditions (Tian et al., 2011). Unsaturated and/or variably saturated transport experiments are closer to natural conditions in the vadose zone. Transport processes are much more complicated under unsaturated than saturated conditions because of the presence of the air phase, although greater retention is expected under unsaturated conditions (Gargiulo et al., 2007b; Tian et al., 2011).

The objective of this research was to investigate transport and retention of MWCNT in natural, undisturbed soils under environmentally relevant conditions like low MWCNT concentrations and low flow rates. Two soil types (a silty loam and a loamy sand) were investigated in laboratory column experiments at water contents close to saturation. Additionally, the nanoparticles were applied to a field lysimeter filled with the loamy sand soil. For all experiments, MWCNT concentrations in the effluent and in the soils were determined. Finally, the observed data was numerically modeled. To our knowledge, this is the first study providing information on MWCNT fate in undisturbed soil and in a lysimeter.

2. Materials and methods

2.1. Carbon nanotubes

Transport experiments were performed using radioactively (^{14}C) labeled MWCNT (Bayer Technology Services GmbH, 51368 Leverkusen, Germany) with a specific radioactivity of appr. 3.2 MBq mg^{-1}. The average outer diameter of the MWCNT was 10–15 nm and the average length was 200–1000 nm (Kasel et al., 2013). Prior to transport experiments, the MWCNT were functionalized by boiling in 70% nitric acid (Sigma–Aldrich Chemie GmbH, 89555 Steinheim, Germany) for 4 h under reflux (Nagasawa et al., 2000). The MWCNT were removed from the acid by filtering through a 0.45 μm polytetrafluoroethylene (PTFE) membrane and rinsing with deionized water until a neutral pH-value was achieved in the filtrate (Mattison et al., 2011). After drying the functionalized MWCNT at 45 °C in an oven, the material was stored at room temperature until needed.

Kasel et al. (2013) characterized many properties of the MWCNT using unlabeled functionalized material. A brief summary is provided below. The acid treatment was demonstrated to remove a significant amount of the metal catalysts (using ICP-MS) and induced oxygen containing functional groups (via XPS-spectra, appr. 6 wt% oxygen) on the MWCNT surfaces. These functional groups are known to enhance the

stability of CNT in the aqueous phase (Smith et al., 2009). Transmission electron microscope (TEM, Philips CM20 FEG, FEI Company, 5651 GG Eindhoven, the Netherlands) images revealed that the size distribution of MWCNT was very heterogeneous. The hydrodynamic radius of MWCNT dispersed in 1 mM KCl was determined to range between 170 and 210 nm using dynamic light scattering (DLS, Zetasizer Nano, Malvern Instruments GmbH, 71083 Herrenberg, Germany). The electrophoretic mobility for MWCNT in 1 mM KCl solution (pH 8.5) was measured using the Zetasizer Nano to be -2.85×10^{-8} m^2 V^{-1} s^{-1}.

For transport experiments, nanoparticle suspensions with concentrations of 10 mg L^{-1} were prepared by adding 1 mg of ^{14}C-labeled functionalized MWCNT to 100 mL of 1 mM KCl solution. The suspension was sonicated for approximately 10 min at 65 W using a cup horn ultrasonicator (Branson Sonifier$^®$ W-250, Danbury, CT 06813-1961, USA) until no aggregates were visible. Afterward, five 0.5 mL aliquots were each added to 2.5 mL of scintillation cocktail (Insta-Gel Plus, PerkinElmer, 63110 Rodgau, Germany) and 2 mL of water, shaken, and the radioactivity was measured using a liquid scintillation counter (LSC, PerkinElmer, 63110 Rodgau, Germany). The low standard deviation of the radioactivity measured in the five replicates indicated that the MWCNT suspensions were homogeneous. For each transport experiment a fresh suspension was prepared.

2.2. Soil

Soil samples from the upper 30 cm of two well characterized agricultural field sites in Germany were used as natural porous media for transport experiments. In particular, a loamy sand (Gleyic Cambisol) from the test site in Kaldenkirchen-Hülst (KAL) and a silty loam (Orthic Luvisol) from the test site in Merzenhausen (MRZ) (Unold et al., 2009a) were employed. The electrophoretic mobility of the soils (0.1 wt %) in 1 mM KCl solution (pH 8.5) was measured using the previously described Zetasizer Nano. The physicochemical characteristics of the two soils are summarized in Table 1.

Undisturbed soil samples were collected in columns made of polyvinyl chloride (PVC) with a length of 10 cm and an inner diameter of 8 cm using a metal adaptor with a sharp front. The adaptor was mounted on the bottom of the PVC column and placed on top of the soil. The column was then pushed stepwise into the plough layer of the soil using a water-level. Between the pushing steps, the surrounding soil was removed. Finally, the soil at the end of the column was cut using a knife to obtain an even surface. For repacked soil columns, the soil was first sieved to a fraction <2 mm, air dried, and then the soil was wet packed into the column.

2.3. Experimental setup

The soil columns were mounted on acrylic glass plates covered with a high conductivity 20 μm nylon mesh. The air-entry value of the nylon mesh was approximately 50 mbar. The undisturbed soil columns were slowly saturated from the bottom with 1 mM KCl. The water-saturated columns (repacked and undisturbed) were equipped with two tensiometers (inserted at 2.5 and 7.5 cm below the soil surface) to monitor the pressure head inside the columns. Software controlled equipment (Unold et al., 2009a) was used to achieve unit gradient, steady-state flow conditions in the columns. In brief, the columns were irrigated from the top with 1 mM KCl and suction was applied to the bottom. A unit gradient in the matrix potential (monitored using the two tensiometers) was achieved by automatically changing the irrigation rate and the bottom suction. The irrigation rate was recorded by weighing the storage bottle of the irrigation solution. The electrical conductivity of the leachate was measured over the duration of the experiment.

The columns were flushed with 1 mM KCl until the conductivity of the leachate and the matrix potentials (water contents) were constant. Afterward, a 1 h pulse of 10 mM KCl was applied to the columns as conservative tracer and its breakthrough curve was detected by measuring the conductivity of the leachate. The columns were flushed again with 1 mM KCl until the conductivity remained constant at background levels. Following the tracer experiment, 5 mL of MWCNT suspension (10 mg L^{-1}) were pipetted evenly on top of the soil. The columns were flushed again

Table 1
Physical and chemical properties of the soils from two experimental test sites Kaldenkirchen-Hülst (KAL, loamy sand) and Merzenhausen (MRZ, silty loam).

	Unit	KAL	MRZ
Clay (<2 μm)[a]	% mass	4.9	15.4
Silt (2–63 μm)[a]	% mass	26.7	78.7
Sand (>2000 μm)[a]	% mass	68.5	5.9
pH (0.01 M CaCl$_2$)[a]		5.9	6.2
Total organic matter[a]	% mass	1.1	1.3
Cation exchange capacity[a]	cmol$_c$ kg^{-1}	7.8	11.4
Iron[b]	%	0.8	1.5
Electrophoretic mobility	m^2 V^{-1} s^{-1}	−2.7E-8	−3.2E-8

[a] Data adapted from Unold et al. (2009a).
[b] Data adapted from Kasteel et al. (2010).

with 1 mM KCl and the leachate was collected using a fraction collector. The leachate was analyzed using a liquid scintillation counter and the experiment was stopped when the radioactivity in the effluent was below the detection limit.

After termination of the transport portion of the experiment, the soil was removed in 1 cm thick increments, dried at 45 °C in an oven, and then homogenized using a mill. Five replicates (500 mg) of each sample were combusted at 900 °C using a biological oxidizer (OX 500, R.J. Harvey Instrumentation Corporation, Tappan, NY 10983, USA). Before measuring the radioactivity using the liquid scintillation counter, the emerging $^{14}CO_2$ was dissolved in vials filled with scintillation cocktail (Oxisolv®, MERCK KGAA, 64293 Darmstadt, Germany). Table 2 summarizes column properties determined from the conservative tracer experiments and mass balance information for MWCNT.

2.4. Lysimeter

A stainless steel lysimeter with a surface area of 0.5 m^2 and a depth of 1.15 m was used for larger scale transport experiments (Burauel and Führ, 2000). The lysimeter contained an undisturbed soil monolith from the test site in Kaldenkirchen-Hülst (KAL). It represents a long-term outdoor experiment on a larger scale. The lysimeter was equipped with two time-domain reflectometry (TDR) probes at depths of 5 and 30 cm to observe the water content during the experiment. The lysimeter was covered with a stainless steel plate to prevent evaporation, precipitation, and plant growth. It was artificially irrigated twice a week with 5 L of tap water to achieve a precipitation rate of 1200 mm y^{-1}. Slight ponding at the lysimeter surface was observed immediately after irrigation.

First, a pulse of 5 L of potassium bromide solution (appr. 16.5 g KBr in total) was applied as a conservative tracer uniformly onto the soil's surface. One week later, the same procedure was repeated with 5 L of ^{14}C-MWCNT suspension (appr. 25 mg MWCNT in total). The leachate ran into a stainless steel pan at the bottom of the lysimeter and was collected in regular intervals. The bromide concentration in the leachate was determined using a high performance liquid chromatograph (STH 585, Dionex, Sunnyvale, CA, USA) equipped with a UV-detector (UV2075, Jasco, Essex, UK). The liquid scintillation counter was again used to determine the radioactivity. After termination of the experiment (8 month after MWCNT application), soil samples were taken at different points using a Pürckhauer soil corer (Schierholz et al., 2000) to obtain information on the MWCNT distribution in the soil profile following a similar approach to the columns.

2.5. Mathematical modeling

The HYDRUS-1D code was used to analyze the transport experiments. It is a finite element model which can simulate the one-dimensional movement of water, heat, and multiple solutes in variably saturated media (Šimůnek et al., 2008). The inverse fitting of model parameters to experimental breakthrough curves (BTCs) and retention profiles (RPs) was performed using a nonlinear least squares optimization routine in the code. The column's porosity and dispersivity (Table 2) were obtained by fitting the advective dispersive equation (ADE) parameters to the conservative tracer BTC for each column.

The transport of MWCNT was simulated using the ADE with terms for one site kinetic retention. The total mass balance equation is written as (Gargiulo et al., 2007a):

$$\frac{\partial \theta C}{\partial t} + \rho \frac{\partial S}{\partial t} = \frac{\partial}{\partial x}\left(\theta D \frac{\partial C}{\partial x}\right) - \frac{\partial qC}{\partial x} \quad (1)$$

where θ [-] is the volumetric water content, ρ is the bulk density of the porous media [$M\,L^{-3}$, where M and L denote units of mass and length, respectively], t is the time [T; T denotes units of time], x is the spatial coordinate [L], q is the flow rate [$L\,T^{-1}$], C is the particle concentration in the aqueous phase [$N_c\,L^{-3}$, where N_c is the number of MWCNT], S is the solid phase particle concentration [$N_c\,M^{-1}$], and D is the dispersion coefficient [$L^2\,T^{-1}$]. The corresponding solid phase particle mass balance equation is given as:

$$\rho \frac{\partial S}{\partial t} = \theta k_1 \left(\frac{d_c + x}{d_c}\right)^{-\beta} C - k_2 \rho S \quad (2)$$

where k_1 [T^{-1}] is the first-order retention coefficient [T^{-1}], k_2 is the first-order detachment coefficient [T^{-1}], d_c [L] is the median diameter of the soil grains, and β [-] is an empirical variable that controls the shape of the retention profile.

This model was already utilized by Kasel et al. (2013) to simulate BTCs and RPs of MWCNT in quartz sand, as well as for bacteria and colloid transport by many others (Bradford and Bettahar, 2006; Bradford et al., 2005; Gargiulo et al., 2008). The model formulation shown in Eq. (2) can account for retention profiles that are exponential or hyper-exponential with depth. The depth-dependent retention term equals 1 when $\beta = 0$ and predicts an exponential distribution of retained MWCNT with depth similar to conventional filtration theory. Conversely, when $\beta > 0$ is employed the retention profile of MWCNT exhibits a hyper-exponential shape (e.g., a higher deposition rate close to the column inlet). The optimal value for β was estimated to be 0.765 for MWCNT based on literature information (Kasel et al., 2013; Wang et al., 2012). The estimated model parameters for all experiments are listed in Table 3.

3. Results and discussion

3.1. Comparison of two water-saturation levels

Transport and retention of MWCNT in an undisturbed soil core of a loamy sand (KAL) were investigated at water contents close to saturation (appr. 96 and 85%, respectively). The negative charge on both MWCNT and soil, and the low ionic strength conditions suggest that highly unfavorable attachment conditions existed for MWCNT during the transport experiments.

There was no detectable breakthrough of MWCNT in the soil core at a water content of 96%. Quantification of the retention profile (Table 2) revealed that 91% of MWCNT were retained in the soil. The main fraction of MWCNT was retained close to the column inlet and the retention profile exhibited a hyper-exponential shape. The same shape was observed by Kasel et al. (2013) for functionalized MWCNT in saturated sand columns and was attributed to a depth-dependent retention mechanism. The determined retention profile for the soil column was simulated using the previously described model and is shown in Fig. 1. The retention coefficient accounting for depth-dependency was able to describe the shape of the experimental retention profile (RP) well.

At lower water saturation (appr. 85%), no breakthrough of MWCNT was observed and 98% of the applied radioactivity was detected in the soil profile. The shape of the retention profile was also hyper-exponential (Fig. 1) and was fitted well using a model including a depth-dependent retention term (Eq. (2)).

Though both experiments were performed at different water-saturation levels and thus, different amounts of air in the column, the retention profiles were similar. Complete retention occurred already at 95% water-saturation but reduction of the water content to 85% changed the MWCNT distribution in the soil. When comparing the profiles (Fig. 1), the MWCNT concentrations in layers deeper than 2 cm were higher at the higher water content than for the lower water content. This implies that MWCNT transport was slightly enhanced at the higher water content. An increase in

Table 2
Experimental conditions, hydraulic parameters, and mass balance information (as fractions of the total applied mass) for all column experiments. The electrolyte was 1 mM KCl.

Type of core	Soil type	Water saturation [%]	q [cm min^{-1}]	Porosity	Disp.[a] [cm]	CNT eff[b]	CNT soil[c]	Total mass balance
Undisturbed	KAL	96	0.0064	0.37	0.60	<0.01	0.91	0.91
Undisturbed	KAL	85	0.0084	0.32	0.69	<0.01	0.98	0.98
Repacked	KAL	96	0.0067	0.38	0.37	<0.01	0.86	0.86
Undisturbed	MRZ	95	0.0063	0.49	2.41	<0.01	1.01	1.01
Lysimeter	KAL	n.d.	0.0003	0.23	17.88	<0.01	n.d.	n.d.

n.d. − no data.
[a] Disp. is the longitudinal dispersivity estimated on basis of the conservative tracer BTC.
[b] CNT eff is the total amount of CNT in the liquid phase.
[c] CNT soil is the total amount of CNT in the solid phase.

Table 3
Fitted model parameters for the retention profiles of the different experiments. Correlation of observed and fitted data is reflected by R^2.

Type of core	Soil type	Water saturation [%]	R^2	β	k_1 [min^{-1}]	Standard error k_1	k_2 [min^{-1}]	Standard error k_2
Undisturbed	KAL	96	0.89	0.765	10.93	16.87	0.62E-02	0.89E-02
Undisturbed	KAL	85	0.96	0.765	2.56	1.55	0.16E-02	0.13E-02
Repacked	KAL	96	0.86	0.765	0.42	0.59	NF	NF
Undisturbed	MRZ	95	0.97	0.765	0.21	0.25	NF	NF

NF – not fitted.

retention was expected with decreasing water-saturation because of a larger air–water interfacial area and a greater amount of flow through small pore spaces (Gargiulo et al., 2008). In contrast to the expected trend, the fitted retention coefficient (k_1) was higher at the higher water content (Table 3). One potential explanation is due to insensitivity in k_1 when complete retention occurs. This hypothesis is supported by the high standard error for k_1 for the experiment at 85% water content (Table 3).

Nevertheless, for both experiments, no significant transport to distances greater than 10 cm occurred and the highest fraction of MWCNT was retained in the top layer of the soil. In consistency with our results, Jaisi and Elimelech (2009) reported limited transport of CNT in a particular fraction of soil (420–1000 μm) in water-saturated column experiments. Based on their findings and our results, we assume that there is no transport of functionalized MWCNT through the studied loamy sand soil at water contents lower than 85%.

It is known that CNT suspensions can be stabilized by natural organic matter (Hyung et al., 2006) and that humic acid can enhance CNT transport (Wang et al., 2008). Nevertheless we did not find any breakthrough of MWCNT in the loamy sand soil containing appr. 1% organic carbon. Similarly, Wang et al. (2010) observed complete retention of Fullerene (C_{60}) nanoparticles in saturated columns packed with two different soils containing 0.75 and 3.3% organic carbon, respectively. One possible explanation for the high retention of MWCNT in soils compared to quartz sand might be adsorption via negatively charged carboxylic groups of the MWCNT onto positively charged metal oxides. However, the iron content of the soil from KAL was relatively low (Table 1). Thus, we assume that physical factors (e.g., straining) play a dominant role for the MWCNT retention in soil (Jaisi and Elimelech, 2009; Kasel et al., 2013). Since MWCNT are non-spherical particles, they are easily

trapped in small pore spaces and may create additional retention locations (Kasel et al., 2013; Pan and Xing, 2012). Another reason for enhanced MWCNT retention may be the low, but environmentally relevant, flow rate (0.006 and 0.008 cm min^{-1}) in our experiments. It is already known, that the flow rate strongly influences MWCNT transport and that retention increases with decreasing flow rate (Liu et al., 2009). In addition, the chemical heterogeneity of soils may also enhance MWCNT retention compared to quartz sand (Pan and Xing, 2012). Aggregation also influences CNT mobility in porous media (Pan and Xing, 2012) but could not be measured in this study.

In summary, results show that even at a water content close to saturation (96%) no detectable breakthrough of functionalized MWCNT occurred in undisturbed cores of the loamy sand soil from KAL. The observed high retention of MWCNT in soil at experimental conditions might be due to an interplay of low flow rate (Liu et al., 2009), soil composition (Fang et al., 2009), heterogeneous pore size distribution (Pan and Xing, 2012), and the presence of an air phase (Gargiulo et al., 2008). Based on the results of our environmentally relevant setup (undisturbed soil core, precipitation from the top, point application of MWCNT, leaching from top to bottom, and low particle concentrations) we expect no significant transport of MWCNT in the loamy sand soil through the vadose zone.

3.2. Comparison of undisturbed and repacked soil

An additional experiment was performed in a repacked column with soil from KAL at a water content of appr. 96% and compared with the experiment performed in the undisturbed column at the same conditions (Fig. 2). The dispersivity of the undisturbed soil column was almost twice as high as that for the repacked column (Table 2), indicating more heterogeneity in the undisturbed soil
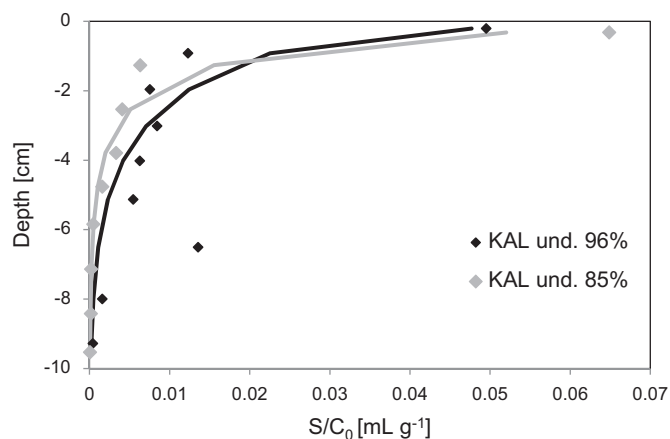

Fig. 1. Observed and simulated retention profiles for MWCNT in undisturbed (und.) loamy sand soil cores from the test site in Kaldenkirchen-Hülst (KAL) at two water-saturation levels (85 and 96%). For detailed experimental conditions see Table 2. The dots are the experimental data and the lines represent the model fits.
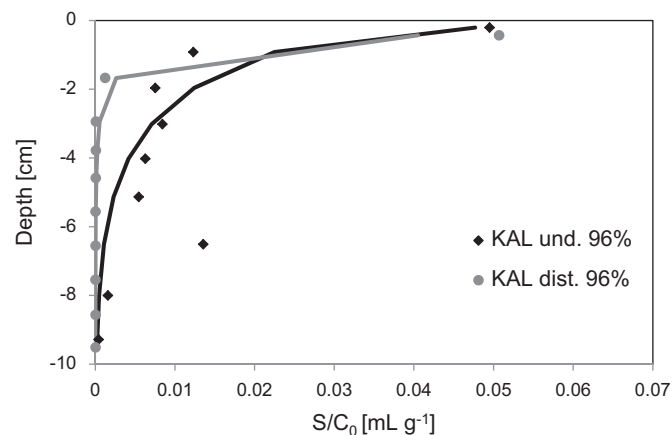

Fig. 2. Observed and simulated retention profiles for MWCNT in a disturbed (dist.) soil column from the test site in Kaldenkirchen-Hülst (KAL) compared with the previously shown RP for the undisturbed soil column from the same test site. The water-saturation was around 96%. For detailed experimental conditions see Table 2. The dots are the experimental data and the lines represent the model fits.

(Unold et al., 2009b). Additionally, the conservative tracer BTCs (data not shown) were described well for both repacked and undisturbed soil columns using the classical ADE model. This finding indicates that physical non-equilibrium processes (e.g., preferential flow) did not play a dominant role in our experiments (Unold et al., 2009b). In general, preferential flow will be more prominent in fully water-saturated media because macropores drain fast when the water level falls below full saturation, unless high rainfall intensities occur (Beven and Germann, 1982).

The transport results were similar for both undisturbed and repacked column experiments. The only difference was that the MWCNT concentration in layers deeper than 2 cm was higher in the undisturbed soil compared to the disturbed soil (Fig. 2). This observation suggests a higher transport potential in the undisturbed soil. Nevertheless, no breakthrough was found in both columns. In the repacked column, more than 86% of MWCNT were recovered in the RP which also exhibited a hyper-exponential shape (Fig. 2). This result indicates that the structure of the undisturbed loamy sand soil was very homogeneous without fractures or macropores, similar to the structure of the repacked soil column.

3.3. Comparison of two soil types

In addition to the previously described experiments with a loamy sand, an experiment with a silty loam (MRZ) at conditions close to water-saturation (96%) was performed. In general, soil from MRZ was expected to exhibit stronger sorption than the loamy sand soil from KAL due to a higher clay content which causes a larger specific surface area (Unold et al., 2009b). For CNT, straining is expected to be the dominant retention mechanism in soil (Jaisi and Elimelech, 2009). Soil texture (e.g., clay content) also affects the pore size distribution in the soil and thus, straining. For TiO_2 nanoparticles, Fang et al. (2009) described a significantly increased retention with increasing clay contents.

The comparison of KAL and MRZ soils at similar experimental conditions did not reveal any detectable differences in transport behavior of MWCNT in both soils. No MWCNT breakthrough was detected and more than 90% was recovered in the soil profile of MRZ soil. The retention profiles in the two soils (Fig. 3) were very similar despite significant differences in their dispersivity and porosity (Table 2). In fact, the MWCNT concentration in layers
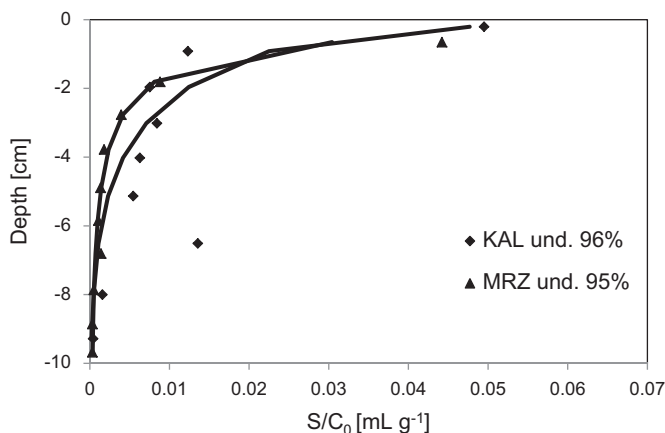
Fig. 3. Observed and simulated retention profiles for MWCNT in an undisturbed loam soil from the test site in Merzenhausen (MRZ) compared with the previously shown RP for the undisturbed loamy sand soil from the test site in Kaldenkirchen-Hülst (KAL). The water-saturation was around 96%. For detailed experimental conditions see Table 2. The dots are the experimental data and the lines represent the model fits.
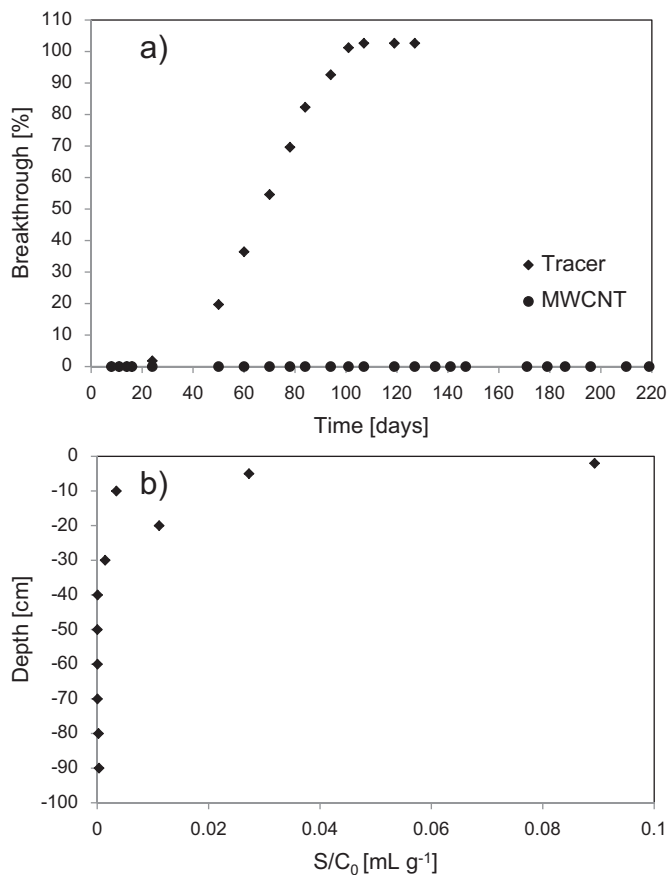
Fig. 4. Cumulative breakthrough of tracer (Br$^-$) and radiolabeled MWCNT (a) as well as an averaged retention profile (b) 220 days after application of MWCNT to a lysimeter. The lysimeter was filled with an undisturbed loamy sand soil from the test site in Kaldenkirchen-Hülst.

deeper than 2 cm was slightly higher for the KAL soil that had less clay. Thus in the absence of preferential flow, we do not expect any transport of MWCNT through the vadose zone in the silty loam MRZ soil because of its higher clay content and lower water contents.

In summary, results indicated that the transport behavior of MWCNT was not significantly different for these two soils. We hypothesize that physical filtration mechanisms are the dominant processes controlling MWCNT retention in these natural soils. These processes are expected to be influenced by water content (Gargiulo et al., 2007a), flow rate (Liu et al., 2009), and particle concentration (Kasel et al., 2013).

3.4. Lysimeter

The results of the lysimeter experiment revealed that 100% of the bromide tracer was recovered in the effluent after 107 days. In dramatic contrast, no radioactivity was detected in the lysimeter effluent after 220 days (Fig. 4a) even at a relatively high irrigation rate (1200 mm y^{-1}). Therefore, the lysimeter experiment was stopped and the MWCNT distribution in the soil profile was determined. The corresponding RP (Fig. 4b) exhibited the same hyper-exponential shape as repacked and undisturbed columns. The main fraction of MWCNT was retained in the upper 20 cm of the soil column. Consistent with the findings of Jaisi and Elimelech (2009), our column experiments indicate that there was no significant CNT transport in that undisturbed loamy sand soil under unsaturated conditions.

The lysimeter experiment proved that complete retention of MWCNT occurred in undisturbed soil at an environmentally relevant irrigation rate for a time period of 8 month. Nevertheless, the influence of certain weather conditions and environmental factors (e.g., preferential flow paths, uptake by organisms, oversaturation due to heavy rainfall, drainage and imbibition) needs to be further considered when evaluating potential risks of MWCNT to humans and the environment.

4. Conclusions

This study revealed almost complete retention of functionalized MWCNT in undisturbed cores of two well characterized soils. Experiments showed no detectable breakthrough of MWCNT. More than 86% of MWCNT were recovered in the soil profile at conditions close to saturation. At lower water-saturation, MWCNT retention in the upper soil layers was enhanced. A long-term study confirmed that the MWCNT were retained in the top soil layer. Soils are therefore expected to act as an effective sink for MWCNT. Reasons for the high retention of MWCNT in soil might be physical and chemical heterogeneity, particle aggregation, the heterogeneous soil pore size distribution, and the presence of an air phase. It is known that organic matter is able to stabilize CNT and enhance their transport. This could not be proven in our experiments, possibly due to the low organic carbon content (appr. 1%) in the soils. Collectively, our results suggest little potential for MWCNT transport through the vadose zone and for subsequent groundwater contamination in the considered soils. Nevertheless, MWCNT transport to deeper soil layers and groundwater under conditions of heavy rainfall and/or preferential flow cannot be fully excluded. In addition, transient drainage and imbibition events might remobilize retained particles.

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References

Beven, K., Germann, P., 1982. Macropores and water flow in soils. Water Resources Research 18, 1311–1325.

Bradford, S.A., Bettahar, M., 2005. Straining, attachment, and detachment of oocysts in saturated porous media. Journal of Environmental Quality 34, 469–478.

Bradford, S.A., Bettahar, M., 2006. Concentration dependent transport of colloids in saturated porous media. Journal of Contaminant Hydrology 82, 99–117.

Bradford, S.A., Simunek, J., Bettahar, M., Tadassa, Y.F., van Genuchten, M.T., Yates, S.R., 2005. Straining of colloids at textural interfaces. Water Resources Research 41, W10404.

Burauel, P., Führ, F., 2000. Formation and long-term fate of non-extractable residues in outdoor lysimeter studies. Environmental Pollution 108, 45–52.

Camobreco, V.J., Richards, B.K., Steenhuis, T.S., Peverly, J.H., McBride, M.B., 1996. Movement of heavy metals through undisturbed and homogenized soil columns. Soil Science 161, 740–750.

Chen, W., Duan, L., Zhu, D., 2007. Adsorption of polar and nonpolar organic chemicals to carbon nanotubes. Environmental Science & Technology 41, 8295–8300.

Cheng, X., Kan, A.T., Tomson, M.B., 2005. Study of C_{60} transport in porous media and the effect of sorbed C_{60} on naphthalene transport. Journal of Materials Research 20, 3244–3254.

Fang, J., Shan, X.-Q., Wen, B., Lin, J.-M., Owens, G., 2009. Stability of titania nanoparticles in soil suspensions and transport in saturated homogeneous soil columns. Environmental Pollution 157, 1101–1109.

Farré, M., Gajda-Schrantz, K., Kantiani, L., Barceló, D., 2009. Ecotoxicity and analysis of nanomaterials in the aquatic environment. Analytical and Bioanalytical Chemistry 393, 81–95.

Gargiulo, G., Bradford, S., Šimůnek, J., Ustohal, P., Vereecken, H., Klumpp, E., 2007a. Bacteria transport and deposition under unsaturated conditions: the role of the matrix grain size and the bacteria surface protein. Journal of Contaminant Hydrology 92, 255–273.

Gargiulo, G., Bradford, S.A., Šimůnek, J., Ustohal, P., Vereecken, H., Klumpp, E., 2007b. Transport and deposition of metabolically active and stationary phase *Deinococcus radiodurans* in unsaturated porous media. Environmental Science & Technology 41, 1265–1271.

Gargiulo, G., Bradford, S.A., Simunek, J., Ustohal, P., Vereecken, H., Klumpp, E., 2008. Bacteria transport and deposition under unsaturated flow conditions: the role of water content and bacteria surface hydrophobicity. Vadose Zone Journal 7, 406–419.

Handy, R., von der Kammer, F., Lead, J., Hassellöv, M., Owen, R., Crane, M., 2008. The ecotoxicology and chemistry of manufactured nanoparticles. Ecotoxicology 17, 287–314.

Hyung, H., Fortner, J.D., Hughes, J.B., Kim, J.-H., 2006. Natural organic matter stabilizes carbon nanotubes in the aqueous phase. Environmental Science & Technology 41, 179–184.

Iijima, S., 1991. Helical microtubules of graphitic carbon. Nature 354, 56–58.

Jaisi, D.P., Elimelech, M., 2009. Single-walled carbon nanotubes exhibit limited transport in soil columns. Environmental Science & Technology 43, 9161–9166.

Jaisi, D.P., Saleh, N.B., Blake, R.E., Elimelech, M., 2008. Transport of single-walled carbon nanotubes in porous media: filtration mechanisms and reversibility. Environmental Science & Technology 42, 8317–8323.

Kasel, D., Bradford, S.A., Šimůnek, J., Heggen, M., Vereecken, H., Klumpp, E., 2013. Transport and retention of multi-walled carbon nanotubes in saturated porous media: effects of input concentration and grain size. Water Research 47, 933–944.

Kasteel, R., Mboh, C.M., Unold, M., Groeneweg, J., Vanderborght, J., Vereecken, H., 2010. Transformation and sorption of the veterinary antibiotic sulfadiazine in two soils: a short-term batch study. Environmental Science & Technology 44, 4651–4657.

Köhler, A.R., Som, C., Helland, A., Gottschalk, F., 2008. Studying the potential release of carbon nanotubes throughout the application life cycle. Journal of Cleaner Production 16, 927–937.

Lam, C.-W., James, J.T., McCluskey, R., Arepalli, S., Hunter, R.L., 2006. A review of carbon nanotube toxicity and assessment of potential occupational and environmental health risks. Critical Reviews in Toxicology 36, 189–217.

Li, C., Schäffer, A., Séquaris, J.-M., László, K., Tóth, A., Tombácz, E., Vereecken, H., Ji, R., Klumpp, E., 2012. Surface-associated metal catalyst enhances the sorption of perfluorooctanoic acid to multi-walled carbon nanotubes. Journal of Colloid and Interface Science 377, 342–346.

Liu, X., O'Carroll, D.M., Petersen, E.J., Huang, Q., Anderson, C.L., 2009. Mobility of multiwalled carbon nanotubes in porous media. Environmental Science & Technology 43, 8153–8158.

Lu, C., Chung, Y.-L., Chang, K.-F., 2005. Adsorption of trihalomethanes from water with carbon nanotubes. Water Research 39, 1183–1189.

Ma-Hock, L., Treumann, S., Strauss, V., Brill, S., Luizi, F., Mertler, M., Wiench, K., Gamer, A.O., van Ravenzwaay, B., Landsiedel, R., 2009. Inhalation toxicity of multiwall carbon nanotubes in rats exposed for 3 months. Toxicological Sciences 112, 468–481.

Mattison, N.T., O'Carroll, D.M., Kerry Rowe, R., Petersen, E.J., 2011. Impact of porous media grain size on the transport of multi-walled carbon nanotubes. Environmental Science & Technology 45, 9765–9775.

Mauter, M.S., Elimelech, M., 2008. Environmental applications of carbon-based nanomaterials. Environmental Science & Technology 42, 5843–5859.

Nagasawa, S., Yudasaka, M., Hirahara, K., Ichihashi, T., Iijima, S., 2000. Effect of oxidation on single-wall carbon nanotubes. Chemical Physics Letters 328, 374–380.

Nowack, B., Bucheli, T.D., 2007. Occurrence, behavior and effects of nanoparticles in the environment. Environmental Pollution 150, 5–22.

Pan, B., Xing, B., 2012. Applications and implications of manufactured nanoparticles in soils: a review. European Journal of Soil Science 63, 437–456.

Peng, X., Li, Y., Luan, Z., Di, Z., Wang, H., Tian, B., Jia, Z., 2003. Adsorption of 1,2-dichlorobenzene from water to carbon nanotubes. Chemical Physics Letters 376, 154–158.

Petersen, E.J., Akkanen, J., Kukkonen, J.V.K., Weber, W.J., 2009a. Biological uptake and depuration of carbon nanotubes by *Daphnia magna*. Environmental Science & Technology 43, 2969–2975.

Petersen, E.J., Pinto, R.A., Landrum, P.F., Weber, J.W.J., 2009b. Influence of carbon nanotubes on pyrene bioaccumulation from contaminated soils by earthworms. Environmental Science & Technology 43, 4181–4187.

Petersen, E.J., Zhang, L., Mattison, N.T., O'Carroll, D.M., Whelton, A.J., Uddin, N., Nguyen, T., Huang, Q., Henry, T.B., Holbrook, R.D., Chen, K.L., 2011. Potential release pathways, environmental fate, and ecological risks of carbon nanotubes. Environmental Science & Technology 45, 9837–9856.

Saleh, N.B., Pfefferle, L.D., Elimelech, M., 2008. Aggregation kinetics of multiwalled carbon nanotubes in aquatic systems: measurements and environmental implications. Environmental Science & Technology 42, 7963–7969.

Schierholz, I., Schäfer, D., Kolle, O., 2000. The Weiherbach data set: an experimental data set for pesticide model testing on the field scale. Agricultural Water Management 44, 43–61.

Schlagenhauf, L., Chu, B.T.T., Buha, J., Nüesch, F., Wang, J., 2012. Release of carbon nanotubes from an epoxy-based nanocomposite during an abrasion process. Environmental Science & Technology 46, 7366–7372.

Schwab, F., Bucheli, T.D., Lukhele, L.P., Magrez, A., Nowack, B., Sigg, L., Knauer, K., 2011. Are carbon nanotube effects on green algae caused by shading and agglomeration? Environmental Science & Technology 45, 6136–6144.

Šimůnek, J., van Genuchten, M.T., Šejna, M., 2008. Development and applications of the HYDRUS and STANMOD software packages and related codes. Vadose Zone Journal 7, 587–600.

Sinnott, S.B., 2002. Chemical functionalization of carbon nanotubes. Journal of Nanoscience and Nanotechnology 2, 113–123.

Smith, B., Wepasnick, K., Schrote, K.E., Cho, H.-H., Ball, W.P., Fairbrother, D.H., 2009. Influence of surface oxides on the colloidal stability of multi-walled carbon nanotubes: a structure-property relationship. Langmuir 25, 9767–9776.

Tian, Y., Gao, B., Silvera-Batista, C., Ziegler, K., 2010. Transport of engineered nanoparticles in saturated porous media. Journal of Nanoparticle Research 12, 2371–2380.

Tian, Y., Gao, B., Ziegler, K.J., 2011. High mobility of SDBS-dispersed single-walled carbon nanotubes in saturated and unsaturated porous media. Journal of Hazardous Materials 186, 1766–1772.

Tian, Y., Gao, B., Wang, Y., Morales, V.L., Carpena, R.M., Huang, Q., Yang, L., 2012. Deposition and transport of functionalized carbon nanotubes in water-saturated sand columns. Journal of Hazardous Materials 213–214, 265–272.

Unold, M., Kasteel, R., Groeneweg, J., Vereecken, H., 2009a. Transport and transformation of sulfadiazine in soil columns packed with a silty loam and a loamy sand. Journal of Contaminant Hydrology 103, 38–47.

Unold, M., Simunek, J., Kasteel, R., Groeneweg, J., Vereecken, H., 2009b. Transport of manure-based applied sulfadiazine and its main transformation products in soil columns. Vadose Zone Journal 8, 677–689.

Wang, P., Shi, Q., Liang, H., Steuerman, D.W., Stucky, G.D., Keller, A.A., 2008. Enhanced environmental mobility of carbon nanotubes in the presence of humic acid and their removal from aqueous solution. Small 4, 2166–2170.

Wang, Y., Li, Y., Kim, H., Walker, S.L., Abriola, L.M., Pennell, K.D., 2010. Transport and retention of fullerene nanoparticles in natural soils. Journal of Environmental Quality 39, 1925–1933.

Wang, Y., Kim, J.-H., Baek, J.-B., Miller, G.W., Pennell, K.D., 2012. Transport behavior of functionalized multi-wall carbon nanotubes in water-saturated quartz sand as a function of tube length. Water Research 46, 4521–4531.