



Roles of cation valance and exchange on the retention and colloid-facilitated transport of functionalized multi-walled carbon nanotubes in a natural soil



Miaoyue Zhang^{a, d}, Scott A. Bradford^{b, *}, Jirka Šimunek^c, Harry Vereecken^a, Erwin Klumpp^a

^a Agrosphere Institute (IBG-3), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

^b United States Department of Agriculture, Agricultural Research Service, U. S. Salinity Laboratory, Riverside, CA 92507, USA

^c Department of Environmental Sciences, University of California Riverside, Riverside, CA 92521, USA

^d Institute for Environmental Research (Biology V), RWTH Aachen University, Worringerweg 1, 52074 Aachen, Germany

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ABSTRACT

Saturated soil column experiments were conducted to investigate the transport, retention, and release behavior of a low concentration (1 mg L^{-1}) of functionalized ^{14}C -labeled multi-walled carbon nanotubes (MWCNTs) in a natural soil under various solution chemistries. Breakthrough curves (BTCs) for MWCNTs exhibited greater amounts of retardation and retention with increasing solution ionic strength (IS) or in the presence of Ca^{2+} in comparison to K^+ , and retention profiles (RPs) for MWCNTs were hyper-exponential in shape. These BTCs and RPs were well described using the advection-dispersion equation with a term for time- and depth-dependent retention. Fitted values of the retention rate coefficient and the maximum retained concentration of MWCNTs were higher with increasing IS and in the presence of Ca^{2+} in comparison to K^+ . Significant amounts of MWCNT and soil colloid release was observed with a reduction of IS due to expansion of the electrical double layer, especially following cation exchange (when K^+ displaced Ca^{2+}) that reduced the zeta potential of MWCNTs and the soil. Analysis of MWCNT concentrations in different soil size fractions revealed that >23.6% of the retained MWCNT mass was associated with water-dispersible colloids (WDCs), even though this fraction was only a minor portion of the total soil mass (2.38%). More MWCNTs were retained on the WDC fraction in the presence of Ca^{2+} than K^+ . These findings indicated that some of the released MWCNTs by IS reduction and cation exchange were associated with the released clay fraction, and suggests the potential for facilitated transport of MWCNT by WDCs.

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1. Introduction

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical-shaped nanostructure (Iijima, 1991). They have been utilized in numerous commercial applications (Gohardani et al., 2014) such as electrical cables and wires (Janas et al., 2014), solar cells (Guldi et al., 2005), hydrogen storage (Jones and Bekkedahl, 1997), radar absorption (Lin et al., 2008) and considering as adsorbents for environmental remediation and water treatment

(Camilli et al., 2014; Li et al., 2012; Mauter and Elimelech, 2008; Pan and Xing, 2012; Zhang et al., 2010) due to their unique electric, chemical, and physical properties. The widespread commercial and potential environmental applications will undoubtedly result in their release into the subsurface. Current studies have investigated the transport behavior of CNTs in different porous media, which is affected by various physical and chemical conditions including ionic strength (IS), water content, grain size, input concentration and dissolved organic matter (Kasel et al., 2013a, 2013b; Tian et al., 2012; Yang et al., 2013). However, most of these studies were conducted in model soil systems such as rigorously cleaned sand or glass beads, which do not reflect the full complexity and heterogeneity of natural soils (e.g. complex grain size distribution and pore structure, and surface roughness and chemical heterogeneity)

* Corresponding author. United States Department of Agriculture, Agricultural Research Service, U. S. Salinity Laboratory, 450 W. Big Springs Road, Riverside, CA 92507, USA.

E-mail address: scott.bradford@ars.usda.gov (S.A. Bradford).

(Cornelis et al., 2014). Kasel et al. (2013b) found limited transport of functionalized multi-walled carbon nanotubes (MWCNTs) in an undisturbed, natural soil. However, information on CNTs interactions with soil colloids and the potential for colloid-facilitated transport of CNT is still limited. Furthermore, the detachment or release of retained engineered nanoparticles (ENPs) like CNTs from the solid phase is important for predicting the ultimate fate and transport of ENPs in the subsurface, but has received little research attention.

Previous studies have demonstrated that pore-water chemistry plays an important role in controlling the retention of ENPs in soils (Badawy et al., 2010; Gao et al., 2006; Tian et al., 2012; Wang et al., 2014, 2015). Retention of ENPs is enhanced at higher ionic strength (IS) because the adhesive force increases with compression of the electric double layer (EDL) and a decrease in the magnitude of the surface potential (Elimelech et al., 2013; Israelachvili, 2011; Khilar and Fogler, 1998). Retention of ENPs is also higher in the presence of similar concentrations of divalent than monovalent cations (Torkzaban et al., 2012; Yang et al., 2013) because the double layer thickness and magnitude of the surface potential decreases and the IS increases to a greater extent (Elimelech et al., 2013; Israelachvili, 2011; Khilar and Fogler, 1998). In addition, adsorbed divalent cations, such as Ca^{2+} , can enhance retention of ENPs by creating nanoscale chemical heterogeneity on the solid surface that can neutralize or reverse the surface charge at specific locations (Grosberg et al., 2002) and/or produce a cation bridge between negatively charged sites on the surface of clays and ENPs (Torkzaban et al., 2012). The relative importance of solution IS and cation type on retention of ENPs is therefore expected to depend on the presence of soil colloids, but these complexities have not yet been fully resolved for natural soils.

A reduction in solution IS and cation exchange (monovalent displacing divalent cations) decreases the adhesive force and thereby induces release of clay particles and ENPs (Bradford and Kim, 2010; Grolimund and Borkovec, 2006; Liang et al., 2013; Torkzaban et al., 2013). The migration of soil colloids can facilitate the transport of pollutants and/or nanoparticles (Bradford and Torkzaban, 2008; Grolimund and Borkovec, 2005; Liang et al., 2013; Yan et al., 2016; Zhu et al., 2014). For example, Liang et al. (2013) provided experimental evidence that release of soil colloids with IS reduction and cation exchange can facilitate the transport of silver nanoparticles. Water-dispersible colloids (WDCs) are indicators for mobile soil colloids (de Jonge et al., 2004); e.g., WDCs are particles from the soil clay fraction that are less than 2 μm in size that are easily dispersible from soil with aqueous solution (Jiang et al., 2012, 2014). Knowledge of the interaction and association between ENPs and WDCs is therefore important for better understanding the fate of ENPs in soil. The effects of perturbations in solution chemistry on the release and colloid-facilitated transport of MWCNTs in soil have not yet been studied.

The objective of this study is to better understand roles of soil colloids, solution IS, and cation type on the transport, retention and release behavior of functionalized MWCNTs (1 mg L^{-1}) in a natural soil. Breakthrough curves and retention profiles for MWCNTs were determined in column experiments, and a numerical model was employed to simulate their fate. The retained concentration of MWCNTs was subsequently determined for the different soil size fractions (e.g., sand, silt, and WDCs). Other experiments were conducted to study the release of soil colloids and MWCNTs with perturbations in solution chemistry (e.g., IS reductions and cation exchange). Results provide valuable insight on the roles of cation type, chemical perturbations, and soil colloids on the retention, release and colloid-facilitated transport of MWCNTs. This knowledge can be useful for environmental applications and risk management of MWCNTs.

2. Materials and methods

2.1. Soil and MWCNT

Soil samples were collected from the upper 30 cm of an agricultural field site in Germany (Kaldenkirchen-Hülst, Germany), sieved to a fraction < 2 mm, and air dried. The soil was classified as a loamy sand with 4.9% clay (<2 μm), 26.7% silt (2–63 μm), and 68.5% sand (63–2000 μm). It had a median grain size (d_{50}) of 120 μm , a total organic carbon content of 1.1%, a cation exchange capacity of $7.8 \text{ cmol}_c \text{ kg}^{-1}$, a pH value of 5.9 (0.01 M CaCl_2), a specific surface area of $1.7 \text{ m}^2 \text{ g}^{-1}$, and 0.8% iron. The clay fraction was composed of illite, montmorillonite, and kaolinite minerals (Kasel et al., 2013b; Liang et al., 2013).

Radioactively (^{14}C) labeled and unlabeled functionalized MWCNTs (Bayer Technology Services GmbH, Leverkusen, Germany) were boiled with 70% nitric acid (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) for 4 h to create additional oxygen-containing functional groups (e.g., carboxylic groups) on their surfaces (Kasel et al., 2013a). The functionalization and characterization of MWCNTs were previously described by Kasel et al. (2013a, 2013b). In brief, a transmission electron microscope was used to characterize morphological properties of MWCNTs, X-ray photoelectron spectroscopy was used to identify oxygen containing functional groups on MWCNTs, and inductively coupled plasma-mass spectrometry was used to determine the amount of metal catalysts before and after acid treatment of MWCNTs. The MWCNTs have a median diameter of 10–15 nm and a median length of 200–1000 nm (Pauluhn, 2010).

Suspensions of MWCNT at selected IS were prepared in deionized water with KCl and CaCl_2 . These suspensions were dispersed by ultrasonication the stock suspension for 15 min at 65 W, and then repeating this process 10 min before injection into soil columns. This low energy of sonication does not damage the MWCNTs (Li et al., 2012).

The hydrodynamic radius measured by dynamic light scattering (DLS) does not reflect the real geometric particle diameter for non-spherical particles like MWCNTs (Hassellöv et al., 2008; Pecora, 2000). Nevertheless, it can be used to study the aggregation behavior of functionalized MWCNTs suspensions. The hydrodynamic radius of unlabeled functionalized MWCNTs suspended in KCl and CaCl_2 at IS = 10 mM were measured 0, 1, and 4 h after suspension preparation by DLS using a Zetasizer Nano (Malvern ZetaSizer 4). The surface charge characteristics and electrophoretic mobility values of unlabeled functionalized MWCNT (pH \approx 5.4) and crushed soil (pH \approx 6) in selected electrolyte solutions were also determined using the Zetasizer Nano apparatus.

2.2. Transport and retention experiments

Saturated MWCNT transport experiments were conducted at different IS (1, 4, and 10 mM KCl) and different cation type at the same IS (1 mM KCl and CaCl_2 , molar concentration 0.33 mM L^{-1} CaCl_2) by using stainless steel columns (3 cm inner diameter and 12 cm length) that were wet-packed with soil. Each side of the column was fitted with a stainless steel plate (1 mm opening) and double PTFE mesh (100 μm openings) to support the soil and to uniformly distribute the flow. The columns were wet packed by incrementally filling the column with soil and Milli-Q water, and then gently tapping the columns with a rubber mallet to ensure complete water saturation. Steady-state flow was achieved using a peristaltic pump, with the flow direction from the column bottom to the top. The saturated hydraulic conductivity and bulk density of the packed soil column was approximately 0.73 cm min^{-1} and 1.5 g cm^{-3} , respectively.

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