Carbon black retention in saturated natural soils: Effects of flow conditions, soil surface roughness and soil organic matter

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A B S T R A C T

We evaluated factors affecting the transport, retention, and re-entrainment of carbon black nanoparticles (nCBs) in two saturated natural soils under different flow conditions and input concentrations using the two-site transport model and Kelvin probe force microscopy (KPFM). Soil organic matter (SOM) was found to create unfavorable conditions for the retention. Despite an increased flow velocity, the relative stability of the estimated maximum retention capacity in soils may suggest that flow-induced shear stress forces were insufficient to detach nCB. The KPFM observation revealed that nCBs were retained at the grain boundary and on surface roughness, which brought about substantial discrepancy between theoretically-derived attachment efficiency factors and the ones obtained by the experiments using the two-site transport model. Thus, decreasing ionic strength and increasing solution pH caused re-entrainment of only a small fraction of retained nCB in the soil columns.

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1. Introduction

In a recent Ceresana report (Ceresana, 2013), the annual production of carbon black nanoparticles (nCBs) was estimated to be more than 7.8 million tons in 2011, of which the largest share of those used for tire production. Surface modification used to enhance the dispersability of nCB in aqueous solutions can also facilitate the release of nCB into aquatic environments (surface and subsurface water systems). Because of its large number of particles, high surface areas and surface impurities, nCBs can generate reactive oxygen species and induce oxidative stress within lung cells (Koike and Kobayashi, 2006). Despite the environmental importance, the transport of nCB in natural soils has not yet been examined.

Recent studies revealed that complex transport behaviors of colloids in soils are qualitatively influenced by the heterogeneous nature of soil grains, both physically (size, shape, and roughness) and chemically (e.g. surface charge, cation exchange capacity) (Jaisi and Elimelech, 2009; Sagee et al., 2012; Zhang et al., 2012). In natural systems, electrostatic colloid—surface interaction forces are predominately unfavorable for attachment since the surface charges of both the particle and the collector surface are the same (Fang et al., 2009; Jaisi and Elimelech, 2009; Sagee et al., 2012). Removal of colloids from the aquatic phase under unfavorable conditions can be influenced by surface roughness, surface charge heterogeneity, straining (i.e., particle entrapment in pore throats that are too small to pass), and deposition in a secondary energy minimum at greater separation distances from the interaction energy barrier (Bradford et al., 2003; Tong and Johnson, 2006; Torkzaban et al., 2008).

Among these influencing factors, the role that surface roughness plays on the retention of colloids in porous media has recently received much attention; however, few studies have reported the contribution of surface roughness on the retention of nCB and other carbonaceous nanoparticles in natural soils. Wang et al. (2013b) suggested that although the sand was 99.9% quartz and had been thoroughly washed, surface charge heterogeneity and surface roughness, and thus retention in low-velocity regions, was the probable explanation for less than 100% effluent mass recovery of biochar nanoparticles; however, the role of surface roughness was not experimentally elucidated in their studies.

There are a few studies that have assessed the effect of soil physical properties on retention and re-entrainment (Fang et al., 2009; Sagee et al., 2012), but these do not typically include direct microscopic evidence (Zhang et al., 2012). Kelvin probe force

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microscopy (KPFM) is a useful tool to determine the local contact potential difference between a conducting atomic force microscopy (AFM) tip and a sample, giving surface potential maps with high resolution and relatively high energy sensitivity (Barth and Henry, 2007; Melitz et al., 2011). nCBs can facilitate the transport of electric current, which increases with decreasing average particle size (Donnet and Voet, 1976) or concentration of surface oxygen and sulfur functional groups (Pantea et al., 2001). Thus, KPFM can be used to distinguish nCB from other attached soil colloids by the difference in electrical properties.

In addition, while some insights regarding nCB transport might be drawn from previous studies based on other carbonaceous nanoparticles such as biochar nanoparticle (Wang et al., 2013a, 2013b), C_{60} (Tong et al., 2010; Wang et al., 2010) and functionalized multi-walled carbon nanotubes (functionalized MWCNT) (Kasel et al., 2013), carboxylated nCB can posses different physical and chemical properties. Typically, nCBs are composed of several spheroidal primary particles with a pronounced ordering of the graphene layers and chemisorbed oxygen complexes (i.e., carboxylic, quinonic, lactonic, or phenolic groups) on their surfaces to varying degrees depending on the condition of manufacturing (Boehm, 1994). Consequently, the specific retention and re-entrainment mechanisms of nCB might not necessarily be the same as those governing other nanoparticles.

The goals of the current study are to (i) analyze the retention of carboxylated nCB as a function of influent concentration and flow velocity using a modified advection–dispersion equation that includes two retention sites; (ii) examine re-entrainment of deposited nCB by changing the ionic strength (IS) and pH of solutions in a four-step column experiment; (iii) examine the effects of soil organic matter (SOM) on the retention and release of nCB; and (iv) evaluate the effect of surface roughness on the nCB retention by AFM. Two soils were selected for their differences in particle size distribution, organic carbon (OC) content and composition, surface roughness, and cation exchange capacity (CEC).

2. Materials and methods

2.1. Soils and carbon black nanoparticle (nCB)

Two soil core samples were collected from the same borehole (A-I: 1.80 m in depth, 15.4 kg; A-II: 4.40 m in depth, 22.2 kg, to represent vertical differences of natural soils) under turf on the Hongo campus of the University of Tokyo, Japan. Each soil sample was thoroughly mixed, gently sieved by passing through a 1-mm-mesh screen (0.4–1.0 mm aggregate) and air-dried at 45 °C for 3 days (Jaisi and Elimelech, 2009). About 40 g of dried soil A-I was thermally treated at 450 °C for 4 h (soil A-Ih) to decompose OC and stored in a desiccator until use. The pore size distribution of the soils A-I and A-Ih was measured by N_2 gas adsorption to confirm that heating the soil A-I did not change the porosity of the soil minerals and soil structure (Fig. S1, Supplementary information, SI). The soils A-I and A-II were classified as clay and silty clay loam, respectively, based on the USDA Textual Soil Classification Diagram. A soil grain size distribution curve and X-ray diffraction pattern of both soils are provided in Figs. S1 and S2 (SI), respectively.

Table 1 summarizes the surface characteristics of the soil samples. According to Ley et al. (1994) and Fang et al. (2009), the soil collector diameters were calculated by the weighted averages of the sand, silt and clay particle diameters (0.175, 0.02, and 0.0015 mm respectively). The CEC of soils A-I, A-Ih, and A-II, determined by means of ammonium acetate extraction (Sagee et al., 2012), was 22.3, 18.9, and 8.1 meq kg^{-1} respectively. The OC contents, extracted following the procedure introduced by Swift (1996), were 1.1 wt% for soil A-I and 0.5 wt% for soil A-II. The surface topography of soil aggregates was measured by AFM in the KPFM mode. A soil surface of 1.00 μm^2 was scanned four times so that the reported roughness statistics (i.e., average roughness, R_a; root-mean-square (RMS) roughness, R_q) was representative of each soil.

Carboxylated nCBs (Aqua-Black 001, Tokai Carbon Co. Ltd., Japan) were used as a model of nCB in the subsurface environment. The mean diameter of the nCB was confirmed by dynamic light scattering (DLS) analysis to be 132 ± 6 nm ($n = 12$). The mean nCB size measured by AFM was 71 ± 34 nm ($n = 6$) (Fig. S3). This difference in the measured particle size was due to the fact that whereas AFM analyzes the size of individual particles, DLS depends on a single intensity averaged value for representing the entire distribution of hydrodynamic diameters. Thus, a few large aggregates can mask the presence of small particles in the sample.

2.2. Column experiments

The soil samples were wet-packed into glass chromatography columns (inner diameter 14 mm, length 88 mm) and conditioned using procedures detailed in SI (Text S1). The porosity (cm^3 cm^{-3}) of packed columns was determined to be 0.48 for soil A-I, 0.42 for soil A-Ih, and 0.43 for soil A-II from analysis of breakthrough curves (BTCs) of a non-reactive tracer (KNO$_3$) (Kretzschmar et al., 1997).

nCB solutions with initial influent concentrations (C_0) of 1, 5, and 10 mg L^{-1} (hereafter referred to as 1nCB, 5nCB, and 10nCB) were stored in 3 mM KCl at pH 7.3, giving both soil grain and nCB a

Table 1
Particle size distribution and surface characteristics of nCB and soil media.

	nCB	Soil A-I	Soil A-Ih	Soil A-II
Particle size distribution	–	Sand (35%), silt (24%), and clay (41%)	–	Sand (18%), silt (52%), and clay (30%)
Diameter (nm)	126 ± 6[a]	67 × 10^{3}[b]	–	42 × 10^{3}[b]
Average roughness R_a (nm)	–	43.8	47.1	26.5
RMS roughness R_q (nm)	–	58.6	60.5	33.3
BET surface area (m^2/g)[c]	144	81	69	203
Point of zero charge	6.3–6.5	5.0	7.8	6.8
Zeta potential (mV) at pH 7.3	−23.7	−19.2	6.8	−10.0
CEC (meq/kg)	–	22.3	18.9	8.1
Extractable humic content (wt%)[d]	–	1.1	0	0.5
Soil pH (measured in water)[e]	–	7.60	8.20	6.24

[a] Median diameter.
[b] The weighted-average soil collector diameter (the sum of the sand, silt and clay particle diameters of 0.175, 0.02 and 0.0015 mm multiplied by their respective percentage contents in the soil (Fang et al., 2009; Ley et al., 1994).
[c] Based on a volumetric N_2 gas adsorption (BELSORP-miniII, BEL Japan Inc.).
[d] Humic extraction procedure was recommended by Swift (1996).
[e] Soil pH was measured at soil to Milli-Q water ratio of 3:10 (w/v) using an Orion (4-star) pH meter with Sure–Flow combination electrode (Orion 9165BNWP).