Journal of Contaminant Hydrology 181 (2015) 3–16

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

Abiotic soil changes induced by engineered nanomaterials: A critical review

Ishai Dror *, Bruno Yaron, Brian Berkowitz

Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot 76100, Israel

A R T I C L E I N F O

Article history:
Received 13 January 2015
Received in revised form 4 April 2015
Accepted 9 April 2015
Available online 17 April 2015

Keywords:
Engineered nanoparticles (ENMs)
ENM retention
Modified soil properties
Change in soil matrix
Environmental contamination
ENM related soil chemistry

A B S T R A C T

A large number of research papers on the fate of engineered nanomaterials (ENMs) in the soil–water system have appeared in recent years, focusing on ENM transport, persistence and toxicological impact. It is clear from these publications that soil is a major sink for ENMs, and that only a small portion degrades or is mobilized further into groundwater. However, to date, very few studies have examined the impact of ENMs on the natural soil–subsurface matrix and its properties. Moreover, it is now well accepted that chemical contaminants are capable of changing soil properties either by inducing direct chemical or physical changes, or through indirect changes by, e.g., influencing biological activity that in turn modifies soil properties. Here, we review studies on the deposition, retention, and accumulation of ENMs in soil, indicative of the extent to which soil acts as a major sink of ENMs. We then examine evidence of how these retained particles lead to modification of surface properties, which are manifested by changes in the sorption capacity of soil for other (organic and inorganic) solutes, and by surface charges and composition different than the natural surfaces. Finally, we demonstrate how this results in physical and hydrological changes to soil properties, including hydraulic conductivity, swelling capacity and wettability. The overall picture revealed in this critical review sheds light on a perspective that has received little attention thus far. These aspects of soil change, due to exposure and subsequent accumulation of ENMs, may ultimately prove to be one of the most important impacts of ENM releases to the environment.

1. Introduction

Over the last years, it has been observed that irreversible changes in natural soils occur following contact with various chemical contaminants of anthropogenic origin (e.g., Ben-Moshe et al., 2013; Berkowitz et al., 2014; Chen et al., 2000; Pignatello, 2006, 2012; Yaron et al., 2008). The term “irreversible changes” refers to long-term, stable, and persistent transformations of soil physical and chemical properties – on a human time scale – which are also resistant to remediation procedures and to natural attenuation. Some of these changes occur following chemical contaminant adsorption–desorption processes, with irreversibility implied by both hysteresis and soil conditioning phenomena. Due to their size and associated chemical properties, one can question if engineered nanomaterials (ENMs) have a similar impact on the soil solid phase as other groups of chemicals.

ENMs form a new class of non-biodegradable pollutants that may reach the land surface as suspended particles in aqueous solution. ENMs are being incorporated into a wide variety of industrial and technological applications, and in consumer products, in increasing quantities. ENM residues are subsequently discharged in industrial and municipal wastewater, which may reach soils via diffuse releases, following effluent disposal and sewage sludge application, and via point releases. Comprehensive information on ENM fate, transport, persistence and toxicological impact as affected by soil solution chemistry and solid phase surface properties appears in many review articles (e.g., Bakshi et al., 2014; Bertsch et al., 2012; Bin et al.,

---

* Corresponding author. Tel.: +972 8 9344230.
E-mail address: ishai.dror@weizmann.ac.il (I. Dror).

http://dx.doi.org/10.1016/j.jconhyd.2015.04.004
0169-7722/

2011; Chen et al., 2008, 2010, 2012; Garner and Keller, 2014; Hotze et al., 2010; Ju-Nam and Lead, 2008; Nowack and Bucheli, 2007; Pan and Xing, 2010, 2012; Peralta-Videa et al., 2011; Petosa et al., 2010; Qafoku, 2010; Riding et al., 2014; Wang, 2014; Yang et al., 2014).

Existing studies have often been performed on inert porous media materials (e.g., glass beads, quartz, or sand) and, to date, only limited research has appeared that focuses on the impact of ENMs on physical and chemical properties of natural soils. Careful examination of the existing literature, however, indicates modifications of natural soil matrix and properties following exposure to ENMs. This review presents and discusses ENM interactions with natural soils that may alter soil matrix composition and surface properties. Here, the focus is on abiotic ENM-induced changes following direct physicochemical interactions. The effect of ENMs on microbial populations and activity in soil has been studied relatively intensively in recent years (e.g., Frenk et al., 2013; Mohanty et al., 2014; Shah et al., 2014a, 2014b; Yadav et al., 2014); these effects are beyond the scope of the current review.

Because chemical contaminants may, under specific conditions, change the matrix and properties of the soil and soil constituents, it is logical to consider that irreversible retention of ENMs on the soil solid phase may also change the soil matrix and its properties. Studies by Elimelech et al. (1995), Brant et al. (2007), and Jiang et al. (2009) were among the first to suggest these possibilities. Here, we present selected evidence for the accumulation of ENMs in soil (Section 2). We then discuss and demonstrate in Sections 3 and 4 how the retention of ENMs in soil can change soil properties and structure.

2. ENM deposition and retention in soils

2.1. ENM–soil solution interactions

In the soil liquid phase, the behavior of ENMs is controlled by the solution chemistry, characterized mainly by pH, ionic strength and ionic composition, as well as by the presence of natural organic and inorganic suspended colloids. These colloids can be discrete organic particles, clays, or other phyllosilicates (Citeau et al., 2006). The soil solution also contains dissolved humic substances which may form an amorphous domain coating the suspended minerals, and colloids with a fibril structure expressed in a transect profile by a dimension of 1 nm or less (Wilson et al., 2008). Solution pH and ionic strength can control precipitation of dissolved humic substances and the dissociation of functional groups of humic acids that can modify the negative charge of some ENMs, and consequently define the extent of electrostatic repulsive forces. In natural soil solutions, changes in the humic substance molecules are often due to contractions, which occur when the entire aggregate is compacted following addition of cations (Baalousha et al., 2006). Humic molecule configurations may also change as a result of chelating processes that are affected by the ionic composition and concentration in the soil solution (Jung et al., 2005; Pranzas et al., 2003). In a similar manner, dissolved organic matter in soil solutions may adsorb or even coat ENMs, changing their original surface properties and in turn their interactions with soil solid phase.

Aggregation and deposition are the primary processes governing ENM redistribution from the land surface to groundwater (Lowry and Casman, 2009). In the soil solution, both homo- and hetero-aggregation of ENMs may occur; aggregation between similar particles is known as homo-aggregation, while aggregation between different particles is called hetero-aggregation. By summing van der Waals and electric double layer forces, expressed as a function of separation distance between ENMs, Hotze et al. (2010) demonstrated that ENMs can have a net attraction in a primary well (minimum), irreversibly forming aggregates, or in a secondary well, where ENMs are reversibly aggregated. In the soil–water environment, ENM aggregation can be prevented by adsorption of natural polymers and polyelectrolytes, which favors electrostatic repulsions.

2.2. ENM deposition from soil solution to soil solid phase

The deposition of ENMs in a soil layer occurs mainly via two distinct pathways: (1) free flow through aggregate channels, and (2) diffuse movement into aggregate pore space. ENM interactions with the soil solid phase may occur within or on the surface of the soil aggregates. The deposition of ENMs in soil can be a result of surface interaction of natural minerals (e.g., clays) and organic matter (e.g., humic acids), or by direct sequestration within the soil pores. The ENM deposition process is often described in terms of the colloid attachment efficiency, a parameter related to the rate between favorable and unfavorable deposition (Petosa et al., 2010; Tufenkji and Elimelech, 2004). Unfavorable slow deposition may occur when the water solution chemistry favors dominating repulsive interactions, which leads to limited ENM deposition. These conditions require the overcoming of considerable energy barriers between ENMs and soil surfaces. In contrast, favorable fast ENM deposition on soil surfaces may occur when the chemistry of the soil solution favors non-repulsive forces between ENMs and soil surfaces. Under these conditions, ENM deposition rates should approach the mass transport limited rate. Suspended particles in the soil solution may be subject to repulsive interactions due to a negative charge of the soil matrix.

An abrupt change in the chemistry of the soil solution may alter the deposition pattern. For example, the effect of pH increase on the decrease of hematite content deposited on a quartz surface, due to disappearance of the detachment energy barrier, has been reported (Ryan and Gschwend, 1994). ENM retention on the soil solid phase is not only a result of adhesive interaction, but may be affected by the pore structure and hydrodynamic forces (Bradford and Torkzaban, 2008; Torkzaban et al., 2007). Experimental results of Torkzaban et al. (2007) on deposition and detachment of carboxylate-modified polystyrene latex microspheres, in Ottawa sand and glass bead collectors, showed that significant hysteresis occurred. The extent of this phenomenon was a function of changes in solution chemistry and differences in solid surface morphology. This behavior was attributed to weak adhesive interactions, which depend on the double layer thickness, colloid mass transfer on the solid phase (controlled by the number of grain contacts), and surface roughness. Recently, Landkamer et al. (2013) defined particle population heterogeneity as an additional paradigm to be considered in colloid deposition and re-entrainment pathways. Some suspended ENMs with specific physico-chemical characteristics may be captured by a secondary minimum and retained irreversibly on the soil solid phase. The soil constituents and soil