Effects of metal oxide nanoparticles on soil properties

Tal Ben-Moshe [a], Sammy Frenk [b], Ishai Dror [a,*], Dror Minz [b], Brian Berkowitz [a]

[a] Department of Environmental Sciences and Energy Research, Weizmann Institute of Science, Rehovot 76100, Israel
[b] Institute for Soil, Water and Environmental Sciences, Agricultural Research Organization, Bet Dagan 50250, Israel

HIGHLIGHTS

► Microscopic properties of soil are affected by nanoparticles.
► Changes in soil humic matter are observed by 3D-FTIR.
► Nanoparticles affect the soil bacterial community composition.
► Macroscopic properties of soil are unaffected by nanoparticles.

GRAPHICAL ABSTRACT
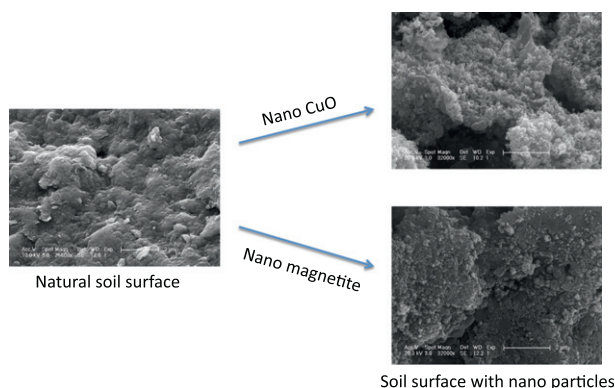
Natural soil surface → Nano CuO / Nano magnetite → Soil surface with nano particles

ABSTRACT

In recent years the behavior and properties of nanoparticles released to the environment have been studied extensively to better assess the potential consequences of their broad use in commercial products. The fate, transport and mobility of nanoparticles in soil were shown to be strongly dependent on environmental conditions. However, little is known about the possible effects of nanoparticles on soil chemical, physical and biological properties. In this study, two types of metal oxide nanoparticles, CuO and Fe_3O_4 were mixed into two types of soil and the effects of the nanoparticles on various soil properties were assessed. Metal oxide nanoparticles were shown previously to catalyze the oxidation of organic pollutants in aqueous suspensions, and they were therefore expected to induce changes in the organic material in the soil, especially upon addition of an oxidant. It was found that the nanoparticles did not change the total amount of organic materials in the soil or the total organic carbon in the soil extract; however, three-dimensional fluorescence spectroscopy demonstrated changes in humic substances. The nanoparticles also affected the soil bacterial community composition, based on denaturing gradient gel electrophoresis (DGGE) fingerprinting, but had little impact on the macroscopic properties of the soil.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

The behavior of nanoparticles in the environment has attracted considerable interest in recent years due to the dramatic increase in nanoparticle production and consumer use, which has resulted in increasing exposure and release to the environment. Transport, retention and mobility in saturated porous media were investigated for different types of nanoparticles including fullerenes, carbon nanotubes and metal oxides (Lecoanet and Wiesner, 2004; Cheng et al., 2005; Espinasse et al., 2007; Wang et al., 2008). In general, the behavior of nanoparticles was shown to be strongly dependent on environmental conditions such as dissolved organic matter, pH and ionic strength. For example, soil organic matter was demonstrated to adsorb readily to nanoparticles, significantly enhancing their suspension stability in aqueous solution

* Corresponding author. Tel.: +972 8 9344230; fax: +972 8 9344124.
E-mail address: ishai.dror@weizmann.ac.il (I. Dror).

and increasing their mobility in porous media (Xie et al., 2008; Johnson et al., 2009).

Few studies have investigated the opposite phenomenon, namely, the effects of nanoparticles on the environment in general, and on soil properties in particular. Elliott and Zhang (2001) injected bimetallic (Fe/Pd) nanoparticles to a test area to demonstrate the reduction of trichloroethene and other chlorinated aliphatic hydrocarbons. The porosity of the soil was not affected by the nanoparticles, and clogging was shown to be minimal. A few studies investigated the effects of nanoparticles on soil microbiology. Fullerene nanoparticles were found to have little impact on soil microbial communities and microbial processes (Nyberg et al., 2008). Multi-walled carbon nanotubes were shown to reduce enzymatic activity in the soil as well as microbial biomass C and N (Chung et al., 2011). Metal oxide nanoparticles were also investigated; Ge et al. (2011) studied the impact of TiO_2 and ZnO on soil microbial communities and demonstrated that both nanoparticles reduced microbial mass and diversity. Pradhan et al. (2011) investigated the effects of copper oxide and silver nanoparticles on leaf microbial decomposition showing that exposure to these nanoparticles led to a decrease in leaf decomposition rate. Furthermore, the decrease in decomposition was accompanied by changes in the structure of the microbial communities.

Study of the interactions between nanoparticles and soil is complicated by the high variability in properties, caused by differences in environmental conditions and soil composition, as well as by the large number of types of available nanoparticles. In this study, two types of metal oxide nanoparticles were chosen, copper oxide (CuO) and magnetite (Fe_3O_4). These types of nanoparticles have wide, potential application: as gas sensors, magnetic phase transitions, catalysts and superconductors for copper oxide (Zhu et al., 2004), and in magnetic recording, magnetic data storage devices, toners and inks for xerography, and magnetic resonance imaging, wastewater treatment, bioseparation, and medicine for iron oxide (Mohapatra and Anand, 2010). Both nanoparticles have low stability in aqueous suspension and tend to aggregate rapidly. They were shown previously to have limited mobility in saturated porous media (Ben-Moshe et al., 2010). Because of their low mobility, large quantities of the nanoparticles are retained in the soil upon release to the environment.

The objectives of this study, therefore, were to investigate the interactions between nanoparticles (copper oxide and magnetite) and natural soils and the possible impact these nanoparticles may have on soil properties. For this investigation, the nanoparticles were mixed with two types of soil, at different concentrations, and a broad survey was performed to determine which physical, chemical and microbial properties of the soil are affected by the presence of nanoparticles.

2. Materials and methods

2.1. Materials

Magnetite (Fe_3O_4) and copper oxide (CuO) nanoparticles (size < 50 nm for both), concentrated nitric acid, humic acid sodium salt (technical) and magnesium nitrate (98%) were purchased from Aldrich. Hydrogen peroxide solution H_2O_2/H_2O (30%) was purchased from Frutarom. Ethanol and hydrochloric acid (32%) were purchased from Gadot. Sodium hydroxide pellets (99%) and nickel chloride hexahydrate were purchased from Merck, Germany. Quartz sand (Accusand, 50/70 mesh, 256 μm) was purchased from Unimin Corp. Deionized water (18.2 MΩ cm) was used in all experiments.

2.2. Preparation of soil samples

Two types of Israeli soil, from Bet Dagan (Red Sandy clay loam Mediterranean soil) and Yatir (Rendzina soil from a forest in an arid zone), were chosen for the experiments. The samples were taken from the upper layer (0–10 cm) of the soil and were sieved through 60 mesh (250 μm). The sand, silt, clay and organic carbon contents of the soil samples – which differ significantly in terms of clay content – are given in Tables 1S and 2S for Bet Dagan and Yatir, respectively. To prepare samples with nanoparticles, 1% or 5% (w/w) of CuO or Fe_3O_4 were added to the dry soil and mixed overnight (18 h). These two relatively high concentrations were chosen to enable detection of potential, prominent effects on soil properties. It should be further noted that both soils have natural amounts of Fe in them, especially the Bet Dagan soil (Singer, 2007). The samples were then packed in a column and water was injected at 0.6 mL min^{-1} for 24 h to remove some of the unattached nanoparticles. The soil samples were then dried at 40 °C in air. Samples without nanoparticles were prepared by the same procedure for comparison. The samples were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) and the amount of nanoparticles deposited on the soil was determined by digesting the soil samples with nitric acid and measuring metal concentration by inductively coupled plasma–mass spectrometry (ICP–MS).

2.3. Characterization of soil macroscopic properties

Several "macroscopic" and "microscopic" properties of the soil samples were studied. The macroscopic properties of the soil that were investigated include porosity, hydraulic conductivity, amount of organic matter, cation exchange capacity (CEC) and nickel (Ni) sorption isotherms. The porosity of the soil samples was measured by the water evaporation method. Hydraulic conductivity was measured by the constant head method (McWhorter and Sunada, 1977).

CEC was measured by the ammonium acetate method (Sumner and Miller, 1996). An excess of 1 N NH_4OAc at pH 7 was added to the soil samples. The samples were mixed thoroughly and centrifuged at 1360×g. The liquid was then separated from the soil and kept in a different container. The process was repeated five times to ensure the complete replacement of exchangeable cations with ammonium. The concentration of the exchangeable cations (Ca^{2+}, K^+, Mg^{2+}, Na^+) in the ammonium solution was measured by ICP–MS. The soil was washed with ethanol to remove any excess of the saturating solution. The adsorbed ammonium was extracted by addition of an excess of magnesium nitrate solution several times and centrifugation. The concentration of adsorbed ammonium in the magnesium nitrate solution was determined by the phenate method (Solorzano, 1969).

Sorption isotherms of nickel (Ni) were prepared by addition of solutions with different initial concentration of $NiCl_2·6H_2O$ (0, 1, 10, 50, 100, 500, 1000 mg L^{-1}) to soil samples. The samples were shaken for 72 h. This mixing time was determined in preliminary kinetic experiments to be sufficient to reach equilibrium. The samples were then filtered and the concentration of Ni in the solution was determined by ICP–MS.

The amount of organic matter was measured by heating a sample with a known weight at 105 °C for 24 h to evaporate water. The sample was weighed again to determine the water content. It was then heated at 400 °C overnight and weighed again. The difference in weight is an estimate of the amount of organic carbon. All of the experiments in this section were prepared in duplicates or triplicates.