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The fate of silver nanoparticles in soil solution — Sorption of solutes and aggregation

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HIGHLIGHTS

- Soil solution reduces the release of ionic silver from Ag NP.
- The stabilizing effect of sorbed organic matter is dependent on Ag NP concentration.
- Short-chained DOM is preferentially adsorbed over long-chained, aromatic DOM.
- Ag NP may form a sink for Ag^+ ions in the soil.

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ABSTRACT

Nanoparticles enter soils through various pathways. In the soil, they undergo various interactions with the solution and the solid phase. We tested the following hypotheses using batch experiments: i) the colloidal stability of Ag NP increases through sorption of soil-borne dissolved organic matter (DOM) and thus inhibits aggregation; ii) the presence of DOM suppresses Ag oxidation; iii) the surface charge of Ag NP governs sorption onto soil particles. Citrate-stabilized and bare Ag NPs were equilibrated with (colloid-free) soil solution extracted from a floodplain soil for 24 h. Nanoparticles were removed through centrifugation. Concentrations of free Ag ions and DOC, the specific UV absorbance at a wavelength of 254 nm, and the absorption ratio $\alpha_{254}/\alpha_{410}$ were determined in the supernatant. Nanoparticle aggregation was studied using time-resolved dynamic light scattering (DLS) measurement following the addition of soil solution and 1.5 mM Ca^{2+} solution. To study the effect of surface charge on the adsorption of Ag NP onto soil particles, bare and citrate-stabilized Ag NP, differing in the zeta potential, were equilibrated with silt at a solid-to-solution ratio of 1:10 and an initial Ag concentration range of 30 to 320 μg/L. Results showed that bare Ag NPs sorb organic matter, with short-chained organic matter being preferentially adsorbed over long-chained, aromatic organic matter. Stabilizing effects of organic matter only come into play at higher Ag NP concentrations. Soil solution inhibits the release of Ag^+ ions, presumably due to organic matter coatings. Sorption to silt particles was very similar for the two particle types, suggesting that the surface charge does not control Ag NP sorption. Besides, sorption was much lower than in comparable studies with sand and glass surfaces.

1. Introduction

Engineered inorganic nanoparticles (EINPs) can enter soils through various sources and pathways such as the application of fertilizers and plant protection products (Batley et al., 2013), biosolids (Benn and Westerhoff, 2008), the irrigation of sewage water (Gottschalk et al., 2009) or the flooding of floodplains (Lecoanet et al., 2004). According to a material flow analysis from a life-cycle perspective of EINP-containing products, an increasing soil exposure to Ag NP has to be expected (Gottschalk et al., 2009). Silver NPs are considered to have a

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cumulative impact on environmental and human health (Anjum et al., 2013).

Once nanoparticles (NPs) have entered the soil, they are subject to reactions with the soil solution as well as with the (mobile and stationary) solid phase. Nanoparticle stability in soils is affected by various processes and environmental factors. With the study presented here we address Ag NP (1) and their coating by dissolved organic matter (DOM), (2) their dissolution and (3) their sorption to soil particles. Thereby our study represents one of the first screenings of important soil processes and an assessment of their relevance for the fate of nanoparticles determined through the use of a natural soil extract.

Coating by dissolved organic matter. The coverage through dissolved organic matter is reported to influence NP stability (Lecoanet et al., 2004). Several authors found an increase in Ag NP stability through the sorption of fulvic and humic acids (Li et al., 2010) as well as Suwannee River Humic Acid (Huynh and Chen, 2011). However, to the best of our knowledge, the sorption of soil-borne dissolved organic matter to Ag NP has so far not been investigated. The presence of divalent cations is known to decrease the stability of pedogenic colloids as well as of NP as they screen the surface charge of particles, thus facilitating aggregation (Klitzke and Lang, 2009; Klitzke et al., 2012; Li et al., 2010). Despite these two counteracting processes, i.e. stabilization through dissolved organic matter sorption and cation-induced aggregation, it is widely assumed that reactions occurring in soils might increase NP stability and thus enhance NP mobility (Darlington et al., 2009; Nel et al., 2006).

Dissolution. The dissolution of NP may release toxic compounds into the environment (Batley et al., 2013). The release of Ag^+ from Ag NP has been observed in different sample matrices, e.g. in well-defined aqueous media with varying pH, concentrations of natural organic matter (NOM) and ocean salts (Liu and Hurt, 2010) as well as in artificial soil solution (Cornelis et al., 2012). On the basis of the results by Liu and Hurt (2010), who found Ag^+ release to be highest at low pH (ie. pH 4) and in the absence of NOM, one may presume Ag NP oxidation in neutral soil solutions to play only a minor role. Oxidized Ag ions may sorb to Ag NP surfaces (Liu and Hurt, 2010), from where they may diffuse away from NP surface into the bulk solution (Borm et al., 2006). While NOM was reported to inhibit Ag NP oxidation (Liu and Hurt, 2010), the presence of cations would promote Ag oxidation as it may displace Ag^+) ions from the particle surface, thus enhance oxidation (Li et al., 2010). So far, it is unclear, to which extent Ag^+ ions oxidized by components of the soil solution are released into the bulk solution, i.e. which fraction remains adsorbed on NP surface as an exchangeable ion with the NP surface acting as a sink of Ag^+ ions.

Sorption to soil particles. The surface charge is considered to be an important parameter governing heteroaggregation (Cornelis et al., 2013) and sorption to silica surfaces is supposed to decrease with increasing negative particle charge (Thio et al., 2012).

The aim of this work was to assess the impact of the soil solution of a flood plain soil on the fate and stability of Ag NP as well as the interaction of Ag NP with natural soil particles by testing the following hypotheses:

i) Colloidal stability of Ag NP increases through the sorption of soil-borne dissolved organic matter and thus inhibits aggregation.
ii) The presence of soil-borne DOM suppresses Ag oxidation and thus reduces the amount of exchangeable Ag^+ adsorbed on Ag NP surfaces.
iii) The surface charge of Ag NP governs sorption onto soil particles, i.e. bare Ag NP show higher sorption to soil particles than Ag NP which are stabilized through additional charges.

These hypotheses were tested with batch experiments.

2. Material and methods

2.1. Preparation of silver nanoparticle suspensions

Citrate-coated Ag NPs were prepared according to the following procedure: Synthesis of Ag NP was performed using Turkevich method (Turkevich et al., 1951) which was modified for Ag. One millimole silver nitrate ($AgNO_3$, ≥99.9%, p.a., Roth) and 5 mmol trisodium citrate ($Na_3C_6H_5O_7$, Sigma-Aldrich) were dissolved in 50 mL and 950 mL demineralised water (18.2 MΩ cm, Direct-Q UV, Millipore) respectively. In the solution of trisodium citrate the pH value was adjusted to 11 using 1 mol/L sodium hydroxide solution (NaOH, 1 N standard solution, Roth). Solution of trisodium citrate was heated to boiling in a covered beaker glass under magnetic stirring (RCT basic, IKA Labortechnik). After the boiling started 50 mL silver nitrate solution was added dropwise to the trisodium citrate solution within 4.5 min. The colour of the reaction solution changed from transparent-colourless to yellow and later to greyish-turbid. The reaction solution was then boiled for 20 min. After this period the solution was cooled to room temperature. The prepared silver nanoparticle stock dispersion was kept at +4 °C in the dark for further use.

Particle size distribution and mean particle diameter (z-average) were determined using dynamic light scattering instrument (Delsa Nano C Particle Analyser, Beckman Coulter). Particle size was measured before and after dilution of silver nanoparticle stock dispersion. For dilution, 1 mL stock dispersion was mixed with 2 mL demineralised water directly in the measuring cuvette. Mean hydrodynamic particle diameters (z-average) measured in undiluted and diluted stock dispersions were 31.2 ± 1.2 nm.

To determine dissolved silver concentration in the stock dispersion, nanoparticles were first separated from the liquid phase, and then the Ag concentration was measured in the liquid phase. Dissolved Ag is defined in this work as a fraction with a diameter of <2 nm. To reach this cut-off, the separation of silver nanoparticles from the liquid phase was performed using ultracentrifuge (SORVALL WX 90 Ultra, Thermo Electron Corporation). Silver NP stock dispersion (distributed in two 8.5 mL ultracentrifuge tubes) was centrifuged at 80,000 rpm (396,000 *g*) for 2 h (acceleration time from 0 to 500 rpm: 6 min and from 500 to 80,000 rpm: approx. 4 min; deceleration time from 80,000 to 500 rpm: approx. 4 min and 500 to 0 rpm: 6 min). After centrifugation, 5 mL of supernatant was removed carefully from each tube, mixed together, and stabilised with 1% nitric acid (sub-boiled). The samples were prepared in triplicate. Stabilised samples were analysed using inductively coupled plasma mass spectrometer (ICP-MS, XSeries 2, Thermo Scientifc). Mean concentration of dissolved Ag (<2 nm) in the Ag nanoparticle stock dispersion was 54 ± 26 μg/L (standard deviation).

Bare Ag NPs with a primary particle size (as indicated by the manufacturer) of 35 nm were obtained from Iolitec nanomaterials. For the DOM sorption experiment, dispersions were prepared in duplicate by weighing 40 mg Ag NP in 40 mL Millipore water. The mixtures were sonicated with an ultrasonic finger at 5400 W/mL for 35 min each and subsequently filtered over a 0.2 μm polyether sulfone membrane (Pall). Both suspensions were joined together. The final concentration of Ag NP amounted to 153 μg/L. The measured (intensity-based) particle diameter by dynamic light scattering (HPPS — High Performance Particle Sizer, Malvern Instruments) was 39.5 ± 8.5 nm. Further NP characteristics have been reported by Abraham et al. (2013). To achieve different initial concentrations for the sorption experiment onto silt, the amount of weighed Ag NPs and the volume of Millipore water were varied.

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