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Transport of silver nanoparticles in saturated columns of natural soils

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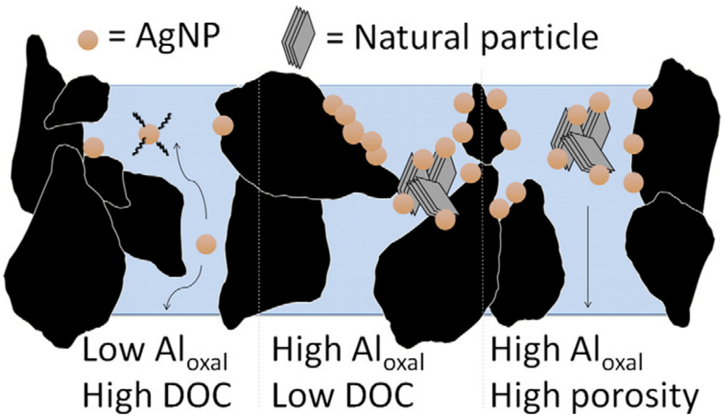
HIGHLIGHTS

- Breakthrough of silver NPs occurred in 8 of 11 columns of natural soils.
- Higher oxalate extractable aluminum meant higher silver breakthrough.
- Heteroaggregation of silver NPs occurred during batch tests.
- Heteroaggregation most likely explains limited NP transport and size exclusion.
- NP modeling in natural soils should consider heteroaggregation.

GRAPHICAL ABSTRACT



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ABSTRACT

With industrialization and urbanization soils are increasingly exposed to engineered nanoparticles (ENP), yet knowledge regarding the transport of ENP in natural soils is lacking, a process that was examined further in the current study. Saturated columns of 11 natural soils with varying physical and chemical properties were spiked with two pore volumes of a solution containing 1.7 mg Ag L^{-1} as polyvinylpyrrolidone (PVP)-coated silver nanoparticles (AgNP) (40 nm actual diameter) and eluted at a constant flow rate of 1 ml min^{-1}. Breakthrough of Ag was analyzed using filtration theory and a HYDRUS-1D transport model that incorporated two-site kinetic attachment–detachment. Separate kinetic batch studies suggested fast heteroaggregation between negatively charged AgNP and positively charged sites on the common soil colloids maghemite or montmorillonite. The concentration of such sites in the soil correlates positively with the oxalate-extractable aluminum concentration of the soils, a measure that correlated positively with collision efficiency. This correlation thus suggested favorable deposition of AgNP and/or enhanced straining following heteroaggregation of AgNP with mobile soils colloids. Occurrence of heteroaggregation was supported by the batch studies, enhanced size-exclusion in the soil with the highest porosity, and reversible attachment–detachment predicted from HYDRUS modeling, whereas straining and favorable deposition were suggested by irreversible attachment. Our study suggests that under similar experimental conditions, PVP-coated AgNP would rapidly interact with natural colloids in soils significantly reducing their mobility and hence potential risk from off-site transport.

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1. Introduction

Engineered nanoparticles (ENP) are defined as particles where $\geq 50\%$ of the particles (monodispersed or aggregated) have at least one dimension in the 1–100 nm size range (EC, 2011). ENP take advantage of the unique properties of nanoparticles that emerge at small dimensions (e.g. high reactivity), but it has been shown that the same properties may also have adverse effects on, for instance, the mortality, reproduction and mobility of organisms once ENP are released to the environment (Shoults-Wilson et al., 2013; Stampoulis et al., 2009). The magnitude of these adverse effects depends on the concentration, bio-availability and possible transformations of ENP in the environment.

Soil environments are a potential main exposure pathway for ENP through land application of wastewater treatment biosolids, accidental spills or intentional applications e.g. as nano-pesticides (Gottschalk et al., 2009; Kah et al., 2012). Soils present a large sink of reactive surfaces where deposition and other reactions of ENP take place, which could influence their bioavailability and mobility (Batley et al., 2012). To assess the potential risk of ENP transport in soils, we need to understand the role that soil physical and chemical properties play on ENP retention and mobility in soils. Transport of ENP has been mostly studied in simple porous media e.g. quartz or glass beads (Petosa et al., 2010). While these studies have provided valuable insight in the mechanisms that control transport of ENP, some specific interactions that occur in natural soils are not taken into account. For example, we previously found that the retention of CeO_2 ENP and silver nanoparticles (AgNP) in batch tests with 16 natural soils correlated predominantly with the granulometric clay content, i.e. the particle fraction < 2 μm (Cornelis et al., 2012; Cornelis et al., 2011). This correlation would not be evident when investigating ENP retention in simple porous media.

AgNP can be toxic to soil invertebrates (Shoults-Wilson et al., 2013) and plants (Stampoulis et al., 2009), but it has been found that the toxicity of AgNP varies with soil type (Shoults-Wilson et al., 2013) possibly because AgNP transport and thus bio-availability varies with soil chemical and physical properties (Sagee et al., 2012). The authors previously found that AgNP retention varied widely in suspensions of natural soils, correlating mainly with the clay content of the soil and it was suggested that this correlation is possibly explained by heterocoagulation of AgNP with naturally occurring colloids (Cornelis et al., 2012). Information is still sparse on the mobility of AgNP in natural soils under dynamic flow conditions, and the effect of soil properties on AgNP transport in soils. To address this need, we conducted flow-through column experiments to investigate the transport of AgNP in 11 natural soils that had various physical and chemical properties. These studies were complemented with batch aggregation kinetic studies of AgNP with soil colloids were investigating the possibility of heteroaggregation of AgNP in soil pore waters.

2. Material and methods

2.1. Nanoparticles

Polyvinylpyrrolidone (PVP) (0.1%) coated AgNP powder (nominal particle size 10 nm) was purchased from the Nanostructured and Amorphous Materials, Inc. (Houston, TX). Stock suspensions were prepared by weighing 0.1 g nanopowder into 50 mL centrifuge tubes followed by sonication (Misonix) at 1500 W L^{-1} for 3 min and centrifugation at 2800 *g* for 15 min. The pristine nanoparticle powder and stock aqueous suspensions were previously characterized in terms of primary particle size, size in suspension, and isoelectric point (IEP) (Cornelis et al., 2012).

2.2. Heteroaggregation kinetics

Heterocoagulation of AgNP with common soil colloids was examined using maghemite and montmorillonite at pH 4. Maghemite (Fe_2O_3) (100 mg L^{-1}) and montmorillonite $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ (100 mg L^{-1}) suspensions (pH 4 adjusted using nitric acid (HNO_3)) were sonicated at 1500 W L^{-1} for 3 min. This was followed by 45 min centrifugation at 4400 *g* for maghemite suspension (final concentration 17.6 mg Fe_2O_3 L^{-1}) and 120 min at 4400 *g* for montmorillonite suspension (final concentration 79.8 mg montmorillonite L^{-1}). A pH value of 4 was selected for this study because heteroaggregation is more rapid than homoaggregation at pH values between the IEP of heteroaggregating particles (Hogg et al., 1966). The AgNP stock suspension (8.4 mg L^{-1}) and the maghemite or montmorillonite suspensions were then mixed at equal volumes. The ionic strength (IS) of the suspensions was varied by the addition of different volumes of sodium perchlorate ($NaClO_4$) solutions to final concentrations of between 0 and 100 mM adjusted to pH = 4. The total volume was maintained at 1 mL. The suspensions were shaken vigorously by hand for *ca.* 3 s. The increase in time-dependent apparent *Z*-average hydrodynamic diameter (d_h), at least up to 150% of the original d_h, was obtained from autocorrelation functions obtained over 6 to 10 s intervals using Dynamic Light Scattering (DLS) (Malvern Zetasizer). The aggregation rate constant (k) at a particular IS is expressed by (Grolimund et al., 2001):

$$k = p \times N_0 \times \left[\frac{\delta d_h}{\partial t}\right]_{t\to 0} \tag{1}$$

where p is a constant factor that depends on material properties and instrument settings, N_0 is the initial particle concentration in the suspension, and $[\delta d_h(t)/\delta t]_{t \to 0}$ is the initial linear d_h increase that corresponds to dimer formation. The measured $[\delta d_h(t)/\delta t]_{t \to 0}$ values were corrected for dilution and the added volume of $NaClO_4$ solutions. At an IS above the critical aggregation concentration (*CCC*), aggregation is diffusion-limited and k attains a constant value k_{fast} corresponding to $[\delta d_h(t)/\delta t]_{fast}$ that is independent of IS. The *CCC* can then be estimated using the dimensionless stability ratio W at each IS by fitting the empirical expression (Grolimund et al., 2001):

$$W = \frac{k_{fast}}{k} = \frac{pN_0\left[\frac{\delta d_h}{\delta t}\right]_{fast}}{pN_0\left[\frac{\delta d_h}{\delta t}\right]_{t\to 0}} = 1 + \left(\frac{CCC}{IS}\right)^{\beta}. \tag{2}$$

The parameter β in Eq. (2) is the slope of log(W) as a function of log(IS) in mol L^{-1}, in the reaction-limited aggregation regime (i.e. $IS < CCC$). Hamaker constants were estimated in this study from homoaggregation kinetics data. First, the Stern potential ψ_δ was calculated using the empirical expression (Elimelech et al., 1995):

$$\beta = -2.06 \times 10^9 \frac{a}{z^2} \tanh^2\left(\frac{ze\psi_\delta}{4kT}\right) \tag{3}$$

where a is the particle radius (m), z is the electrolyte valency, e is the electronic charge, k is the Boltzmann constant (1.38×10^{-23} J K^{-1}) and T is the temperature (298 K). The Hamaker constant can then be estimated using the approximate formula (Elimelech et al., 1995):

$$CCC = \frac{\tanh^4\left(\frac{ze\psi_\delta}{4kT}\right)}{z^6 A^2} \tag{4}$$

where *CCC* is expressed in mol L^{-1} and A is the Hamaker constant in J.

2.3. Soil characterization

Eleven soil samples with various physical and chemical characteristics were collected from the top 15 cm of the profile from three states (New South Wales, Queensland and South Australia) in Australia (Table 3). The soils were air-dried at 25 °C for 1 week and sieved