



Soil–pore water distribution of silver and gold engineered nanoparticles in undisturbed soils under unsaturated conditions



D.S. Tavares^{a,b}, S.M. Rodrigues^{a,*}, N. Cruz^a, C. Carvalho^a, T. Teixeira^a, L. Carvalho^c, A.C. Duarte^a, T. Trindade^c, E. Pereira^a, P.F.A.M. Römkens^d

^a Department of Chemistry and CESAM, University of Aveiro, 3810-193 Aveiro, Portugal

^b Department of Chemistry and CICECO, Aveiro Institute of Nanotechnology, University of Aveiro, 3810-193 Aveiro, Portugal

^c Laboratório Central de Análises, University of Aveiro, 3810-193 Aveiro, Portugal

^d Alterra – Wageningen University and Research Center, PO Box 47, Wageningen 6700 AA, The Netherlands

HIGHLIGHTS

- Both Ag and Au ENPs added to soils were retained almost completely within 24 h.
- The short term solubility of Au was partly controlled by natural soil colloids.
- Ag from Ag ENPs added to soils was present in the pore water mostly as ionic Ag.
- Under aerated soil conditions the actual availability and mobility of Ag and Au ENPs in soils are low.

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ABSTRACT

Release of engineered nanoparticles (ENPs) to soil is well documented but little is known on the subsequent soil–pore water distribution of ENPs once present in soil. In this study, the availability and mobility of silver (Ag) and gold (Au) ENPs added to agricultural soils were assessed in two separate pot experiments. Pore water samples collected from pots from day 1 to 45 using porous (<0.17 μm) membrane samplers suggest that both Ag and Au are retained almost completely within 24 h with less than 13% of the total added amount present in pore water on day 1. UV–Vis and TEM results showed that AuENPs in pore water were present as both homoaggregates and heteroaggregates until day 3 after which the concentration in pore water was too low to detect the presence of aggregates. A close relation between the concentration of Au and Fe in pore water suggests that the short term solubility of Au is partly controlled by natural soil colloids. Results suggest that under normal aerated soil conditions the actual availability of Ag and AuENPs is low which is relevant in view of risk assessment even though the impact of environmental conditions and soil properties on the reactivity of ENPs (and/or large ENPs aggregates) retained in the solid matrix need to be addressed further.

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1. Introduction

During the last decade there was an exponential increase in the use of engineered nanoparticles (ENPs) in commercial goods because of their unique properties related to the small size and enhanced surface area (Gottschalk et al., 2013; Sun et al., 2014). The most produced metal-based ENPs in 2012 were TiO₂, ZnO and AgENPs (Gottschalk et al., 2013; Sun et al., 2014) which represent around 10%, 10%, and 50% of metallic ENPs in commercial

products worldwide, respectively (Yang et al., 2013). In particular AgENPs were adapted for a wide variety of applications (e.g. textiles, paints, nanopesticides) due to well known antimicrobial properties as well as other most relevant characteristics (such as high catalytic efficiency and high nonlinear optical performance) (Tilaki and Mahdavi, 2006; Jiang et al., 2011; Sun et al., 2014). Commercial application of AgENPs leads to their release into the environment both through normal use or intentional applications (Benn and Westerhoff, 2008; Kaegi et al., 2010).

Soils are one of the final sinks of ENPs released into the environment (Sun et al., 2014). This is largely due to the high retention capacity for AgENPs and soil geochemical processes that reduce the dispersibility of AgENPs (Cornelis et al., 2013). Model calculated estimates of concentrations of AgENP in soil vary from 10⁻⁵ to

* Corresponding author at: Departamento de Química – Universidade de Aveiro, 3810-193 Aveiro, Portugal.

E-mail address: smorais@ua.pt (S.M. Rodrigues).

$10^2 \mu\text{g kg}^{-1}$ (Gottschalk et al., 2013). However, these numbers still lack validation which is largely related to the lack of appropriate methods for detecting, characterizing and quantifying ENPs in complex natural media such as soil (Gottschalk et al., 2013).

In addition also the fate of ENPs in soil in view of risks for leaching to ground- and surface water or uptake by plants and organisms has to be further addressed in order to accurately estimate risks of ENPs (Coutris et al., 2012).

Due to the contrasting physico-chemical characteristics of Ag and Au ENPs both Ag and AuENPs were included in this study. Under normal oxidizing soil conditions AgENPs are prone to oxidative dissolution, and their fate depends on inorganic speciation in solution, the affinity of Ag^+ and Ag ENPs to adsorb to soil components and the stability of ENP aggregates in pore water (Benoit et al., 2013). Soil properties (pH, soil organic matter, texture and natural inorganic colloids) have been reported to significantly affect the AgENPs distribution between the soil solid matrix and pore water although many unknowns still exist regarding their fate and actual availability in soil (Coutris et al., 2012; Benoit et al., 2013; Cornelis et al., 2013).

Gold ENPs on the other hand are very stable, resistant to oxidation and generally easily detected in soils due to low background concentrations which makes them stable probes for the analysis of the behavior of metal-based ENPs in complex natural systems (Unrine et al., 2010). Recent studies on both aquatic and terrestrial environments suggest that there is a potential for Au ENPs to be transferred either from the water column or soils to the food web (Ferry et al., 2009; Unrine et al., 2010).

Transport of ENPs in soils has been often studied in column experiments under saturated flow conditions using either coarse-textured, homogeneous, artificial porous media (Tian et al., 2010; Ben-Moshe et al., 2010) or natural soils (Cornelis et al., 2013). A recent study by Liang et al. (2013) on the transport of AgENPs used columns packed with loamy sand soil under unsaturated conditions reported that the mobility of AgENPs in soils can be overestimated when applying artificially high input flow rates of AgENPs.

Hence, further studies are necessary to fully understand the fate of the various ENPs in soils under undisturbed and natural flow conditions, to properly describe the interactions of AgENPs and AuENPs with natural soil colloids and to determine the effects of these interactions on ENPs availability in soils (Sagee et al., 2012; Cornelis et al., 2014).

The main objective of this study was to quantify the soil–pore water distribution of Ag and AuENPs after addition to soils under environmentally relevant conditions, i.e. aerated soils and to infer on their potential mobility. Pot experiments with agricultural soils were performed to identify the degree to which ENPs added to aerated soils remain chemically available. Agricultural soils were used since the regular application of biosolids is likely to result in the preferential accumulation of metal-based ENPs in agricultural areas (Gardea-Torresdey et al., 2014). Finally the results of this study were evaluated in view of implications for risk assessment.

2. Materials and methods

2.1. Sampling and characterization of soil samples

Samples from agricultural sites from three different areas in Portugal (urbanized/mining/industrial) reflecting commonly observed soil types have been selected for this study, including samples from:

- “Grande Porto” urban area (Urb1–Urb5).
- Estarreja industrial area (samples Ind1–Ind5).
- Aljustrel and Lousal mining areas (samples Min1–Min5).

Soils (0–10 cm) from all locations were sampled in grassland/pasture areas using a plastic spade. Soils were air dried at room temperature until constant weight and sieved at <2 mm using a nylon sieve. The <2 mm soil fraction was used for subsequent soil analyses and pot experiments.

Details on the methods for characterization of soil properties are given in [Supplementary Information](#).

2.2. Synthesis and characterization of AgENPs and AuENPs

AgENPs were synthesized by reduction of AgNO_3 with an excess of NaBH_4 as described by Mulfinger et al. (2007). AuENPs were synthesized by reduction of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ with $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, as described previously by Schneider et al. (2006) and Pinto et al. (2007). Details of these methods are given in [Supplementary Information](#).

The morphology of the Ag and AuENPs was evaluated by transmission electron microscopy (TEM) using a Hitachi H-9000 TEM microscope operating at 300 kV and equipped with energy-dispersive X-ray spectroscopy (EDX). Samples for TEM analysis were prepared by putting one drop of the colloidal ENPs onto a carbon-coated copper grid and then let the solvent to evaporate. The average size of the Ag and AuENPs was assessed by direct measurements on the TEM images. Mean ENPs diameter and size ranges were quantified based on measurements of at least 100 individual particles using ImageJ software. UV–Vis absorption spectra for the Ag and AuENPs were recorded on a Jasco V-560 UV–VIS spectrophotometer (300–700 nm). Quartz cuvettes with 1 cm-pathlength were used as sample holder for all UV–Vis analysis. A Malvern Zeta-Sizer Nano-ZS was used to determine the zeta potential using phase analysis light scattering. Five replicate measurements of zeta potential were performed for each sample.

The pH of the Ag and Au colloids was 6.6 and 8.0, respectively. Total concentrations of Au and Ag in colloids were determined by elemental analysis by ICP-OES following microwave-assisted *aqua regia* digestion using Teflon vessels (microwave oven: MARS model, CEM). A sub-sample of 2 mL of each colloid was digested with 2 mL *aqua regia*. The detection limits were: 0.01 mg L^{-1} for Ag and 0.12 mg L^{-1} for Au.

In the pot experiments (see Section 2.3) both Ag and AuENPs were added in different concentration ranges using different dilution (in ultra pure water) of the initially prepared colloids. The dilution ranges and the resulting Ag and Au input concentrations are shown next:

- AgENPs – colloid A: $[\text{Ag}] = 25 \text{ mg L}^{-1}$; colloid B: $[\text{Ag}] = 5.0 \text{ mg L}^{-1}$; colloid C: $[\text{Ag}] = 2.5 \text{ mg L}^{-1}$.
- AuENPs – colloid A: $[\text{Au}] = 16 \text{ mg L}^{-1}$; colloid B: $[\text{Au}] = 8.5 \text{ mg L}^{-1}$; colloid C: $[\text{Au}] = 3.5 \text{ mg L}^{-1}$.

2.3. Pot experiments

2.3.1. Pot experiment 1: influence of ENP input concentration on the soil-pore water distribution of Ag and AuENPs

In pot experiment 1, 21 pots containing 500 g (dry weight (dw)) of soil Ind1 (air dried, sieved to <2 mm) were prepared. Two pore water samplers (Rhizon flex) were placed in each pot: the first one at a depth of 3 cm below the soil surface (surface sampler – SF) and the second at 6 cm below the soil surface (sub-surface sampler – SB). The pore water samplers include a microfiltration membrane with a nominal pore size of 0.12–0.17 μm . Thus it should be noticed that Ag or Au amounts measured in pore water samples correspond to either dissolved metal ions from oxidized particles or ENPs (and their aggregates) with size <0.12–0.17 μm . This filter is an inert polymer with no ion exchange properties, to minimize sorption.

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