



Sorption behavior of copper nanoparticles in soils compared to copper ions



Dorit Julich ^{a,*}, Stefan Gäth ^b

^a Institute of Soil Science and Site Ecology, TU Dresden, Piener Str. 19, 01737 Tharandt, Germany

^b Institute of Landscape Ecology and Resources Management, Justus-Liebig-University, Heinrich-Buff-Ring 26C, 35392 Giessen, Germany

ARTICLE INFO

Article history:

Received 6 September 2013

Received in revised form 23 June 2014

Accepted 6 July 2014

Available online 15 July 2014

Keywords:

Copper nanoparticles

Copper

Sorption

Freundlich isotherm

ABSTRACT

Metallic nanoparticles have special physical and chemical properties which determine a particular behavior in environmental systems and organisms. While several studies investigated the differences in the toxicity of metallic nanoparticles compared to their ionic forms or salts, there is little knowledge about processes in complex environmental media. For instance, the sorption processes in soils crucially influence accumulation, transport and/or release into other media (water, biota, etc.). Our study assessed the sorptivity of copper oxide nanoparticles (CuO-NPs) in comparison to copper ions (Cu²⁺) in batch experiments. The results showed significant differences in the solid to liquid distribution at equilibrium and indicated much stronger sorption of CuO-NPs at soil components compared to Cu²⁺. The sorption isotherms of both variants were fitted to the Freundlich equation showing clear differences of the Freundlich parameters K_F and n . The values for Cu²⁺ sorption were in the range of agricultural soils in Germany (log K_F : 2.6–4.1, n : 0.9–1.6). On the contrary the isotherms for the CuO-NP experiments were strongly shifted to the solid phase (log K_F : 4.0–9.0, n : 1.3–3.7). Both Cu²⁺ and CuO-NP sorptions (expressed as log K_F) were significantly correlated ($P < 0.05$) to pH, carbonates, soil organic carbon and amorphous Fe in the soils. However, a larger data set is needed to generate reliable statistical results. Further, more research is required to identify reasons for the detected differences in sorption behavior between nanoparticulate copper and copper ions.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Nanoparticles (NPs) are characterized by at least one average dimension of <100 nm and have special physical and chemical properties based on their size, distribution, morphology and phase (Christian et al., 2008; Nel et al., 2006). Therefore, NPs may differ considerably from their bulk counterparts resulting in different behaviors in environmental systems and organisms (Taylor and Walton, 1993). As a result of increasing industrial production, the release of engineered nanoparticles (ENPs) into the environment is highly probable (Biswas and Wu, 2005; Ma et al., 2010; Nel et al., 2006). Furthermore, many studies demonstrated adverse effects (toxicity) of NPs on plants and other organism (e.g. Karlsson et al., 2008; Midander et al., 2009; Mishra and Kumar, 2009; Nair et al., 2010; Navarro et al., 2008; Nowack and Bucheli, 2007). Such NP-related adverse effects are very complex and strongly depend on the physico-chemical characteristics and interrelation of these properties. Luyts et al. (2013) therefore linked specific properties of NPs separately to their toxicity. Regarding metallic NPs, additional toxicity may be caused by dissolution of metal ions from the particles or by involved redox-processes.

The present study focuses on copper oxide nanoparticles (CuO-NPs) which are widely used in industrial production (e.g. electrics, ceramics, films, polymers, inks, metallics, coatings) and have specific optical, electrical, and catalytic properties (e.g. Lee et al., 2008). Copper is an essential element for organisms but is toxic above a species-dependent tolerance limit. Several recent studies revealed differences in toxicity of copper salts or ions compared to nanoparticulate copper (Amorim and Scott-Fordsmand, 2012; Gomes et al., 2012; Griffitt et al., 2008; Meng et al., 2007). These studies also indicated that the negative effects were not fully caused by released Cu ions from the particles, but primarily induced nanoparticle-specific. Though dissolved metal ions may contribute to toxicity, more stable particles can accumulate and persist inside an organism (Midander et al., 2009). Nair et al. (2010) summarized the effects of metallic NPs (including CuO-NP) on plant growth and suggested that an aggregation/agglomeration of NPs may block pores and channels resulting in higher phytotoxicity of the metal ions which are more mobile within plants. Nevertheless, studies of Lee et al. (2008) and Stampoulis et al. (2009) indicated that comparatively high concentrations of copper nanoparticles are needed to cause visible effects on plant vitality where plant species was an important influencing factor.

However, there is a lack of knowledge about mobility and sorption behavior of metallic NPs in soils as crucial accumulation and transfer zone as well as potential source for NPs in ecosystems (Klaine et al., 2008; Ma et al., 2010). The main problems of investigating metallic

* Corresponding author.

E-mail addresses: dorit.julich@tu-dresden.de (D. Julich), stefan.a.gaeth@umwelt.uni-giessen.de (S. Gäth).

NPs in the complex medium soil are the separation of natural NPs (colloids) from ENPs and the implementation of an appropriate experimental set-up (homogeneous mixing, prevention of aggregation, etc.). Additionally, there is still no information available on dissolution and transformation processes of metallic NPs after addition to a test medium which considerably will influence their fate and effects in the terrestrial environment (Klaine et al., 2008). In general, soils provide a large and reactive sink for substances with high surface reactivity. Strong sorption processes of metallic NPs in soils are therefore conceivable (Klaine et al., 2008). Several studies assessed the behavior of metallic NPs in porous or artificial soil media and demonstrated the dependency of ENPs-mobility from properties of the nanoparticles, test media and test conditions like solution pH and ionic strength (Christian et al., 2008; Fang et al., 2009; Jones and Su, 2012; Lecoanet et al., 2004; Nowack and Bucheli, 2007). However, porous media cannot sufficiently represent complex soil systems where sorption processes on heterogeneous soil constituents occur. Fang et al. (2011) examined the copper transport in soil columns in the presence and absence of TiO₂-NPs and derived pedotransfer functions (Freundlich and Langmuir) to describe the sorption processes. Collins et al. (2012) demonstrated in a field study that Cu- and ZnO-NPs are not completely adsorbed to soil constituents but are mobile in agricultural soils. The sorption of metallic NPs on soil colloids (e.g. clay, organic matter, iron oxide, other minerals) or incorporation into such colloids may be of particular relevance for metal transport through soil profiles (Gilbert et al., 2009; Klaine et al., 2008).

In the presented study we examined the sorption behavior of copper oxide nanoparticles in comparison to copper ions in different soils by batch experiments. Batch experiments are a common method to assess the sorption behavior of heavy metals in soil where the effect of contaminant concentration on sorption processes can be included by conduction tests with varying spike concentrations (Krupka et al., 1999). Besides ionic strength and pH value of the batch solution, which affect the position of the sorption isotherm (Utermann et al., 2005) considerably, the size distribution (aggregation/agglomeration) will influence the results of the experiments with nanoparticles (Bian et al., 2011). However, it has to be considered that batch experiments provide the liquid/solid partitioning at equilibrium (K_D value) but contain no information on behavior in flow conditions and on metal bonding forms (ion exchange, chemisorptions, bound to complexes and/or precipitates). The main questions in our study were: (1) are there differences in sorption behavior of Cu²⁺ ions and CuO-NPs? (2) Can sorption isotherms for both Cu²⁺ and CuO-NP describe sorption processes? (3) Which soil parameters influence Cu²⁺/CuO-NP sorption?

2. Materials and methods

2.1. Soil samples

In this study, six different top soils from agricultural managed sites in Hesse/Germany were analyzed. The sampling strategy and information about local characteristics are given in Z rner (2010). The main parameters for the selected soils are listed in Table 1. The dried (40 °C) soil

samples were sieved for 2 mm and stored at room temperature. The particle size distribution was analyzed by K ohn-pipette procedure (German standard DIN 18123). Soil pH values were determined in 0.01 M CaCl₂ suspension with a soil/solution ratio of 1:2.5 wt/vol and the content of carbonates was measured with a Scheibler-apparatus according to the German standard DIN 19684-5. The analysis of soil organic carbon (SOC) was conducted with a C/N-Analyzer (German standard DIN ISO 10694). Cation exchange capacity CEC was calculated according to Krogh et al. (2000) using measured SOC and clay contents (Eq. (1)).

$$CEC = 0.95 + 2.90 * 1.72 * SOC + 0.53 * clay. \quad (1)$$

The background concentrations of Cu in soil were determined by aqua regia digestion for total Cu contents and by extraction with 0.025 M Na₂-EDTA (90 min, soil/solution ratio 1:10 wt/vol) to estimate adsorption involved Cu (potentially mobile fraction) (Welp and Br ummer, 1999; Z rner, 2010). The contents of amorphous iron (Fe_{ox}), manganese (Mn_{ox}) and aluminum (Al_{ox}) were determined by extraction with oxalate (Schlichting et al., 1995). All extracts were measured by inductively coupled mass spectroscopy (ICP-MS Agilent 7500ce) (Table 1).

2.2. Copper ions and nanoparticles

For the sorption experiments with Cu²⁺ ions, the spike Cu solutions were prepared from copper(II)-nitrate-trihydrate (Cu(NO₃)₂ * 3H₂O) in deionized water. The CuO-NPs were purchased from IoLiTec (Ionic Liquid Technology GmbH, Germany) as dispersion in water (100 g CuO/L water). The particle size provided by IoLiTec was in the range from 40 to 80 nm. A nanoparticle tracking analysis (NTA) for CuO-NPs diluted in water was conducted on a NanoSight LM14 device (NanoSight Ltd., Amesbury, UK) with a 532-nm laser (50 mW). The results revealed a heterogeneous distribution of the particle sizes of the manufactured NPs with a mean size of 173 nm (sd 75 nm). To achieve well mixed dispersion and to minimize aggregation and agglomeration, the nanoparticle solution was shaken and ultrasonicated (stabilization step) before applied in the batch experiments (cf. Lee et al., 2008).

2.3. Batch experiments

The batch sorption experiments were performed by mixing 10 g air dried soil (<2 mm) with 25 mL of 0.01 M Ca(NO₃)₂ solution, spiked with different amounts of Cu (copper(II)-nitrate-trihydrate) and CuO-NPs respectively, all in duplicates. Since the initial levels in the nanoparticle variants were adjusted to copper oxide-levels, the effectively added Cu concentrations of the single levels are lower compared to the Cu²⁺ variants (Table 2). The soil-solution mixtures were shaken horizontally for 16 h at room temperature. Subsequently, the samples were centrifuged at 1500 rpm for 30 min and filtered through disposable 0.45 µm syringe filters. For stabilizing the samples until Cu analysis they were immediately acidified with 150 µL HNO₃. The Cu concentrations were analyzed with ICP-MS (Agilent 7500ce).

Table 1
Selected soil characteristics of the six test soils (agricultural top soils from Hesse/Germany).

Sample	pH _{CaCl₂} [–]	CaCO ₃ [wt.%]	SOC [wt.%]	CEC ^a [cmol _c kg ⁻¹]	Sand [wt.%]	Silt [wt.%]	Clay [wt.%]	Cu _{tot} ^b [mg kg ⁻¹]	Cu _{EDTA} ^c [mg kg ⁻¹]
A	7.1	0.08	1.09	15.8	46.2	36.0	17.8	13.12	3.49
B	6.7	0.05	1.26	18.2	17.0	62.4	20.6	15.80	5.15
C	7.4	0.64	1.49	26.3	3.3	62.9	33.8	17.77	5.44
D	6.2	0.03	0.99	14.6	29.7	53.9	16.4	14.13	4.04
E	5.4	0	0.91	15.6	44.3	36.7	19.0	13.73	2.96
F	5.8	0	1.18	24.7	3.6	62.7	33.7	17.32	4.11

^a CEC calculated from Eq. (1) (Krogh et al., 2000).

^b Total Cu content in soil (aqua regia digestion).

^c Na₂-EDTA-extractable Cu content in soil.

Download English Version:

<https://daneshyari.com/en/article/4573311>

Download Persian Version:

<https://daneshyari.com/article/4573311>

[Daneshyari.com](https://daneshyari.com)