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Impact of water chemistry on the behavior and fate of copper nanoparticles☆

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ABSTRACT

A full-factorial test design was applied to systematically investigate the contribution and significance of water chemistry parameters (pH, divalent cations and dissolved organic carbon (DOC) concentration) and their interactions on the behavior and fate of copper nanoparticles (CuNPs). The total amount of Cu remaining in the water column after 48 h of incubation was mostly influenced by divalent cation content, DOC concentration and the interaction of divalent cations and DOC. DOC concentration was the predominant factor influencing the dissolution of CuNPs, which was far more important than the effect of pH in the range from 6 to 9 on the dissolution of the CuNPs. The addition of DOC at concentrations ranging from 5 to 50 mg C/L resulted in a 3—5 fold reduction of dissolution of CuNPs after 48 h of incubation, as compared to the case without addition of DOC. Divalent cation content was found to be the most influential factor regarding aggregation behavior of the particles, followed by DOC concentration and the interaction of divalent cations and DOC. In addition, the aggregation behavior of CuNPs rather than particulate dissolution explained most of the variance in the sedimentation profiles of CuNPs. These results are meaningful for improved understanding and prediction of the behavior and fate of metallic NPs in aqueous environments.

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1. Introduction

Metallic nanoparticles (NPs) are increasingly applied in industrial and consumer products. The release of NPs into the aquatic environment can occur via different routes like industrial and municipal wastewater discharges (Boxall et al., 2007), runoff (Osmond and McCall, 2010) and leaching from consumer products (Hendren et al., 2011). Fueled by the inevitable release of NPs into the aqueous environment, concern about the adverse effects of these materials on aquatic biota has been growing. Among other particles, copper NPs (CuNPs) have been demonstrated to be highly toxic to a wide range of aquatic organisms (Hua et al., 2014; von Moos and Slaveykova, 2014; Song et al., 2015). It is therefore essential to comprehensively understand the behavior and fate of CuNPs in the aquatic environment across a range of water chemistry, in order to better interpret and predict their hazards to organisms.

After being emitted into aquatic environments, NPs are subject to undergo a series of environmental processes. These processes include dissolution and aggregation and subsequent sedimentation, which consequently affect their ultimate fate, bioavailability and hazards to organisms. Currently, it is widely known that the behavior and fate of NPs are highly dependent on the water chemistry. In particular, environmental parameters like pH, electrolytes (especially divalent cations) and natural organic matter (NOM) can strongly influence the ultimate fate of NPs in the environment. For example, pH can affect the aggregation and dissolution of metallic NPs by influencing the surface potential of the NPs (von der Kammer et al., 2010; Peng et al., 2017). The divalent cations Ca^{2+} and Mg^{2+} are able to efficiently compress the electrical double-layer of NPs and consequently enhance aggregation of NPs (Zhang et al., 2009; Van Hoecke et al., 2011). NOM has been widely reported to enhance the stability of metallic NPs via electrostatic and/or steric repulsion (Gao et al., 2012; Romanello and Fidalgo de Cortalezzi, 2013), and to alter their dissolution profiles through chelation and/or complexation of the metallic NPs (Majedi et al.,

2014; Wang et al., 2015). Destabilizing effects of NOM on metallic NPs have also been reported, especially in the presence of divalent cations. This is due to the formation of bridges between NOM and cations (Stankus et al., 2011). Nevertheless, few studies have systematically investigated the issue of the extent in which environmental parameters present at environmental relevant concentrations affect the behavior and fate of NPs (Majedi et al., 2014; Son et al., 2015). This is amongst others due to a lack of full-factorial experiments to quantitatively investigate the individual and interactive effects of each environmental parameter on the behavior and fate of NPs in environment.

In this study, a factorial test design was applied to systematically investigate the behavior and fate of CuNPs in various aqueous matrices. The aim of this study is to evaluate the contribution and significance of each environmental parameter (i.e., pH, divalent cation content, and NOM concentration) and their interactions to the variations of behavior and fate of CuNPs across a range of water chemistry. This study is meaningful for improving our understanding and predictive potential of behavior and fate of NPs in freshwater environments.

2. Materials and methods

2.1. Preparation of CuNP suspensions

CuNPs (spherical surface area 30–50 m^2/g; purity 99.9%) were purchased from IoLiTec, with a nominal size of 25 nm. Stock suspensions of CuNPs (250 mg/L) were freshly prepared in MilliQ water after 30 min of bath-sonication to disperse the particles, prior to each experiment.

For the study design, CuNP suspensions under a range of water chemistry conditions were prepared. The divalent cation composition of the exposure media was modified by adding $CaCl_2 \cdot 2H_2O$ and $MgSO_4 \cdot 7H_2O$ in a fixed molar ratio of 4:1. Aldrich humic acid (sodium salt) (HA) was used as a surrogate to natural dissolved organic carbon (DOC). A stock solution was prepared by dissolving HA in 0.002 N NaOH solution, followed by stirring for 24 h, filtration through a 0.2 μm cellulose acetate membrane, and storage at 4 °C prior to use. The total organic carbon (TOC) content of the prepared stock HA solutions was determined by a TOC analyzer (TOC-VCPH, Shimadzu Corporation). The pH values of the exposure media were adjusted by 0.1 M NaOH or 0.1 M HCl to reach values in between 6 and 9. It is worth to point out that the pH of the exposure media was adjusted to the desired value after mixing the DOC with the CuNP suspensions. CuNP suspensions were prepared freshly for all aqueous matrices tested. A factorial experiment design was adopted with 3 pH (6, 7.8, 9) × 3 divalent cation concentrations (0, 2.5, 10 mM) × 4 DOC concentrations (0, 5, 25, 50 mg C/L, Table 1). The range of each parameter employed in this study encompasses the range commonly observed in natural environments (Vijver et al., 2008; Ottofuelling et al., 2011; Hammes et al., 2013).

2.2. CuNP characterization

The morphology and primary size of the CuNPs in the exposure medium with 2.5 mM of divalent cations (composition of $CaCl_2 \cdot 2H_2O$ and $MgSO_4 \cdot 7H_2O$ in a fixed molar ratio of 4:1) and pH of 7.8 were characterized using transmission electron microscopy (TEM, JEOL 1010, JEOL Ltd., Japan). The hydrodynamic diameters of CuNP suspensions during 48 h of incubation were determined in triplicate by dynamic light scattering (DLS) on a Zetasizer Nano-ZS instrument (Malvern, Instruments Ltd., UK). At the same time points, the zeta-potential of each NP suspension was measured by ZetaPALS software based on the Smoluchowski equation. During the 48 h of incubation, all the prepared NP suspensions were stored

Table 1
Overview of the systematic modification of the matrices used for testing the fate of CuNPs.

Trial no.	pH value	Cation conc. (mM)	DOC conc. (mg/L)
1	6	0	0
2	6	0	5
3	6	0	25
4	6	0	50
5	6	2.5	0
6	6	2.5	5
7	6	2.5	25
8	6	2.5	50
9	6	10	0
10	6	10	5
11	6	10	25
12	6	10	50
13	7.8	0	0
14	7.8	0	5
15	7.8	0	25
16	7.8	0	50
17	7.8	2.5	0
18	7.8	2.5	5
19	7.8	2.5	25
20	7.8	2.5	50
21	7.8	10	0
22	7.8	10	5
23	7.8	10	25
24	7.8	10	50
25	9	0	0
26	9	0	5
27	9	0	25
28	9	0	50
29	9	2.5	0
30	9	2.5	5
31	9	2.5	25
32	9	2.5	50
33	9	10	0
34	9	10	5
35	9	10	25
36	9	10	50

Conc. = concentration.

in a climate chamber under a 16:8-h light-dark cycle (20 ± 1 °C). To maintain the desired pH value during the 48 h incubation, the pH of the exposure media was adjusted carefully with 0.1 M NaOH or 0.1 M HCl every 24 h. In addition, the actual divalent cation concentration (i.e., Ca^{2+} and Mg^{2+}) and actual DOC concentration in exposure suspensions were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) and listed (Table S1).

The variations of the concentration of total Cu and dissolved Cu-ions shedding from CuNPs in the water column, were monitored within 48 h of incubation. The actual concentration for each CuNP exposure suspension was around 800 μg/L, which is in the range (10–920 μg/L) of the predicted CuNP concentration in aquatic environments (Chio et al., 2012). The prepared CuNP suspensions across a range of water chemistry, as prepared according to Table 1, were stored in the climate chamber (16:8-h light-dark cycle; 20 ± 1 °C). At each sampling point (1, 12, 24, 36 and 48 h after preparation), two independent CuNP suspensions with the same water chemistry as duplicates were used to analyze the concentration of each Cu fraction. For each exposure suspension, a 5 mL sample collected carefully from the position around 2 cm below the surface of each NP suspension, was digested by addition of 1 drop of 65% nitric acid at room temperature for at least 1 d prior to ICP-OES analysis. In this way, the total amount of Cu remaining in the water column, including dissolved Cu and suspended particulate Cu was determined. Kinetics of the sedimentation of CuNPs within 48 h of incubation could be analyzed by determining the change of concentration of total Cu in the water column. At each sampling point,