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Influence of daylight on the fate of silver and zinc oxide nanoparticles in natural aquatic environments☆

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ABSTRACT

Nanoparticles, such as silver (Ag-NP) and zinc oxide (ZnO-NP), are increasingly used in many consumer products. These nanoparticles (NPs) will likely be exposed to the aquatic environment (rain, river, lake water) and to light (visible and UV) in the products where they are applied, or after those products are discharged. Dissolution of Ag-NP and ZnO-NP is an important process because the dissolved Ag^+ and Zn^{2+} are readily available and toxic for aquatic organisms. The objective of this study was to investigate the role of daylight (UV and visible) for the fate of engineered Ag-NP and ZnO-NPs in different types of natural waters. Ag-NP and ZnO-NP were exposed to rainwater, river Rhine, and lake waters (Greifen, Lucerne, Cristallina, Gruère) under different light conditions (no light, UV 300–400 nm and visible light 400–700 nm) for up to 8 days. Stronger agglomeration of Ag-NP was observed in the waters with higher ionic strength in comparison to those with lower ionic strength. Visible light tended to increase the dissolution of Ag-NP under most natural water conditions in comparison to dark conditions, whereas UV-light led to decreased dissolved Ag^+ after longer exposure time. These effects illustrate the dynamic interactions of Ag-NP with light, which may lead both to increased oxidation and to increased reduction of Ag^+ by organic compounds under UV-light. In the case of ZnO-NP, agglomeration occurred at higher ionic strength, but the effects of pH were predominant for dissolution, which occurred up to concentrations close to the solubility limit of ZnO(s) at pH around 8.2 and to nearly complete dissolution of ZnO-NP at lower pH (pH 4.8–6.5), with both visible and UV-light facilitating dissolution. This study thus shows that light conditions play an important role in the dissolution processes of nanoparticles.

1. Introduction

Silver nanoparticles (Ag-NP) and zinc oxide nanoparticles (ZnO-NPs) are among the most widely used engineered nanoparticles and are present in many nanotechnology based consumer products (http://www.nanotechproject.org). These nanoparticles will thus likely be released into the aquatic environment (rain, river, lake water) and exposed to light (visible and UV) in the products where they are applied, or after those products are discharged, as demonstrated by model predictions of the environmental fate of nanoparticles (Sun et al., 2015, 2016). The release of Ag-NPs from commercial textiles during washing and from outdoor facades after rainfall events was reported in several studies (Geranio et al., 2009; Kaegi et al., 2010). ZnO-NP are used in sunscreens and other cosmetic products from which they can easily be released to the aquatic environment (Smijs and Pavel, 2011). After exposure to aqueous media, the particles will likely be transformed by forming agglomerates and by partly dissolving (Unrine et al., 2012; Li et al., 2010; Tejamaya et al., 2012; Cheng et al., 2011; Odzak et al., 2014).

Toxicity of metallic nanoparticles may be due to internalization of nanoparticles, depending on organism types as well as on environmental conditions, and/or to the release of dissolved cations, e.g. Ag^+ (Navarro et al., 2008, 2015; Yang et al., 2012; Yue et al., 2015). Toxicity may also be linked to the catalytic properties of metallic nanoparticles and the redox reactivity of nanoparticle surfaces, leading to the production of reactive oxygen species (ROS) (Adams et al., 2006; Auffan et al., 2009; Lyon et al., 2007; Skjolding et al., 2016). Dissolution is a critical step in determining nanoparticle fate and bioavailability. Toxic effects of dissolved metal forms (ionic, labile inorganic and organic complexes) are very well documented (Batley et al., 2004; Campbell et al., 2002; Sigg and Behra, 2005). In particular, Ag^+ ions are highly toxic to various

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aquatic organisms (Behra et al., 2013; Navarro et al., 2008, 2015; Xiu et al., 2012; Yang et al., 2012). Toxicity of zinc oxide nanoparticles has been shown to be mostly dependent on dissolved zinc ions (Franklin et al., 2007; Tong et al., 2015). In contrast to uptake of dissolved ions, internalization of nanoparticles in cells does not appear to occur in algae (Adam et al., 2015; Piccapietra et al., 2012a), but has been observed for example in fish cells by endocytic mechanisms (Yue et al., 2015).

Dissolution is thus an important process that determines the fate and effects of NPs. The fate of nanoparticles in natural waters is also critically influenced by agglomeration, which results in larger particles with different properties. Dissolution and agglomeration depend on the nanoparticle characteristics (e.g. type, size, coatings) and on environmental conditions, e.g. pH, ionic strength, DOC, oxygen content in water and on exposure to daylight. (Odzak et al., 2014; Unrine et al., 2012; Navarro et al., 2015; Liu and Hurt, 2010). Whereas effects of water composition with respect to pH, natural organic matter and other components have already been extensively examined, few studies have considered effects of daylight or of UV-light on nanoparticle dissolution and agglomeration (Cheng et al., 2011; George et al., 2014; Gorham et al., 2012; Yu et al., 2016). Possible effects of light include formation of ROS (reactive oxygen species), especially by interactions with natural organic matter, and thus increased oxidation processes. On the other hand, reduction processes of silver-ligand complexes may also be favoured in the presence of light, as demonstrated for example by Yin et al. (2012) and Hou et al. (2013) for reduction of Ag^+ in natural waters and in the presence of humic acids. The combination of these processes may thus lead to both increased dissolution and agglomeration of Ag-NP, as shown for example by Gorham et al. (2012). In a study on behaviour of Ag-NPs exposed to natural aqueous media and sunlight, Yu et al. (2014) suggest that Ag-NPs would undergo oxidation and reduction simultaneously, along with release of Ag^+ ions and formation of “new” Ag-NPs. Another study on the toxicity of Ag-NPs under simulated solar light indicated that surface oxidation and dissolution to Ag^+ caused increased bioavailability of silver to a fish cell line and to zebrafish embryos (George et al., 2014). These effects are expected to be of lesser importance for ZnO-NP, as ZnO dissolution is mostly affected by pH. Nevertheless, it was shown that under UV-light dissolution of ZnO-NP and ROS production increased (Adam et al., 2015; Ma et al., 2014).

The results of our previous study on the fate of Ag-NP and ZnO-NPs, exposed to five different natural waters under dark conditions, showed that agglomeration and sedimentation were important processes for both NPs, but that large differences were apparent with respect to dissolution (Odzak et al., 2015). Relatively small amounts of Ag-NP dissolved (1–4%) compared to 30–60% dissolved ZnO-NPs. Low ionic strength led to a better colloidal stability of nanoparticles. Natural organic matter, as measured by dissolved organic carbon (DOC), was on one hand stabilizing the nanoparticles, and on the other hand complexing the dissolved Ag^+ or Zn^{2+}. Dissolution of Ag-NP and ZnO-NP in natural aqueous media in the dark was pH dependent, with higher dissolved Ag^+ and Zn^{2+} at lower pH, whereas DOC effects did not show a clear tendency (Odzak et al., 2015).

We hypothesize that agglomeration and dissolution may be enhanced when Ag-NP and ZnO-NPs in natural waters are exposed to daylight and that these processes are dependent on the natural water composition, in particular with respect to natural organic matter content and to pH. The main objective of this study was to investigate the role of daylight (UV and visible) on the fate of engineered Ag-NP and ZnO-NPs in different types of natural waters. For this purpose, Ag-NP and ZnO-NPs were exposed to several natural waters, namely rainwater, river (Rhine) and lake waters (Greifen, Lucerne, Cristallina, Gruère), which represent a typical range of composition, and to various light conditions (no light, UV (300–400 nm) and visible light (400–700 nm)). Agglomeration of these NPs and dissolution to Ag^+ and Zn^{2+} were examined over a period of 8 days as a function of these various parameters.

2. Materials and methods

2.1. Selection of nanoparticles

For this study we used silver nanoparticles (Ag-NP) and zinc oxide nanoparticles (ZnO-NPs). Ag-NPs coated with citrate were produced by NanoSys, Wolfhalden, Switzerland. The particles were supplied in a water suspension with total Ag concentration of 1 g L^{-1} and average size of 15 nm. ZnO-NPs were produced by Bühler AG and supplied in an ethanol suspension (40 wt % ZnO) with particle size of $\leq$130 nm, as given by the producer.

2.2. Sampling of natural waters

The experiments were performed in different types of natural water, with a wide range of pH, ionic strength and dissolved organic carbon (DOC) content, which were collected in Swiss aquatic systems: rainwater from an urban/industrial area (Dübendorf); Lake Greifen (Maur), a eutrophic lake; Lake Lucerne (Kastanienbaum), an oligotrophic lake; Lake Cristallina (Val Maggia), a mountain lake with low ionic strength; Etang de la Gruère (Saignelégier), a peat bog lake with high humic acid content and river Rhine (Rheinsfelden), which is representative with respect to ionic strength, calcium and DOC concentrations for Swiss rivers in the midland region.

Water samples were collected from the shore at around 2 m distance and depth of 0–20 cm, using a Teflon (PTFE) 1L-bucket on a 1.5 m plastic stick (HDPE). At the experimental sites the water temperature and pH were measured. At the same time the water was sampled (in duplicate) for total and dissolved metal concentrations and for major elements. For total metal concentration, the samples were taken in previously acid cleaned 15-mL plastic vials, acidified (HNO_3, Merck Suprapure) at the site and stored until being analysed by ICP-MS (inductively coupled plasma mass spectrometry). For dissolved metal concentrations in natural waters the samples were filtered at the site using 0.2 μm filter disks (Sartorius) and plastic syringes. Water samples for the experiments were also filtered through 0.2 μm cellulose nitrate filters (Sartorius) immediately after return to the laboratory.

2.3. Experimental set-up

All experiments were performed at constant room temperature (22.5 ± 0.1 °C) and at pH close to original values measured at the sampling sites. To adjust pH to its original values, water samples were spiked with HNO_3 or NaOH (Merck, Suprapure).

The concentration of Ag-NPs used throughout the study was 0.22 mg L^{-1} (2 μM), and experiments with ZnO-NPs were run at the concentration of 4.1 mg L^{-1} (50 μM). These concentrations were selected to obtain well measurable dissolved Ag and Zn concentrations. Before use in these experiments, Ag-NPs in their original suspension and ZnO-NPs after dilution in deionized water to the concentration of 1 g L^{-1} were ultrasonicated for 30 min in ultrasonic bath Bandelin Sonorex RK 52. Nanoparticles were suspended in natural aqueous media with the composition described above for a maximum of 8 days. During the experiments, the water