



Silver nanoparticles in seawater: A dynamic mass balance at part per trillion silver concentrations



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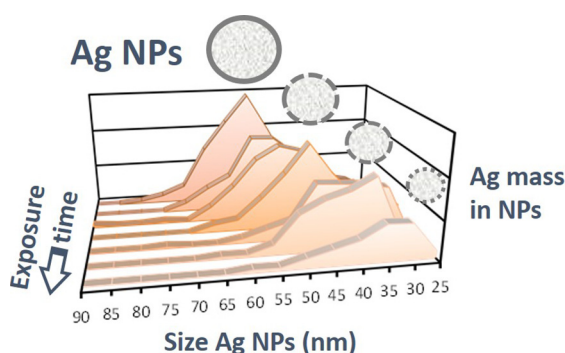
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HIGHLIGHTS

- spICP-MS was used to investigate the transformation of Ag NP in seawater medium.
- Dissolution was the predominant process of Ag NP transformation.
- Higher stability of BPEI-coated Ag NPs was observed for all investigated NP sizes.
- An extra Ag NP peak was observed in the low size range at high spiking levels.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the dynamic processes affecting silver (Ag) nanoparticles that have been spiked into seawater at environmentally relevant concentrations (200 and 2000 ng Ag L⁻¹). Seawater samples were taken at regular time intervals from multiple microcosm tanks and analysed rapidly, without any sample preparation, using a recently developed flow injection on-line dilution single particle inductively coupled plasma mass spectrometry method. Dissolution was found to be the predominant process of Ag nanoparticle transformation, with its rate being influenced by the type and thickness of the nanoparticle organic coating. More specifically the branched poly(ethyleneimine) coating provided additional stability to the 40 and 60 nm Ag nanoparticles that were tested, compared to the poly(vinylpyrrolidone) coated ones. At high Ag nanoparticle spiking levels and after 24 h of exposure an extra Ag-containing nanoparticle peak appeared at the low range of the NP size distribution histogram. This peak corresponds to Ag-containing particles that contain Ag mass equivalent to 25–30 nm Ag nanoparticles (assuming spherical shape). However, the composition and the “real” size of these particles remains unknown as the particles may have formed from the in-situ reduction of dissolved silver or they originate from other processes involving nanocrystal formation, as has been shown to occur in sewage sludge, or interaction with natural organic matter. Overall, this study provides additional insight into the physicochemical mechanisms behind Ag nanoparticle behavior in marine media.

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1. Introduction

The novel properties arising from the size reduction of bulk materials to the nanometer scale has created a whole new range of applications in medicine, environmental monitoring and remediation, optics, energy harvesting and healthcare (Lohse and Murphy, 2012). However, current use as well as projected high use of such materials has been translated into obvious concerns about the potential impact of nanomaterials on ecosystems, since they have been shown to have an enhanced ecotoxicological effect compared to bulk materials (Hansen and Baun, 2012; Pettitt and Lead, 2013). Hence, it is crucial to assess their behavior in different media, including how environmental parameters influence their dissolution and aggregation patterns (Pasricha et al., 2012).

Paradigmatic is the case of silver (Ag) in the form of nanoparticles (NPs), whose dynamic balance between its elemental state (Ag(0)) and its oxidized form (Ag(I)) is intensified by its relatively low redox gap (i.e. -0.80 V). Recently, the Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) has deliberated an opinion on the toxicity of nano-silver where it stated that toxic effects on aquatic organisms are unlikely, but cannot be excluded (SCENIHR, 2014), thus a thorough monitoring of Ag NPs in all different aquatic media is of paramount importance for improved exposure and modeling studies.

Several studies have already dealt with Ag NP interactions in the presence of organic matter (Gao et al., 2012; Sharma et al., 2014; Yang et al., 2014) and sunlight (Hou et al., 2013; Yin et al., 2012; Yu et al., 2014), as well as their transformation as a function of pH (El Badawy et al., 2010; Pokhrel, 2014) and ionic strength (Chambers et al., 2014; El Badawy et al., 2012) of the matrix in which they reside. Although these investigations have only “shined a dim light” on Ag NP behavior, they have not clarified what occurs at environmentally relevant concentrations, e.g. ng Ag L^{-1} as opposed to the μg or mg Ag L^{-1} used in most studies. The latter high concentrations are required because of the insufficient limits of detection and matrix effects observed when using conventional techniques, namely dynamic light scattering (DLS), nanoparticle tracking analysis (NTA), electron microscopy and ultraviolet–visible spectroscopy.

Recently, the development and application of single particle (sp) inductively coupled plasma mass spectrometry (ICP-MS) has made it possible to monitor the fate of Ag NPs at such low concentrations in complex media. Indeed, as this technique is based on detecting individual metal-containing NPs from the metal atom ion plumes generated in the high temperature argon plasma of the ICP-MS (Laborda et al., 2014, 2013), their number concentration, metal mass fraction and metal equivalent diameter (i.e. by assuming a spherical shape) can be determined (Liu et al., 2014; Mitrano et al., 2012).

Thus spICP-MS is potentially a powerful tool for assisting in routine risk assessment of nanomaterials thanks to its rapid analysis capabilities and minimum sample pre-treatment requirements (Mitrano et al., 2014). More specifically, assessment of metal-containing nanomaterial fate and transformation has been performed by spICP-MS mainly in freshwater, drinking water and estuarine river matrices (Mitrano et al., 2014; Heithmar, 2011), with limited applications in seawater systems (Heithmar, 2011). With respect to the latter, a suitable method for monitoring Ag NPs by spICP-MS in seawater media, without prior seawater dilution, has been lacking. Indeed, the analysis of high salt matrices necessitates extensive dilution or matrix removal prior to analysis with ICP-MS since it causes cone clogging, spectral and non-spectral interferences. However, extensive sample dilution or matrix removal may cause NP artifact formation, e.g. de-agglomeration or agglomeration, respectively, and should therefore be avoided.

The determination of the mass balance for engineered Ag nanoparticles in seawater will allow for their modelling in exposure studies, in order to define their repartition in the total environment more accurately. At present, our understanding of Ag NP mass balance, resulting from

physical as well as chemical transformations occurring in complex matrices, have been limited to studies in wastewater (Gartiser et al., 2014; Kaegi et al., 2011), biofilm formation (Han et al., 2016; Herrling et al., 2016; Hsueh et al., 2015) and freshwater systems (Auffan et al., 2014).

The objective of the present study was to investigate Ag NP behavior in seawater media by employing the recently developed flow injection on-line (FI-OD) spICP-MS methodology, which does not require sample pretreatment, for NP analysis in seawater microcosm experiments. Of particular interest was the investigation of how physicochemical properties of selected Ag NPs, including their initial nominal diameter, as well as their organic coating thickness and type affect their persistence in seawater systems when added at environmentally relevant concentrations.

2. Materials and methods

2.1. Materials

Two different Ag NP organic coatings were selected for this study (branched polyethyleneimine (BPEI) and poly(vinylpyrrolidone) (PVP)) with Ag NPs at two different nominal diameters each, i.e. 40 and 60 nm (NanoXact, Nanocomposix, San Diego, CA, 99.99% silver purity). Other relevant physicochemical properties of the Ag NPs used in this study are listed in the Supplementary information (SI) Table S1.

All other chemicals employed in this work were purchased from Sigma-Aldrich unless stated otherwise. The solutions were prepared by weighing (± 0.1 mg) of the purchased reagents and diluting them using ultrapure 18.2 M Ω cm Milli-Q water (Millipore).

Seawater for the microcosm experiments and for the preparation of standards were collected from the Mediterranean Sea in open water close to the seaside of Gournes, Heraklion (Greece), where the Hellenic Center for Marine Research (HCMR) is located. Its composition in terms of pH, organic matter and dissolved ions is summarized in the SI Table S2. No visible sediments or fish were included in these samples.

2.2. First microcosm experiment

Addition of Ag NPs (AgPVP and AgBPEI at 40 and 60 nm) at a single concentration level for time exposure experiments was performed on 10/2014 by adding each type of Ag NP to oligotrophic seawater contained in separate 10 L low-density Nalgene polyethylene tanks (Fig. S1).

The four types of Ag NPs tested were PVP and BPEI capped, each having nominal diameters of 40 and 60 nm. The Ag NPs added to each microcosm tank resulted in a 200 ng Ag L^{-1} concentration, whereas the exposure was for two days. Each type of Ag NP was added into three tanks in order to account for any batch-to-batch variation of environmental and physical parameters, stirring, organic matter composition, biological and sampling variations. In addition, three tanks were used as controls, i.e. no Ag NPs added to the seawater. The tanks were allowed to float in a large seawater pool which provided thermo-regulation and mild agitation resulting from a central running seawater stream.

2.3. Second microcosm experiment

Addition of Ag NPs (60 nm AgBPEI) at 200 and 2000 ng Ag L^{-1} , for a total seawater exposure time of five days, was conducted at HCMR on 03/2015. Once again 10 L low-density polyethylene tanks were filled with oligotrophic seawater and then individually spiked, in triplicate, with the specified Ag NP concentrations. The tanks were allowed to float in the same seawater pool as already described for the 1st microcosm study.

2.4. spICP-MS

An X-series ICP-MS (Thermo Fischer Scientific, Winsford, UK) was employed for the first microcosm study whereas, in the second

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