

Monitoring the Fate and Transformation of Silver Nanoparticles in Natural Waters

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Received: 11 April 2016 / Accepted: 8 July 2016 / Published online: 20 July 2016
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Abstract There is potential for silver nanoparticles (AgNPs) to be released into surface waters and thus affect aquatic organisms. However, agglomeration, dissolution, surface modifications and chemical speciation are important transformation processes that control the toxicity of AgNPs. Analytical methods are needed to determine the size distribution, mass and form of AgNPs and other silver species in natural waters. Cloud point extraction, single particle inductively coupled plasma mass spectrometry (spICP-MS) and asymmetric flow field flow fractionation with on-line ICP-MS (AF4-ICP-MS) are analytical techniques that show potential for quantitative analysis of AgNPs in aquatic matrices at environmentally relevant concentrations. In this review, we discuss the fate processes for AgNPs in natural waters and the analytical methods that can be used to determine the distribution of AgNPs and their transformation products.

Keywords Nanosilver · Analysis · Fate · Nanoparticles

Background

Silver nanoparticles (AgNPs) are used in several hundred products, including additives to medical equipment, antibacterial creams and clothing (Vance et al. 2015). AgNPs are used primarily because of their high reactivity

and their antibacterial properties. There are concerns about the potential for these nanomaterials to adversely affect the integrity of aquatic ecosystems (Kahru and Dubourguier 2010). Wastewater treatment plant (WWTP) effluents are a major point source, although AgNPs are expected to go through transformations and accumulate in biosolids in these systems (Kaegi et al. 2013; Lombi et al. 2013; Ma et al. 2014). Nonetheless, depending upon the degree of removal of AgNPs in the WWTP, there is potential for AgNPs to be released into rivers and lakes with predicted environmental concentrations (PECs) in the ng L^{-1} range (Gottschalk et al. 2013). However, more accurate estimates of the PECs for AgNPs are difficult to calculate because of a lack of knowledge of critical parameters, including the factors that influence environmental fate and behaviour (Gottschalk et al. 2009). More recent estimates of emissions of nanomaterials into the environment are up to 70 times greater than previous model estimates, due to the rapid increase in production volumes (Sun et al. 2014). Due to analytical challenges, there are few data on measured environmental concentrations (MECs) of AgNPs for comparison to PECs derived from model estimates. There are analytical data that indicate that AgNPs are present at $\sim 1 \mu\text{g L}^{-1}$ in the influent of WWTPs, leading to effluent concentrations in the low ng L^{-1} range (Hoque et al. 2012; Li et al. 2013). In addition to inputs from WWTPs, AgNPs may enter aquatic ecosystems from diffuse sources, such as run-off from agricultural fields treated with biosolids (Blaser et al. 2008).

Once released into aquatic ecosystems, AgNPs can adversely affect aquatic organisms. However, the mechanisms of toxicity of AgNPs are not entirely understood (Völker et al. 2013). It is currently under debate whether toxicity is a nanoparticle-specific effect or is caused by the release of free silver ion (Ag^+) by oxidative dissolution of

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the AgNPs. There is evidence that the majority of AgNP toxicity results from exposure to released Ag^+ (Notter et al. 2014). On the other hand, Laban et al. (2010) showed that AgNPs cause developmental effects in early life stages of fish that were not observed in fish exposed to Ag^+ . The relevance of these modes of toxic action is influenced by the fate of the AgNPs. For instance, Furtado et al. (2015) showed in lake mesocosms spiked with AgNPs that there was very little dissolved silver (which includes Ag^+) present in the natural lake water due to complexation of the dissolved Ag species with organic matter.

Fate

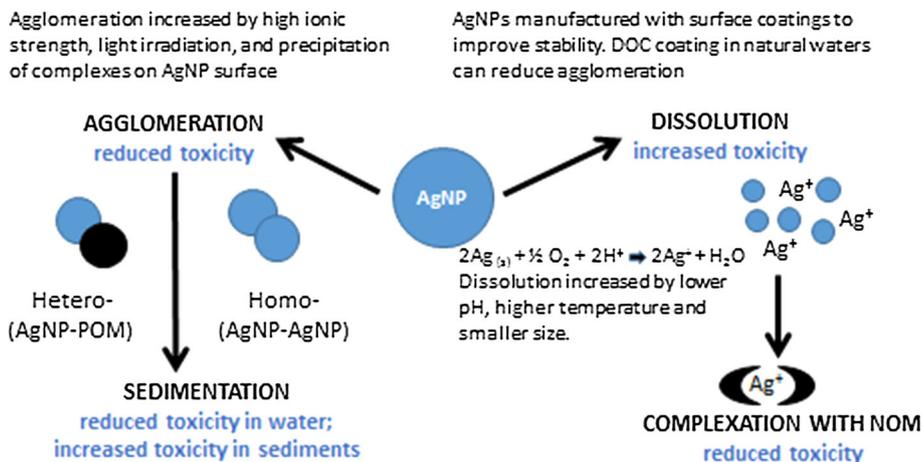
AgNP dissolution and agglomeration are the most important transformation processes that alter fate and toxicity (Unrine et al. 2012). The formation of soluble $\text{AgCl}_{(x)}$ complexes, for instance, did not alter AgNP toxicity to bacteria (Levard et al. 2013), whereas the formation of insoluble $\text{AgCl}_{(s)}$ (Levard et al. 2013) and $\text{Ag}_2\text{S}_{(s)}$ (Choi et al. 2009) greatly reduced bacterial toxicity. Understanding the extent of AgNP dissolution and resulting Ag^+ concentrations in aquatic systems is essential for estimating environmental risks (Fig. 1). The extent of these transformations will depend on physicochemical conditions, such as dissolved organic carbon (DOC), pH, ionic strength, redox, particle specific properties (i.e. size and surface coating), and concentration (Mitreveli et al. 2016).

AgNP dissolution occurs in the presence of dissolved oxygen where Ag^0 at the AgNP surface is oxidized to Ag_2O and “dissolves” to release Ag^+ (Li et al. 2012). However, Zhang et al. (2016) point out that AgNP dissolution can also take place under anoxic conditions. Particle size influences the rate of dissolution (Peretyazhko et al. 2014), and aggregation of nanoparticles has been shown to slow down the rate of dissolution (Liu and Hurt 2010).

Some studies indicate that dissolution is influenced by particle coating (Dobias and Bernier-Latmani 2013), while other studies have shown variable results for the effect of capping agent on rates of dissolution (Mitrano et al. 2014). The physicochemical properties of the surrounding medium also control the rates of dissolution, as this process increases at low pH (Peretyazhko et al. 2014) and is accelerated at high temperatures (Liu and Hurt 2010). Moreover, dissolution of the Ag_2O surface layer can be prevented by the adsorption and accumulation of Ag^+ at the particle surface (Li et al. 2010). In contrast, electrolytes (i.e. Cl^-) can promote dissolution by increasing Ag_2O solubility or replacing adsorbed Ag^+ . However, AgNP dissolution rates are slower at low Cl^- concentrations due to the formation of insoluble $\text{AgCl}_{(s)}$ species, whereas at high Cl^- concentrations, soluble $\text{AgCl}_x^{(x-1)}$ species dominate and increase dissolution (Levard et al. 2013). The presence of DOC in the medium, such as humic acids (HA), can slow dissolution (Liu and Hurt 2010; Mitrano et al. 2014), likely by forming a coating on the nanoparticles' surface or acting as reductants, converting Ag^+ to Ag^0 . In contrast to HA, cysteine, a low molecular weight thiol amino acid, increases dissolution. This pattern may be explained by similar processes to those suggested for Cl^- , or are the result of reduced agglomeration imparted by coating with thiol groups (Gondikas et al. 2012).

Once dissolved, the properties of the surrounding medium will directly determine the fate and toxicity of Ag^+ . Free Ag^+ is unlikely to be present in natural waters at high concentrations due to its cationic nature and strong affinity for ligands (Ratte 1999). In freshwater ecosystems, Ag^+ is expected to preferentially complex with thiol-containing ligands present in DOC, while little complexation to $\text{AgCl}_{(x)}$ is expected due to the low Ag/Cl ratios and because of the much higher stability constants associated with thiols in DOC, compared to Cl^- (Levard et al. 2012). In anaerobic environments where inorganic sulphur is

Fig. 1 AgNP transformations in aquatic ecosystems and their effect on fate and toxicity



present (i.e. S_2^{2-}), silver sulfide complexes will dominate due to their high formation constant, $\log K = \sim 13$ (Levard et al. 2012). Similar patterns are expected in surface waters with very low Ag^+ ($ng\ L^{-1}$) but relatively high inorganic sulphur concentrations (Reidy et al. 2013). The presence of reduced sulphur in oxygenated water is attributed to its complexation with iron, copper or zinc that stabilizes HS^- and S^{2-} species and prevents them from becoming oxidized. Ag^+ is then able to displace iron, copper, or zinc, and bind to the reduced sulphur species (Bianchini and Bowles 2002). Finally, both ionic Ag and complexed Ag also readily adsorb to particulate matter (Ratte 1999).

Besides dissolution, the agglomeration of AgNPs is a fundamental process influencing the ecotoxicology of these particles (Unrine et al. 2012). As illustrated in Fig. 1, AgNPs either agglomerate together (i.e. homo-agglomeration) or with other organic or inorganic particles (i.e. hetero-agglomeration). The latter seems more likely in natural aquatic ecosystems, given the substantially higher concentrations of other particles compared to nanoparticles. Irrespective of the form of agglomeration, the process is often governed by the Derjaguin and Landau, Verwey and Overbeek (DLVO) theory of colloidal stability. This theory suggests that the tendency of AgNPs to agglomerate depends on van der Waals attractive forces overcoming the energy barrier caused by the repulsive forces between particles induced by an electrical double layer on the particles (Hotze et al. 2010). The agglomeration rate is controlled by several factors, including the surface coating of the nanoparticle (Huynh and Chen 2011), as well as the particle concentration and the presence of cations in solution (Mitreveli et al. 2016). In the latter case, multivalent cations in the surrounding medium screen the surface charge, ultimately reducing the electrical double layer that surrounds particles. More specifically, once ion concentrations exceed the critical coagulation concentration, the energy barrier is completely eliminated, resulting in a change in kinetic regimes from slow, reaction limited cluster agglomeration to rapid, diffusion limited cluster agglomeration (Mitreveli et al. 2016). Agglomeration can also be induced by precipitation of Ag complexes on AgNP surfaces that form connections between particles (Li et al. 2012). Conversely, organic matter generally improves stability by adsorbing to AgNP surfaces and inducing steric and electrostatic repulsion (Mitreveli et al. 2016). However, even in waters with elevated natural organic matter, high concentrations of divalent cations will promote aggregation, possibly by bridging between the cations and negatively charged functional groups on the nanoparticle (Stankus et al. 2011).

As a consequence of agglomeration, AgNPs are expected to precipitate out of suspension, reducing exposure and

toxicity to pelagic organisms, but increasing risks for benthic species (Fig. 1), as demonstrated for other nanoparticles (e.g., Dabrunz et al. 2011). At the same time, agglomerated AgNPs are less toxic due to their size and reduced ability to interact with cell membranes and release toxic Ag^+ (Seitz et al. 2015). Thus, it is important to understand the transformations of nanoparticles in aquatic systems. The following section discusses the analytical techniques that may be considered to address this knowledge gap.

Analysis

Currently there are a limited number of analytical techniques that are available for quantifying and characterizing nanoparticles at environmentally relevant concentrations in aquatic matrixes, including their transformation status (Howard 2010). Appropriate techniques and instrumentation are lacking due to the low concentrations of the nanoparticles, the complexity of the matrix, difficulties in sample preparation, artefacts and sample stability, polydispersity, and the lack of reference and standard materials for calibration (von der Kammer et al. 2012). Commonly used techniques for characterizing the size of AgNPs, such as dynamic light scattering (DLS) do not allow for quantification of the nanoparticles and/or lack sensitivity, with detection limits much higher than expected environmental concentrations. Other techniques such as electron microscopy that require isolation of the nanoparticles from the aqueous matrix can introduce artifacts such as aggregation/agglomeration (Laborda et al. 2015). Size fractionation by filtration, cloud-point extraction (CPE), asymmetric flow field flow fractionation with online ICP-MS (AF4-ICP-MS), and single-particle-inductively coupled mass spectroscopy (spICP-MS) are techniques that can be used to quantify the size and/or form (i.e. dissolved versus particulate) of AgNPs at environmentally relevant concentrations (Furtado et al. 2014). These analytical techniques show potential for use in studies of the fate and ecotoxicology of AgNPs.

Fractionation of AgNPs by filtration is frequently used to operationally characterize the size distribution of AgNPs. For instance, Farmen et al. (2012) used filtration to determine the size distribution of Ag in toxicological experiments and defined particulate Ag as that retained by a 0.22 μm membrane and colloidal Ag as that retained by a 10 kDa membrane ($3\ nm > Ag < 220\ nm$). This filtration approach was also used by Furtado et al. (2015) to characterize the size distribution of AgNPs in lake mesocosms. Following this rationale, particulate Ag can be associated with bacteria (0.2–1 μm), algae (>1 μm), and other forms of particulate organic matter, which are commonly referred

to as “seston” in limnological literature. Colloidal Ag would be operationally defined as material with sizes between 3 and 200 nm, which could include AgNPs defined as <100 nm in size. Ag passing through a 3–10 kDa ultrafiltration (UF) membrane has been operationally defined as dissolved Ag (dAg) in the majority of the literature. The dAg includes Ag^+ and Ag^+ complexes that are less than the nominal pore size (i.e. 1–3 nm) of the ultra-filtration membrane (Liu and Hurt 2010). Interactions of AgNP/ Ag^+ with the filter, pore blockage as a result of filter cake formation, and membrane polarization are common artefacts that reduce recovery in the filtrate (e.g. Mitrano et al. 2012a). However, the advantages of filtration include simplicity and the ability to use sensitive analytical techniques (e.g. ICP-MS) to quantify the Ag concentration in each fraction.

CPE pre-concentrates AgNP by amending the aqueous medium with a surfactant (e.g. Triton X-114) at a concentration that exceeds the critical micelle concentration, followed by heating to its “cloud point” temperature (Hartmann et al. 2013). Consequently, micelles form and an additional surfactant rich phase is created containing non-polar substances (i.e. AgNPs), while polar substances (i.e. dAg) remain in the aqueous phase. Following centrifugation, the supernatant containing AgNPs can be analyzed directly. To optimize AgNP extraction efficiency, the pH of the solution is adjusted to the zero point charge and thiosulfate ($\text{S}_2\text{O}_3^{2-}$) is added to complex with any Ag^+ adsorbed onto the AgNP surface (Liu et al. 2009). Advantages of CPE method include the relatively low-cost, as well as the ability to pre-concentrate samples, which improves detection limits. Furthermore, CPE preserves the size and shape of AgNPs, offering the potential for characterizing the nanoparticles by electron microscopy (e.g. TEM) or by energy dispersive x-ray spectroscopy (Liu et al. 2009). CPE has been used to detect AgNPs in natural waters at low $\mu\text{g L}^{-1}$ concentrations (Liu et al. 2009; Chao et al. 2011). However, Furtado et al. (2014) identified low recoveries in complex matrixes using CPE that require resolution before this technique can be widely applied to studies in natural waters.

Flow field flow fractionation comprises a family of analytical techniques where separation of particles takes place within an elongated channel without a stationary phase through the action of an external field applied perpendicularly to the laminar flow of the mobile phase (Baalousha et al. 2011). Briefly, analyte separation takes place along a thin channel with one permeable wall covered by an ultrafiltration (UF) membrane. A longitudinal flow moves the particles through the channel, while a cross flow is applied perpendicular to the channel and pushes the particles towards the UF membrane. The diffusion of particles opposes the cross flow force, causing smaller

particles with higher diffusion coefficients to move further away from the UF membrane than larger particles. Due to the parabolic flow profile of the longitudinal flow, velocity decreases towards the walls. The smaller particles that move closer to the center of the flow channel have shorter retention times (Baalousha et al. 2011). A standard UV–Vis detector can be used as a non-specific detector system for nanoparticles, although limits of detection are typically in the mg L^{-1} range. For detection of metallic nanoparticles, such as AgNPs at environmentally relevant concentrations (i.e. $\mu\text{g L}^{-1}$) an ICP-MS can be coupled to the AF4 to monitor the size distribution (i.e. AF4-ICP-MS), or fractions collected as they elute from the AF4 can be analyzed off-line by ICP-MS (Hoque et al. 2012).

The hydrodynamic diameter of particles can be calculated by either AF4 theory or by an external calibration curve using different sized NP standards. Additionally, the mass concentration of particles can be determined by external calibration with NP standards or by flow injection with dAg standards. Because of the large size range of particles (1 nm–50 μm) that can be detected, AF4-ICP-MS is a promising method for AgNP analysis (Poda et al. 2011; Mitrano et al. 2012b; Furtado et al. 2014). It also has utility in studying dAg complexes detected at early retention times in the AF4 fractograms (Furtado et al. 2014; Mitrano et al. 2012b; Unrine et al. 2012). However, particle-membrane interactions remain the biggest challenge for AF4-ICP-MS analysis, limiting analyte recoveries to <50 % or resulting in incorrect particle size estimations due to analyte adsorption and thus delayed particle elution (Baalousha et al. 2011). AF4 methods thus require careful optimization, particularly for the magnitude of the cross-flow and the composition of the mobile phase (Fig. 2). Furthermore, since separation in AF4 is related to hydrodynamic diameter, retention times may be skewed if particles become coated with organic material (Mitrano et al. 2012b).

Analysis by spICP-MS is an emerging method that has demonstrated great utility for environmental monitoring. Originally developed by Degueldre et al. (2006), this analytical technique has now been widely applied to evaluate the fate of nanoparticles in aquatic matrixes (Mitrano et al. 2012a; Furtado et al. 2014). In contrast to traditional ICP-MS that determines total Ag concentrations from the intensity of Ag ions that reach the detector over a long dwell time of 0.2–1 s, spICP-MS can distinguish between AgNPs and dAg by operating with a short dwell time (i.e. <10 ms). Thereby, spICP-MS measures each individual spike in signal intensity over time, and dAg is monitored as a continuous background signal. AgNPs (or its aggregates) are identified as a pulse in intensity above dAg level as a cluster of Ag^+ ions that are generated in the nebulizer and reach the detector simultaneously. The

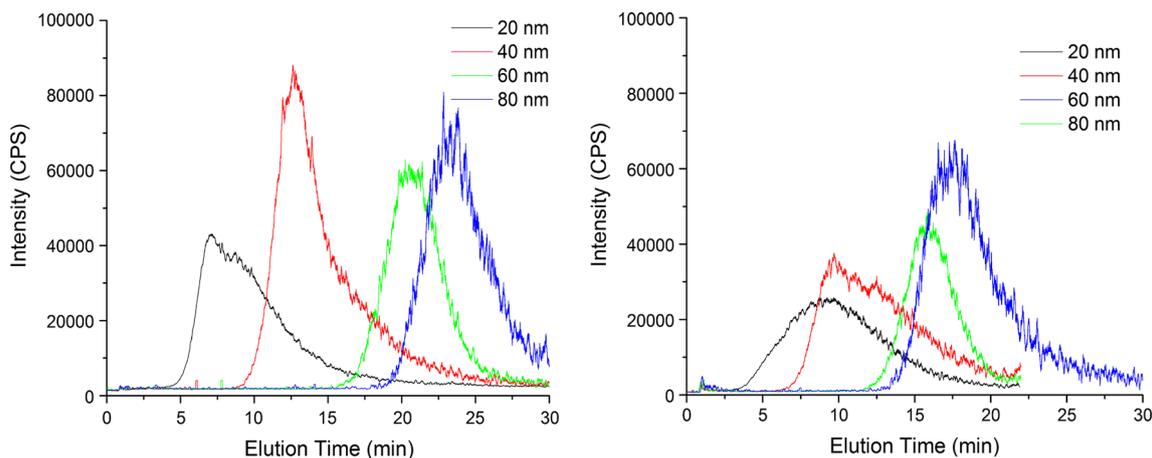


Fig. 2 AF4-ICP-MS fractograms for various sizes of PVP-capped AgNPs purchased from Nanocomposix (San Diego, CA, USA) analyzed at a cross-flow of 1.0 mL/min (*left*) and 0.7 mL/min (*right*)

particle number can be determined by the frequency of pulses and the particle size can be calculated from the signal intensity using an algorithm that relates intensity to particle size. The pulse intensity is related to particle size using dAg standards and the transport efficiency (Pace et al. 2012).

The greatest advantage of spICP-MS is that it can provide detailed qualitative and quantitative information about different Ag forms, including the particle size distribution and number, and the mass concentration of dAg and AgNPs. Furthermore, it has detection limits for AgNP that cover expected environmental concentrations. Isotope dilution techniques using ^{109}Ag -enriched standards even allow for reliable characterisation in complex matrixes (Telgmann et al. 2014). Moreover, relative to AF4-ICP-MS, spICP-MS offers rapid sample throughput, and requires little additional method development for each matrix or AgNP type. The largest limitation, however, is the size detection limit, which until recently, was around 20 nm (Laborda et al. 2013). However, recent advances in instrumentation and manipulation of the data generated by spICP-MS are expanding the lower range of sizes that can be detected (Cornelis and Hassellöv 2014; Montañó et al. 2014). Figure 3 illustrates the size distribution of AgNPs analyzed using a high resolution ICP-MS instrument that is capable of operating with dwell times $<50\ \mu\text{s}$. Since spICP-MS analysis generates data from which the size of the particle core is determined, it is useful to simultaneously use other analytical techniques, such as AF4-ICP-MS to determine the hydrodynamic size of the particles (Mirano et al. 2012b; Furtado et al. 2014).

While advances have been made in developing analytical techniques for AgNPs in aquatic matrixes, there are significant challenges to be overcome in analyzing the distribution of AgNPs at environmentally relevant

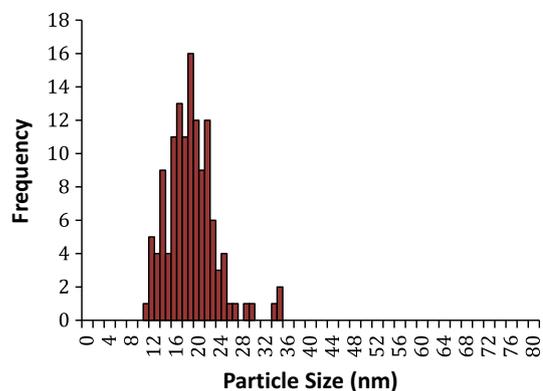


Fig. 3 The size distribution determined by spICP-MS analysis of a suspension prepared from citrate-capped AgNPs with a median size range of 20 nm, according to the supplier, Nanocomposix. The samples was analyzed with a Nu AttoM ICP-MS in single particle mode with a dwell time of 30 μs , as described by Newman et al. (accepted)

concentrations in more complex matrixes, such as sediments (Rabajczyk 2016) and biological tissues (Gray et al. 2013). Laborda et al. (2015) reviewed the current state of development of analytical techniques for nanoparticles in complex matrixes and concluded that there are a number of techniques that show promise for analytical applications. If there are sufficiently high concentrations of AgNPs in these complex matrixes, it is also possible to generate information on the speciation of Ag and the transformation products of AgNPs using X-ray absorption spectroscopy (XAS) and X-ray absorption near edge structure (XANES) techniques (Lombi et al. 2013; Leonardo et al. 2016). Clearly, the challenge for future work in this field is to develop analytical techniques that can be used to evaluate the concentrations and forms of AgNPs once they partition into sediments or are accumulated by aquatic organisms.

Conclusions

Although no one analytical technique can generate all of the information required to characterize the size, concentration and transformation of AgNPs in the aquatic environment, there are now a range of methods that can be applied for this purpose. The insights provided by these techniques are fundamental for linking AgNPs properties with adverse effects in aquatic ecosystems.

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