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**Review Article**

# Role of Silver Nanoparticles: Behaviour and Effects in the Aquatic Environment – A Review

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**Abstract**

This review summarizes and evaluates the present knowledge on the behaviour, the biological effects and the routes of uptake of silver nanoparticles (AgNps) to organisms, with considerations on the nanoparticle physico-chemistry in the Eco-toxicity testing systems used. Different types of AgNps syntheses, characterization techniques and current and future concentrations in the environment are also outlined. This review focuses with a set of recommendations for the advancement in understanding the role of silver nanoparticles in the field of environmental and Eco-toxicological research.



**Key Words:** Silver Nanoparticles, Eco-Toxicity, Aquatic Environment

## Introduction

Silver nanoparticles (AgNPs) possess many unique properties, which has inspired their extensive application in antimicrobial materials, biological labeling, optoelectronics, catalysis systems, and as fluorescent probes used for *in vivo* imaging (Jin *et al.,*2001; Sun and Xia, 2002 and Sun *et al.,*2003). Silver nanoparticles have extremely large surface area-to-mass ratios and have a high percentage of their component atoms on the surface, which gives them unique biological activity or toxicity (Colvin, 2003; Warheit, 2008 and Griffitt *et al.,* 2009). Recently, *in vitro* tests were performed to evaluate the cytotoxicity and mechanisms involved in the toxicity of multifarious metallic nanoparticles, which indicated that silver nanoparticles (sizes: 15 and 100nm) had the highest cytotoxicity compared to other metallic nanoparticles such as $MoO_3$ and $Fe_3O_4$ (Braydich-Stolle *et al.,*2005; Hussain *et al.,*2005). Additional *in vitro* experiments demonstrated that AgNPs exhibited significant cytotoxicity to human cells (Asharani *et al.,* 2009; Kawata *et al.,* 2009). Despite these studies being well performed, understanding the potential *in vivo* toxicity of silver nanoparticles still remains unclear (Julia Fabrega *et al.*, 2011). Nanotechnology manipulates matter at the Nano-scale (1–100nm) (Moore, 2006; Nel *et al.,*2006) producing Nano products and nanomaterial's (NMs) that can have novel and size-related physicochemical properties differing significantly from those from larger particles. The novel properties of NMs have been exploited widely for use in medicine (Salata, 2004; Barnett *et al.,* 2007; Dong and Feng, 2007), cosmetics (Lens, 2009), renewable energies (Pavasupree *et al.,* 2006), environmental remediation (Zhang, 2003 and Tungittiplakorn *et al.,* 2004), and electronic devices (Kachynski *et al.,* 2008).

AgNps have distinctive physico-chemical properties, including a high electrical and thermal conductivity, surface-enhanced Raman scattering, chemical stability, catalytic activity and non-linear optical behaviour (Capek, 2004; Frattini *et al.,* 2005). These properties make them of potential value in inks (Tay and Edirisinghe, 2002 and Perelaer *et al.,* 2009), microelectronics (Wu *et al.,* 2006), and medical imaging (Jain *et al.,* 2008). However, it is the exceptional broad spectrum bacteriocidal activity of silver (Ratte, 1999; Silver, 2003; Silver *et al.,* 2005; Luoma, 2008) and relatively low cost of manufacturing of AgNPs (Capek, 2004), that has made them extremely popular in a diverse range of consumer materials, including plastics, soaps, pastes, metals and textiles (Frattini *et al.,* 2005) increasing their market value. Silver is considered relatively harmless to humans. Indeed, silver's

bactericidal properties have been exploited by certain groups commercializing colloidal silver suspensions as 'health supplements'. However, the beneficial effects on health are not proven, and high exposures to silver compounds can cause argyria, an irreversible condition in which the deposition of Ag in the body tissue results in the skin turning bluish in colour (Hill, 1941 and Rosenman *et al.,* 1979). In addition, there is a potential impact on gut microflora affecting the population size of certain types of bacteria (Sawosz *et al.,* 2007).

The environmental impacts of AgNps are, still unknown. However, previous knowledge on the environmental and physiological implications of exposure to dissolved silver ions and silver salts in freshwater and seawater organisms provides a baseline for assessment and a reason for concern. From this baseline only, the potential effects and impacts of AgNps to organisms and to ecosystems can be developed. Prior to the interest in NPs, the silver ion ($Ag^{+}$(aq)) was considered the most toxic form of silver in water (Ratte, 1999). As with all metals, the chemistry of the surrounding environment affects association of silver ions with various ligands, in turn influencing bioavailability and toxicity (Luoma *et al.,* 1995; Adams and Kramer, 1998 and Erickson *et al.,* 1998). For instance, in freshwater systems, organic matter and sulfide, with a high silver affinity, probably dominate Ag speciation and reduce silver bioavailability. In seawater systems, the silver chloro complex is highly bioavailable and it is the primary form in waters of salinity greater than about 3 NTU; (Luoma *et al.,* 1995 and Luoma, 2008). The uptake rates of the chloro complexes by fish are not as rapid as with the free Ag ion, but concentrations of chloro complexes are much higher than free Ag ion concentrations in most aquatic systems. Thus, the marine organisms are more likely to bioaccumulation of Ag than freshwater organisms (Luoma, 2008), under equivalently contaminated conditions.

The purpose of this review is to critically evaluate the existing knowledge on AgNps as a potential problem for environmental health, taking into consideration the characteristics, behaviour, bioavailability and biological effects of AgNps in aqueous suspensions. From the current information on AgNps and their role in the environment, one can identify and priorities the key current knowledge gaps (Julia Fabrega *et al.,* 2011).

**Release of silver nanoparticles into the environment**

Worldwide, the present production of AgNps is estimated at about 500 t/a (Mueller and Nowack, 2008), and a steady increase on the volume manufactured is predicted for the next few years (Boxall *et al.,* 2008). AgNps may be discharged to the environment by several routes, including during synthesis, during manufacturing and incorporation of the NPs into goods, during the use phase of the good containing NPs, and while recycling or disposal of goods and AgNps (Köhler *et al.,* 2008). In 2008, a study on analysing the risk from the release of AgNps to freshwater ecosystems predicted that by 2010, 15% of the total silver released into water in the European Union would come from biocidal plastics and textiles (Blaser *et al.,* 2008). There are few experimental data reporting partitioning between and within environmental compartments by NP mass and none by particle number or even how partitioning might differ between discharges that are primarily AgNps vs Ag itself. However, there are data showing that manufactured nanomaterials used in consumer goods will accumulate in surface waters (Benn and Westerhoff, 2008 and Kaegi *et al.,* 2008). Modelled and experimental data (Luoma, 2008; Mueller and Nowack, 2008; Geranio *et al.,* 2009 and Gottschalk *et al.,* 2009) suggest that μg $L^{-1}$ may be present in surface waters and exponential increases are predicted due to the increase usage and consequently discharge levels.

**Influence of environmental conditions.**

Navarro *et al.* (2008a) also emphasized the importance of understanding the chemical nature of the exposure medium in determining AgNps bioavailability. As noted earlier, pH, ionic strength and composition, NOM, temperature, and nanoparticle concentration all interact to affect aggregation or stabilization of AgNps. Solubility determines the proportional exposure of organisms to $Ag^{0}$, $Ag^{+}$ or complexes Ag. For example, thermodynamics would generally indicate that NPs of $Ag^{0}$ are not equilibrium species and will not persist in aquatic environments containing dissolved oxygen (Liu and Hurt, 2010), although there is no any relevant data on kinetic of loss but this kinetics of dissolution at near neutral pH are likely to be slow (Julia Fabrega *et al.,* 2011). Aggregation determines the particle size of AgNps to which organisms are exposed and influences which dose metric needs to be quantified in exposure. The paucity of data actually testing the influence on bioavailability of exposure medium chemistry has led to very different assumptions, or conclusions, about the influence of processes like dissolution and aggregation.

In summary, there are beginnings to understand the processes that influence the bioavailability of NPs in general, although much more study is needed to support any broad conclusions specifically for AgNps. The nature of the particle and the chemistry of the environment will interact with physico-chemical and environmental dynamics to influence the form of Ag and AgNps present in an environment. These are likely to affect the bioavailability of the Ag and AgNps, but the characteristics of different biological species and all potential routes of exposure must be considered to adequately predict ecological risks (Julia Fabrega *et al.,* 2011).

**Effects of AgNps to aquatic organisms, fish**

Ag ion toxicity *in vivo* has been researched in some detail in freshwater fish species (Janes and Playle, 1995; Wood *et al.,* 1996 and Zhou *et al.,* 2005) with $LC_{10}$ values as low as 0.8 μg $L^{-1}$ for certain freshwater fish species (Birge and Zuiderveen, 1995). Ag ions in solution can reach the bronchial epithelial cells via the Na+ channel coupled to the proton ATPase in the apical membrane of the gills, travel to

the basolateral membrane of the gill and block the $Na^+$ $K^+$ ATPase affecting ion regulation of $Na^+$ $Cl^-$ ions across the gills (Bury and Wood, 1999). At high concentrations (μM), there are important physiological consequences such as blood acidosis which can ultimately lead to circulatory collapse and death (Wood *et al.,* 1996; Morgan *et al.,* 1997; Hogstrand and Wood, 1998 and Grosell *et al.,* 1999). Only a handful of studies have investigated *in vivo* the effects of AgNps in fish (Bilberg *et al.,* 2010; Chae *et al.,* 2009; Griffitt *et al.,* 2009; Scown *et al.,* 2010; Yeo and Pak, 2008). Initial results indicate that 10–80 nm AgNps affect early life stage development that include spinal cord deformities, cardiac arrhythmia and survival (Asharani *et al.,* 2008; Yeo and Pak, 2008). AgNps can also accumulate in the gills and liver tissue affecting the ability of fish to cope with low oxygen levels and inducing oxidative stress (Bilberg *et al.,* 2010; Scown *et al.,* 2010). However, the threshold at which such effects occur is variable among these experiments, even for the same species. Such variability may reflect differences in choices of experimental conditions and/or differences in particle behaviour or character that were undefined. In general, juvenile zebra fish and Japanese medaka have shown to be more susceptible to AgNps than to equal mass concentrations of $AgNO_3$, at least under conditions that maximize free ion Ag concentrations for the latter.

Some authors have suggested that the toxicity is unlikely to be attributable to particle dissolution only (Chae *et al.,* 2009; Griffitt *et al.,* 2009 and Yeo and Yoon, 2009). Other exposure studies with equal mass of AgNps and $AgNO_3$ (as low as $10^{-20}$ μg $L^{-1}$ for embryonic studies and 1 mg $L^{-1}$ for juveniles) have supported the contention for different mechanisms of action, with differential uptake and transcriptomic responses for AgNps compared with $AgNO_3$ (Asharani *et al.,* 2008; Yeo and Kang, 2008 and Yeo and Pak, 2008). Indeed, a differential uptake of Ag compounds has been shown in zebra fish and rainbow trout: in zebra fish embryos, high exposure concentrations (0.4 and 100 mg $L^{-1}$) showed that AgNps aggregates were incorporated into blood vessels, skin, brain, heart and yolk (Yeo and Yoon, 2009), whereas Ag ions concentrated in organelles, the nucleus and the yolk only (Julia Fabrega *et al.,* 2011).

**Recommendations**

The use of nanomaterials and their potential environmental and human health risks (Helfenstein *et al.,* 2008; Andujar *et al.,* 2009) are of increasing concern and social debate (Dean, 2009; Feder, 2006; RS/RAE, 2004) and have been the subject of many government reports. This review has outlined the current knowledge and gaps on AgNps as a potential problem for environmental health. With the existing information, one can identify the current research mentioned earlier gaps and needed areas of research as follows; (Julia Fabrega *et al.,* 2011).

1. There is a pressing need to develop analytical and metrological methods which can detect, quantify and characterize AgNps; such data will strongly inform both exposure and hazard our nature of experimental studies.
2. Improved hazard data is also required, significant improvements in understanding dose, physicochemical properties, bio uptake and toxicity processes need to be made.
3. Assessing the potential harmness of AgNps in aquatic environments requires well characterized AgNps and to study AgNps in a well dispersed state to identify Nano related effects.
4. Better information is needed on current usage and release rates of dissolved and nanoparticles of silver from consumer products and from industrial processed. Ideally, this information needs to be integrated into readily accessible models.
5. Advancement of models for use in studies on AgNps (and other NPs). Models that can be adapted for this purpose derive from studies on other environmental pollutants, in areas of exposure (Blaser *et al.,* 2008 and Mueller and Nowack, 2008), bioavailability (biodynamics, Luoma and Rainbow, 2005), toxicity (BLM, Paquin *et al.,* 2002) and structure activity relationships (Puzyn *et al.,* 2009).
6. Such models need to be challenged with appropriate high quality data and modified to account for any 'Nano-specific' effects. This will be a continuing and iterative process, but with the provision of high quality data in the areas highlighted earlier, this should allow improvements in models to be effects rapidly (Julia Fabrega *et al.,* 2011).

**Conclusion**

Nanostructure compounds and devices have shown unique physicochemical and high specific surface properties, leading to their application in electronics, optics, textiles, medical devices, drug delivery systems, in addition to environmental remediation (DeWild *et al.,*2003; Oberdörster *et al.,*2005 and Balbus *et al.,*2007). With the widespread application of engineered nanoparticles (NPs), numerous nano-scale compounds might consequently be released into the aquatic environments and elicit an impact not only on the ecosystems but also on the human health (Nel *et al.,* 2006; Benn and Westerhoff, 2008). At present, toxicological information on nanoparticles remains insufficient; thus frameworks for future toxicological assessments on nano-sized materials have been promoted (Colvin, 2003; Balbus *et al.,* 2007).

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