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## Mini-review

# Predicting the environmental impact of nanosilver



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## ABSTRACT

Silver nanoparticles (AgNPs) are incorporated into many consumer and medical products due to their antimicrobial properties; however, the potential environmental risks of AgNPs are yet to be fully understood. This mini-review aims to predict the environmental impact of AgNPs, thus supplementing previous reviews on this topic. To this end, the AgNP production, environmental release and fate, predicted environmental concentrations in surface water, sediment, and sludge-activated soil, as well as reported toxicity and proposed toxic mechanisms are discussed, focusing primarily on fish. Furthermore, knowledge gaps and recommendations for future research are addressed.

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## 1. Introduction

Nanotechnology is rapidly moving into every sector of human life; its global market was valued at \$20.1 billion in 2011 and is expected to double by 2017 (BCC, 2012). This is not surprising as engineered nanomaterials (ENMs) possess unique properties attributed mainly to their size (<100 nm in at least one dimension) and their high surface area to volume ratio, which allow for increased uptake and interactions with biological systems and unique catalytic and oxidative reactions on the ENM surface (Auffan et al., 2009; Nel et al., 2009). Thus, ENMs are applicable in many domains, including optics, engineering, alternative energy, remediation, and consumer products (Oberdörster et al., 2007). In fact, as of October 2013 there were 1628 reported consumer products containing ENMs (Nanotech Project, 2014). ENMs could also be used for drug-delivery, diagnostic, and investigative purposes (Oberdörster et al., 2005; Nel et al., 2006). For example, a sensitive nanosensor chip for the detection of early cancer biomarkers was recently developed (Nanotech News, 2009).

Silver nanoparticles (AgNPs) are the most common ENM, incorporated into 383 or 23.5% of all reported consumer and medical products as of October 2013 (Nanotech Project, 2014). Their prevalence reflects the well-known antimicrobial properties of silver, whose efficacy is improved through the incorporation of AgNPs into such products (Kim et al., 2007; Chernousova and Epple, 2013). The bactericidal activity of AgNPs is attributed to the controlled release of silver ion (Ag<sup>+</sup>) and nano-specific effects of AgNPs. Ag<sup>+</sup> interacts strongly with thiol groups, thus inactivating important enzymes, including those involved with the electron-transport chain and thus cellular oxidation, and DNA replication (Morones et al., 2005; Gordon et al., 2010). In addition, Ag<sup>+</sup> denatures DNA and RNA (Fong and Wood, 2006), and leads to DNA condensation (Feng et al., 2000), ultimately affecting DNA replication and RNA translation. Ag<sup>+</sup> can also bind to electron donor groups in DNA and proteins, making them unavailable for cellular processes (Clement and Jarrett, 1994). Furthermore, Ag<sup>+</sup>-mediated generation of reactive oxygen species (ROS) has also been reported (Gordon et al., 2010). In addition, AgNPs attach to the cell membrane, disrupting proper cellular function (Sharma et al., 2009), and generating ROS (Hwang et al., 2008; Foldbjerg et al., 2009). The broad-spectrum bactericidal action of AgNPs is effective against Gram negative and Gram positive strains, as well as drug-resistant bacteria (Lara et al., 2010). The antiviral capacity of AgNPs against human immunodeficiency virus type 1 (Elechiguerra et al., 2005) and hepatitis B virus (Lu et al., 2008) has also been reported.

However, recent studies reporting adverse effects of ENMs in general and AgNPs in particular (see below) have raised safety concerns across the world. Thus, the aim of this mini-review is to examine the available information on AgNP

use/production, environmental release, fate, and toxicity, as well as to address the existing knowledge gaps, thereby supplementing previous reviews on this topic.

## 2. AgNP production and use

Unlike most other ENMs, the synthesis and use of AgNPs is not new (Fig. 1). The comprehensive review by Nowack et al. (2011) noted that historically AgNPs were referred to as ‘colloidal silver’ and that the addition of the prefix ‘nano’ does not automatically make ‘nanosilver’ a new chemical. In fact, the synthesis of AgNPs was first reported by Lea (1889), who reported the formation of ‘finely divided silver’ and described a method to produce ‘allotropic gold–yellow and copper-colored’ forms of silver. These allotropic forms of silver are essentially AgNPs, which are recognized by their yellowish hue and a corresponding surface plasmon at ~400 nm (Thomas et al., 2008).

Nowack et al. (2011) also provided several historical examples of products that incorporated AgNPs. These included the colloidal silver formulation Collargol (prepared in 1894 by Heyden and Radebeul for wound treatment), a silver-proteid compound Protargol (prepared in 1897 by Friedrich Bayer and Co. to treat gonorrhea) (Kolthoff, 1925), and a protein-stabilized silver solution Argyrol (prepared in 1901 by Barnes to treat conjunctivitis) (Schack, 1960). The use of such compounds in the first half of the 20th century was widespread, but declined with the introduction of antibiotics in the 1940s (Alexander, 2009; Davies and Davies, 2010). It is important to note that with the advent of antibiotic resistance in the 1960s, the use of AgNPs in medicine returned in the late 1990s with applications in wound dressings (e.g. Acticoat) and catheters as reviewed by Chaloupka et al. (2010). However, Argyrol remains available for purchase (e.g. <http://www.argyrol.com/agprotein.phtml>).

In addition to its medicinal uses, AgNPs were also applied as biocidal additives (e.g. Algaedyn, registered in the US, 1954) and incorporated into water filters (e.g. 989 Bacteriostatic Water Filter Media, registered in 1988) (Nowack et al., 2011), and thanks to the emergence of nanotechnology such biocidal products are widespread on the market today (Nanotech Project, 2014). Unfortunately, historic data on AgNP production are not available (Nowack et al., 2011) and the production of AgNPs after the emergence of nanotechnology is still largely unknown.

To date there remains little information on the production of AgNPs. This information is essential to predict the environmental concentrations and thus the risk associated with AgNPs. Mueller and Nowack (2008) estimated the global production of AgNPs at 500 tons per annum (t/a). This estimate is based on the global production of silver (25,620 t/a), of which 95% is used for jewelry, photography, and industrial

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