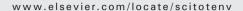


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Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles

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ABSTRACT

Products with antimicrobial effect based on silver nanoparticles are increasingly used in Asia, North America and Europe. This study presents an analysis of risk to freshwater ecosystems from silver released from these nanoparticles incorporated into textiles and plastics. The analysis is presented in four stages; (i) silver mass flow analysis and estimation of emissions, (ii) assessment of the fate of silver in a river system and estimation of predicted environmental concentrations (PECs), (iii) critical evaluation of available toxicity data for environmentally relevant forms of silver and estimation of predicted no-effect concentrations (PNECs), and (iv) risk characterization. Our assessment is based on estimated silver use in the year 2010, focusing on the Rhine river as a case study. In 2010, biocidal plastics and textiles are predicted to account for up to 15% of the total silver released into water in the European Union. The majority of silver released into wastewater is incorporated into sewage sludge and may be spread on agricultural fields. The amount of silver reaching natural waters depends on the fraction of wastewater that is effectively treated. Modeled PECs in the Rhine river are in satisfactory agreement with monitoring data from other river systems. Because a complete characterization of the toxicity of environmentally relevant silver species is lacking, only a limited risk assessment is possible at this time. However, our study indicates that PEC/PNEC ratios greater than 1 cannot be ruled out for freshwater ecosystems, in particular sediments. No risk is predicted for microbial communities in sewage treatment plants.

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1. Introduction

The use of silver nanoparticles incorporated in consumer products has become common in the last years because of the biocidal effect of the silver ion. Industry makes use of this new technology in food contact applications, in the interior of automobiles such as steering wheels and in building materials such as sanitary tubing and coverings. Another field of application for products with antimicrobial effect based on silver ions is medical equipment such as catheters, infusion

systems and medical textiles (The Silver Institute, 2001; Markarian, 2002; Simpson, 2003; Markarian, 2006.). Worldwide, markets for silver-containing nano-functionalized products have started to grow significantly (The Silver Institute, 2001; Markarian, 2006; Rundle, 2006).

The increasing use of antimicrobial silver nanoparticles requires an environmental risk assessment for such products. Here we evaluate the impacts of silver released from silver-containing plastics and textiles on freshwater ecosystems. The relevance of the topic is given by the EU directive concerning the

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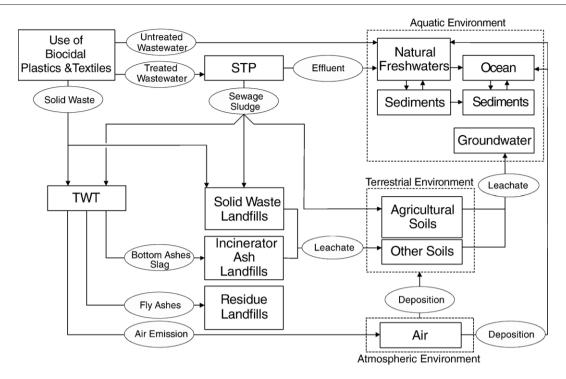


Fig. 1 – Overview of silver flows triggered by biocidal plastics and textiles. Arrows represent silver flows; dashed lines indicate different environmental spheres. TWT=thermal waste treatment; STP=sewage treatment plant.

placing of biocidal products on the market (European Parliament and Council, 1998) and the recent announcement of regulation of silver nanoparticle technology by the US Environmental Protection Agency (Weiss, 2006). There are projections of strong growth in the silver nanoparticle market for the coming years (HeiQ, 2006).

The biocidal mechanism of silver-containing products results from a long term release of silver ions (Ag⁺) by oxidation of metallic silver (Ag⁰) in contact with water (Kumar et al., 2005). In plastics and textiles silver nanoparticles are embedded in the polymer matrix; another possible approach is to apply a silver-containing surface coating to the polymer (Marini et al., 2007). Here we focus on silver released from nanoparticles embedded in the polymer and assume that only silver ions and not entire nanoparticles are released. The Ag⁺ ion inhibits the enzymes for the P, S, and N cycles of nitrifying bacteria (Ratte, 1999). In addition, ionic silver can block DNA transcription and interrupt bacterial respiration and adenosine triphosphate (ATP) synthesis (Kumar et al., 2005).

The antimicrobial spectrum of silver is extensive, and silver has also been reported to be effective against a variety of virus types (Han et al., 2005). Silver ions also have fungicidal and algicidal effects (Ratte, 1999).

Silver is classified in the "soft" metal group and binds very strongly with reduced sulfur groups such as thiolates and sulfides (Stumm and Morgan, 1996). Because reduced sulfur is found in most natural waters (Kramer et al., 2007), free silver ions exist only at very low concentrations in the aquatic environment.

The objectives of this study are (i) to estimate, in comparison to current silver releases from various other applications, the incremental amount of silver that will be released to

the environment by biocidal plastics and textiles in a nearfuture scenario, and (ii) to evaluate for the total of silver releases from biocidal and other applications whether predicted silver concentrations in freshwater and sediments could have adverse effects. Releases from other biocidal applications of silver such as cosmetics or exterior paints are not considered because they are very difficult to quantify.

Our assessment is presented in four stages. First, the system boundaries are defined, mass flows of silver are quantified, and three emission scenarios are defined. Second, the behavior of silver in natural freshwater is reviewed, and a mass balance model is applied to calculate predicted environmental concentrations (PECs) for freshwater and freshwater sediments. PECs are also estimated for sewage treatment plants (STPs) and sewage sludge. The uncertainty of the results is assessed and predicted concentrations are compared to empirical data. Third, toxicity data for environmentally relevant silver compounds are compiled and predicted noeffect concentrations (PNECs) are determined where possible. Finally, the potential for risk caused by the release of silver into freshwater is evaluated using all available data.

2. Emission scenarios

2.1. Temporal scale and spatial boundary

The market for silver-containing biocidal products is undergoing rapid expansion. The Silver Institute (2001) estimated that the use of silver as a biocide would increase by about 500 times between 2000 and 2004 in Europe (with an estimate of 30 t/yr for 2004). We selected the year 2010 in order to take into

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