Particulate and colloidal silver in sewage effluent and sludge discharged from British wastewater treatment plants

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HIGHLIGHTS

- Average silver removal during sewage treatment in 9 British plants was high at 98%.
- Mean silver in effluent was 84 ng L^{-1}, of which 6 ng L^{-1} was colloidal (2–450 nm).
- Estimates for British rivers were typically <1, and up to 4 ng L^{-1} colloidal silver.
- Total silver in sewage sludge solids was 3–14 mg kg^{-1} dry weight (median 3.6).
- Applied to soil, this would add up to 11 µg kg^{-1} yr^{-1} silver to the upper 20 cm.

GRAPHICAL ABSTRACT
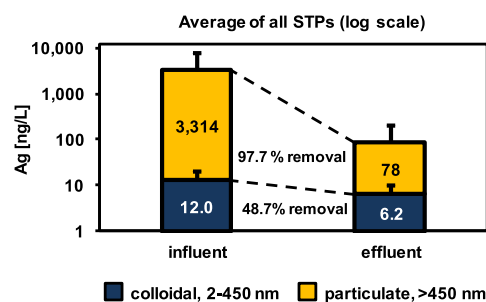
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ABSTRACT

Differential filtration was used to measure silver (>2 nm) entering and leaving nine sewage treatment plants (STPs). The mean concentration of colloidal (2–450 nm) silver, which includes nanosilver, was found to be 12 ng L^{-1} in the influent and 6 ng L^{-1} in the effluent. For particulate silver (>450 nm) the mean values were 3.3 µg L^{-1} for influent and 0.08 µg L^{-1} for effluent. Thus, removal was around 50% and 98% for colloidal and particulate silver respectively. There was no significant difference in performance between the different types of STP investigated (three examples each of activated sludge, biological filter and biological filter with tertiary treatment located across England, UK). In addition, treated sewage sludge samples (biosolids) were taken from several STPs to measure the total silver likely to be discharged to soils. Total silver was 3–14 mg kg^{-1} DW in the sludge (median 3.6), which if the sludge were added at the recommended rate to soil, would add 11 µg kg^{-1} yr^{-1} to the top 20 cm soil layer. Predicted concentrations using the LF2000-WQX model for all the rivers of England and Wales for nanosilver were typically in the 0–1 ng L^{-1} range but levels up to 4 ng L^{-1} are possible in a high discharge and low flow scenario. Predicted concentrations for the total particulate forms were mostly below 50 ng L^{-1} except for a high discharge and low flow scenario where concentrations could reach 135 ng L^{-1}.

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1. Introduction

Silver is a minor constituent of the earth's crust with an average content of 0.1 mg kg^{-1} (Purcell and Peters, 1998). Silver has been used in and discharged from a range of industrial applications for over 150 years (Rozan et al., 1994). In the early 1990s the main demands for silver were the photographic business, catalysts, jewelry, electronics industry, brazing alloys, battery manufacture, bearings and dental/medical applications all of which generated some silver waste (Purcell and Peters, 1998; Eckelman and

Graedel, 2007). There are now concerns over the discharge of engineered nanoparticulate silver into the environment (Depledge et al., 2010) particularly with the use of nanosilver in medical antimicrobial products and in some clothing products (Bondarenko et al., 2013). Recent predictions have suggested effluent discharges between 8.4 μg cap^{-1} d^{-1} with a 96% removal rate (Gottschalk et al., 2009) and 114 μg cap^{-1}d^{-1} (Blaser et al., 2008, medium risk scenario). If a per capita effluent discharge of 160 L d^{-1} were assumed these predictions would suggest a range of 50–700 ng L^{-1} to be present in sewage effluent. However, a recent study of German sewage treatment plant effluents found only 5 ng L^{-1} nanoparticulate silver (Li et al., 2013). There remains considerable uncertainty over both the true size of the nanosilver market and the quantities likely to be released from products on a daily basis.

To improve the risk assessments for nanosilver it would be highly desirable to quantify the engineered variety in sewage effluent, but unfortunately this remains difficult. We can however measure colloidal silver which may be taken to represent a worst case, or upper boundary (precautionary) value, for nanosilver entering receiving waters. We used 450 nm as the cut-off point between solid and colloidal size silver, as this is the most commonly used pore size when separating water samples into a solid and "dissolved" fraction and at the lower end we used a pore size of approximately 2 nm, which was the closest available to the common definition of nanoparticles as 1–100 nm in size. Therefore particles between 1 and 2 nm diameter may have been missed, but in an analysis of sewage sludge with a relatively high silver content, silver was found in small clusters of silver sulfide particles with the individual particles having sizes of 5–20 nm (Kim et al., 2010). Similarly, it would be very helpful to assess how much silver we might be adding to soil through sewage sludge disposal. If we cannot distinguish nanosilver in sewage sludge then the total silver content could be seen as representing the upper boundary value for nanosilver.

The objectives of this study were therefore to:

• Measure colloidal (2–450 nm) and particulate (>450 nm) silver entering and leaving a group of nine sewage treatment plants (STPs), which were representative of different regions and treatment processes in England.
• Measure total silver in the sludge product of a representative group of nine STPs.
• To use the effluent and sludge values as a basis to predict ranges of concentrations that might be found in rivers and soils in the UK.
• To assess whether these predicted environmental concentrations would exceed currently known toxicity thresholds.

2. Materials and methods

2.1. Wastewater sampling

The selection of STPs was designed to reflect both the most numerous types and a geographic spread across the country (Table 1).

An ISCO Avalanche cooled sampler was programmed to collect a 24 h composite sample by collecting 0.4 L every 30 min, thus accumulating about 19 L over the sampling period. Two samplers were deployed to collect influent and effluent simultaneously. The samples were kept at $\leqslant$4 °C during and after sampling. Prior to use, the polypropylene sampling bottles were soaked overnight in 2% HNO$_3$ (1.42SG Primarplus, Fisher Scientific, Loughbourough, UK) and rinsed with de-ionized water and the tubing of the sampler was rinsed with sample before each 0.4 L sample was taken. The composite samples were then fractionated by particle size as described below.

2.2. Separation of large particulate fraction (>450 nm)

Particulate samples were prepared by filtering 25 ml of influent or 250 mL effluent through each of 8–16 pre-weighed 0.45 μm cellulose nitrate filter membranes (Sartorius 11306-47-N, 47 mm diameter) per influent or effluent sample. For samples with unusually high or low solids contents, these volumes were adjusted up or down by up to a factor of about two to achieve a good amount of solids without excessive blocking of the filters. The filtrate was used as part of the colloidal silver determination (see below). The filters were then air dried and transferred to a desiccator with silica gel and re-weighed after a few days to determine the suspended solids content before using the filters with attached solids for particulate silver analysis. Additional pre-weighed filters were wetted with de-ionised water and dried and weighed along with the samples to determine any apparent weight fluctuations, due to atmospheric conditions.

2.3. Separation of colloidal fraction (2–450 nm)

To remove >0.45 μm particles from the remaining unfiltered sample, it was pre-filtered through sandwiched glass fiber filters (Fisher MF100, ca. 1.6 μm pore size and MF150, ca. 1.0 μm pore size, 90 mm diameter), replacing the filters whenever they started blocking, before being passed through a high throughput 0.45 μm disposable filter cartridge (hydrophobic PVDF membrane, Millipore Durapore Opticap XL4), which had been rinsed and wetted thoroughly with at least 5 L de-ionized water before use. Each filter cartridge was first used for an effluent sample and then for the corresponding influent sample, rinsing it thoroughly with de-ionized water between the two samples. The filtrate from the 0.45 μm membrane and cartridge filters was combined and concentrated with a cross-flow ultrafiltration membrane unit (1 kDa or ca. 2 nm pore size, regenerated cellulose, Millipore Pelicon 2) in recirculation mode. Ideally a 1 nm pore size should have been used to capture all particles under the usual definition of nanoparticles, but that was not available. The pressure in the ultrafiltration unit was adjusted to 10 bar at the outlet and the cross flow to about 1.5 L min^{-1}, leading to 30–40 mL min^{-1} permeate flow. When the retentate volume had reduced to about 750 mL, the cross flow equipment was rinsed with 250 mL permeate which was added to the retentate bottle. At the end of this process the retentate was about 15–20 times concentrated and should contain all colloids between 2 and 450 nm sizes. The ultrafiltration membrane was thoroughly rinsed with de-ionized-water before and after every use and stored wet at 4 °C. The peristaltic tubing was soaked overnight in 2% HNO$_3$ (1.42SG PrimarPlus, Fisher Scientific, Loughbourough, UK) and rinsed with de-ionized water between use.

2.4. Digestion method for particulate and colloidal silver

For the >450 nm particulate material collected on filters, the method used by Shafer et al. (1998) was adopted. To get sufficient sample, three filters for the influent and 4–6 filters for effluent samples were used. The filters were cut into eighths using ceramic scissors and the portions were added to nitric acid cleaned Teflon bottles. To each bottle 20 mL of ultrapure water and 0.4 mL of ultrapure nitric acid was added and the bottles were gently swirled to ensure all filter portions were covered by the dilute acid. All bottles were sealed and double bagged in polyethylene bags and heated overnight at 60 °C in a temperature controlled oven.

For the colloidal 2–450 nm fraction, 2 mL of ultrapure nitric acid (Baker Ultrex II) was added to a 200 mL aliquot of the sample and then evaporated to dryness in an acid cleaned Teflon beaker. The dry residue was re-dissolved in 1 mL of ultrapure nitric acid with gentle heating and diluted to a final volume of 10 mL with