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

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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 in the influent and 6 ng/L in the effluent. For particulate silver (>450 nm) the mean values were 3.3 µg/L for influent and 0.08 µg/L 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 DW in the sludge (median 3.6), which if the sludge were added at the recommended rate to soil, would add 11 µg/kg/yr 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 range but levels up to 4 ng/L are possible in a high discharge and low flow scenario. Predicted concentrations for the total particulate forms were mostly below 50 ng/L except for a high discharge and low flow scenario where concentrations could reach 135 ng/L.

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Silver, nanoparticles, exposure, river, sewage effluent

1. Introduction

Silver is a minor constituent of the earth's crust with an average content of 0.1 mg/kg (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/d with a 96% removal rate (Gottschalk et al., 2009) and 114 µg/cap/d (Blaser et al., 2008, medium risk scenario). If a per capita effluent discharge of 160 L/d were assumed these predictions would suggest a range of 50-700 ng/L to be present in sewage effluent. However, a recent study of German sewage treatment plant effluents found only 5 ng/L 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 hr 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 $\leq 4^{\circ}\text{C}$ during and after sampling. Prior to use, the polypropylene sampling bottles were soaked overnight in 2% HNO_3 (1.42SG Primarplus, Fisher Scientific, Loughborough, 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 $0.45\ \mu\text{m}$ 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, leading to 30-40 ml/min 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, Loughborough, 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 ultrapure water (Millipore, Milli-Q, >18 MΩ). In this way a clear solution was obtained after digestion and a further concentration factor of ca. 20 times was achieved, making the total concentration factor from the original sample to the digest 300-400 fold.

For the two methods described above spike recovery checks were set up using two commercially available nanosilver products (NGAP NP Ag-2103-w, 42 nm silver dispersion in water, Nanogap, Spain and 50 nm silver powder, Amepox Ltd, Poland). Specifically, for the determination of the >450 nm fraction, filters were loaded with known weights of sewage influents previously equilibrated with known amounts of nanosilver. For the determination of the colloidal 2-450 nm fraction, filtered sewage influents and effluents were spiked by adding known amounts nanosilver.

2.5. Collection of sewage sludge samples

Anaerobically treated and partially dewatered sewage sludge known as “cake” was collected from eight STPs and one dedicated sludge processing facility across England. In all cases the sludge included biosolids from other STPs in the area transported there for treatment. All samples of “cake” were of the final product which is ready to be used in agriculture, or landscaping etc. Sludge cake was collected in a plastic bucket using a spade and taking samples from a few different areas of the pile. The bucket was closed with an airtight lid and kept cool until processing in the laboratory. A sub-sample was taken from different parts of the bucket and placed in portions on a sheet of aluminium foil and wet weight determined. The sample was then dried at 105°C before being weighed again to determine the water content. The dried sample was then ground in a ball mill prior to analysis.

2.6. Sewage sludge digestion and certified reference materials

A dried 1.5 g sample was placed in a 100 ml Kjeldahl digestion tube., then 10.5 ml concentrated hydrochloric acid and 3.5 ml concentrated nitric acid (both Aristar grade, VWR, UK) were added and the tube was closed off with a glass marble and left to start the reaction at room temperature overnight in a fume hood. The tubes were then placed in a digestion block and heated to 140°C for 2.5 hours.

Once cooled down, the sample was filtered through copper nitrate treated filter paper (Whatman no 540, soaked for 30 min in 0.1M copper nitrate solution and then washed with ultrapure water). Complete silver transfer was ensured by rinsing the digestion tubes and closure marbles several times with 0.5M nitric acid and adding this to the sample to be filtered and rinsing the filter with more 0.5M nitric acid after the sample had passed through. The samples were then made up to 100 ml with 0.5M nitric acid and stored in the

dark until analysis. Certified reference materials and blanks of HNO₃ and oleic acid washed sand were included with each batch. The reference materials were LGC 6181 (dried digested sewage sludge, LGC, Teddington, UK), which has a silver content of 55 µg/g (close to the maximum value found in the sludge samples below) and NCS 73034 (NCS Testing Technology, China National Analysis Center for Iron and Steel, Beijing, China) which has a silver content of only 0.13 µg/g.

2.7. Sample analysis

The digests were measured undiluted using a Perkin Elmer Elan DRC II inductively coupled plasma mass spectrometer (ICPMS) instrument. Both Ag stable isotopes (¹⁰⁷Ag and ¹⁰⁹Ag) were measured, with the concentration data for ¹⁰⁷Ag being reported. Corrections were made for both Mo and ZrO spectral interferences. The use of both ¹⁰⁷Ag and ¹⁰⁹Ag as analytical isotopes allowed cross validation of the concentration data obtained. For all measurements the difference in concentration determined using both Ag isotopes was less than 5%. The ICPMS instrument was calibrated using Ag standards over the range 0-10 µg/L in 10% v/v ultrapure nitric acid matrix using ¹¹⁵In as an internal standard to compensate for matrix effects and possible drift in instrument sensitivity. The ICPMS instrument detection limit was 0.14 µg/l (mean blank + 3σ for the reagent blank, n=10) which corresponds to 0.3-0.5 ng/L for the colloidal fraction of the original samples and the instrument method had a precision of 1.4 % (coefficient of variation, nominal Ag concentration 5 µg/l, n = 10).

To check for contamination with the particulate silver method, unused filters were extracted alongside the samples and gave a reading of 0.95 (SD 0.02) µg/L silver in the filter extracts. To confirm this value, more blank filters were extracted on a separate occasion giving a reading of 0.98 (SD 0.62) µg/L silver in the filter extracts. The 0.95 µg/L value (which was measured at the same time as the samples) was used to correct the readings of the

sewage samples for background contamination. To check for contamination for the colloidal silver method, blanks containing ultrapure acid treated like the 2-450 nm fraction were analyzed along with the digests and had non-detectable silver levels.

2.8. Predicting nano and total particulate silver concentrations in all English and Welsh rivers based on measured discharge

The LF2000-WQX model was used to predict the concentrations in 21,450 km of rivers across England and Wales. The model has been described in detail elsewhere (Williams et al., 2009) and applied to a range of different contaminants released through STPs including, triclosan (Price et al., 2010), dishwasher additives (Janna et al., 2011), and pharmaceuticals (Rowney et al., 2009; Kugathas et al., 2012). In a recent test with estrogens it was found to simulate well the measured river concentrations (Williams et al., 2012). The model uses per capita loads and effluent flow rates to estimate concentrations of a contaminant discharging to the river network from all major STPs. These are in turn combined with the river flows at each site to calculate the concentrations in the receiving water taking account of any mass loads transported from upstream. Thus, working from the low order streams at the head of the river network to the outlet from the river basin, the model accounts for the accumulation of point loads and the accumulation of water in which these loads are diluted.

LF2000-WQX is a hybrid deterministic/stochastic model: the core is deterministic, describing removal and dilution processes, and a stochastic layer is added using Monte Carlo simulations based on statistical descriptions of the per capita-discharge loads, sewage discharge flows and estimated flow duration curves. The simulations are run multiple times each run a combination of discrete samples from the input distributions. A distribution of concentrations is then estimated from each river reach; the mean prediction can be thought to approximate to the concentration that would be seen in the river under the normal range

of river flow and discharge conditions. The 90%ile prediction is the concentration that will only be expected to be exceeded 10% of the time and when used in a risk assessment is more protective than the mean. Such a scenario might reflect a high discharge and low river flow situation.

For the modeling study the measured effluent concentrations from the nine separate STPs were assumed to be typical of the UK and converted to per capita effluent loads (pc_eff, µg/cap/d). This calculation required the estimated dry weather flow (DWF, m³/d) for the STP and the population served (p) thus;

$$pc_eff = (\text{measured concentration (ng/L)} \times \text{dwf}) / (p \times 1000)$$

In these simulations the colloidal silver per capita loads were described by a normal distribution and the total particulate silver loads by a log normal distribution. Comparison of the mean and median values calculated across the STPs suggested that the total particulate silver per capita loads were skewed from the normal. It was also assumed that there was no loss of particulate silver as it was transported along the rivers.

3. Results and discussion

3.1. Spike recoveries

The spike recovery checks used to validate the methods for the determination of silver in the >450 nm and 2-450 nm fractions gave the following mean recoveries (%) respectively: 125 (range 85 – 153, n=6) and 90 (range 57 – 123, n=8).

It was important to check the methods for the determination of silver in the >450 nm and 0-450 nm fractions by using spike recovery tests with real nanosilver. In the absence of suitable well defined certified reference materials, two commercially available silver

nanoparticle products were used. These, one suspension (NGAP NP Ag-2103-W, 42 nm silver dispersion in water, Nanogap, Spain) and one powder (50 nm silver powder, Amepox Ltd, Poland), required extensive preparation before use and in this context the spike recoveries appeared reasonable. Our results confirm that we did not experience any major losses of nanosilver when using the methods used for the determination Ag in the >450 nm and 2-450 nm fractions.

3.2. Particulate silver (>450 nm) in the sewage influents and effluents

There was a wide variation in particulate silver influent values ranging from 90 to 15,000 ng/L (table 2). This is a wider range than that found by Li et al. (2013) who measured silver in German STPs and found typically 400 ng/L up to a maximum of 1,700 ng/L for particulates in the influent. In the effluent an average of 78 ng/L particulate silver was measured (range from 8.5 to 409 ng/L, table 2). These values were similar to measurements of total particulate silver in effluent at North American sites sampled in the mid 1990's to 2001 where 28-180 ng/L total was reported (Shafer et al., 1998; Adams and Kramer, 1999; Wen et al., 2002). With one exception (SB1) all the STPs, regardless of type, removed more than 93% of the particulate silver in the influent (table 2), confirming previous assessments made in the US in the late 1990s on the efficiency of silver removal in sewage treatment (Shafer et al., 1998). It is noteworthy that the overall removal of suspended solids as measured in the same samples was 96%; suggesting particulate silver was most likely removed with the sludge in the settlement process. Indeed, when expressed per g suspended solid the silver concentration generally changed little during treatment (table 2).

3.3. Colloidal silver (2-450 nm) in the sewage treatment plants, including the nano component

The colloidal silver in the influent was only a very small proportion of the total with a range of 2-27 ng/L and a mean of 12 ng/L (table 2). The colloidal silver will include the nanoparticle fraction. Higher influent values were reported in Germany, using a different approach, with typically 312 ng/L being reported (lowest 60 ng/L) (Li et al., 2013). Some removal from influent to effluent was apparent in the present study with the mean dropping to 6 ng/L or half the influent value. This value agrees well with the recent German study of 5 ng/L (Li et al., 2013) and is slightly less than the 16-53 ng/L observed in North American STP effluents a decade ago (Adams and Kramer, 1999; Wen et al., 2002).

3.4. Predicted nano and total particulate silver concentrations in all English and Welsh rivers based on measured discharge

The monitoring results showed some considerable variation between STPs (table 2), but there was no evidence statistically that these differences in per capita load could be ascribed to the type of STP. Since there was no significant difference in effluent per capita daily load by type, all the data were pooled to provide a mean per capita load. Thus, the combined monitoring data indicated a mean loading of 1.7 µg/cap/d (SD 1.4) for the colloidal (assumed here for risk assessment purposes to be all nanosilver) and 23.6 µg/cap/d (SD 31.9) for total particulate silver. The model output for all 21,450 km of rivers being fed by over 2,000 STPs can be displayed as a series of cumulative frequency distributions (Fig. 1). For total particulate silver around 62% of values were predicted to be 10 ng/L or less using the mean concentration (Fig. 1). At the 90%ile prediction more occasions of concentrations in excess of 50 ng/L are shown (19%) but with the majority of sites still likely to be 20 ng/L or below. For the assumed nano fraction it can be seen that most concentrations would fall between 0

and 4 ng/L with a very small fraction over 10 ng/L for the 90th percentile prediction. These predictions are corroborated by a recent monitoring study of <450 nm silver in British rivers (Peters et al., 2011) where three quarters of the samples were below a 6.6 ng/L limit of quantification and over half below a 3 ng/L limit of detection. The mean of the maximum concentrations in that study was 6.1 ng/L.

3.5. Measured total silver in sewage sludge

There was a good agreement between the duplicate analyses and between the quantification ion Ag107 and the confirmation ion Ag 109 (data not shown).

The recoveries for the high silver containing sludge reference material LGC 6181 was close to 100% (average: 101%, range: 97-112%, n=5), but for the low concentration reference material the recoveries were less good (average: 142%, range 107-173%, n=5). However, the silver concentrations in the samples were a factor 18-300 higher than this low standard and up to a factor of 20 lower than the higher reference material, so they fell in a region where the analysis was expected to perform well.

The values for silver in sludge at all the sites except sludge 7 were similar at 2-7 mg/Kg (table 3). Perhaps the outlier was linked to its high industrial input compared to other plants in the study. A previous predictive exercise suggested 1.3 to 4.4 mg/kg nanosilver might be found in European sludge (Gottschalk et al., 2009) which is similar to these values for total silver. These silver sludge measurements can be compared with the amount of silver found on the particulates (>0.45 µm) in the influent (although they only represent a brief snapshot of what might arrive in the sludge). These particulate values were 0.7-38.8 mg/kg DW which is in a similar range to that found in the final sludge products (2.3-42 mg/kg DW).

3.6. Estimating silver concentrations in soils

Good agricultural practice advises limiting total N applications to 250 kg/ha/year N. As sludge is considered to contain a minimum of 3% N by dry weight (Hogan et al., 2001), up to 8.3 tonnes dw/ha sludge may be applied. Assuming the median silver found in sludge from the 9 STPs studied here was representative (table 3) that would result in an inadvertent application of silver of 29.5 g/ha (2.95 mg/m² Ag) if this recommended agricultural practice was followed. The typical plough depth is 20 cm and a typical soil DW bulk density is 1.3 t/m³ (Hallett, 2008), so 1 m² ploughed to 20 cm gives a soil volume of 0.2 m³, or 260 kg by weight of soil. Thus, for the median value of silver in sludge, 2,950 µg Ag/260 kg soil would yield a 11.3 µg/kg silver concentration in soil (61.5 µg/kg DW soil at 90%ile). There are still few studies on silver toxicity to soil flora and fauna, but harmful effects have been observed with plants grown in suspension (El-Temseh and Joner, 2012; Yin et al., 2012) exposed to 10 mg/L silver.

4. Conclusion

The silver concentrations entering and leaving UK sewage treatment plants measured here were relatively low. The effluent colloidal (including nanoscale) value of 6 ng/L is practically identical to that recently reported in Germany (Li et al., 2013). Perhaps the market penetration in Europe of silver and nanosilver products is not as large as predicted, or the release from products is less than expected (Geranio et al., 2009; Benn et al., 2010). Combining these sewage effluent measurements with a water quality model for England and Wales suggests 4 ng/L nanosilver would be exceptional and values less than 1 ng/L the norm. These concentrations are around 3-orders of magnitude below the current lowest reported effect values for aquatic organisms (EC50 of 1 µg/L for *Daphnia magna* 21 d reproduction test (Ribeiro et al., 2014)).

However, the total particulate silver, to which nanosilver contributes, was predicted to exceed 50 ng/L at 19% of locations using the 90th percentile concentration (typical of low flows). A concentration of 50 ng/L was proposed as an environmental quality standard back in 1996 (Murgatroyd et al., 1996). However, the risks of particulate and nanosilver in the environment may be less than expected due to the favorable reaction of silver with sulphide (a common ion in sewage) to form precipitates and complexes which are stable even in oxidizing conditions (Choi et al., 2009; Kim et al., 2010; Kaegi et al., 2011) and importantly reducing the release of the toxic Ag ion (Levard et al., 2011). This form appears to reduce the toxicity of silver (Levard et al., 2013). It remains to be seen to what extent the diversion of silver to land through sewage sludge poses environmental risks.

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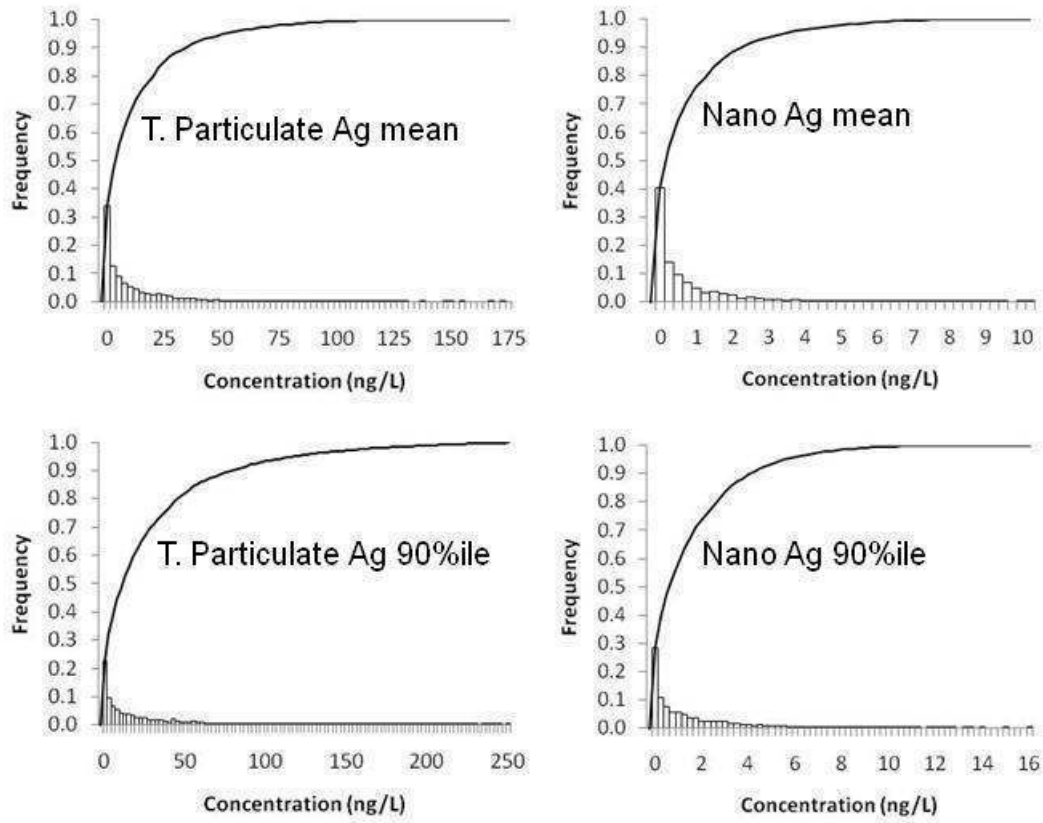


Figure 1. Frequency and cumulative frequency plots of predicted total particulate and nanosilver mean and 90%ile concentrations in all river reaches downstream, of STPs in England and Wales

Table 1 Sewage treatment plants sampled in the survey

Name*	Region	Human PE (k)	Ave. Dry weather flow (m3/d)	Sampling dates
SAS1	South	23.7	5000	01/02.11.10
SAS2	Midlands	188.7	62000	02/03.08.10
SAS3	North West	205.6	64759	25/26.10.10
SB1	North West	120.6	49670	17/18.10.10
SB2	South	7.0	1269	18/19.08.10
SB3	South	5.9	1368	14/15.07.10
TB1	South	11.3	2406	07/08. and 10/11.11.10**
TB2	East	16.2	4200	26/27.09.10
TB3	North West	140.6	40907	04-06.10.10

*SAS standard activated sludge, SB standard biological filter, TB biological filter with tertiary treatment. ** Influent and effluent were sampled on different days

Table 2 Summary of silver monitoring results

Name	Influent			Effluent			Removal	
	2-450 nm [ng/L]	> 450 nm [ng/L]	> 450 nm [µg/g solids]	2-450 nm [ng/L]	> 450 nm [ng/L]	> 450 nm [µg/g solids]	2-450 nm	> 450 nm
SAS1	2.1	14,850	38.1	2.7	28	1.3	none	99.8%
SAS2	10.3	4,790	10.4	9.1	68	6.9	11%	98.6%
SAS3	14.3	260	0.9	< 0.5	16	3.3	>96%	93.8%
SB1	4.0	340	0.7	12.3	171	5.3	none	49.5%
SB2	24.0	190	0.8	12.7	12	1.2	47%	93.5%
SB3 summer	10.5	9,670	39.2	4.6	409	49.5	56%	95.8%
SB3 autumn	6.3	1,450	4.6	5.7	45	4.1	10%	96.9%
TB1	16.2	380	1.2	7.9	17	4.6	51%	95.4%
TB2	12.0	1890	5.8	4.5	8.5	2.2	62%	99.6%
TB3 infl1 (dom.)	27.0	90	0.8	2.8	12	2.5	81%*	99.2%*
TB3 infl2 (mixed)	5.5	2,540	10.1	5.3	69	9.8	68%*	94.7%*
Median	10.5	1,450	4.6	5.3	28	4.1	49.7%**	98.1%**
Average	12.0	3,310	10.2	6.2	78	8.2	48.7%**	97.7%**
(SD)	(8.0)	(4,780)	(14.5)	(4.0)	(120)	(13.8)	NA	NA

*using combined influent concentrations calculated as the average of the two measurements weighted according to the flows of 45:55 domestic:mixed on 4/5.10.10 and 50:50 on 5/6.10.10

** calculated from averages (respectively medians) of all influent and effluent concentrations

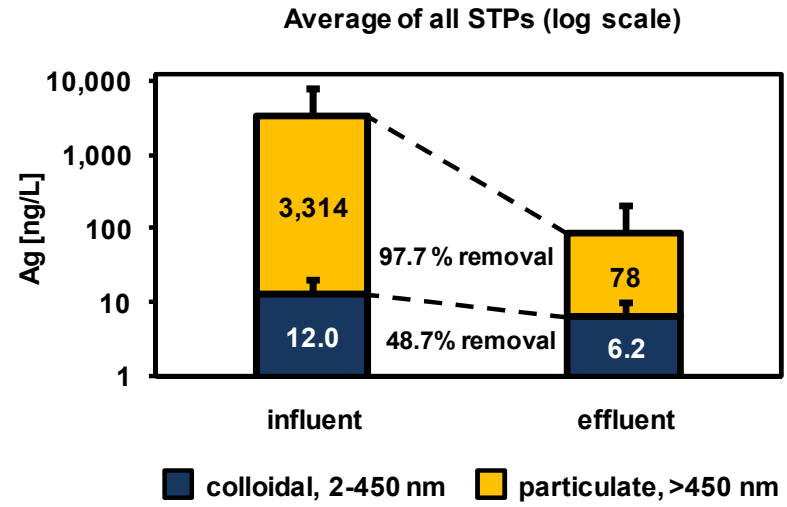
NA SD not calculated

Table 3 Silver concentrations in sludge cake from 9 sewage or sludge treatment works

Name	Region	date	may include sludge from	Moisture % of sludge cake	Ag (107) [mg/kg DW]
Sludge 1	South	19.10.12	SB2, SB3, TB2	21.2	3.48 (3.36, 3.59) ^a
Sludge 2	South	24.10.12	SB2	16.3	3.56
Sludge 3	Midlands	13.11.12	SAS2	18.8	7.34 (7.51, 7.17) ^a
Sludge 4 ^b	North West	21.11.12	SAS3	26.3	4.62
Sludge 5 (SB1)	North West	22.11.12	SB1	29.2	2.88
Sludge 6	North West	21.11.12		23.4	2.34
Sludge 7 (TB3)	North West	27.11.12	TB3	29.1	42.10
Sludge 8	Middle	13.12.12	TB2	26.6	3.98 (4.10, 3.85) ^a
Sludge 9	Middle	13.12.12	TB2	30.4	2.92
Low: 10% ile					2.77
Median					3.56
High: 90% ile					14.3

^a duplicate digestions, the average and the individual measurements are given

^b dedicated sludge treatment plant



HIGHLIGHTS

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