Challenges in assessing the environmental fate and exposure of nano silver.

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Abstract. There are significant challenges in assessing the fate and exposure of nanoparticles (NPs) owing to the lack of information on their use and potential pathways and sinks in the environment. This paper discusses these issues using nanosilver as a case study. The approach taken is to assess the production of nanosilver, the range of products that utilise its properties, potential environmental release pathways and subsequent fate. Estimates of UK nanosilver released into the environment have been made and sewage sludge identified as an important receiving compartment. This work aims to highlight the on-going challenges faced when assessing NPs in the environment. Using nanosilver as an example, difficulties in assessing production, use and release are discussed. The study also recommends a potential approach to assess the fate and behaviour assessment of nanosilver in the environment.

1. Introduction

Nanoparticles (NPs) released into the environment have the potential to cause significant impact as a result of their unique properties and potential widespread use and application [1]. However, many challenges exist in assessing their environmental fate and exposure, as well as identifying whether the release of nanoparticles into the environment could result in detrimental effects.

The approach taken in this study to assess the environmental fate and exposure of nanosilver has initially involved reviewing their production and the lifecycle of products that use nanoparticles. Reviewing the production and use of a particular NP is challenging owing to the lack of information on use of NPs. Attempts to record products that may contain NPs have been made by some organisations, such as the Woodrow Wilson Centre in the US (Project on Emerging nanotechnologies (PEN) consumer inventory)[2], and by UK Defra’s Voluntary Reporting System (VRS)[3]. Clarifying whether the products actually contain the nano form or not, is an issue faced by these organisations. However, it is apparent that the use of NPs in consumer products is increasing by comparison to their bulk counterparts. The burden on the environment from widespread and extensive use is not yet known and current research is incomplete.

This study has focussed on UK use and the fate and exposure of nanosilver in the environment. The potential for large quantities of nanosilver being released into the environment raises the questions about the form of nanosilver once released. Data regarding the environmental form of silver is important when designing a best approach for environmental measurements.
Regulation covering the manufacture of nanoparticles, their use and release, lags behind rapid scientific and industrial advancements. A key example is represented by the recent EU Regulation REACH (Registration Evaluation Authorisation Restriction of Chemicals), which came into force on the 1st June 2007. The current REACH regulation applies to all chemicals manufactured or imported in quantities of more than 1 tonne per year into the EU, including chemicals manufactured in the nano form. A potential risk with regulating NPs is the low NP tonnages will fall outside the radar of regulation. There are also further limitations for REACH regulating NPs as their properties vary significantly from their bulk counterpart. Various endpoints have been suggested for testing of NPs such as specific surface area, zeta potential (surface charge) and surface chemistry.

Attaining a clearer understanding of the NPs fate and behaviour, and chemical and physical form in the environment will help support the development of effective regulation [4].

2. Nano Silver production and use
Nanosilver is increasingly applied and used in products for its antimicrobial properties. In order to better understand the impact of nanosilver upon the environment, our approach has first been to investigate global and historic uses of bulk silver and the emerging uses of nanosilver in the UK market. In this instance nanosilver refers to silver nanoparticles which are described as ‘nanoscale clusters of metallic silver atoms’ [5]. The total surface area maximises the effect of the silver and the presence of both metallic and ionic form will characterise many nanosilver products [1]. Commonly most commercially available silver nanoparticles have a diameter of 10 nm with specific surface area 9-11 m²g⁻¹ [6].

Silver is a familiar metal in modern society and has been in use for many hundreds of years. As a transition metal group which is soft, white, and lustrous, it has many beneficial properties. It is ductile, malleable and has high electrical and thermal conductivity which lend its use to many applications. Silver, as well as nanoparticles of silver have antimicrobial properties [7], which have been applied for uses in cosmetics, coatings, and medical applications. The primary advantage nanosilver has over its bulk counterpart is the potential to use less material in application thus providing weight and cost reductions.

Globally the use of silver has been dependent on the available supply driven by discovery of new silver mines and the application of new extraction techniques. The global demand of silver has been approximately 25,000 t/yr over the past 10 year [8]. Dips in demand have occurred, for example during 2009 a drop in fabrication has been noted due to the global financial crisis 2009, which led to fabrication figures similar to that in 2003 [8].

2.1. UK Nanosilver demand
In order to estimate the potential demand for nanosilver in the UK, we used information on existing global demand levels for silver. Global demand levels as sourced from the Silver Institute include Industrial Applications, Photography, Jewelry, Silverware, Coins & Medals. The sum of these demands is referred to as the Total Fabrication amount. The UK is assumed to use 8% of the total fabrication demand for silver, as seen in figure 1. However the maximum demand of nanosilver could be assumed to be just the silver industrial application demand, while minimum or lowest level is assumed to be the 5% of the industrial application. Figure 1 shows the output estimations for nanosilver demand in the UK.
3. Environmental release

Establishing potential or actual environmental release routes and quantities is required to better understand the nanoparticles fate and exposure. There have been a small number of studies on release. For example Geranio and Heuberger et al. (2009) [9] investigated nine textile types with nanosilver incorporated into the cotton, polyester or polyamide fibre. During washing the total Ag released varied from 1.3 to 35% of the total Ag in the fabric, although the amount lost after subsequent washes decreased. The coarse fraction >450 nm sized particles were identified as the greatest lost from textiles which were attributed to the mechanical stress during the washing process [9]. This study confirms that there would be some release into waste water from silver articles during the washing process. Kaegi et al. (2010) [10] reported the release of nanosilver from painted facades. The initial runoff from leaching from a painted façade gave a maximum concentration of 145 mg/l. The study determined that 0.5 mg/m² was the total amount of Ag released from the paint during one year of exposure which was about 30% of the applied Ag [10]. Another study demonstrated that nanosilver impregnated socks lose nearly 100% of their silver content within four washings [11].

Data developed from direct studies on release during product use can be used to estimate the quantity of nanosilver that is potentially present in environmental compartments. The figure can then be compared against the natural background levels of silver in the environment. Previous work that has modeled release in the environment includes [12] and [13].

4. Environmental fate and challenges

The environmental form that nanosilver takes is one of the more complex issues in studying its behaviour in the environment. Understanding the transformation and speciation of silver in the environment is important for analysis, assessment of toxicity, and understanding its fate and behaviour [14].

Four oxidation states of silver exist: 0, 1+, 2+, and 3+; the most commonly found form in the environment being 0 and 1 [15]. Nanosilver has a propensity to change form and bind with other elements. Silver has a strong affinity to bind with sulphur and is commonly found in a sulphur form in the environment [16]. Silver can be present in the form of silver oxide, silver nitrate, silver halides (Floride, Chloride, Bromide), silver sulphate, silver thiosulphate complexes and silver sulphide. The
solubility and toxicity of these forms varies and their presence in particular compartments will be dictated by the concentration of other chemicals, pH and organic matter [17].

Silver has been reported to be removed efficiently by wastewater treatment (WWT) plants (>94%) [18,16]. Settling and filtration are the main form of removal which also relates to the high particle-water partition coefficient (Kd) (Shafer et al., 1998 [18]). However, removal efficiencies vary and contamination of receiving waters from WWT plants is thought to be likely. Sewage sludge remains an important potential source of silver to the environment where it binds efficiently with sulphur. Kim (2010) [19] found nanoAgS in sludge which was hypothesised to have formed insitu via reduced sulphur reacting with the Ag NPs and soluble Ag species.

During 2004 nearly 1.4 million tons of dry solids were produced in England and Wales with 1.6 million estimated for 2010. Of this 62% of sewage sludge was applied to over 80,000 hectares of agricultural land with other disposal outlets such as incineration (19%), land reclamation (11%), other (7%) including compost, industrial crops, and landfill (1%) accounting for the rest [20].

Sludge applied to land is regulated for some metals and pathogens and maximum permitted concentrations in soils have been set by the European Community Directive 86/278/EEC (CEC, 1986), details of which have been implemented in England, Scotland and Wales by The Sludge (Use in Agriculture) Regulations. Metal concentrations within sludge must be regularly analysed with soil analysis undertaken before and after application. However, there is no concentration limit set for silver. Within the literature Beckett (1978) [21] reports a value of silver in a UK dried digested sludge at 200 mg/kg. A more recent analysis of silver in UK sludge has not been identified although a typical concentration would be approximately 25 mg/kg dry weight [22].

Soil quality is dependent on chemical, physical and biological factors [23]. The application of municipal sludge onto land for agricultural purposes has the potential to improve aspects of soil quality. The accumulation of metals on agricultural land remains a concern for soil quality for risks such as phytotoxicity. Smith (2009) [24] concluded that the ‘risks to the environment, human health, crop quality and yield and soil fertility, from heavy metals in MSW-compost are minimal’. However, this review excluded silver.

5. Challenges for environmental exposure
Before considering environmental exposure it is worth briefly discussing occupational exposure to silver and nanosilver. Dermal and ingestion exposure are the two main potential human pathways during nanosilver production and use. There is also the potential for accidental ingestion and although silver is not an essential trace element in the body it is readily absorbed and commonly present in the bloodstream at low levels <2.3 μg/L [25]. There is also some evidence that inhalation exposure to airborne metals is possible in the workplace, Park et al. (2009) [26] monitored Ag NPs that were released in a commercial production facility during liquid-phase production of Ag.

Identification of nanosilver in the environment has only been confirmed in a handful of studies. The presence of nanosilver in the environment is not necessarily due to engineered nanosilver usage. However, new usage could have an impact and there are complications with existing tools and techniques for the identification of nanosilver in the environment. To better establish nanosilver in the environment we have expanded upon the potential exposure pathways from current usage.

5.1. Nanosilver exposure pathways
Products containing nanosilver that are potentially in use within the UK have been divided into a number of product categories. This is not a definitive list and the information has come from existing databases including PEN’s project consumer inventory [2], Defra’s VRS [3] and internet searches. These product categories were used to derive potential exposure pathways as displayed in table 1.
Table 1. The potential exposure pathways of nanosilver from products used in the UK into the environment has been summarized.

| Category              | Release Pathway                                           | Number of products in category |
|-----------------------|-----------------------------------------------------------|-------------------------------|
| Medical Application   | Medical Incineration, Landfill                            | 1                             |
| Health and Fitness    | Wastewater, Landfill                                      | 11                            |
| Home and Garden       | Wastewater, Landfill, Runoff, direct & diffuse pathway to aquatic environment | 3                             |
| Food and Beverage     | Landfill, Recycled, Lost, Ions to water                   | 2                             |
| Appliances            | Wastewater                                                | 1                             |

Items with silver impregnated into their structure such as plastics are most likely to end up in landfill or be recycled. Plastic containing silver is designed to release ions for the effect of antimicrobial action to take place. The lifecycle of these plastics has been measured and assumed to be about 3 years [27]. On disposal the product may go to landfill and uncertainty exists as to whether the disposed product still contains silver. Silver ions are also used in shower filter systems which may then be released from the filter and enter the wastewater treatment system.

Nanosilver is also used in paint products for anti-mold protection and so there is potential release via runoff, direct & diffuse pathway to aquatic environment [10]. The disposal of medical equipment and clothing is controlled with hazardous waste going to incineration or other waste going to landfill.

Clothing and sheets may also release nanosilver in the indoor environment. Abrasion against skin of socks and towels during use may cause release of particles in indoor and outdoor environment. Household cleaning equipment may remove some of the released material which would normally be disposed into waste or via landfill. Socks and material washed in washing machines containing nanosilver are known to be released into wastewater [9]. Once items are no longer required, clothing/material/socks maybe recycled or disposed of to landfill.

Nanosilver roll on deodorant is designed to adhere to skin but this is likely to be washed off and pass into the wastewater system. Spray deodorant is directed at the skin but may also be accidentally sprayed on other household surfaces. Deodorant may also transfer onto clothing which again may be washed and any remains may go to wastewater. Also inhalation may occur if developed into spray products.

5.2. Potential release estimates
Some assumptions have been made to calculate potential quantities of nanosilver released into sludge and water. The results are shown in table 2. Kaegi et al. 2010 [10] estimated that more than 30% of the total nanosilver is released to the environment from painted facades. This figure is applied to the nanosilver demand for the UK, as calculated from the '5% UK Industrial application'. Removal efficiencies of waste water treatment suggest that a suitable figure to apply is 90% with the remaining 10% potentially releasing into water and aquatic environments.

Table 2. Assumptions and quantities of nanosilver in UK environment 2009.

| Assumption                           | Quantity (tonnes) |
|--------------------------------------|-------------------|
| Assume nano goes in waste water system | 13.1              |
| Assume nano goes 90% to sludge       | 11.8              |
| Assume nano goes 10% to water        | 1.3               |
6. Future considerations
Nanosilver is likely to continue to be developed for its antimicrobial properties and applied to many consumer products. Clarification of the environmental form of silver will enable better understanding of its fate in the environment. There are currently a lack of studies detailing environmental measurements and detection using standard equipment. Detection and measurement of silver in the environment remains challenging but will support fate studies.

The exposure scenarios for nanosilver can only be comprehensive if information on product types and use becomes available. In the meantime only estimates can be made about production of nanosilver and use. Commercially sensitive data covering production volumes remains restricted. Progressing work in field experiments, measuring release will help test exposure scenarios and support models predicting release.

Although this work has not considered the toxicity of nanosilver it is something that must acknowledged. Nanosilver has been found to be toxic to some aquatic species, detail of which can be found in the literature [28, 29]. However until further research is conducted the impact remains unclear.

It is important that the necessary understanding of the environmental fate and exposure of nanosilver is developed and can support the risk assessment process. As highlighted above, current REACH regulation applies to all chemicals manufactured or imported in more than 1 tonne per year into the EU, including chemicals manufactured in the nano form. This regulation uses a risk assessment process to protect human health and the environment. To adequately mitigate the risk, validated nano form specific data and knowledge will be required. Various endpoints have been suggested for testing NPs such as specific surface area, zeta potential (surface charge) and surface chemistry. The lack of knowledge and information available on nano particles in the environment remains an issue. Regulation and standardisation will not be achieved in the nano arena until further research has been undertaken to resolve the knowledge gaps. In the meantime industrial output will likely continue to increase.

References
[1] Panyala NR, Pena-Mendez EM, Havel J 2008 Silver or silver nanoparticles: a hazardous threat to the environment and human health? J. Appl. Biomed. 6 (3):117-29.
[2] PEN PoEN 2010 Consumer Products. [23rd April 2010]; Available from: http://www.nanotechproject.org/inventories/consumer/.
[3] DEFFRA, 2008 [cited UK Voluntary Reporting Scheme for engineered nanoscale materials: Available from: http://www.defra.gov.uk/environment/quality/nanotech/documents/vrs-nanoscale.pdf.
[4] Handy RD, Owen R, Valsami-Jones E 2008 The ecotoxicology of nanoparticles and nanomaterials: current status, knowledge gaps, challenges, and future needs. Ecotoxicology. 17 (5):315-25.
[5] Marambio-Jones C, Hoek EMV 2010 A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment. J. Nanopart. Res. 12 (5):1531-51.
[6] Navarro E, Baun A, Behra R, Hartmann NB, Filser J, Miao AJ, et al. 2008 Environmental behavior and ecotoxicity of engineered nanoparticles to algae, plants, and fungi. Ecotoxicology. 17 (5):372-86.
[7] Morones JR, Elechiguerra JL, Camacho A, Holt K, Kouri JB, Ramirez JT, et al. 2005 The bactericidal effect of silver nanoparticles. Nanotechnology. 16 (10):2346-53.
[8] The Silver Institute Demand and Supply in 2009. [3rd November 2010]; Available from: http://www.silverinstitute.org/supply_demand.php#demand.
[9] Geranio L, Heuberger M, Nowack B 2009 The Behavior of Silver Nanotextiles during Washing. Environmental Science & Technology. 43 (21):8113-8.
[10] Kaegi R, Sinnet B, Zuleeg S, Hagendorfer H, Mueller E, Vonbank R, et al. 2010 Release of silver nanoparticles from outdoor facades. Environ. Pollut. 158 (9):2900-5.

[11] Benn TM, Westerhoff P 2008 Nanoparticle silver released into water from commercially available sock fabrics (vol 42, pg 4133, 2008). Environmental Science & Technology. 42 (18):7025-6.

[12] Mueller NC, Nowack B 2008 Exposure modeling of engineered nanoparticles in the environment. Environmental Science & Technology. 42 (12):4447-53.

[13] Gottschalk F, Sonderer T, Scholz RW, Nowack B 2009 Modeled Environmental Concentrations of Engineered Nanomaterials (TiO2, ZnO, Ag, CNT, Fullerenes) for Different Regions. Environmental Science & Technology. 43 (24):9216-22.

[14] Bell RA, Kramer JR 1999 Structural chemistry and geochemistry of silver-sulfur compounds: Critical review. Environmental Toxicology and Chemistry. 18 (1):9-22.

[15] Purcell TW, Peters JJ 1998 Sources of silver in the environment. Environmental Toxicology and Chemistry. 17 (4):539-46.

[16] Kramer JR, Bell RA, Smith DS 2007 Determination of sulfide ligands and association with natural organic matter. Appl. Geochem. 22 (8):1606-11.

[17] Mukherjee B, Weaver JW 2010 Aggregation and Charge Behavior of Metallic and Nonmetallic Nanoparticles in the Presence of Competing Similarly-Charged Inorganic Ions. Environmental Science & Technology. 44 (9):3332-8.

[18] Shafer MM, Overdier JT, Armstrong DE 1998 Removal, partitioning, and fate of silver and other metals in wastewater treatment plants and effluent-receiving streams. Environmental Toxicology and Chemistry. 17 (4):630-41.

[19] Kim B, Park C-S, Murayama M, Hochella MF 2010 Discovery and Characterization of Silver Sulfide Nanoparticles in Final Sewage Sludge Products. Environmental Science & Technology.null-null.

[20] Water UK 2006 Recycling of Biosolids to Land. [3rd November 2010]; Available from: http://www.water.org.uk/home/news/press-releases/biosolids-and-agriculture/-final-revised-biosolids-briefing-pack-2006-v8.pdf?s1=sludge&s2=properties.

[21] Beckett PHT 1978 An all-element analysis of digested sewage sludge. Water Pollution Control. 77 (4):539-46.

[22] Gray NF 2005 Water technology : an introduction for environmental scientists and engineers. 2nd ed. ed.(Oxford: Elsevier Butterworth-Heinemann)

[23] Wander MM, Drinkwater LE 2000 Fostering soil stewardship through soil quality assessment. Applied Soil Ecology. 15 (1):61-73.

[24] Smith SR 2009 A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge. Environ. Int. 35 (1):142-56.

[25] Lansdown ABG 2007 Critical observations on the neurotoxicity of silver. Crit. Rev. Toxicol. 37 (3):237-50.

[26] Park J, Kwak BK, Bae E, Lee J, Kim Y, Choi K, et al. 2009 Characterization of exposure to silver nanoparticles in a manufacturing facility. J. Nanopart. Res. 11 (7):1705-12.

[27] Blaser SA, Scheringer M, MacLeod M, Hungerbuhler K 2008 Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles. Science of the Total Environment. 390 (2-3):396-409.

[28] Scown TM, Santos EM, Johnston BD, Gaiser B, Baalousha M, Mitov S, et al. 2010 Effects of Aqueous Exposure to Silver Nanoparticles of Different Sizes in Rainbow Trout. Toxicological Sciences. 115 (2):521-34.

[29] Ratte HT 1999 Bioaccumulation and toxicity of silver compounds: A review. Environmental Toxicology and Chemistry. 18 (1):89-108.