



CrossMark
click for updates

Cite this: DOI: 10.1039/c6en00023a

Durability of nano-enhanced textiles through the life cycle: releases from landfilling after washing†‡

Denise M. Mitrano,^{*a} Pawena Limpiteeprakan,^b Sandhya Babel^b and Bernd Nowack^a

By taking a life cycle approach to study the potential for silver nanoparticle (AgNP) release from functionalized textiles, we can estimate the relative importance of different phases to the release of Ag over time. Alongside the fastness of the AgNPs during the use phase (e.g. washing), we further explored the release potential of NPs from fabrics disposed of in a landfill (*i.e.* the end of life stage). Three different laboratory-prepared nano-enhanced fabrics (60 nm and 100 nm citrate-capped Ag as reactive particles; 60 nm citrate-capped Au as a non-reactive control) were subjected to 1 or 10 washing cycles under different laundering conditions (detergents with and without oxidants). The total metal released varied significantly depending on NP incorporation and the washing pattern variant. Au served to contrast the mechanical release of NPs with the (additional) chemical release the detergents induced to the Ag textiles, where the Ag : Au ratio released from the fabric was as high as 3, suggesting more predominant chemical mechanisms for silver release in those cases. Textile disposal was simulated by the Toxicity Characteristic Leaching Procedure (TCLP), where pre-laundered fabrics were subjected to this sequential exposure. The results show that the active landfill environment cannot readily mobilize the NPs from the fabric surface as easily after washing compared to unwashed textiles. Without washing, simulated landfilling released between 35–45% of the total Ag incorporated into the fabric (and only 20% of Au), but after laundering, most variants released less than 0.5%. Therefore, larger releases of NPs from textiles were observed during the use phase of the life cycle rather than the disposal phase, where an important portion of the released NP was in the dissolved phase. Large variations in releases at the end of life stage are determined under pre-washing conditions, which proves the necessity of life-cycle aging sequences to properly assess the likelihood and characteristics of materials released from nano-enhanced textiles.

Received 27th January 2016,
Accepted 10th March 2016

DOI: 10.1039/c6en00023a

rsc.li/es-nano

Nano Impact

Understanding the transformation and release of nanoparticles from nano-enhanced products depends on crafting studies that rely on realistic consumer patterns representing multiple and sequential phases of a product life cycle. Here, textiles are studied with known nanoparticle incorporation (production phase), various washing conditions (use phase) and landfilling (disposal phase) to understand the dynamics of the silver nanoparticle behavior in each step. The use of well-controlled fabrics, unreactive reference materials and a life cycle-based experimental regime is paramount to understanding silver specific responses to laundering and/or landfilling of these nano-composite fabrics and thus better predicting factor(s) responsible for silver releases over time.

1 Introduction

Nanoparticles (NPs) are added to textiles to impart various functionalities such as antimicrobial properties, self-cleaning ability or dirt repellency.¹ A large variety of textiles on the market today contain silver (Ag) in various forms (*e.g.* Ag⁰, Ag/TiO₂ and AgNPs) acting as an antimicrobial agent.^{2,3} AgNP incorporation into textiles makes up an important share of AgNP use across all possible applications.⁴ This use of nano-silver has stirred quite some public and scientific debate about its possible adverse effects, resulting in a large body of literature on the fate and effects of nano-Ag.^{5–7} During product use, both environmental and human activities can stress

^a Technology & Society Laboratory, Empa – Swiss Federal Laboratories for Materials Science and Technology, CH-9014 St. Gallen, Switzerland.

E-mail: denise.mitrano@empa.ch; Tel: +41 58 765 78 61

^b School of Biochemical Engineering and Technology, Sirindhorn International Institute of Technology, Thammasat University, P. O. Box 22, Pathum Thani 12121, Thailand

† The authors declare no competing financial interests.

‡ Electronic supplementary information (ESI) available: Supporting information contains metal content released from fabrics during the TCLP procedure, results of particle stability experiments (Fig. 6) including the amount of metal recovered from the experimental containers after an acid wash and zeta potential measurements of 60 nm AuNPs in water and TCLP solutions under different conditions. See DOI: 10.1039/c6en00023a

a nano-product resulting in NP transformation(s) and releases. In order to obtain a holistic view about the possible fate of Ag in textiles, all life-cycle stages need to be evaluated, including production, use and disposal.⁸ Choices made during textile fabrication can dictate both the concentration of NPs loaded onto the material and the possible releases if NPs do not securely adhere to the fabric surface.^{9,10} During the use phase of the life cycle of a textile, environmental and consumer use patterns can vary significantly¹¹ and so NP transformations and releases may diverge from a textile made by the same fabrication process.¹² For example, exposure to sunlight during outdoor use, sweat contact, washing, drying, ironing and finally disposal (either in a landfill or by incineration) may all have variable effects on the durability and fastness of the NPs in each textile formulation.^{8,13} There are a suite of studies that targeted the release during washing^{14–17} and the exposure of humans through release into sweat.^{17–20} These studies have shown that, depending on the textile investigated, release can range from below 1% to more than 50% of the Ag contained in the textile during one single washing. It was also shown that significant transformation of metallic Ag to AgCl and AgS occurred during laundering.^{2,16,21} Furthermore, differences in wash conditions (e.g. detergent type) can drastically affect possible Ag transformations once particles are released into the solution.²²

The fate and behavior of Ag in textiles in the end of life (EoL) stage have received significantly less attention than washing textiles. Since textiles and other similar nano-enhanced consumer goods will often be finally disposed of in landfills, a better understanding of the potential for AgNPs to be released into and transported in landfill leachates is needed. The release of Ag under landfill conditions from some consumer products, including textiles, has been reported by Benn and co-workers, but no distinction between dissolved and particulate silver was made.²³ Through other leaching tests, it has been suggested that nano-Ag-containing textiles should not be considered hazardous waste, yet it is important to evaluate the release potential of textiles with high silver concentrations under relevant reactive landfill conditions.²⁴ The influence of the antimicrobial activity of silver on the biological activity in landfills has been studied to some extent. The application of AgNPs on cotton fabrics suppressed the biodegradation of the fabrics in soil.²⁵ The resistance against bacterial attack of AgNP-treated cotton, wool and silk was enhanced compared to non-treated textiles during a soil burial test, and the fiber breaking load was reduced in all fibers without nano-treatment.²⁶ Furthermore, even low concentrations of AgNPs were shown to have small impacts on the composting process.²⁷

Detailed studies on the fate and behavior of Ag nano-enhanced textiles during the EoL phase are scarce, especially those connecting the EoL stage with the previous use stage(s) of the life cycle. The toxicity characteristic leaching procedure (TCLP) is a standard test applied to investigate release under landfill conditions.²⁸ The TCLP test mimics the type of processes that waste might be exposed to under natural condi-

tions in a landfill. If hazardous components migrate from the disposal site into a water source, drinking water supplies may be contaminated. The TCLP test consists of extraction of contaminants using an acetic acid buffer solution followed by analysis of the resultant extract. If a TCLP test determination indicates that these elements are present at concentrations that exceed the associated regulatory limits, then the original waste is considered to be toxic and is subject to stringent disposal regulations. The study by Benn and co-workers²⁹ has used this test to quantify the release of Ag from various consumer products in the past.

The objective of this study is to highlight the characterization of AgNP releases from lab-prepared fabrics under two sequential life-cycle phases: washing and subsequent simulated landfill conditions. In order to include the variations in consumer use and represent realistic household washing conditions, fabric swatches were washed one or ten times with one of two detergents (with and without oxidizing agent). The release of NPs from textiles can be due to different factors, both chemical and physical. To explore the differences between chemical and physical (mechanical) release of Ag during the washing and leaching process, we included fabrics made with nano-Au as a non-reactive control NP. Characterization of the system was accomplished in several phases: (1) multiple wash cycles in different detergent chemistries, (2) simulated landfill tests of previously washed fabrics, (3) total metal remaining on the textile (both after washing and after landfilling) as measured by fabric digestion and total metals analysis, (4) differentiation between particulate and dissolved metal in wash water and landfill leachate extract and (5) analysis of the stability of NPs in landfill leachates to understand the likelihood of mobility of particles once they are in the landfill.

2 Materials and methods

2.1 Nanoparticles, fabric liquors and standards

60 nm and 100 nm citrate-capped spherical AgNPs with stock concentrations of 20 mg L⁻¹ were purchased from Sigma Aldrich (Germany) alongside 60 nm AuNPs (50 mg L⁻¹) from nanoComposix (San Diego, CA, USA). Dissolved standards used for ICP-MS calibration (AgNO₃ and Au; Merck) were diluted in 2% nitric acid or 3% HCl with concentrations ranging from 1 to 200 µg L⁻¹.

2.2 Application of nanomaterials to polyester fabric

The fabrics consisted of 100% woven polyester (PET). The fabrics, sized A4, were treated on a dual-roll padder operated at 2 m s⁻¹ with a roll pressure of 4 bar. Nanoparticles were added to a fabric liquor to treat the woven polyester fabric. A typical liquor composition included 25 mL of stock NPs, 1 mL of the binder, 0.05 mL of the fabric wetting agent, 0.01 mL of citric acid and 1 mL of water. The binder used was Effect SAX (HeiQ Materials AG, Switzerland), which is a blocked linear isocyanate with cationic character, which starts to de-block above 150 °C (*i.e.* in the curing phase). Typical liquor

absorption was 35–40% wet pick-up by weight before drying at 120 °C for 2 min in a laboratory stenter and subsequent curing at 160 °C for 2 min. Fabric sheets were processed twice through this process for maximal NP adhesion given the relatively dilute NP concentration in the fabric liquor. The fabric sheets were trimmed and cut into squares approximately 1 cm² in size, mixed and separated into batches of approximately 1 g for treatments of washing, simulated landfill exposure, or washing with subsequent simulated landfill exposure.

2.3 Washing procedure

In order to investigate the potential for nano-Ag to be released during the use phase of the product life cycle, sequential washing was performed with analysis of fabrics after one wash and after ten washes. Additionally, to highlight the variety of home washing conditions, which was recently reported to significantly affect NP transformations through the wash cycle,²² two types of powder detergent were bought from a grocery store. As outlined in Mitrano *et al.*, where all washing detergent chemistry can be found,²² one detergent contained no oxidizing agents (“color”) and one contained 13% by weight oxidants (“oxi”), where the differing washing detergent chemistry was postulated to be responsible for variations in NP degradation/dissolution.

The washing procedure was based on ISO standard 105-C06:2010, which describes testing of the color fastness through domestic and commercial laundering, with further amendments made according to our previous washing studies.^{10,15,16} The wash liquor was prepared by dissolving 4 g of detergent per liter of water. Approximately 1 g of fabric was placed into polyethylene bottles (50 mL with a tight fitting cap to withstand the extra pressure created by oxidizing agents in some solutions) containing 5 polyethylene balls and 20 mL of wash solution. A 45 min program at 40 °C and 40 ± 2 rpm with steel vessels (75 ± 5 mm diameter, 125 ± 10 mm height, 550 ± 50 mL) tumbling end-over-end with two rinse cycles was followed, as per our previous publications.^{10,15,16,22} After each wash cycle, the fabrics were removed and dried at 60 °C in an oven before the next wash cycle commenced. The fabrics after 1 and 10 wash cycles were either analyzed directly for loss of metal NP content during the washing procedure or employed for the leaching test representing disposal in a landfill (TCLP test; more information in section 2.4). Note that each replicate of washing or combination of washing with subsequent leachate exposure was individually processed, *i.e.* 3 separate treatments of 10 washes with subsequent TCLP exposure were performed as opposed to “bulk” washing of fabrics 10 times and then exposure to the TCLP liquid. This inherently means that the standard deviation between samples is cumulative throughout the entire experimental process (*i.e.* addition of washing differences between samples plus TCLP differences).

The wash water was saved after 1 and 10 washes of the nano-Ag fabrics to determine the ionic Ag content. Centrifugation

ultrafiltration was performed using spin filters with porous cellulose membranes with a 10 kDa size cutoff (Vivaspin 6, GE Healthcare, Bioscience, USA); effectively a nominal particle size limit of 1 to 2 nm. The suspensions were centrifuged for 15 min at 3500 rpm. The solution was acidified with 2% HNO₃ and analyzed by ICP-MS (Agilent 8800 Triple Quad).

2.4 Simulated leaching test (TCLP)

One set of three unwashed fabrics underwent the TCLP test (The EPA Standard Method 1311; Toxicity Characteristic Leaching Procedure) to determine the leaching behavior from this procedure alone. Triplicate samples of fabric swatches washed once or ten times (in either color or oxi detergent) were also submitted to the TCLP test. The extraction fluid was prepared by adding 5.7 mL of glacial acetic acid to 500 mL of deionized water. Then, 64.3 mL of 1 N NaOH was added and diluted to a volume of 1 L. The pH was 4.93 ± 0.05. As called for by the standard TCLP leaching test, the solid-to-liquid ratio was fixed at approximately 1:20 by mass, which equated to 1 g of fabric in 20 mL of extraction fluid. The sample was rotated end-over-end at 40 ± 2 rpm and 23 ± 2 °C for a period of 18 h. The speed of rotation was adapted to equal that of the washing test since the same end-over-end rotation device was used for both protocols. The fabrics were removed from the extraction fluid, dried and saved for *aqua regia* digestion to determine the amount of total metal remaining on the fabric. An aliquot of the extraction fluid was processed through a 10 kDa cutoff ultracentrifugal filter and another aliquot was saved for total metal analysis. Both were acidified to 2% HNO₃ for further analysis by ICP-MS.

2.5 Metal (NP) content on fabrics

The total metal content in the fabrics was obtained by *aqua regia* digestion of both Ag- and Au-treated fabrics. The total metal content (Ag and Au) in untreated (blank), treated (unwashed) and experimental (washed and/or exposed to leachate) PES fabrics was quantified by ICP-MS after microwave digestion with *aqua regia*. When analyzing the Ag-treated fabrics, the total metal concentration was kept in the range of 50 to 250 µg L⁻¹ to minimize Ag precipitation. With Au-treated fabrics, digests were further diluted in the range of 5 to 50 µg L⁻¹ to avoid carryover of Au between samples.

2.6 Stability of particles in TCLP solution

In addition to determining the total amount of metal that leached from the fabrics during the TCLP test, we determined the stability of these particles in the leachate solution in terms of both the leachate matrix and the test conditions (*i.e.* end-over-end rotation). Both Ag and Au NPs (60 nm) were used to investigate possible aggregation and settling of particles under several test conditions. Solutions of 500 µg L⁻¹ 60 nm Au particles and (separately) 200 µg L⁻¹ 60 nm Ag particles in DI H₂O or TCLP extraction fluid were suspended in plastic containers to monitor the total metal concentration in solution for 18 hours while solutions were either resting on

the bench top, moderately stirred, or rotated (*i.e.* end-over-end rotation as in the TCLP test). The matrix of experiments was further expanded to include each of these variants with the addition of 2% surfactant (sodium dodecyl sulfate, SDS) to further promote stability under test conditions, which could be used as a “best case scenario” for further particle stability. Finally, a dissolved indium (In) internal standard of $300 \mu\text{g L}^{-1}$ was used throughout to monitor general metal stability in the solutions over the experimental regime. Sampling time points consisted of 0, 4, 8 and 18 hours in which the solutions were sampled from the top of the experimental container and acidified to 2% HNO_3 for total metals analysis by ICP-MS.

After 18 hours, the samples were disposed of and the sample containers were washed with a high concentration of acid for metal recovery. For silver solutions, a 20 mL mixture of 10% HNO_3 and 1% H_2O_2 was added to the empty experimental containers and shaken for 24 hours, with subsequent ICP-MS analysis to determine the amount of metal sorbed to the vessel walls. For Au-containing experiments, 10% HCl was used.

2.7 Zeta potential analysis

The zeta potential of 60 nm Au NPs (3 mg L^{-1}) in DI water and TCLP solutions (standing and shaking) were measured on a Malvern Zetasizer instrument at time points of 0, 1, 2, 4 and 8 hours. At each time point, triplicate measurements were obtained, each consisting of 100 sub-runs to evaluate the zeta potential. An average of the three main measurements with the standard deviation representing triplicate measurements is reported.

3 Results

3.1 Metal release from textiles during laundering and TCLP test

Total Ag and Au contents in impregnated PES fabrics before and after wash were assessed by *aqua regia* digestion and subsequent ICP-MS analysis (Fig. 1). The Ag and Au concentrations were obtained from washing and TCLP exposure of the samples in triplicate. Because the initial NP loading varied between textile treatments, a more direct way to observe trends across particle types is to assess the relative percent of metal remaining on the fabric compared to the unwashed samples (Fig. 2; A–C). Oxi washing detergents (blue bars) released a higher amount of metal than color detergents (orange bars) across all NP inclusions. Likewise, fabric swatches subjected to 10 wash cycles (darker shaded bars of each color) released more metal than those which underwent a single wash, especially Ag-embedded fabrics washed in oxi detergent. Nevertheless, some differences between the washed fabrics can be found depending on the NP inclusion. The 60 nm Ag NP fabric released more metal into the wash solution under every experimental condition compared to the 100 nm Ag fabric. This suggests the size preference for the release of smaller particles. Statistical analysis was performed

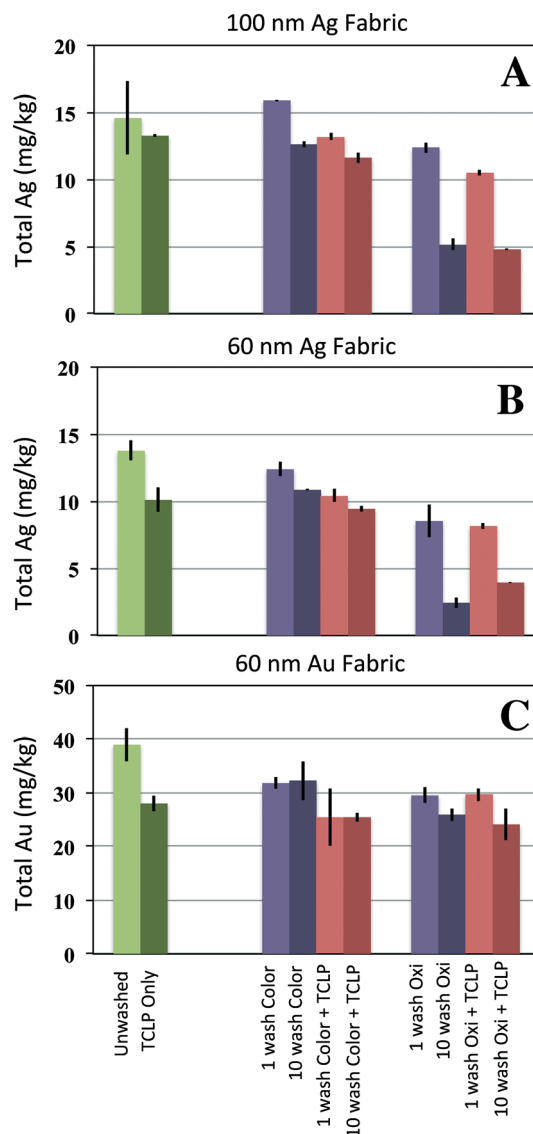


Fig. 1 Total metal analysis from fabric digests for 100 nm Ag-treated fabric (panel A), 60 nm Ag-treated fabric (panel B) and 60 nm Au-treated fabric (panel C). Green bars are indicative of fabrics that did not undergo a washing procedure, with the unwashed (raw) fabric sample and the TCLP test only in light and dark green bars, respectively. Purple bars indicate the total metal in fabrics that were only washed once (light purple) or 10 times (dark purple). Red bars depict fabric samples which were first washed then exposed to the TCLP test, with one wash indicated by light red bars and 10 washes by dark red bars. Samples washed with color detergents are in the center group while fabrics washed with oxi detergents are in the right group.

through a two-way ANOVA test considering all variables, which indicated that both particle size and washing treatment significantly ($p \lll 0.05$) affected Ag release from the textiles, where 60 nm Ag fabrics released more metal than 100 nm variants, color washes released less Ag than oxi washes, and washing multiple times released more Ag than washing once. Additional one-way ANOVA tests comparing individual treatments between the 60 nm and 100 nm Ag treatments (*e.g.* both fabrics washed under the same conditions)

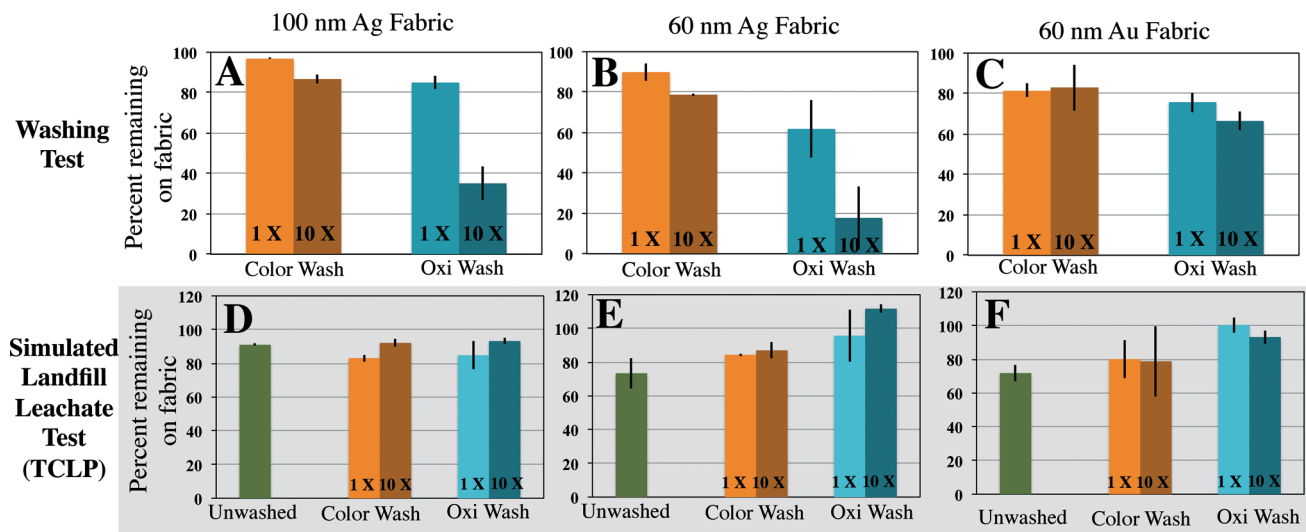


Fig. 2 Relative percentages of metal remaining on each fabric after washing in comparison to the unwashed fabrics are displayed in panels A–C (100 nm Ag fabric, 60 nm Ag fabric and 60 nm Au fabric). Fabric swatches washed with color detergents are indicated in orange while those washed with oxi variants are shown in blue. In both cases, the lighter shade indicates one washing cycle and the darker shade indicates 10 washing cycles. Results of the percent of metal remaining on the fabric after the simulated landfill leachate test (TCLP) are shown in panels D–F in comparison to the corresponding treatment before the TCLP test. Note that the scale on the lower graphs exceeds 100.

also revealed a significant difference in Ag release between the two NP sizes ($p < 0.05$).

In many cases, the 60 nm Au fabric released the least amount of metal under a given set of washing conditions. Because Au is an inert metal, the loss of these particles from the fabrics represents (1) the portion of particles which were not strongly physically attached to the textile surface during manufacturing and/or (2) the fraction of metal which was released due to the mechanical/physical stress from washing the fabrics. Since Ag undergoes additional chemical reactions which can significantly enhance possible release, namely the oxidative dissolution of the particles, it is reasonable to find that these textile treatments release more metal, especially under oxidative conditions, compared to the inert tracer material. The preferential chemical release of Ag compared to the physical release of Au during washing is depicted in Fig. 3A, where the ratio of Ag/Au release of Ag textiles washed in a given detergent/cycle number, which is related to the amount of Au released from the textiles, is indicated by the green and orange symbols for 60 nm Ag and 100 nm Ag NP inclusions, respectively. A ratio higher than one indicates preferential release of Ag over Au. The unit for comparison was mg of metal released per kg of fabric. Here, it becomes more evident that smaller Ag particles are always released from the fabric in higher concentrations than the larger Ag particles and additional washes in the oxi detergent release more Ag than Au.

Additional Ag and Au were released from many textile variants during the simulated landfill leachate test (Fig. 2, panels D–F). Depending on the particle inclusion, the TCLP test removed between 10 and 30% of metal from the unwashed textiles (green bars). The percentages of metal remaining on the fabrics after the TCLP test for all variants that also included a washing step were directly compared to the corresponding

washed only samples. For example, the amount of metal remaining on the textile after the washing step (Fig. 2, panels A–C) was taken to be the total possible metal for release in the TCLP step (Fig. 2, panels D–F), *i.e.* if no metal was released during the TCLP test, the total value would be 100%. Therefore, the total amount of metal released from one full exposure (washing then TCLP) must be assessed as a combination of the top and bottom rows of Fig. 2. Again, we find that Ag from 60 nm doped fabrics is released in higher concentrations than that from the 100 nm counterparts. In these experimental sets, a slightly higher amount of metal was released for fabrics first washed in the color detergents as opposed to those washed in the oxi variants, where the highest amount of metal was released in those sets that underwent only one wash. This suggests that the fraction of material which remains on the textiles that were exposed to harsher washing conditions (*i.e.* increased washing replicates and/or oxi washing detergent) is less likely to be released during the TCLP test. In these instances, the washing conditions promoted a higher likelihood of metallic release from the textiles than when the textile reached the EoL phase in the landfill. In short, under these conditions, the use phase of the life cycle appears to be responsible for the higher metal release rather than the disposal phase. Comparing the relative Ag release to the Au release upon TCLP test exposure (Fig. 3B), we find that the Ag fabrics that were first washed in the oxi detergent subsequently release more Ag into the TCLP solution than the corresponding Au fabric variants.

3.2 Characteristics of metal released to TCLP solution

Total metal concentrations and the dissolved fraction of metal after ultrafiltration in the TCLP leaching solution were

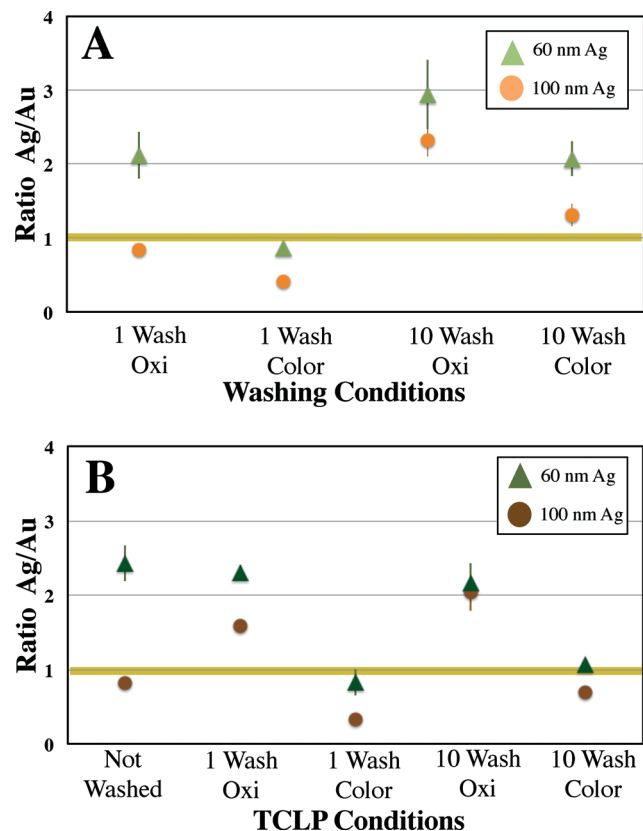


Fig. 3 Ratio analysis of preferential chemical release of Ag compared to mechanical release of Au with (A) washing only conditions and (B) washing with subsequent TCLP exposure. The yellow line at one represents the release of Au from fabrics under each corresponding experimental condition. Green triangles represent fabrics containing 60 nm Ag NPs and orange dots indicate 100 nm AgNP fabrics (light and dark colors indicating washing only conditions and sequential exposure, respectively, in panels A and B). Error bars represent propagation of error of triplicate measurements of Ag and Au nano-enhanced fabric washes.

analyzed for all samples (Table S1[†]). When translated into the amount of metal leached from the fabric under each experimental variant, the highest amount of metal leached from the unwashed fabrics and a significantly lower amount leached from the pre-washed fabrics (Fig. 4). When un-

washed textiles were directly exposed to the TCLP extraction fluid, nearly all of the metal detected in solution from either 100 nm Ag or 60 nm Au doped fabrics was particulate (Fig. 4A) but the 60 nm Ag textiles were of mixed characteristics (*i.e.* dissolved and particulate metal was detected in solution). Additionally, Ag fabrics which were first washed had a much higher variability in the released material measured in the TCLP solution, where between 20–50% of Ag passed through the centrifugal ultrafilter (Fig. 4, panels B and C). In all cases, the fabrics released less than 2 mg kg⁻¹ metal into the TCLP solution and in most cases the amount released was less than 0.5 mg kg⁻¹. The amount of metal measured in the TCLP solution can be further linked to the total metal remaining on the fabric after the initial washing step (Fig. 5). In this context, a significant fraction of metal was released from fabrics which were not washed first (green bars), but a much lower amount of material was extracted from the TCLP solution from fabrics which had first underwent any type of washing procedure. Therefore, in both absolute and relative terms, the amount of metal recovered during the simulated landfill test is small, especially when compared to the release of metal from the unwashed textiles. This further indicates the necessity of life-cycle aging sequences to properly assess the likelihood and characteristics of material released from nano-enhanced textiles.

3.3 Stability of NPs in DI H₂O and TCLP extraction fluid

The inconsistency between the percentage of metal released from the fabrics during the leaching test (Fig. 2, panels D–F) and the amount recovered from the TCLP solution (Fig. 4) points to the (in)stability of the particles themselves in the TCLP solution. We therefore further investigated this aspect of particle stability in the TCLP solution (Fig. 6). The total recoverable Ag is higher in the DI H₂O variants under all conditions except shaking without the SDS surfactant (panel A) than in the experiments in the TCLP extraction fluid without an additional surfactant (panel B). Here, while the addition of SDS appears to stabilize the particles in terms of total recovery from the solution, when no SDS is added, the particles have an enhanced probability of sticking to the experimental

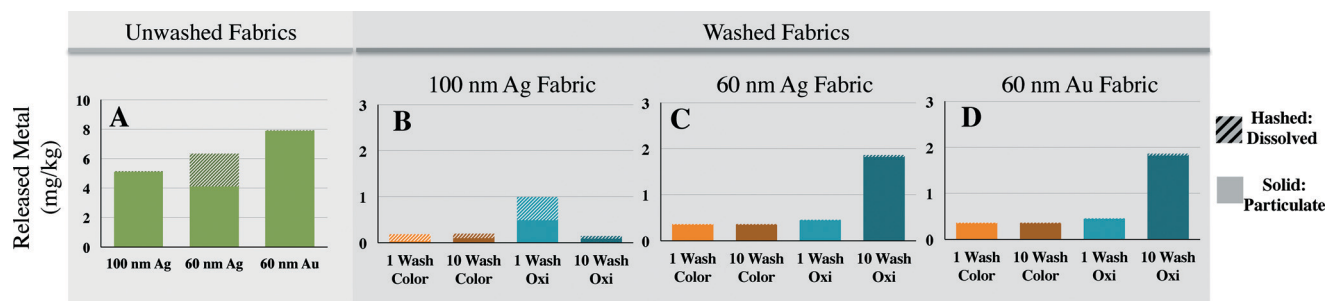


Fig. 4 Concentration of metal released into the TCLP extraction fluid based on fabric weight. (A) Unwashed fabrics (where the x-axis corresponds to fabric type) and washed fabrics: (B) 100 nm Ag fabrics, (C) 60 nm Ag fabrics and (D) 60 nm Au fabrics (where the x-axis corresponds to washing treatment). Solid portions of bars represent particulate matter with hashed sections indicating dissolved metal. Unwashed fabrics are indicated in green, washed with color detergents in orange and washed with oxi detergents in blue, with ten washes in darker variants.

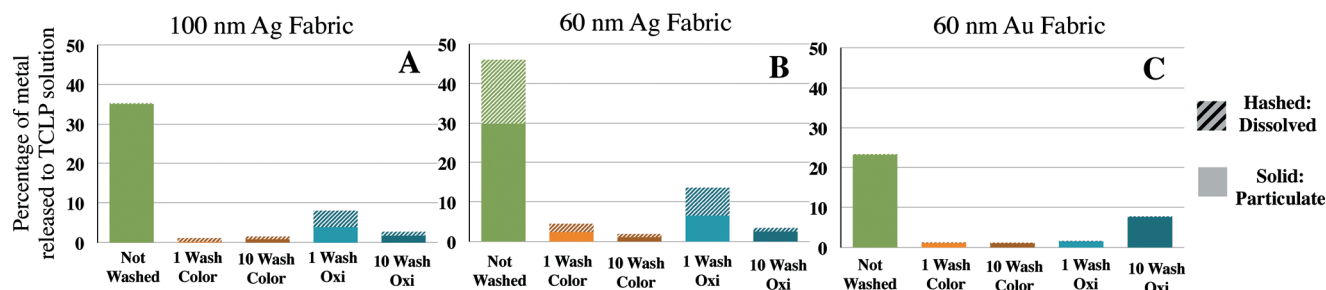


Fig. 5 Percentage of metal released to TCLP solutions after initial washing steps for (A) 100 nm Ag-treated fabric, (B) 60 nm Ag-treated fabric and (C) 60 nm Au-treated fabric. Solid portions of bars represent particulate matter with hashed sections indicating dissolved metal. Unwashed fabrics are indicated in green, washed with color detergents in orange and washed with oxi detergents in blue, with ten washes in darker variants.

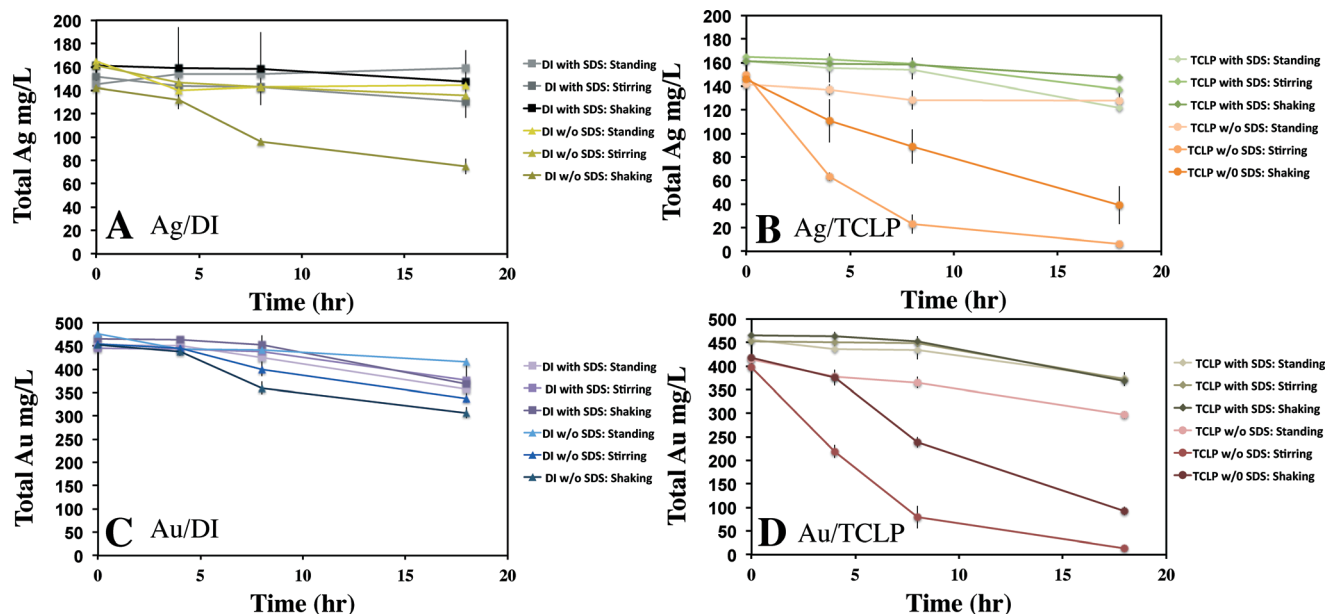


Fig. 6 Stability of 60 nm Ag (panels A and B; initial concentration 200 mg L^{-1}) and 60 nm Au (panels C and D; initial concentration 500 mg L^{-1}) NPs in DI H_2O or TCLP extraction fluid under different physical aging conditions (standing, stirring, shaking) with or without the addition of surfactant (SDS) as a stabilizing agent. Error bars indicate the standard deviation of triplicate experiments.

container wall, especially with additional agitation (e.g. panel B, stirring or shaking, medium orange or dark orange traces, respectively). Notably, the same overall trends can be observed when studying the AuNPs despite the different particle chemistries. Again, in these experimental sets, more than 90% of the total Au is recoverable from the DI H_2O experiments under all conditions (panel C), whereas a drastic decrease in Au recovery is found with AuNPs suspended in the TCLP extraction liquid when additional agitation is applied without the presence of a surfactant (panel D). In short, for both Ag and AuNPs spiked into the TCLP solutions containing no surfactant, the particle stability was severely decreased in a short amount of time upon any agitation to the system.

Furthermore, the form of agitation promoted various degrees of instability, where bottles which were allowed to stand on the bench top appeared to have the best stability, followed by stirring and finally shaking (the conditions under

which the tests with the fabrics were performed). Because the ionic In internal standard concentrations remained stable between the measurements at time 0 and 18 h (see Table S2[†]), a particle aggregation and/or sticking effect is seemingly at play. When the experimental containers were rinsed with acid to recover the metal that adhered to the container wall, a significant fraction was recovered from systems where particle recovery from the solution was the lowest (Table S2[†]).

4 Discussion

Two phases of the product life cycle were examined in this suite of experiments: the use phase and the disposal phase. By examining the washing of textiles under various conditions, we can begin to understand the range of concentrations of particles that will be released from nano-enhanced fabrics under conditions that increasingly represent normal use. By continuing the life-cycle thinking and performing

sequential exposure of the fabrics to simulated landfilling, we can suggest approximations of release from this environmental compartment. The study of both scenarios works in tandem to create a more holistic picture of the behavior of metallic NPs incorporated into textiles and the release profiles they may undergo over time. Nevertheless, the trends suggested by this study cannot be applied to all particulate incorporations in textiles. For example, we have shown in this manuscript that Ag and Au NPs behave quite differently with respect to release under the same conditions, and so the incorporation of *e.g.* TiO₂ into a textile or variously capped/coated Ag or Au NPs could have different release profiles that deviate from the trends we found here. Additionally, specific consumer use patterns will influence how much metal is released in which of the life cycle phases.

4.1 Textile use phase

As suggested from our previous work involving various detergents and their effect(s) on NP transformations,²² the oxi wash releases more metal than the color wash, and more washes equals more release. Given that the release ratios (Ag/Au NP release, *e.g.* Fig. 3) exhibit higher releases for Ag under many conditions, this indicates that some chemical interactions are more important than physical (mechanical) washing. This is also supported by the stronger chemicals (*i.e.* oxi detergent) causing a larger release of metal upon washing the fabric, especially upon multiple washes (up to 3 times higher release).

Nevertheless, in nearly half of the experimental sets, significant additional Ag release was not observed suggesting that particles are released by (1) a set proportion of NPs not being well bound to the fabric surface in the first place, in which case the textile manufacture process could be improved, or 2) mechanical stress during washing. These factors are difficult to separate definitively in this series of studies, but by comparing different formulations of chemical binders and/or methods of NP incorporation into textiles and assessing releases after washing, we could better correlate the materials science of textile engineering with environmental releases. Chemical treatment of fabrics using AgNPs can be employed *ex situ* or *in situ*. The *ex situ* approach (securing previously prepared AgNPs onto the fabric) is facilitated by the readily available AgNPs on the market but many *ex situ* treatments lack durability. The influence of AgNP formulation and incorporation into the fabric can have a large effect on the morphological, antimicrobial, durability and physical properties of the fabrics.⁹ In this project, we chose only one industry-standard blocked linear isocyanate binder and treated the surface of the PES fabric with pre-formed NPs, resulting in an average release of 24% across all experimental conditions. We can then compare the durability of fabrics in this experiment to that observed in other studies that washed fabrics with known details of silver application and incorporation methods (*i.e.* no commercially purchased fabrics) (Table 1). While not intended as an exhaustive review, a sum-

mary of some AgNP textile formulations and the general durability that the authors described during washing provides some context to these present washing studies. There were many more examples of fabrics synthesized under different conditions, but full investigation into the durability of the fabrics in terms of the percentage of Ag released during each wash was often lacking from the reports.

From this summary, a few relevant points can be brought to the readers' attention: (1) more silver is released in the first few washing cycles compared to the latter washing cycles,^{30–33} (2) metal release drastically varies between the fabrics produced, (3) no clear trend emerged for textiles which released more or less metal when considering the fabric material, binder composition, incorporation method, or other metrics we recorded and (4) despite the large release of metal, those studies which took into account the antimicrobial efficiency of the fabrics after washing did not note a significant difference in efficacy despite the lack of NP treatment durability, indicating that only a small amount of material is needed to produce the desired effects.

4.2 Textile disposal phase

Total metal analysis detected a lower amount of metal in the TCLP liquid than would be suggested by the results from the fabric digest, but this can be explained by the particle instability in the solution itself. The discrepancy between the loss from the textile and the detection in the TCLP liquid is likely caused by NPs (both Ag and Au) adhering to the experimental container walls under TCLP conditions. With a pH of 4.9, the acid groups of the citrate coating are still mainly deprotonated, so the charge on the particle surface should still be negative. However, there is potential that the acetate in the TCLP solution exchanges the citrate on the NP surface and thus the particles are less stable. Measurements of the zeta potential in the TCLP solution using the 60 nm citrate-capped Au NPs do suggest that these charge differences cause some instability (Fig. S1†), where the initial zeta potential of the NPs in DI water was -43 mV, but upon initial suspension in the TCLP extract, the zeta potential immediately decreased to -25 mV, with further reduction of charge over time to about -10 mV. The instability of charge can cause sorption to the container walls and this sorptive tendency is expedited when the solution is under additional physical movement (*e.g.* shaking as opposed to stirring) because there is an increased likelihood that NPs will come into contact with the container.

The sorption of nanomaterials to the laboratory plastic during testing has been studied before,^{36,37} and a combination of particle size, particle concentration, particle surface functionality, test vessel surface properties and exposure media all played a role in the significance of the sorbed fraction of NPs. Therefore, because of the propensity of the nanomaterial to adsorb to container walls, the amount of metal released from the textiles is most reliable when determined by fabric digestion, rather than by ICP-MS measurements in the TCLP solution, at least under these test conditions.

Table 1 Summary of Ag release from known textile incorporations, including multiple washings

Fabric	Binder and other chemical treatments	Ag incorporation method	Particle capping agent	Particle size	Application method	Number of wash cycles	Washing detergent characteristics	Average Ag release after the last wash cycle	Misc. info	Author
Ex situ Ag NP treatment on fabrics										
Polyester	Blocked linear isocyanate with cationic character	Commercial pre-formed particles	Citrate	60 and 100 nm	Roll to roll padder	1 or 10	Standard and bleaching detergents	24%	Increased release with oxi-containing detergents; more smaller particles released	Mitrano <i>et al.</i> (this study)
Polyester	Blocked linear isocyanate with cationic character	Commercial pre-formed particles	Citrate	20 nm	Roll to roll padder and bulk incorporation	1	Phosphate-free ECE detergent without optical brightener	10% (surface) or 1% (bulk)	Lower release compared to conventional Ag additives	Mitrano <i>et al.</i> 2015 (ref. 22)
Polyester	Blocked linear isocyanate with cationic character	Commercial pre-formed particles	Citrate and PEG	20, 60 and 100 nm	Roll to roll padder (surface application)	1	Suite of 7 detergents	5–75%	Oxi-containing detergents release more Ag; sunlight irradiation inhibits release	Mitrano <i>et al.</i> (submitted) (ref. 12)
Cotton	None	In-house synthesis of pre-formed Ag NPs	Tri-sodium citrate powder	20–60 nm	Immersed in Ag NP solution with stirring; then padded to ensure even coating	5 and 10	Non-ionic detergent (Ultravon CN Ciba)	25% and 50% for 5 and 10 wash cycles	Aggregation of NPs at high concentrations; less durable than <i>in situ</i> preparation by the same authors	Pasricha <i>et al.</i> 2013 (ref. 9)
Cotton	With and without butane tetracarboxylic acid (BTCA)	Commercial pre-formed particles	SHP	60 nm	Series of bath submersions, padded at the end	10, 20 and 30	Non-ionic detergent, short bath wash	Decrease over multiple wash cycles	Cross-linking with BTCA entraps Ag NPs with the cellulose	Montazer <i>et al.</i> 2012 (ref. 34)
Cotton, polyester and blends of cotton/polyester and polyester/spandex	Some variants dyed before experiments, no binder specified	Pre-formed ethanol-based nanosilver colloids (spheres)	Not specified	2–5 nm	Padder with constant pressure	5, 10, or 20	Not specified	93%	The majority of release in the first 5 washes; antimicrobial effectiveness preserved after all laundering	Lee <i>et al.</i> 2003 (ref. 30)
Cotton, wool, nylon	None	In-house synthesis of pre-formed Ag NPs	None used	3–6 nm	Textile bath submersion	3	Not specified	12–25%	Most loss in the first wash; after the third wash the fabrics leached detectable amounts of Ag	Pasricha <i>et al.</i> 2012 (ref. 31)

Table 1 (continued)

Fabric	Binder and other chemical treatments	Ag incorporation method	Particle capping agent	Application method	Number of wash cycles	Washing detergent characteristics	Average Ag release after the last wash cycle	Misc. info	Author
<i>In situ</i> Ag NP treatment of fabrics									
Polyester	Dopamine-modified polyester surface	<i>In situ</i> AgNO ₃ reduction	Polydisperse, N/A including aggregates	Textile bath submersion	1 to 30	Not specified	75%	Doped fabrics adsorbed more Ag; most Ag loss between 1 and 10 washes then steady Ag concentration remained	Xu <i>et al.</i> 2013 (ref. 32)
Cotton	None	AgNO ₃ solution irradiated using UV lamp	Not specified	Textile bath submersion	5 and 10	Non-ionic detergent (Ultravon CN Ciba)	<20%	Uniform distribution of particles; more durable than <i>ex situ</i> preparation by the same authors	Pasricha <i>et al.</i> 2013 (ref. 31)
Cotton	With and without binder (1%); Printo® Fx based on acrylate solutions	AgNO ₃ reduction by alkali-hydrolyzed maize starch	Not specified	Pad-dry-cure	5, 10 or 20	2 g L ⁻¹ Na ₂ CO ₃ and 2 g L ⁻¹ commercial detergent	39–44%	Without binder, more metal released	El-Rafie <i>et al.</i> 2014 (ref. 35)
Polyamide	Alanine and sunlight lamp irradiation	Ag reduced onto fabric impregnated with TiO ₂ NPs	Not specified	Textile bath submersion	1 to 10	5 g L ⁻¹ Society of Dyers & Colourists (SDC) and standard detergent	85%	Half of Ag released after the first wash, most released in the first 4 cycles	Milošević <i>et al.</i> 2015 (ref. 33)

It should be noted that this control experiment was initially performed because we found it impossible to measure the amount of individual particles in solution using the single particle (sp)ICP-MS method^{38,39} in the TCLP solution. Initially, we envisioned relaying additional information about (potential) particle size changes in the TCLP solution after they were released from the laboratory-prepared textiles, yet because of the instability of particles in solution and the sorption to the container walls, this was not possible. In previous studies, we successfully froze solutions at given time points (either entirely or diluted) to be later analyzed by spICP-MS,^{22,40} but the matrix and/or sorption of the unstable particles did not promote good recovery even in our spICP-MS control experiments. This reiterates the importance of two key factors when studying nanomaterials in a slew of different environmental or ecotoxicity experimental regimes: (1) relevant control experiments should be included whenever new types of NPs or test vessels are used to define the extent of sorption and (2) method validation (in this case, of spICP-MS) needs to be continued for each new matrix and/or variant in the experimental protocol to ensure that one understands the properties which are actually being measured in the test system.

The particle stability experiments in the test media suggest that NPs do not remain suspended in solution without the addition of a surfactant – so under landfill conditions, NPs may not be readily mobile either. Much more metal was recovered in the TCLP solution from exposing the fabrics which were not washed compared to fabrics which had undergone a laundering step, which further proves the necessity of life-cycle aging sequences to properly assess the likelihood and characteristics of material released from nano-enhanced textiles.

Conclusions

In the scope of the environmental science and toxicology literature, the release of NPs from textiles generally takes an environmental focus (*e.g.* NP transformations, risk, fate, *etc.*). However, better understanding of the properties of the materials for a discussion of the NP fastness for different AgNP incorporations and relative release rates, especially upon multiple washings, is called for. Of course, the releases (and effectiveness) can vary greatly depending on how the fabrics are produced; yet surprisingly, this is a topic that is largely missing from the environmental literature. By fabricating textiles using known production methods and with particles of known size and then subjecting them to various washing conditions, the factors that most affect particle release can be parsed out. However, because of the instability of the NPs in the test solution (especially in the TCLP liquid), direct measurement of the fabric swatches by digestion was found to be the most dependable way to assess the total amount of material removed from the fabric during the different aging tests.

Based on the TCLP test, NPs will likely not be readily mobilized in the solution as particles due to the depressed zeta

potential. Thus, we would only expect to see a small release from the fabrics under these circumstances and, if/when this fraction of material were to be released, it may not be very mobile through a reactive landfill. Generally, under these experimental conditions, the use phase of the life cycle appears to be responsible for the higher metal release rather than the disposal phase. However, we also need to consider the release kinetics – the TCLP test just tests the short-term (about 1 day) release, whereas in landfills, many decades are available for release. The washed textiles released a significant portion of the Ag in the dissolved form and we could expect that, under prolonged landfill conditions, the dissolution of Ag inside the coating and release as dissolved Ag become even more important over longer timescales.

Furthermore, by monitoring the fabrics through their life cycle and simulating the landfilling of already washed fabrics, we can better estimate the true risk of further transportation of nanomaterials originating from fabrics into various environmental compartments. This can be shown especially well by the TCLP test, where fabrics that were not laundered first released a much higher proportion of metal during the experimental regime than their laundered counterparts. Therefore, by monitoring the sequential aging which matches with actual product use patterns, we can better estimate a more realistic release of NPs through each phase of the product life cycle. We can further make a link between these experimental results and the current materials flow modeling scheme which depicts landfills as a final sink,^{4,8} *i.e.* no further transport to other technical or environmental compartments after entering the landfill. From the results garnered from this study, we can say with more certainty that the release of NPs from landfills into the environment due to disposal of nano-enabled textiles is likely small since the particles are unstable in landfill leachates.

Acknowledgements

This work was funded by the European Commission within the Seventh Framework Program (FP7; NanoMILE Project Grant Agreement NMP4-IA-2013-310451). Additional financial support was provided by the Royal Golden Jubilee PhD Program (RGJ) under the organization of the Thailand Research Fund (TRF) (Grant No. PHD/0307/2552).

References

- 1 R. Mishra, J. Militky, V. Baheti, J. Huang, B. Kale, M. Venkataraman, V. Bele, V. Arumugam, G. Zhu and Y. Wang, The production, characterization and applications of nanoparticles in the textile industry, *Text. Prog.*, 2014, **46**(2), 133–226.
- 2 E. Lombi, E. Donner, K. Scheckel, R. Sekine, C. Lorenz, N. von Götze and B. Nowack, Silver speciation and release in commercial antimicrobial textiles as influenced by washing, *Chemosphere*, 2014, **111**, 352–358.
- 3 N. S. Tulve, A. B. Stefaniak, M. E. Vance, K. Rogers, S. Mwilu, R. F. LeBouf, D. Schwegler-Berry, R. Willis, T. A. Thomas and

- L. C. Marr, Characterization of silver nanoparticles in selected consumer products and its relevance for predicting children's potential exposures, *Int. J. Hyg. Environ. Health*, 2015, 218(3), 345–357.
- 4 T. Y. Sun, F. Gottschalk, K. Hungerbühler and B. Nowack, Comprehensive probabilistic modelling of environmental emissions of engineered nanomaterials, *Environ. Pollut.*, 2014, 185, 69–76.
 - 5 M. Boholm and R. Arvidsson, Controversy over antibacterial silver: implications for environmental and sustainability assessments, *J. Cleaner Prod.*, 2014, 68, 135–143.
 - 6 R. Arvidsson, S. Molander and B. A. Sanden, Assessing the Environmental Risks of Silver from Clothes in an Urban Area, *Hum. Ecol. Risk Assess.*, 2014, 20(4), 1008–1022.
 - 7 N. Seltenrich, Nanosilver: Weighing the Risks and Benefits, *Environ. Health Perspect.*, 2013, 121, A220–A225.
 - 8 D. M. Mitrano, S. Motellier, S. Clavaguera and B. Nowack, Review of nanomaterial aging and transformations through the life cycle of nano-enhanced products, *Environ. Int.*, 2015, 77, 132–147.
 - 9 S. Perera, B. Bhushan, R. Bandara, G. Rajapakse, S. Rajapakse and C. Bandara, Morphological, antimicrobial, durability, and physical properties of untreated and treated textiles using silver-nanoparticles, *Colloids Surf., A*, 2013, 436, 975–989.
 - 10 D. M. Mitrano, E. Rimmele, A. Wichser, R. Erni, M. Height and B. Nowack, Presence of Nanoparticles in Wash Water from Conventional Silver and Nano-silver Textiles, *ACS Nano*, 2014, 8(7), 7208–7219.
 - 11 H. Wigger, S. Hackmann, T. Zimmermann, J. Köser, J. Thöming and A. von Gleich, Influences of use activities and waste management on environmental releases of engineered nanomaterials, *Sci. Total Environ.*, 2015, 535, 160–171.
 - 12 D. M. Mitrano, E. Lombi, Y. Arroyo Rojas Dasilva and B. Nowack, *Unraveling the Complexity in the Aging of Nano-Enhanced Textiles: a Comprehensive Sequential Study on the Effect of Sunlight and Washing*, Submitted.
 - 13 H. Wigger, S. Hackmann, T. Zimmermann, J. Köser, J. Thöming and A. von Gleich, Influences of use activities and waste management on environmental releases of engineered nanomaterials, *Sci. Total Environ.*, 2015, 535, 150–171.
 - 14 T. M. Benn and P. Westerhoff, Nanoparticle silver released into water from commercially available sock fabrics, *Environ. Sci. Technol.*, 2008, 42(11), 4133–4139.
 - 15 L. Geranio, M. Heuberger and B. Nowack, The Behavior of Silver Nanotextiles during Washing, *Environ. Sci. Technol.*, 2009, 43(21), 8113–8118.
 - 16 C. Lorenz, L. Windler, N. von Goetz, R. Lehmann, M. Schuppler, K. Hungerbühler, M. Heuberger and B. Nowack, Characterization of silver release from commercially available functional (nano) textiles, *Chemosphere*, 2012, 89(7), 817–824.
 - 17 J. Hedberg, S. Skoglund, M.-E. Karlsson, S. Wold, I. Odnevall Wallinder and Y. Hedberg, Sequential studies of silver released from silver nanoparticles in aqueous media simulating sweat, laundry detergent solutions and surface water, *Environ. Sci. Technol.*, 2014, 48(13), 7314–7322.
 - 18 N. von Goetz, C. Lorenz, L. Windler, B. Nowack, M. Heuberger and K. Hungerbühler, Migration of Ag- and TiO₂- (Nano)particles from Textiles into Artificial Sweat under Physical Stress: Experiments and Exposure Modeling, *Environ. Sci. Technol.*, 2013, 47(17), 9979–9987.
 - 19 K. Kulthong, S. Srisung, K. Boonpavanitchakul, W. Kangwansupamonkon and R. Maniratanachote, Determination of silver nanoparticle release from antibacterial fabrics into artificial sweat, *Part. Fibre Toxicol.*, 2010, 7, 8.
 - 20 M. E. Quadros, R. Pierson, N. S. Tulve, R. Willis, K. Rogers, T. A. Thomas and L. C. Marr, Release of Silver from Nanotechnology-Based Consumer Products for Children, *Environ. Sci. Technol.*, 2013, 47, 8894–8901.
 - 21 D. M. Mitrano, E. Rimmele, A. Wichser, R. Erni, M. Height and B. Nowack, Presence of Nanoparticles in Wash Water from Conventional Silver and Nano-silver Textiles, *ACS Nano*, 2014, 8, 7208–7219.
 - 22 D. M. Mitrano, Y. Arroyo Rojas Dasilva and B. Nowack, Effect of Variations of Washing Solution Chemistry on Nanomaterial Physicochemical Changes in the Laundry Cycle, *Environ. Sci. Technol.*, 2015, 49(16), 9665–9673.
 - 23 T. Benn, B. Cavanagh, K. Hristovski, J. Posner and P. Westerhoff, The Release of Nanosilver from Consumer Products Used in the Home, *J. Environ. Qual.*, 2010, 39, 1875–1882.
 - 24 K. D. Hristovskil, Regulatory Implications for Commercial Fabrics Containing Nanosilver: Hazardous Waste or Not?, *J. Environ. Manage.*, 2012, 10, 4–5.
 - 25 V. Lazić, M. Radoičić, Z. Šaponjić, T. Radetić, V. Vodnik, S. Nikolić, S. Dimitrijević and M. Radetić, Negative influence of Ag and TiO₂ nanoparticles on biodegradation of cotton fabrics, *Cellulose*, 2015, 22(2), 1365–1378.
 - 26 D. Chattopadhyay and B. Patel, Improvement in physical and dyeing properties of natural fibres through pre-treatment with silver nanoparticles, *Indian J. Fibre Text. Res.*, 2009, 34(4), 368.
 - 27 A. Gitipour, A. El Badawy, M. Arambewela, B. Miller, K. Scheckel, M. Elk, H. Ryu, V. Gomez-Alvarez, J. Santo Domingo and S. Thiel, The impact of silver nanoparticles on the composting of municipal solid waste, *Environ. Sci. Technol.*, 2013, 47(24), 14385–14393.
 - 28 EPA, *Standard Method 1311*, Toxicity Characteristic Leaching Procedure.
 - 29 T. Benn, B. Cavanagh, K. Hristovski, J. D. Posner and P. Westerhoff, The Release of Nanosilver from Consumer Products Used in the Home, *J. Environ. Qual.*, 2010, 39(6), 1875–1882.
 - 30 H. Lee, S. Yeo and S. Jeong, Antibacterial effect of nanosized silver colloidal solution on textile fabrics, *J. Mater. Sci.*, 2003, 38(10), 2199–2204.
 - 31 A. Pasricha, S. L. Jangra, N. Singh, N. Dilbaghi, K. Sood, K. Arora and R. Pasricha, Comparative study of leaching of silver nanoparticles from fabric and effective effluent treatment, *J. Environ. Sci.*, 2012, 24(5), 852–859.
 - 32 H. Xu, X. Shi, Y. Lv and Z. Mao, The preparation and antibacterial activity of polyester fabric loaded with silver nanoparticles, *Text. Res. J.*, 2013, 83(3), 321–326.

- 33 M. Milošević, A. Krkobabić, M. Radoičić, Z. Šaponjić, V. Lazić, M. Stojković and M. Radetić, Antibacterial and UV protective properties of polyamide fabric impregnated with TiO₂/Ag nanoparticles, *J. Serb. Chem. Soc.*, 2014(00), 125–125.
- 34 M. Montazer, F. Alimohammadi, A. Shamei and M. K. Rahimi, Durable antibacterial and cross-linking cotton with colloidal silver nanoparticles and butane tetracarboxylic acid without yellowing, *Colloids Surf., B*, 2012, **89**, 196–202.
- 35 M. El-Rafie, H. B. Ahmed and M. Zahran, Characterization of nanosilver coated cotton fabrics and evaluation of its antibacterial efficacy, *Carbohydr. Polym.*, 2014, **107**, 174–181.
- 36 A. Malysheva, A. Ivask, C. Hager, G. Brunetti, E. R. Marzouk, E. Lombi and N. H. Voelcker, Sorption of silver nanoparticles to laboratory plastic during (eco) toxicological testing, *Nanotoxicology*, 2015, 1–6.
- 37 R. Sekine, K. Khurana, K. Vasilev, E. Lombi and E. Donner, Quantifying the adsorption of ionic silver and functionalized nanoparticles during ecotoxicity testing: Test container effects and recommendations, *Nanotoxicology*, 2015(0), 1–8.
- 38 D. M. Mitrano, A. Barber, A. Bednar, P. Westerhoff, C. Higgins and J. Ranville, Silver nanoparticle characterization using single particle ICP-MS (SP-ICP-MS) and asymmetrical flow field flow fractionation ICP-MS (AF4-ICP-MS), *J. Anal. At. Spectrom.*, 2012, **27**, 1131–1142.
- 39 F. Laborda, J. Jimenez-Lamana, E. Bolea and J. R. Castillo, Selective identification, characterization and determination of dissolved silver (I) and silver nanoparticles based on single particle detection by inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.*, 2011, **26**(7), 1362–1371.
- 40 L. M. Furtado, M. E. Hoque, D. F. Mitrano, J. F. Ranville, B. Cheever, P. C. Frost, M. A. Xenopoulos, H. Hintelmann and C. D. Metcalfe, The persistence and transformation of silver nanoparticles in littoral lake mesocosms monitored using various analytical techniques, *Environ. Chem.*, 2014, **11**(4), 419–430.