

Presence of Nanoparticles in Wash Water from Conventional Silver and Nano-silver Textiles

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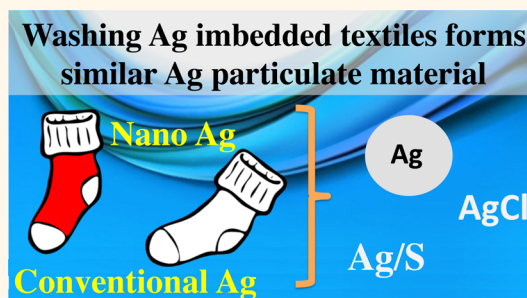
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ABSTRACT Questions about how to regulate nanoeenhanced products regularly arise as researchers determine possible nanoparticle transformation(s). Focusing concern on the incorporation and subsequent release of nano-Ag in fabrics often overshadows the fact that many “conventional silver” antimicrobials such as ionic silver, AgCl, metallic Ag, and other forms will also form different species of silver. In this study we used a laboratory washing machine to simulate the household laundering of a number of textiles prepared with known conventional Ag or nano-Ag treatments and a commercially available fabric incorporating yarns coated with bulk metallic Ag. Serial filtration allowed for quantification of total Ag released in various size fractions ($>0.45\ \mu\text{m}$, $<0.45\ \mu\text{m}$, $<0.1\ \mu\text{m}$, and $<10\ \text{kDa}$), while characterization of particles with TEM/EDX provided insight on Ag transformation mechanisms. Most conventional Ag additives yielded more total Ag and more nanoparticle-sized Ag in the washing liquid than fabrics that used nano-Ag treatments. Incorporating nano-silver into the fiber (as opposed to surface treatments) yielded less total Ag during fabric washing. A variety of metallic Ag, AgCl, and Ag/S particles were observed in washing solution by TEM/EDX to various extents depending on the initial Ag speciation in the fabrics. Very similar particles were also observed when dissolved ionic Ag was added directly into the washing liquid. On the basis of the present study, we can state that all silver-treated textiles, regardless of whether the treatment is “conventional” or “nano”, can be a source of silver nanoparticles in washing solution when laundering fabrics. Indeed, in this study we observed that textiles treated with “conventional” silver have equal or greater propensity to form nano-silver particles during washing conditions than those treated with “nano”-silver. This fact needs to be strongly considered when addressing the risks of nano-silver and emphasizes that regulatory assessment of nano-silver warrants a similar approach to conventional silver.



KEYWORDS: nanoparticle release · Ag nanoparticles · transformation · textile · washing · aging

In the current discussion about risks of engineered nanomaterials (ENM) and consumer products, nanotextiles feature prominently.¹ Regulators often assert that textiles containing ENMs, and specifically nano-Ag, need to be evaluated and controlled more stringently than antimicrobial textiles containing “conventional” Ag.² However, even many silver applications considered as conventional are actually based on nano-Ag, and in fact the U.S. EPA has registered a number of nano-Ag antimicrobial products since 1954.³ Silver-treated textiles achieve their antimicrobial activity *via* a release of silver ions (Ag^+). The antimicrobial efficacy of a silver additive is therefore directly related to the potential for releasing

silver ions.^{3,4} Numerous forms of Ag additives, which effectively act as a source of Ag^+ , have been available for many years in applications including textiles, plastics, and coatings.³ Several investigations have shown that silver-containing textiles, treated with either nano or conventional forms, have the potential to release significant amounts of Ag into washing liquid, with percentages released in the first washing of up to 20–30%.^{5–7} The washing of nano-silver-treated textiles potentially releases both dissolved and particulate silver, with some of the Ag released comprising particles (or aggregates) larger than 450 nm.⁸ For fabrics incorporating metallic silver, oxidation from Ag(0) to Ag(I) is a prerequisite for the

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appearance of Ag^+ in solution.⁶ The sensitivity of nano-Ag to oxygen is well known,⁹ and the chemisorbed Ag^+ , formed either in air,^{10,11} during exposure to water,¹² or when in contact with detergents, can be easily released once the textile is laundered. However, the dissolution process is complex, with the extent and rate of dissolution being dependent on a multitude of factors ranging from solution chemistry to redox environment to particle specific characteristics such as capping agents and method of incorporation into the fabric.¹³ Quadros *et al.* assessed the potential of children to be exposed to nano-Ag from a blanket, plush toy, and a variety of other nontextile items.¹⁴ Methods varied by product to mimic likely release scenarios, but fabric products released the highest quantities of silver, mostly in ionic rather than particulate form.¹⁵ Additionally, von Goetz *et al.* demonstrated that dissolved Ag was released from fabrics exposed to sweat, with Ag-chloro complexes being the major dissolved species due to the high chloride content in sweat.¹⁶

Generally, washing Ag-functionalized textiles has the potential to lead to a spectrum of silver forms in the washing liquid including ionic silver and various particulate compositions. Which Ag forms are directly released from a textile and which (transformed) forms of Ag can be subsequently found in the washing liquid likely depend mainly on (1) the Ag form originally incorporated into the textile, (2) the composition of the washing liquid, and (3) the conditions of the washing procedure, variations of which lead to a multitude of possible transformation pathways. For example, metallic Ag nanoparticles (Ag NPs) have been observed in the effluent of a washing machine that was adding dissolved Ag directly into the washing solution.¹⁷ Also Geranio *et al.*⁶ reported that conventional silver textiles released a portion of the incorporated Ag in nanoparticulate form.

A fundamental feature when considering this system is therefore that silver can speciate between ionic silver, silver salts, and metallic silver. Several recent studies have shown that formation of metallic Ag nanoparticles from dissolved silver under environmental conditions is possible: Maurer *et al.* determined that reduced soil humic acids transform dissolved Ag^+ into metallic silver nanoparticles.¹⁸ Aquatic humic acids of various origins were responsible for forming metallic silver nanoparticles from dissolved ionic Ag.¹⁹ Dissolved organic matter reduced dissolved Ag^+ in the presence of sunlight to metallic nano-silver.²⁰ Superoxide has been shown to reduce Ag^+ to silver nanoparticles.²¹ In the vicinity of parent Ag particles smaller Ag nanoparticles are formed *via* the oxidation to Ag^+ ions and subsequent reduction to form daughter Ag nanoparticles.²² There are therefore several known pathways by which nanoparticulate metallic silver can be formed from dissolved Ag^+ , and we can speculate that similar reactions also take place in

washing liquid; thus, Ag nanoparticles are observed when washing conventional Ag textiles.

The presence of silver in any of these forms—dissolved, nanoparticulate, and/or silver complexes—in the wash water could have consequences for the environment. The fate and transformation of silver in urban wastewater treatment systems, and beyond to receiving waters and biosolid application, should be considered when discussing adverse effects to environmental health.^{23,24} While detailing the risks to either aquatic or terrestrial organisms associated with the release of silver from textiles is beyond the scope of this study, it should be considered that biota will react differently to these various (transformed) silver species.

The aim of this current study was to characterize the quantity and form of Ag derived from washing various silver-treated textiles. Standardized textiles were prepared from both conventional and nano-Ag additives (AgCl, AgCl/TiO₂ composite, Ag-zeolites, Ag NPs, and Ag-SiO₂ composite). Finally, a commercially available textile containing metallic bulk silver was also tested. The silver material found in the washing liquid following standardized washing was quantified, and the nanoparticulate silver forms were characterized. From this, we were able to quantify the proportion of Ag material derived from each textile category. We then could additionally relate how the end Ag particles/complexes differed from one another depending on the starting composition of Ag in each fabric.

RESULTS

The background Ag concentration in the washing liquid (treated in the same way as the samples, including filtration) was 0.8 to 3.9 $\mu\text{g/L}$ for the method blank and 0.1 to 1.8 $\mu\text{g/L}$ for the untreated negative control textile (Figure 1A). The washing liquid is therefore contributing some silver to the solution, and concentrations below about 4 $\mu\text{g/L}$ are considered background.

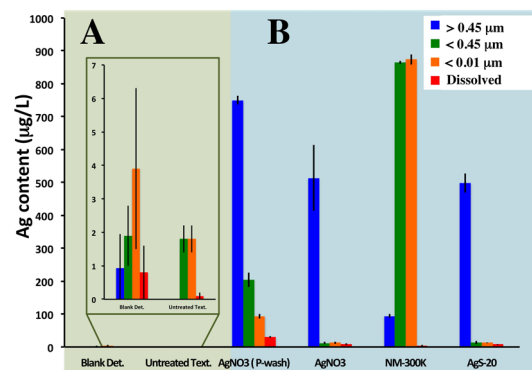


Figure 1. Size fractionation of Ag positive control materials spiked into washing liquids. Spiked Ag concentrations of 1100 $\mu\text{g/L}$ were added as AgNO_3 , NM-300K, or AgS-20. All controls were performed in phosphate-free detergent except where noted, where phosphate-containing detergent was used ("P-washing").

Positive Controls. Positive controls included spiking AgNO_3 , NM-300K, nano-Ag, or AGS-20 Ag/SiO_2 composite directly into the washing liquid. The amount of Ag measured in the small particulate ($<0.45\ \mu\text{m}$), nanoparticulate ($<100\ \text{nm}$), and dissolved fractions ($<30\ \text{kDa}$) in the washing liquid is shown in Figure 1B. Addition of AgNO_3 to the washing liquid resulted in the significant removal of the dissolved Ag fraction, where 46.7% of the total spiked Ag material was recovered in fractions other than the ultrafilter. Similar results were found in the phosphorus-containing washing liquid, where 68.1% of material was found to be particulate matter. When considering not all Ag^+ was recovered, the proportion of particulate matter to total Ag measured became considerably more significant, with 98.1% and 94.5% of Ag being analyzed in the particulate matter for Ag spiked in washing liquid and phosphorus-containing washing liquid, respectively. Therefore, conclusive evidence was found that the addition of AgNO_3 (ionic silver) to washing liquids results in the formation of both particulate and nanoparticulate silver forms. The detergent used for most of these experiments was a phosphate-free standard detergent based on zeolites to remove water hardness. An additional experiment with the addition of AgNO_3 into the phosphate-containing washing liquid was used in previous silver washing studies with commercial textiles^{5,6} and resulted in a much higher percentage of particulate silver forms detected, where again a significant amount of nanoparticulate silver was formed.

Reduced recovery rates of total Ag in the AgNO_3 -spiked washing liquid experiments may be explained by metallic Ag precipitating from solution and adhering to the container walls. In electroless plating of silver on surfaces including glass, ionic silver is reacted with reducing agents, forming a layer of metallic silver on surfaces.²⁵ This process is carried out at high pH with various reducing agents and has also been demonstrated on textiles.²⁶ Indeed, even when the untreated samples were analyzed less than 24 h after washing, measured total Ag was less than 5% of the spiked concentration. The exception to this was the Ag collected on the $0.45\ \mu\text{m}$ filter, which was digested, where appreciable amounts of Ag were detected. This indicates that in our washing experiments concentrations of dissolved/ionic Ag may be significantly underestimated in some of the washing solutions.

When the same total concentration of NM-300K nano-silver was added directly into washing liquid as the amount contained in the textile, approximately 80% passed through both the 0.45 and $0.1\ \mu\text{m}$ filters, indicating the presence of discrete nanoparticulate Ag. The fraction removed by the filter (*i.e.*, larger than $0.45\ \mu\text{m}$) indicates that little Ag was retained by the solids in the washing liquids (*e.g.*, zeolites, *etc.*) or formed Ag agglomerates in the washing liquid. The pristine particle size of NM-300K is approximately

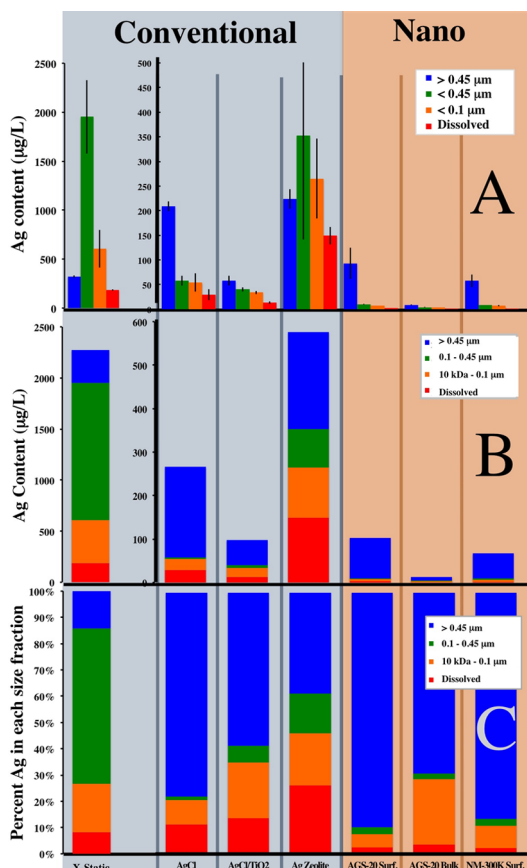


Figure 2. (A) Size fractionation of Ag materials in washing liquids from commercial (for X-Static sample note separate scale) and lab-prepared textiles for both "conventional" additives (shaded blue) and "nano" additives (shaded peach). Ag concentrations in the $>0.45\ \mu\text{m}$ fraction were measured as $0.45\ \mu\text{m}$ filter digests. All treatments were applied to the textile surface, except for the AGS-20 bulk, where silver was incorporated within the fabric fibers. (B) Average values from panel A, stacked to approximate total Ag release from each washed material, and (C) fractions of Ag release normalized to the total Ag recovered from washing each fabric.

$20\ \text{nm}$,²⁷ suggesting that the recovered Ag fraction was the size of the pristine particles. This indicates that if nano-Ag particles are released into washing liquids, they could be expected to remain stable in suspension. Addition of AGS-20 powder (pristine particle size *ca.* $1\ \mu\text{m}$) to the washing liquid resulted in very low recovered concentrations of Ag in all filtrates, suggesting that in principle no release of discrete Ag nanoparticles from the composite occurred. The total [Ag] was not recovered in the $>0.45\ \mu\text{m}$ fraction, which would indicate incomplete digestion of the silicates that contained the Ag during filter digestion.

Release of Silver during Washing Textiles. Among the various treatments, the X-Static fabric showed the highest overall release of Ag to the washing liquid in terms of total absolute concentration (Figure 2), but due to the very high starting concentration of silver on the fabric, only a small proportion ($<1\%$) of the total available Ag in the fabric was released (Figure 3).

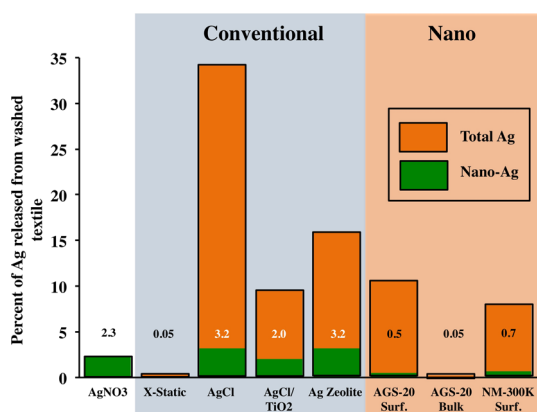


Figure 3. Proportion of silver released (%) from textiles during washing relative to measured total Ag content in the starting fabrics. Green portions of the bars and corresponding numbers indicate percent of total Ag found as nanoparticles in the washing liquid (excluding dissolved Ag). Note that with direct AgNO₃ addition to the washing liquid, 2.3% of the total Ag recovered was in the nano fraction (10 kDa–100 nm), which is also shown in green. Orange portions of the bars account for all other recovered Ag fractions.

The majority of the silver in the washing liquid was in the size range of 0.1–0.45 μm . The dissolved and the >0.45 μm fractions were much lower. There is a seemingly large standard deviation of the <0.45 μm fraction, and this variance may be explained by the inhomogeneity of the blended fabric construction, giving variable Ag recovery from sample to sample.

Among the laboratory-prepared fabrics prepared with conventional Ag additives, the Ag-zeolite proved to release the highest total Ag concentrations to the washing liquid (Figure 2). Additionally, the Ag-zeolite released the highest proportion of Ag relative to Ag incorporated into the fabric of all laboratory-prepared samples (Figure 3). Similar concentrations of Ag were found in the >0.45 μm and <10 kDa (ionic) fractions. Because the >0.45 μm fraction is not notably large, it suggests that the Ag-zeolite additive was not simply rubbed off the fabric surface by mechanical stress.

The second highest Ag concentration was found in the washing liquid from the AgCl-treated fabric (Figure 2). The largest fraction of silver in the washing liquid was found after the filter digest, *i.e.*, >0.45 μm . The fabric allowed for the second highest percentage of Ag to be released, indicating a possible weaker surface fixation of AgCl compared to other textile additives. The AgCl/TiO₂ fabric released the least amount of Ag to the washing liquid for the conventional Ag additive subset (Figure 2). With the smallest amount of standard deviation in Ag recovery, the Ag application to the fabric also seemed to be the most homogeneous.

The washing liquids of the three textiles containing NM-300K and AGS-20 additives exhibited very low concentrations of silver in the fraction smaller than 0.45 μm (Figure 2), less than any of the conventional

textile additives. The main fraction where Ag was detected for all samples was in the larger than 0.45 μm size range. As anticipated, the textiles that were surface treated yielded more total Ag in the washing liquid than the sample with Ag incorporated into the fiber bulk, where the fraction of Ag recovered in the fraction smaller than 0.45 μm was less than 10 $\mu\text{g/L}$, which is less than the control sample of the equivalent amount of AgNO₃ added to washing liquid. About 10–20% of this fraction was dissolved, and the rest of the material was found as particulate matter.

In terms of total Ag released from the textiles to the washing liquid, conventional additives leached considerably higher amounts of Ag than the nanoadditive-treated textiles. Note that the nano treatments yielded the lowest amount of silver release. Some of the prepared fabrics (*e.g.*, Ag-zeolite) had a mottled appearance, indicating inhomogeneous distribution of the applied Ag material in the treatment process. While these areas were generally avoided when choosing fabric swatches to wash, this natural variation in the textile samples accounts for some of the relatively high standard deviations in some of the measurements.

The percentage of Ag released in the nano size range (10 kDa–0.1 μm) of the total Ag in each of the textiles can also be seen in Figure 3 (green bars). The amount of the AgNO₃ control that formed particulate matter, which was added here as a reference, is also shown. After addition of AgNO₃ into the wash media, a sizable portion (2.3%) of silver measured was detected in the nanoparticulate fraction. In contrast, the values of laundered “nano”-treated textiles in this same fraction were significantly lower, with 0.5%, 0.05%, and 0.7% of the silver for the AGS-20 surface, AGS-20 bulk, and NM300 surface samples, respectively. With the exception of the X-Static fabric, which released a small relative amount of its Ag in the nano range (0.05%), the other “conventional” textiles released more nano-Ag than the “nano” textiles.

Speciation Calculations. The speciation modeling calculations revealed that for the chloride levels measured in the washing liquid 73% of Ag is expected to be precipitated as AgCl, assuming all the silver is initially present as ionic silver. Formation of solid phases directly from ionic silver can therefore be expected in all experiments.

Characterization of Ag Forms. Transmission electron microscopy (TEM) with energy-dispersive X-ray spectroscopy (EDX) was used to identify and characterize particles that formed through Ag⁺ transformation(s), those that were directly released into the washing liquid, and particles that transformed during the washing process (chemical changes, agglomeration, *etc.*). Figure 4 presents a matrix of representative TEM images of particles that formed during the wash process from different Ag additives, with the corresponding EDX plots found in Figure S3.

			Starting Silver Form on Textile						
			Control	Conventional				Nano	
			AgNO ₃	X-Static	AgCl	AgCl/TiO ₂	AgZeolite	NM300	AGS-20
			A	B	C	D	E	F	G
NP Forms in Washing Liquid	Ag	1				ND			ND
	AgCl	2		ND	ND	ND	ND		ND
	Ag/S	3			ND				

Figure 4. Representative examples of nanoparticulate Ag particles found in the washing liquid from various Ag-treated textiles. The scale bar in all images represents 50 nm. ND indicates particles not detected or only a single particle not representative of the overall sample. Note the term “Nano” refers here to discrete nano-silver particles and/or nano/microcomposites.

In the positive control sample where AgNO₃ (1100 μ g/L) was added into the washing liquid, numerous Ag nanoparticles were observed. Many of these particles had a fractal shape, as visible in Figure 4 (matrix coordinates A3). The EDX spectrum showed very strong sulfur signals in addition to the Ag signal. A second type of Ag-containing particle is shown in Figure 4 (A2). These particles are much larger and are aggregates of particles with diameters up to 100 nm. There are regions in the aggregate that show only an Ag signal (dense regions) and others that also show Cl and S signals (less dense gray regions). Overlaying the spectra of the two particles, the dense particles have only a Ag signal, whereas the gray regions have Ag in addition to Cl, S, and O signals. Therefore, the dense particles are likely metallic nano-silver, while the gray particles consist of silver sulfide and/or AgCl.

In addition to the phosphate-free detergent used for all washing experiments, 1100 μ g/L AgNO₃ was also added into the P-containing detergent used in previous studies.^{5,6} In these samples, two types of Ag-containing particles were seen. Figure 4 (A1) shows an example of very small (2–5 nm) single nanoparticles that were commonly observed. The EDX signal shows peaks for Ag and sulfur. In some cases the S signal is very small and so is possibly formed from subsequent transformations during storage of the TEM grids.

The commercially available X-Static fabric, which released the highest amount of total Ag of any of the fabrics, produced many metallic Ag particles of approximately 20–30 nm in size (Figure 4, B1). Often these were observed in association with a matrix of Si, originating from the detergent, or with small associated S peaks (Figure 4, B3), formed either during the wash cycle or after exposure to air. While the AgCl

fabric did not contain as much total Ag as the other fabrics, the relative amount of Ag was high and many particles were detected. Ag particles in the size range of 20–30 nm were readily detected and no AgCl particles were observed (Figure 4, C1), corresponding well with the silver speciation calculations (Table 1). Though nominally having a similar total Ag concentration, the AgCl/TiO₂ fabric resulted in different silver-containing particulate material. No metallic Ag particles were observed, but Ag/S particles (approximately 10 nm in size) and TiO₂ particles were observed (Figure 4, D3). Most particles in this washing liquid seemed to be associated with a silica matrix, suggesting possible adhesion of the particles to the Si in the detergent. In the Ag-zeolite treatment metallic Ag particles in the size range of 30–40 nm were observed (Figure 4, E1) in addition to some Ag/S complexes (Figure 4, E3). As with the AgCl/TiO₂ fabric, many of the observed particles were found in association with a Si matrix originating from either the detergent or the zeolite material itself.

After addition of NM-300K nano-Ag into the washing liquid, three particle types were observed (Figure 4); (F1) metallic particles in the size range from a few nanometers to about 20–30 nm; (F2) Ag with associated Cl (*i.e.*, AgCl precipitate); and (F3) small particles a few nanometers in diameter consisting of Ag, Cl, and/or S. The first particle type was in the given size range for the NM300 material,²⁷ indicating that to some extent nontransformed NM-300K nanomaterials were released from the textile.

The washing liquid from the textile with AGS-20 on the surface contained less than 10 μ g/L of silver. Similar to other textile samples, the TEM analysis showed the sample contained various non-silver nanoparticles

originating from the washing liquid or the textile itself (e.g., zeolite and TiO_2 particles). There was only one single 10 nm Ag-containing particle found (Figure 4, G3), which, similar to those particles observed from the other silver additives, was associated with an amorphous matrix of Cl, S, and Si.

DISCUSSION

Release of Total Ag. Washing liquid from the X-Static fabric contained the highest total amount of Ag during the wash cycle ($1985 \pm 362 \mu\text{g/L}$ Ag). This high level is to be expected, as the fabric contained nearly 100 times more Ag than the other silver-treated fabrics (approximately 14 500 mg Ag/kg fabric vs 15–115 mg Ag/kg fabric). Of the “conventional” treatments, the Ag-zeolite fabric released the most Ag, averaging approximately 425 $\mu\text{g/L}$ Ag. The fabric that released the least amount of total Ag was the sample AGS-20 bulk, with silver contained inside the fibers. While beyond the scope of this study, the antimicrobial efficacy of the treated textiles needs to be weighed with potential for Ag release during use.²⁸ Excluding the X-Static and AGS-20 bulk fabrics, which had a very low proportion of Ag released, the other fabrics with both “conventional” and “nano” treatments had similar proportions of total Ag released during washing, indicating that the majority of fabrics tested here are similar in terms of total Ag release, with the “nano” fabrics giving relatively less release compared to the “conventional” fabrics.

Size Fractionation of Recovered Ag. The initial form of silver in the textiles (i.e., ionic, salt, metal) is an important factor for the concentration of various size fractions of the material released after the wash cycle. This relationship is not necessarily intuitive, where releases of Ag^+ may result in higher concentrations of nano-silver particulates in the wash effluent than if the textile was directly treated with nano-silver. For example, the concentration of Ag in nanoparticulate form found in the washing liquid from the two AGS-20 textiles investigated was <0.5% (surface treated) and <0.05% (bulk treated) of the total silver treatment, respectively. This indicates a smaller propensity to release silver from the textile during laundering than conventional silver treatments. For perspective, an equivalent amount of total silver in the form of AgNO_3 added directly to the washing liquid leads to corresponding fractions of 2.3% and 13.5% of the Ag in the nanosize range. Treatments with nano-Ag form can therefore result in less nanoparticulate silver in the washing liquid than if silver nitrate (source of silver ions) was added directly. The large fraction of nanosized particulates from the Ag-zeolite “conventional” textile is consistent with the AgNO_3 result, as the ionic silver within the zeolite matrix is easily released to the washing liquid, where it can subsequently form silver-containing nanoparticles.

Textile treated with nano additives also featured washing liquids with a higher proportion of silver material larger than $0.45 \mu\text{m}$ compared to the conventional textile additives. Indeed, in this study the vast majority (over 90%) of Ag was released in the largest size fraction for fabrics that were surface treated with the nano additives. This could indicate association with abraded fabric fibers, etc., which could not pass through the filter. Particle agglomeration is also a possible explanation for this result. However, the conventional fabric treatments also form nanosized Ag particles, and so we would have also expected these materials to readily agglomerate under similar conditions if this phenomenon were the primary mechanism. The AgCl fabric yielded just over 35% of Ag material in the $>0.45 \mu\text{m}$ size range, and the other fabrics gave significantly less in this larger fraction, with only 2–16% of the material appearing in $>0.45 \mu\text{m}$ range.

The Ag size fractions in the washing liquid may also vary depending on the medium used for washing. Previous studies have used distilled water,⁷ tap water,⁸ and washing solutions^{5,6} to investigate Ag release from commercial and research/test fabrics. In their study soaking socks in distilled water, Benn and Westerhoff reported that up to 86% of Ag released was in the ionic form, whereas the work of Geranio *et al.* and Lorenz *et al.*, who used detergent-based washing solutions, gave much lower Ag^+ concentrations and the particulate fraction was more relevant. In these studies, the majority of silver found in the washing liquids was 75% and 50% as particles $>0.45 \mu\text{m}$ on average for the Geranio and Lorenz studies, respectively. As in the present study, the high pH of the washing solutions and the high concentration of ligands that can interact with the ionic Ag promote Ag complexation and precipitation. This is true if the Ag is derived from either the conventional or nano-treated fabrics. It is thus clear that “washing” in distilled water is a poor proxy for the behavior of Ag in real washing solutions. Therefore, the results from these overly simplistic studies should not be used to make any conclusions about release or transformations of (nano) Ag from textiles under real-world conditions.

Ag Speciation, Particle Formation, and Morphology. A variety of transformation byproducts are produced when AgNO_3 , conventional Ag, or nano-Ag treatments are processed in washing liquid (Figure 5). Regardless of the starting material, some similar Ag species arise and common particles are formed. Initial release of silver from the textile may conceivably occur as Ag^+ and/or nano-Ag from the nano-treated textiles or *via* Ag^+ for the conventional-treated textiles. While these initially released forms may conceivably persist in this initial form, it is likely they subsequently proceed through a transitional phase during the washing cycle where the Ag materials may undergo oxidation, dissolution, reduction, precipitation, and/or sulfidation reactions to

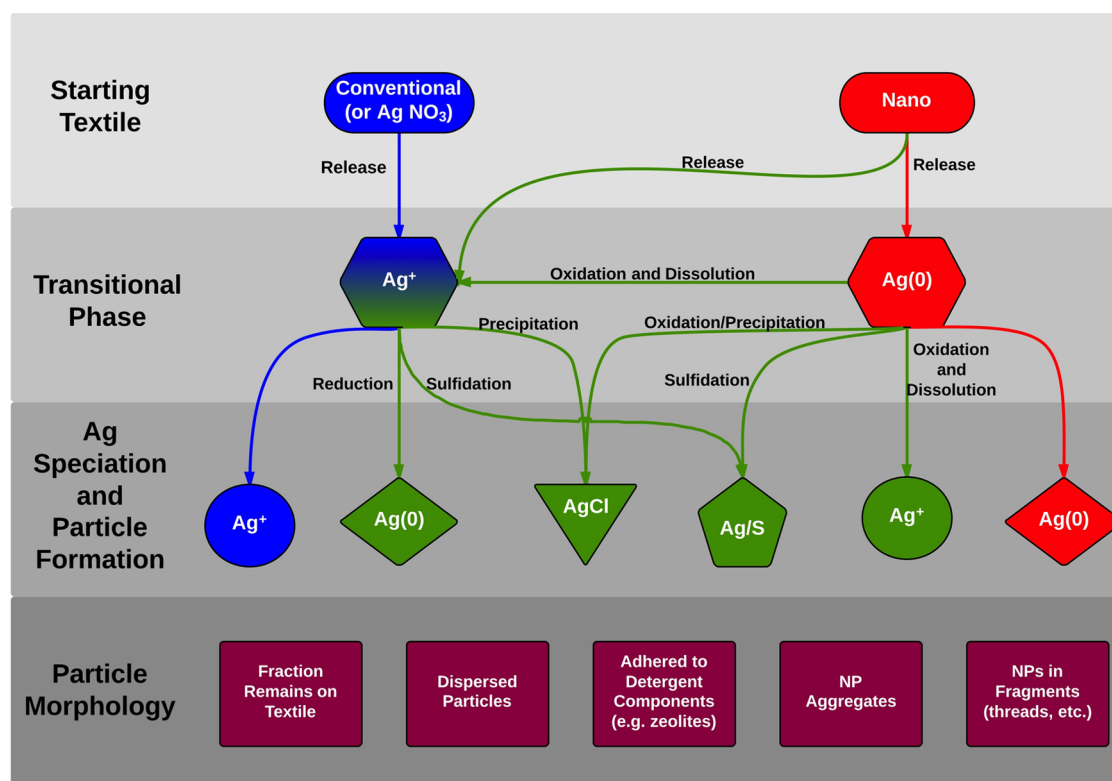


Figure 5. Possible scenarios for silver release and subsequent transformation(s) from silver-treated textiles. Blue shading or lines indicate conventional materials or AgNO_3 that persists through the transformation process, and red shading and lines indicate pristine nanomaterials. Green shading and lines indicate a transformation product or process, respectively. Graded stages of transformation are noted as starting (pristine) material, transitional phase, Ag speciation and particle formation, and particle (population) morphology possibilities, where purple boxes show possible resultant final particle configurations.

form a myriad of possible Ag species, complexes, and particles. It is important to note that difficulty can arise in determining if particles persist unchanged from the initial material (e.g., nano-Ag(0) from the textile) or if a seemingly similar particle was formed *via* other means (e.g., release of Ag(0) from a nanotextile that undergoes oxidative dissolution to form Ag^+ and subsequently is reduced to Ag(0), forming a “new” particle in the wash cycle). The Ag species and particles formed may appear not only as dispersed moieties but also as a spectrum of particle morphologies, including Ag adhered to washing components, particle aggregates, and nano-Ag attached to fabric fragments. Finally, it is important to note that most of the silver material will remain on the textile itself (in some cases a significant portion of the starting material), and while this material is not directly released from the fabric, it too may have altered surface characteristics and/or morphology due to the wash cycle conditions. The solid phase speciation of Ag in original and washed silver textiles was recently investigated by Lombi *et al.*, where the authors found a number of different Ag species coexisting before and after washing.²⁹ Additional experiments are called for to investigate how these transformations affect further Ag release (whether it be in particulate or ionic form) in subsequent washing steps. Different silver species will also have different

biocidal potency.^{30,31} It is beyond the scope of this study to determine the antimicrobial efficiency of the fabrics used in this study or to comment on manufacturers' claims regarding relative antimicrobial qualities of the various treatments. However, of the fabrics used in a study by Lorenz *et al.*, those identified as nanotextiles showed higher antimicrobial activity than fabrics in which traditional forms of silver were incorporated.⁵

Our experiments reveal that different nanoparticulate Ag species including metallic Ag, AgCl, and Ag/S can be formed even when AgNO_3 (dissolved Ag^+) is added to washing liquid. Similar materials were also observed when fabrics treated with conventional Ag additives were washed. EDX spectra show clear evidence for the reduction of AgNO_3 to metallic silver nanoparticles. This was consistently observed in experiments with AgNO_3 , AgCl, and Ag-zeolites. The presence of silver nanoparticles in washing liquid from a textile treated with an unspecified form of silver is therefore clearly an insufficient proof that the original textile was treated with nano-Ag. The formation of AgCl particles in washing liquid is expected based on speciation calculations. The S-containing particles can to some extent be an artifact of air exposure and reactions with sulfur during TEM grid sample storage;³² yet some of the present samples were imaged directly

without storage, and these also exhibited clear S peaks, indicating that sulfur-containing phases were indeed formed in the washing liquid. However, with the analyses we have performed it is not possible to identify the precise form of sulfur, only the presence of S together with Ag. The formation of Ag_2S has been reported numerous times under anaerobic conditions,^{33,34} and Ag_2S nanoparticles have been found in wastewater.^{35,36} Levard *et al.* have shown that Ag_2S is a possible phase in natural systems, even in the presence of chloride.³⁷ In the present study, numerous samples with S-containing silver nanoparticles were identified in the washing liquid. The source of sulfur may be the sulfate present in the washing liquid, which is present at quite a high concentration (the washing powder contains 10% Na_2SO_4). Because Ag_2SO_4 is very soluble, this phase is unlikely to have been formed, and therefore it is reasonable to deduce that reduced sulfur formed these sulfur-containing Ag particles. In addition, in most cases there was no O-signal present within the Ag/S particles, further supporting a reduced form of sulfur as the primary mechanism.

It is noteworthy that in the samples we have imaged with TEM we did not observe any AgCl particles in the solutions from the textiles with AgCl or AgCl/TiO_2 . While one possible explanation is that no release of particulate AgCl occurred, the most likely explanation is that all silver-containing particles in the washing liquid were formed following dissolution of the AgCl to ionic Ag and then subsequent formation of new Ag(0) or Ag/S particles. Any of these different particles may either remain dispersed in solution, aggregate, or complex with silica particles originating from the detergent. Finally, up to 4% of the silver recovered after washing the conventional textiles passed through the 10 kDa filter, indicating that there is only a small possibility for Ag^+ ions to persist in the washing liquid.

Textiles treated with nano additives produce many similar silver forms in washing liquids compared to those formed from the direct release of Ag^+ from conventional Ag textiles. Treated fabrics may directly release Ag^+ into the washing liquid or release metallic nano-Ag particles, which after oxidation and dissolution produce ionic Ag^+ in solution. The Ag^+ can then undergo the identical reaction processes as described in the preceding section. Conversely, metallic Ag particles can undergo (surface) transformations, including reactions with sulfur. The addition of the NM-300K controls to the washing liquid highlights the spectrum of possible particle transformations in the system. Alongside the unchanged NM-300K particles (*i.e.*, metallic Ag), AgCl and Ag/S nanoparticles were also observed. A change from the initial particle size, either smaller (Ag/S) or larger (AgCl) particles, is indicative of a dissolution/precipitation process. Changes to the treatment particle morphology may also occur. Particle aggregation is possible, as particles adhere to

larger fragments (*e.g.*, zeolites) in the washing liquid. However, the high concentration of surfactants in the washing liquid stabilizes the particles, and well-dispersed single particles could be observed. Finally, some fibers may abrade from the textile during the mechanical washing process, where these fragments could contain essentially pristine particles.

Particle transformation could also hypothetically occur before the textiles have been washed. Incorporation of silver into textiles affords easy contact with air. ENM incorporated into products may be stored for some time exposed to the atmosphere including humidity and varying temperatures. During this time changes in crystal structure, particle size, or surface chemistry may occur. Under most atmospheric conditions, Ag becomes tarnished after exposure to air. Formation of Ag_2S is the most common corrosion product in indoor air,¹⁰ while strong oxidants, such as NO_x and ozone, may accelerate Ag_2S formation significantly.^{38–40} Alternatively, transformation of Ag to AgCl is usually more dominant in outdoor environments, where environmental components including ozone, UV light, and humidity can accelerate atmospheric corrosion of silver.^{11,41} In their X-ray absorption spectroscopy (XAS)-study Lombi *et al.* identified in unwashed textiles purchased on the market many different forms of silver including metallic Ag, AgCl, Ag_2S , ionic Ag, and other forms.²⁹ Some of these species represent the original material added to the textile, whereas Ag_2S is clearly a transformation product formed during the technical processes or storage.

In their comparative evaluation of antimicrobials used in textiles, Windler *et al.* had stated that application rates of antimicrobials and their durability are primary drivers of the environmental effects of various antimicrobial treatments.⁴² Nano treatments generally require a much lower total Ag load on the fabric than conventional treatments and therefore have potential to release less silver to the environment. Accordingly, silver treatments that achieve functionality with very low application rates, such as those based on nano-Ag and AgCl, can offer clear potential benefits for textile use.

CONCLUSIONS

The different forms of silver observed in washing liquids can originate from all silver-treated textiles, both from ionic silver and from metallic nano-silver. The various Ag and Ag complexes in washing liquid have consequences for the evaluation of the data from textile washing. Silver in textiles has to release silver ions (Ag^+) in order to have the desired antimicrobial activity, and so precipitation/complexation may potentially decrease the potency of the treatment. A small fraction of dissolved silver was detected in all samples, which in many cases underwent transformation

TABLE 1. Summary of Various Silver Treatments and Fabric Samples Including Measured Ag Content Determined through Fabric Digestion^a

silver additive	trade name	supplier	silver form	particle size	fabric construction	treatment	measured (mg Ag/kg fabric)
Conventional							
AgCl	T25-25	Sanitized	salt	>100 nm	woven	surface, roll to roll	14.6
X-Static (metallic Ag)	X-Static	Noble Biomaterials	metal	fiber	knitted	surface, electrolytic deposition	14 500
AgCl/TiO ₂	JMAC	Clariant	salt	composite Ø ca. 1 µm	woven	surface, roll to roll	19.5
Ag-zeolite	#382280	Sigma-Aldrich	ionic	composite +20 mesh	woven	surface, roll to roll	67.6
Nano							
Ag/SiO ₂	AGS-20	HeiQ Materials	metal	composite Ø ca. 1 µm	woven and knitted	bulk and surface	116 ± 1 (bulk) 18.2 ± 0.3 (surface)
NM-300K	NM300K	EU JRC	metal	<20 nm	woven	surface	15.5 ± 0.6

^a Note that the “Nano” category here refers to discrete nanoparticles and to nano/microcomposites.

and precipitation reactions, forming silver-containing nanoparticles such as metallic Ag, AgCl, and Ag/S. Therefore, the presence of particles in washing solution does not conclusively indicate that nanoparticles were necessarily released from the textiles. In contrast, it may simply be that silver particles in the textile dissolve to Ag⁺ and subsequently form secondary particles in the washing liquid. Significantly, this process would be the same for all forms of silver treatments in textiles, e.g., bulk silver-coated filaments or ionic silver bound in a matrix or AgCl particles. In addition to these transformation pathways it is possible that nanoforms might persist in their original form through the washing process. The inherent diversity of the various transformation and speciation pathways makes the task of determining the exact origin of Ag⁺, Ag salts, and Ag nanomaterials in washing effluent very complex; it is certainly not a simple case of “nano on textile = nano release from textile”.

The present study illustrates that washing any silver-treated textile, regardless of “conventional” or “nano” treatment types, can result in the presence of silver

nanoparticles in the washing liquid. Consequently, we must consider that “conventional forms” of silver also precipitate nanosized silver (complexes) during use, warranting careful reflection regarding the contrasting approaches to the regulatory treatment of nano-silver compared to conventional silver forms. Indeed, we have clearly shown that textiles treated with “conventional” silver have equal or greater propensity to form nano-silver particles during washing conditions than “nano” silver treatments.

This study serves as a vivid example of the inherent complexity of silver behavior in complex environmental conditions. Counterintuitively, the “nano” textile treatments have been found to offer lower exposure potential to nanoparticles than the “conventional” treatment counterparts. Current regulatory distinctions between “nano” and “conventional” silver treatments warrant careful reflection when the similarities in behavior are such that these can legitimately be considered together simply as “silver” treatments for the purpose of assessing environmental exposure from washing.

MATERIALS AND METHODS

Silver Additives, Composites, and Nanoparticles. The silver additives used are shown in Table 1. The AgCl additive T25-25 is commonly used for textiles that come in constant and direct skin contact, such as underwear, work wear, or sportswear, but can also be applied to home textiles and bedding.⁴³ The JMAC material is a Ag chloride/titanium dioxide composite,⁴⁴ containing 20% AgCl and 80% titanium dioxide. The AgCl/TiO₂ composites are approximately 0.5 µm in diameter and contain particles less than 100 nm in size.¹⁵ Ag-zeolite powder was obtained from Sigma-Aldrich (article number 382280) as an analogue to Ag-zeolite forms that are employed in textile applications. The starting raw material is a gray granulate with a particle size of +20 mesh containing 35% Ag.⁴⁵

Two metallic silver additives were used in the course of this study. HeiQ AGS-20 is an antimicrobial textile additive produced by HeiQ Materials AG. The additive was conditionally registered by the EPA in 2011.⁴⁶ It is a composite of silver metal sintered onto amorphous silicon dioxide (SiO₂) with the composites

having a size of approximately 1 µm. The constituent silver includes domains in the range of 1 to 10 nm as described by Egger *et al.*⁴⁷ as well as larger particles including sizes larger than 100 nm. The NM-300K nano-silver material is a standard OECD reference substance characterized by the European Commission Joint Research Centre (JRC).²⁷ It is composed of metallic Ag nanoparticles with a mean size of <20 nm²⁷ and is representative of nano-silver forms that can be used for treating textiles.

Additionally, silver nitrate solution was obtained as 1000 mg/L in 0.5 M HNO₃ (Merck) and diluted accordingly for use as experimental positive controls and as instrument calibration solutions.

Fabrics. Standardized textiles were prepared from each of the Ag additives (Table 1). The textiles were treated using Ag concentrations reflective of application levels used in practice.⁴² The various silver-containing liquid formulations were impregnated into 30 cm × 40 cm 100% polyester fabric pieces using a dual-roll padder operated at 2 m/s with 4 bar roll pressure followed by a stenter frame operated at 120 °C for 2 min and 160 °C for 3 min. The application procedure was carried out

using a laboratory system that is representative of commercial industrial scale textile treatment systems. An edge zone of 1 ± 0.5 cm from each sheet was discarded and not used in the experiments. A knitted fabric with the AGS-20 additive directly incorporated into polyester multifilament yarns (bulk treatment) was also included in the study.

A commercial fabric containing nylon yarns coated with bulk metallic Ag (X-Static) was also included. X-Static samples were taken from commercially available tennis socks, the same type used for a previous study by Geranio *et al.*⁶ The soles of two pairs of socks (size 41–46) were sampled for washing and analysis. The fabric composition was a blend of 79% cotton, 12% polyamide, 6% X-Static, and 1% Lycra. The X-Static material is registered with the U.S. EPA.⁴⁸

The Ag content of the test fabric swatches was determined through microwave digestion with $\text{H}_2\text{O}_2/\text{HNO}_3$ for fabrics containing AgCl, AgCl/TiO₂, and X-Static and HF digestion for fabrics containing Ag-zeolite and AGS-20 using an acid mixture of hydrofluoric acid (HF), nitric acid (HNO_3), and if necessary hydrochloric acid (HCl). Boric acid (H_3BO_3) was used to neutralize HF. The Ag content was measured by ICP-MS (PerkinElmer Elan 6000 or PerkinElmer Elan 6100).

Washing Tests. The washing procedure was carried out as described in previous literature^{6,49,50} with some slight modifications. The washing experiments were performed according to ISO Standard 105-C06:2010. The Washtex-P Roaches laboratory washing machine was operated at 40 ± 2 rpm with steel vessels (75 ± 5 mm diameter, 125 ± 10 mm height, 550 ± 50 mL). Temperature was controlled by a thermostat, keeping the washing medium at a constant temperature of 40 ± 2 °C. For most experiments, a phosphate-free ECE detergent without optical brightener was used (for composition, see Table S1), dissolved in distilled water. A washing liquid volume of 75 mL (reduction from 150 mL standard volume) was placed into polyethylene bottles (275 mL), followed by a fabric sample (4 g), and 5 polyethylene balls (\varnothing 8 mm). Each washing experiment (including all controls) was carried out in triplicate. One test variation with addition of AgNO_3 into phosphate-containing detergent (ECE reference detergent 77 for color fastness) previously used in the Geranio study was also included.⁶ As positive controls, AgNO_3 , AGS-20, and NM300 were added directly into the washing liquid at the same total concentrations similar to the treatment level for the associated textile samples, resulting in a silver concentration of 1100 $\mu\text{g/L}$.

After the washing procedure, the fabrics were removed and the excess liquid was gently pressed from the fabric and collected for analysis. The remaining washing liquid in the vessel was filtered and subsequently acidified to 1% HNO_3 (to ensure ionic Ag stability) and stored in the dark at room temperature in polypropylene vials until ICP-MS analysis (for further information about the washing process see Figure S1). Within 24 h of washing, TEM grids were prepared by centrifuging a 2 mL aliquot of wash solution (0.45 μm filtered) at 5000 rpm for 2 h directly onto a 300-mesh copper grid.

The pH was measured in all solutions using a Metrohm 827 pH meter directly after the experiments. All washing liquids had a pH value of 10.5–10.8, and the phosphate-free washing liquid had a lower pH (9.6) (Table S2). Chloride is an important ion that leads to the precipitation of AgCl and so was measured in the textile washes. The chloride content in the washing liquid of selected washing experiments was measured by ion chromatography in the <0.45 μm filtrate. A Metrohm 733 ion chromatograph equipped with a MetroSep A Supp 5 column was used. The washing powder did not specify any chloride salt added, but it was evidently present as an impurity. The concentration was approximately 7 mg/L in the washing liquid and the textile washes (Table S3).

Fractionation and Characterization of Silver in Washing Liquids. Particle size fractionation of the wash solution was accomplished through serial 0.45 μm , 0.10 μm , and centrifugal (10 kDa) filtrations. The suite of filters used included 0.45 μm cellulose nitrate filters (Sartorius Stedim), 0.10 μm cellulose nitrate and polycarbonate (used interchangeably) (Sartorius Stedim/Whatman) filters, and 10 kDa centrifugal ultrafilters (Sartorius Stedim Vivaspin 6). The Ag content of all solutions was

measured by ICP-MS (PerkinElmer Elan 6000 or PerkinElmer Elan 6100). The 0.45 μm filters from the textile samples were digested using HF and subsequently analyzed for Ag content by ICP-MS. For further information about the fractionation process see Figure S1.

The 0.45 μm filters passed $95.8 \pm 1.3\%$ of the AgNO_3 in Na_2CO_3 solution (mimicking the ionic strength and pH of the detergent solution). The 0.1 μm filters passed $88.9 \pm 1.1\%$ in Na_2CO_3 . The recovery in the 10 kDa filtrate ranged between 40% and 60% for different samples. Therefore, in these solutions, about 50% of the dissolved Ag was lost to the filter, suggesting possible underestimation of dissolved Ag content in the results presented here. The recovery of NM300K nanoparticles in 0.1 g/L SDS after passing through the 0.45 and 0.1 μm filters was $97.0 \pm 0.4\%$ and $91.5 \pm 2.4\%$, respectively (Figure S2), indicating that the filtration does not result in significant loss of these nanoparticles.

Particle images were obtained via scanning transmission electron microscopy (STEM) combined with EDX for element detection using a JEOL JEM 2200 fs operated at 200 kV. The nominal spot size of the STEM probe was 0.7 nm using a beam convergence angle of 10.8 mrad. High-angle annular dark-field STEM micrographs were recorded using an inner detector angle of 100 mrad, while the bright-field STEM images were recorded with a detector angle of approximately 15 mrad. EDX spectra of individual particles were recorded either by positioning the electron probe on a selected particle or by scanning the electron probe on a small frame centered on the particle.

Speciation Calculations. To further explore the speciation of Ag, the precipitation of solid phases was calculated using the VisualMINTQ chemical equilibrium software⁵¹ for AgNO_3 . Input values were the concentration of ions given in Table S1 for the washing liquid, the measured chloride concentration for the washing liquid, and the measured pH values. The total AgNO_3 concentration was considered to be 1100 $\mu\text{g/L}$ Ag (total Ag added in the experiments or expected from total release of Ag from nano-silver-treated textiles).

Conflict of Interest: The authors declare the following competing financial interest(s): Dr. Murray Height is an employee of the company HeiQ Materials AG, which manufactures and markets various silver-based antimicrobial products.

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Supporting Information Available: Includes composition of laundry detergent (Table S1), schematic of fabric washing and wash water filtration/analysis (Figure S1), pH values and chloride content (Tables S2 and S3), percent recovery from filters (Figure S2), and EDX spectra of particles observed in wash water (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES AND NOTES

- Seltenrich, N. Nanosilver: Weighing the Risks and Benefits. *Environ. Health Perspect.* **2013**, 121, A220–A225.
- BfR. *BfR rät von Nanosilber in Lebensmitteln und Produkten des täglichen Bedarfs ab*, Bundesinstitut für Risikobewertung, Germany, Stellungnahme Nr. 024/2010; **2009**.
- Nowack, B.; Krug, H. F.; Height, M. 120 Years of Nanosilver History: Implications for Policy Makers. *Environ. Sci. Technol.* **2011**, 45, 1177–1183.
- Kumar, R.; Howdle, S.; Munstedt, H. Polyamide/Silver Antimicrobials: Effect of Filler Types on the Silver Ion Release. *J. Biomed. Mater. Res. B* **2005**, 75B, 311–319.
- Lorenz, C.; Windler, L.; von Goetz, N.; Lehmann, R.; Schuppler, M.; Hungerbühler, K.; Heuberger, M.; Nowack, B. Characterization of Silver Release from Commercially Available Functional (Nano) Textiles. *Chemosphere* **2012**, 89, 817–824.
- Geranio, L.; Heuberger, M.; Nowack, B. The Behavior of Silver Nanotextiles during Washing. *Environ. Sci. Technol.* **2009**, 43, 8113–8118.

7. Benn, T.; Westerhoff, P. Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics. *Environ. Sci. Technol.* **2008**, *42*, 4133–4139.
8. Benn, T.; B, C.; K, H.; JD, P.; Westerhoff, P. The Release of Nanosilver from Consumer Products Used in the Home. *J. Environ. Quality* **2010**, *39*, 1875–1882.
9. Liu, J.; Hurt, R. Ion Release Kinetics and Particle Persistence in Aqueous Nano-Silver Colloids. *Environ. Sci. Technol.* **2010**, *44*, 2169–2175.
10. McMahon, M.; Lopez, R.; Meyer, H., III; Feldman, L.; Haglund, R., Jr. Rapid Tarnishing of Silver Nanoparticles in Ambient Laboratory Air. *Appl. Phys. B: Laser Opt.* **2005**, *80*, 915–921.
11. Lin, H.; Frankel, G. Accelerated Atmospheric Corrosion Testing of Ag. *Corrosion* **2013**, *69*, 1060–1072.
12. Li, X.; Lenhart, J. J. Aggregation and Dissolution of Silver Nanoparticles in Natural Surface Water. *Environ. Sci. Technol.* **2012**, *46*, 5378–5386.
13. Misra, S. K.; Dybowska, A.; Berhanu, D.; Luoma, S. N.; Valsami-Jones, E. The Complexity of Nanoparticle Dissolution and its Importance in Nanotoxicological Studies. *Sci. Total Environ.* **2012**, *438*, 225–232.
14. Quadros, M.; Pierson, R., IV; Tulve, N.; Willis, R.; Rogers, K.; Thomas, T.; Marr, L. C. Release of Silver from Nanotechnology-Based Consumer Products for Children. *Environ. Sci. Technol.* **2013**, *47*, 8894–8901.
15. Kulthong, K.; Srisung, S.; Boonpavanitchakul, K.; Kangwansupamonkon, W.; Maniratanachote, R. Determination of Silver Nanoparticle Release from Antibacterial Fabrics into Artificial Sweat. *Part. Fibre Toxicol.* **2010**, *7*, 1–9.
16. von Götz, N.; Lorenz, C.; Windler, L.; Nowack, B.; Heuberger, M. P.; Hungerbuehler, K. Migration of Ag- and TiO₂- (Nano) Particles from Textiles into Artificial Sweat under Physical Stress: Experiments and Exposure Modeling. *Environ. Sci. Technol.* **2013**, *47*, 9979–9987.
17. Farkas, J.; Peter, H.; Christian, P.; Urra, J. A. G.; Hasselov, M.; Tuoriniemi, J.; Gustafsson, S.; Olsson, E.; Hylland, K.; Thomas, K. V. Characterization of the Effluent from a Nanosilver Producing Washing Machine. *Environ. Int.* **2011**, *37*, 1057–1062.
18. Maurer, F.; Christl, I.; Hoffmann, M.; Kretzschmar, R. Reduction and Reoxidation of Humic Acid: Influence on Speciation of Cadmium and Silver. *Environ. Sci. Technol.* **2012**, *46*, 8808–8816.
19. Akaighe, N.; MacCuspie, R. I.; Navarro, D. A.; Aga, D. S.; Banerjee, S.; Sohn, M.; Sharma, V. K. Humic Acid-Induced Silver Nanoparticle Formation under Environmentally Relevant Conditions. *Environ. Sci. Technol.* **2011**, *45*, 3895–3901.
20. Yin, Y. G.; Liu, J. F.; Jiang, G. B. Sunlight-Induced Reduction of Ionic Ag and Au to Metallic Nanoparticles by Dissolved Organic Matter. *ACS Nano* **2012**, *6*, 7910–7919.
21. Jones, A. M.; Garg, S.; He, D.; Pham, A. N.; Waite, T. D. Superoxide-Mediated Formation and Charging of Silver Nanoparticles. *Environ. Sci. Technol.* **2011**, *45*, 1428–1434.
22. Glover, R. D.; Miller, J. M.; Hutchison, J. E. Generation of Metal Nanoparticles from Silver and Copper Objects: Nanoparticle Dynamics on Surfaces and Potential Sources of Nanoparticles in the Environment. *ACS Nano* **2011**, *5*, 8950–8957.
23. Kaegi, R.; Voegelin, A.; Ort, C.; Sinnet, B.; Thalmann, B.; Krümer, J.; Hagendorfer, H.; Elumelu, M.; Mueller, E. Fate and Transformation of Silver Nanoparticles in Urban Wastewater Systems. *Water Res.* **2013**, *47*, 3866–3877.
24. Kaegi, R.; Voegelin, A.; Sinnet, B.; Zuleeg, S.; Hagendorfer, H.; Burkhardt, M.; Siegrist, H. Behavior of Metallic Silver Nanoparticles in a Pilot Wastewater Treatment Plant. *Environ. Sci. Technol.* **2011**, *45*, 3902–3908.
25. Koura, N. Electroless plating of silver. In *Electroless Plating: Fundamentals and Applications*; Mallory, G. O.; Hajdu, J. B., Eds.; Noyes Publications/William Andrew Publishing, LLC: New York, USA, 1990; pp 441–462.
26. Yuen, C. W. M.; Jiang, S. X.; Kan, C. W.; Ku, S. K. A.; Choi, P. S. R.; Tang, K. P. M.; Cheng, S. Y. Polyester Metallisation with Electroless Silver Plating Process. *Fibers Polym.* **2013**, *14*, 82–88.
27. Klein, C. L.; Comero, S.; Stahlmecke, B.; Romazanov, J.; Kuhlbusch, T. A. J.; Van Doren, E.; De Temmerman, P.-J.; Mast, J.; Wick, P.; Krug, H.; Locoro, G.; Hund-Rinke, K.; Kördel, W.; Friedrichs, S.; Maier, G.; Werner, J.; Linsinger, T.; Gawlik, B. M. *NM-Series of Representative Manufactured Nanomaterials: NM-300 Silver Characterisation, Stability, Homogeneity*; European Commission Joint Research Centre: Luxembourg, 2011.
28. Nowack, B.; Krug, H. F.; Height, M. 120 Years of Nanosilver History: Implications for Policy Makers. *Environ. Sci. Technol.* **2011**, *45*, 1177–1183.
29. Lombi, E.; Donner, E.; Scheckel, K. G.; Sekine, R.; Lorenz, C.; Goetz, N. V.; Nowack, B. Silver Speciation and Release in Commercial Antimicrobial Textiles as Influenced by Washing. *Chemosphere* **2014**, *111*, 352–358.
30. Levard, C.; Mitra, S.; Yang, T.; Jew, A. D.; Badireddy, A. R.; Lowry, G. V.; Brown, G. E., Jr. Effect of Chloride on the Dissolution Rate of Silver Nanoparticles and Toxicity to *E. coli*. *Environ. Sci. Technol.* **2013**, *47*, 5738–5745.
31. Reinsch, B.; Levard, C.; Li, Z.; Ma, R.; Wise, A.; Gregory, K.; Brown, G., Jr.; Lowry, G. Sulfidation of Silver Nanoparticles Decreases *Escherichia coli* Growth Inhibition. *Environ. Sci. Technol.* **2012**, *46*, 6992–7000.
32. McMahon, M. D.; Lopez, R.; Meyer, H. M., III; Feldman, L. C.; Haglund, R. F., Jr. Rapid Tarnishing of Silver Nanoparticles in Ambient Laboratory Air. *Appl. Phys. B: Laser Opt.* **2005**, *80*, 915–921.
33. Levard, C.; Reinsch, B. C.; Michel, F. M.; Oumahi, C.; Lowry, G. V.; Brown, G. E. Sulfidation Processes of PVP-Coated Silver Nanoparticles in Aqueous Solution: Impact on Dissolution Rate. *Environ. Sci. Technol.* **2011**, *45*, 5260–5266.
34. Reinsch, B. C.; Levard, C.; Li, Z.; Ma, R.; Wise, A.; Gregory, K. B.; Brown, G. E.; Lowry, G. V. Sulfidation of Silver Nanoparticles Decreases *Escherichia coli* Growth Inhibition. *Environ. Sci. Technol.* **2012**, *46*, 6992–7000.
35. Kaegi, R.; Voegelin, A.; Sinnet, B.; Zuleeg, S.; Hagendorfer, H.; Burkhardt, M.; Siegrist, H. Behavior of Metallic Silver Nanoparticles in a Pilot Wastewater Treatment Plant. *Environ. Sci. Technol.* **2011**, *45*, 3902–3908.
36. Kim, B.; Park, C. S.; Murayama, M.; Hochella, M. F. Discovery and Characterization of Silver Sulfide Nanoparticles in Final Sewage Sludge Products. *Environ. Sci. Technol.* **2010**, *44*, 7509–7514.
37. Levard, C.; Hotze, E. M.; Lowry, G. V.; Brown, G. E. Environmental Transformations of Silver Nanoparticles: Impact on Stability and Toxicity. *Environ. Sci. Technol.* **2012**, *46*, 6900–6914.
38. Rice, D.; Peterson, P.; Rigby, E. B.; Phipps, P.; Cappell, R.; Tremoureaux, R. Atmospheric Corrosion of Copper and Silver. *J. Electrochem. Soc.* **1981**, *128*, 275–284.
39. Kim, H. Corrosion Process of Silver in Environments Containing 0.1 ppm H₂S and 1.2 ppm NO₂. *Mater. Corros.* **2003**, *54*, 243–250.
40. Volpe, L.; Peterson, P. The Atmospheric Sulfidation of Silver in a Tubular Corrosion Reactor. *Corros. Sci.* **1989**, *29*, 1179–1196.
41. Watanabe, M.; Shinozaki, S.; Toyoda, E.; Asakura, K.; Ichino, T.; Kuwaki, N.; Higashi, Y.; Tanaka, T. Corrosion Products Formed on Silver After a One-Month Exposure to Urban Atmospheres. *Corrosion* **2006**, *62*, 243–250.
42. Windler, L.; Height, M.; Nowack, B. Comparative Evaluation of Antimicrobials for Textile Applications. *Environ. Int.* **2013**, *53*, 62–73.
43. Sanitized silver for bedding: natural effect against bacteria and dust mites. <http://www.sanitized.com/en/business-partners/trademark-products/active-substances/silver.html>, accessed June 25, 2014.
44. Ash, M.; Ash, I. *Handbook of Preservatives*; Synapse Information Resources: Endicott, NY, 2004.
45. Sigma-Aldrich silver-exchanged zeolite. <http://www.sigmaaldrich.com/catalog/product/aldrich/382280?lang=en®ion=US>, accessed June 24, 2014.

46. USEPA. *Decision document: conditional registration of HeiQ AGS-20 as a materials preservative in textiles*; U.S. Environmental Protection Agency, **2011**.
47. Egger, S.; Lehmann, R. P.; Height, M. J.; Loessner, M. J.; Schuppler, M. Antimicrobial Properties of a Novel Silver-Silica Nanocomposite Material. *Appl. Environ. Microbiol.* **2009**, *75*, 2973–2976.
48. Biomaterials, N. FAQs EPA Registration and Labeling. <http://www.noblebiomaterials.com/category2.asp?itemid=336>, accessed June 24, 2014.
49. Lorenz, C.; Windler, L.; Lehmann, R. P.; Schuppler, M.; Von Goetz, N.; Hungerbühler, K.; Heuberger, M.; Nowack, B. Characterization of Silver Release from Commercially Available Functional (Nano)Textiles. *Chemosphere* **2012**, *89*, 817–824.
50. Windler, L.; Lorenz, C.; von Goetz, N.; Hungerbühler, K.; Amberg, M.; Heuberger, M.; Nowack, B. Release of Titanium Dioxide from Textiles during Washing. *Environ. Sci. Technol.* **2012**, *46*, 8181–8188.
51. Gustafsson, J. P. *VisualMINTEQ* version 3.0; 2011. Available at <http://www2.lwr.kth.se/English/OurSoftware/Vminteq/index.html>.