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

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ABSTRACT Questions about how to regulate nanoenhanced 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 μm, < 0.45 μm, <0.1 μm, and <10 kDa), while characterization of particles with TEM/EDX provided insight on Ag transformation mechanisms. Most conventional Ag additives yielded more total Ag and more nanoparticulate-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.5 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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The sensitivity of nano-Ag to oxygen is well known, and the chemisorbed Ag⁺, formed either in air during exposure to water, 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. 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. 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. 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.

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. Also Geranio et al. 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. Aquatic humic acids of various origins were responsible for forming metallic silver nanoparticles from dissolved ionic Ag. Dissolved organic matter reduced dissolved Ag⁺ in the presence of sunlight to metallic nano-silver. Superoxide has been shown to reduce Ag⁺ to silver nanoparticles. 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. 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 the 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. 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 μg/L for the method blank and 0.1 to 1.8 μg/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 μg/L are considered background.
Positive Controls. Positive controls included spiking AgNO₃, NM-300K, nano-Ag, or AGS-20 Ag/SiO₂ composite directly into the washing liquid. The amount of Ag measured in the small particulate (<0.45 μm), nanoparticulate (<100 nm), and dissolved fractions (<30 kDa) in the washing liquid is shown in Figure 18. Addition of AgNO₃ 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 AgNO₃ (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 AgNO₃ into the phosphate-containing washing liquid was used in previous silver washing studies with commercial textiles⁵,⁶ 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 AgNO₃-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.⁵ 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 μm 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 μm filters, indicating the presence of discrete nanoparticulate Ag. The fraction removed by the filter (i.e., larger than 0.45 μm) 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 80 nm, 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 μm) 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 μm 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).
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.
In the positive control sample where AgNO$_3$ (1100 μg/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 μg/L AgNO$_3$ 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/TiO$_2$ fabric resulted in different silver-containing particulate material. No metallic Ag particles were observed, but Ag/S particles (approximately 10 nm in size) and TiO$_2$ 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/TiO$_2$ 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 μg/L of silver. Similar to other textile samples, the TEM analysis showed the sample contained various non-silver nanoparticles.

<table>
<thead>
<tr>
<th>NP Forms in Washing Liquid</th>
<th>Control</th>
<th>Conventional</th>
<th>Nano</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNO$_3$</td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>X-Static</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>AgCl</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>AgCl/TiO$_2$</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>AgZeolite</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>NM300</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>AGS-20</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Table 1. Comparison of the types of nanoparticulate Ag found in the washing liquid from various Ag-treated textiles.
originating from the washing liquid or the textile itself (e.g., zeolite and TiO₂ 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 ± 362 μg/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 μg/L Ag. The fabric that released the largest 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 concentration 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 AgNO₃ 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 AgNO₃ 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 μm 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 μm size range, and the other fabrics gave significantly less in this larger fraction, with only 2 – 16% of the material appearing in >0.45 μm range.

The Ag size fractions in the washing liquid may vary depending on the medium used for washing. Previous studies have used distilled water,⁷ tap water,⁸ and washing solutions⁵,⁶ 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 particle fraction was more relevant. In these studies, the majority of silver found in the washing liquids was 75% and 50% as particles >0.45 μm 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 AgNO₃, 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...
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. 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. 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.

Our experiments reveal that different nanoparticulate Ag species including metallic Ag, AgCl, and Ag/S can be formed even when AgNO₃ (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 AgNO₃ to metallic silver nanoparticles. This was consistently observed in experiments with AgNO₃, 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; yet some of the present samples were imaged directly.
Particle aggregation is possible, as particles adhere to the treatment particle morphology may also occur. Changes to smaller (Ag/S) or larger (AgCl) particles, is indicative of possible particle transformations in the system. Alongside the unchanged NM-300K particles, metallic Ag particles can 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 particles 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. Changes from the initial particle size, either smaller (Ag/S) or larger (AgCl) particles, is indicative of a dissolution/reprecipitation 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 Ag₂S is the most common corrosion product in indoor air, while strong oxidants, such as NOₓ and ozone, may accelerate Ag₂S formation significantly. 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.

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. 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...
MATERIALS AND METHODS

Silver Additives, Composites, and Nanoparticles. The silver addi-
tives used are shown in Table 1. The AgCl additive T25-2S 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.41 The
JMAB material is a Ag chloride/titanium dioxide composite,41
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.15

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 European Commission Joint Research Centre (JRC).16 It is
composed of metallic Ag nanoparticles with a mean size of <20 nm15
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 experi-
mental 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 impreg-
nated into 30 cm × 40 cm 100% polyester fabric pieces using
a dual-roll padded operation 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
and precipitation reactions, forming silver-containing
nanoparticles such as metallic Ag, AgCl, and Ag/5.
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 trans-
formation pathways it is possible that nanoforms
might persist in their original form through the wash-
ing process. The inherent diversity of the various
transformation and speciation pathways makes the
ability to determine 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 con-
trasting 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 pro-
portion 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 treat-
ments have been found to offer lower exposure potential
to nanoparticles than the “conventional” treatment counter-
parts. Current regulatory distinctions between “nano” and “conventional” silver treat-
ments 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.

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

<table>
<thead>
<tr>
<th>silver additive</th>
<th>trade name</th>
<th>supplier</th>
<th>silver form</th>
<th>particle size</th>
<th>fabric construction</th>
<th>treatment</th>
<th>measured (mg Ag/kg fabric)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>T2S-2S</td>
<td>Sanitized</td>
<td>salt</td>
<td>&gt;100 nm</td>
<td>woven</td>
<td>surface, roll to roll</td>
<td>14.6</td>
</tr>
<tr>
<td>X-Static (metallic Ag)</td>
<td>X-Static Noble Biomaterials</td>
<td>metal</td>
<td>fiber</td>
<td>knitted</td>
<td>surface, electrolytic deposition</td>
<td>14 500</td>
<td></td>
</tr>
<tr>
<td>AgCl/TiO2</td>
<td>JMAB Clariant</td>
<td>salt</td>
<td>composite Ø ca. 1 μm</td>
<td>woven</td>
<td>surface, roll to roll</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>Ag-zeolite</td>
<td>#382280 Sigma-Aldrich</td>
<td>ionic</td>
<td>composite +20 mesh</td>
<td>woven</td>
<td>surface, roll to roll</td>
<td>67.6</td>
<td></td>
</tr>
<tr>
<td>AgSiO2</td>
<td>AGS-20 HeiQ Materials</td>
<td>metal</td>
<td>composite Ø ca. 1 μm</td>
<td>woven and knitted</td>
<td>bulk and surface</td>
<td>116 ± 1 (bulk)</td>
<td></td>
</tr>
<tr>
<td>NM-300K</td>
<td>NM300K EU JRC</td>
<td>metal</td>
<td>&lt;20 nm</td>
<td>woven</td>
<td>surface</td>
<td>15.5 ± 0.6</td>
<td></td>
</tr>
</tbody>
</table>

*Note that the “Nano” category here refers to discrete nanoparticles and to nano/microcomposites.
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.45 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% Lyrcra. The X-Static material is registered with the U.S. EPA.46

The Ag content of the test fabric swatches was determined through microwave digestion with H2O2/HNO3 for fabrics containing Ag-zeolite and AGS-20 using an acid mixture of hydrofluoric acid (HF), nitric acid (HNO3), and if necessary hydrochloric acid (HCl). Boric acid (H3BO3) 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 literature49,50 with some slight modifications. The washing experiments were performed according to ISO Standard 105-C06:2010. The Wasshtex-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), except in experiments with a phosphate-containing detergent (ECE reference detergent 77 for color fastness) present in the washing liquid. The washing liquid contained AgNO3 into phosphate-containing detergent (ECE reference detergent 77 for color fastness) present in 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 μg/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% HNO3 (to ensure ionic Ag stability) and stored in the dark at room temperature in propylene 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 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 concentration, but it was evident present in the washing liquid.

Fractionation and Characterization of Silver in Washing Liquids. Particle size fractionation of the wash solution was accomplished through sequential filtration using a 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/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 75.8 ± 1.3% of the AgNO3 in Na2CO3 solution (mimicking the ionic strength and pH of the detergent solution). The 0.1 μm filters passed 88.9 ± 1.1% in Na2CO3. 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 ± 0.4% and 91.5 ± 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 mrads. High-angle annular dark-field STEM micrographs were recorded using an inner detector angle of 100 mrads, while the bright-field STEM images were recorded with a detector angle of approximately 15 mrads. 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 AgNO3. 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 AgNO3 concentration was considered to be 1100 μg/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 interests(s): Dr. Murray Height is an employee of the company HeiQ Materials AG, which manufactures and markets various silver-based antimicrobial products.

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


46. USEPA. Decision document: conditional registration of HeiQ AGS-20 as a materials preservative in textiles; U.S. Environmental Protection Agency, 2011.


