Potential Environmental Impacts and Antimicrobial Efficacy of Silver- and Nanosilver-Containing Textiles

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Supporting Information

ABSTRACT: For textiles containing nanosilver, we assessed benefit (antimicrobial efficacy) in parallel with potential to release nanosilver (impact) during multiple life cycle stages. The silver loading and method of silver attachment to the textile highly influenced the silver release during washing. Multiple sequential simulated household washing experiments for fabric swatches in deionized water with or without detergent showed a range of silver release. The toxicity of washing experiment supernatants to zebrafish (Danio rerio) embryos was negligible, with the exception of the very highest Ag releases (~1 mg/L Ag). In fact, toxicity tests indicated that residual detergent exhibited greater adverse response than the released silver. Although washing the fabrics did release silver, it did not affect their antimicrobial efficacy, as demonstrated by >99.9% inhibition of E. coli growth on the textiles, even for textiles that retained as little as 2 μg/g Ag after washing. This suggests that very little nanosilver is required to control bacterial growth in textiles. Visible light irradiation of the fabrics reduced the extent of Ag release for textiles during subsequent washings. End-of-life experiments using simulated landfill conditions showed that silver remaining on the textile is likely to continue leaching from textiles after disposal in a landfill.

INTRODUCTION

Silver nanoparticles (AgNPs) are increasingly used in a variety of products, primarily for their antimicrobial properties. These products range from food packaging and coatings, health supplement drinks, textiles, and bandages. This increased use necessitates assessing the potential impacts of this novel technology on humans and the environment. To date, few studies have evaluated the potential risks alongside the benefits of nanotechnology. This paper examines both by considering how product design and composition influence the environmental exposure and hazard (i.e., risk) and the antimicrobial efficacy (i.e., benefits) of textiles containing nanosilver, silver salts, and metallic silver.

The hazard aspect of risk is well-represented in the literature, and exposure modeling provides estimates for concentrations of free NPs (i.e., not incorporated into products) in the environment. Exposure modeling of NPs in the environment, including AgNPs, predicts concentrations in surface water in the ng/L range. Many hazard assessments for NPs, including AgNPs, have been conducted. The toxicity of AgNPs to zebrafish embryos, rats, rainbow trout, Escherichia coli, and Daphnia magna, among many other organisms, has been studied extensively with much discussion centered on the relative toxicity of AgNPs versus Ag ions because AgNPs are among the more soluble NPs. A recent survey of nanotoxicology literature on soluble NPs found that AgNPs are less toxic than Ag ions in 93.8% of studies.
However, given that AgNPs readily dissolve to Ag ions, an accurate assessment of the potential risks associated with silver-enabled product use and the total amount of silver released is needed to weigh against their benefits to society.

Recent research moves beyond discussion of free NPs to focus on quantifying AgNP and silver ion release from consumer products. Several studies focus on the use phase and demonstrate Ag release from textiles during household washing. Lorenz et al. measured Ag release during the washing and rinsing of textiles and found AgCl to be the dominant chemical form of Ag in wash water. Other silver species, such as sulfided and phosphatized Ag, have also been observed in wash water. AgNPs have been sequentially exposed to matrices simulating those likely to be encountered in their life cycle (e.g., sweat, laundry detergent, and surface water). Other products have been tested for extent of Ag release: Kaegi et al. found that over 30% of AgNPs in a house façade exposed to ambient weather conditions were released after one year. Ag release from antimicrobial food containers has also been evaluated.

This study aims to evaluate four silver-containing textile products through their life cycle, examining the antimicrobial efficacy of these textiles, potential silver release from textiles during simulated-use phases, environmental toxicity, and end-of-life for these products. Each textile sample used a different method to integrate silver onto a common textile fabric, polyester, involving: (1) covalently tethered silver nanoparticles, (2) electrostatically attached silver nanoparticles, (3) a silver-salt coating, and (4) metallic-silver-coated fibers. To focus on the use phase of antimicrobial textiles, we performed multiple fabric-washing cycles and quantified the release of silver (both ionic and particulate) using complementary analytical techniques. Exposure of the fabrics to light allowed us to measure how irradiation affects Ag release during subsequent washing. Efficacy tests (antimicrobial assessment) were performed on the textile, and toxicity testing was performed on the wash water (using zebrafish embryos). The mass and forms of silver released during multiple life cycle phases allow us to assess the transformations and implications of silver as an antimicrobial agent in fabrics. The study’s main conclusions are that, although all of the textiles release silver, the attachment method and mass-loading of silver on textiles both strongly influence antimicrobial efficacy and silver release during use. Significant antimicrobial efficacy persists at very low silver levels (only a few ppm) remaining on fabrics after multiple sequential washings that simulate representative use.

**MATERIALS AND METHODS**

**Ag-Containing Textiles.** Athletic T-shirts (100% polyester) were purchased from Asics (Kobe, Japan), and Dune Sciences attached AgNPs on the shirts from aqueous dispersions (11–13 L of 1699 μg/L Ag). A pair of attachment methods were used: (1) an electrostatic method, where the AgNPs were attached to the shirt fibers via surface-charge difference, referred to as “electrostatic-AgNP”; and (2) via a proprietary linker molecule, which serves to tether the AgNP to the fiber through covalent bonds, referred to as “tethered-AgNP”. To supplement the manufactured textiles, we purchased two more silver-containing fabrics. These fabrics were selected because they use different methods of applying Ag to the textile: Ag0-coated fibers woven into the shirt (X-Static, referred to as “Ag0-coated”) and AgCl applied to the fabric (Polygiene, referred to as “Ag-salt-coated”). All four fabrics were used for subsequent washing and antimicrobial efficacy experiments.

**Analysis of Ag-Containing Textiles and Silver Nanoparticles.** The following digestion procedure was used to determine the total Ag loading on each textile. Triplicate samples containing ~10 mg of each textile were placed in Teflon digestion vessels with 5 mL of 70% trace-metal-grade HNO3 and 5 mL of nanopure water. A microwave-assisted reaction system (MARS 5, CEM, Matthews, NC) aided the digestion, and the digestate was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Thermo X-Series II, Thermo, Waltham, MA) after dilution to 2% HNO3. The Ag concentration was normalized to the digest solution volume and textile mass to yield units of μg Ag/g fabric.

To prepare the fibers for scanning transmission electron microscopy (STEM) imaging, we cut pieces of fabric into fine pieces with scissors and dispersed them in nanopure water. Drops of this dispersion were pipetted onto a copper TEM grid with lacy carbon. The prepared TEM grid was dried for 4 h at room temperature before imaging. TEM images were acquired on an FEI Titan high-resolution TEM at an accelerating voltage of 300 keV in scanning TEM mode with a high-angle annular dark field detector. Variable pressure scanning electron microscopy (VPSEM) was conducted using an FEI (Hillsboro, OR) Quanta 200 environmental scanning electron microscope (ESEM)/VPSEM Microscope. The VPSEM was operated at 15 kV. Images were collected in backscatter-electron mode to enhance contrast.

Nanoparticles used by Dune Sciences to treat the fabrics were obtained for independent characterization. Bright-field images were acquired on an FEI Technai Spirit TEM at an accelerating voltage of 120 keV. Samples for imaging were prepared on hydrophilic SMART TEM Grids purchased from Dune Sciences. A particle-size distribution and ζ potential were determined using a Möbius massively parallel phase-analysis light-scattering (MP-PALS) instrument. Measurements were performed at a nanoparticle concentration of 0.01 mg/mL in 5 mM solution of NaHCO3 (pH 7.0). Samples were prepared by diluting a 1 mg/mL suspension of AgNPs and vortexing for 5 s before pipetting into the sample cuvette. Measurements were performed by averaging 20 scans in duplicate at 25 °C. Single-particle ICP-MS was used to measure average AgNP size. Experimental details can be found in the Supporting Information.

**Washing of Ag Textiles.** Half of the fabric samples were washed using a standard American Association of Textile Colorists and Chemists laundry detergent (AATCC 2003 formulation, constituents in Table S1) to mimic conditions used for washing in the home, and the remaining samples were washed using the same procedure but without detergent. The washing protocol was based upon a modification of the ISO Standard 105-C06:2010 method. Concentrated detergent (40 μL) was diluted in 50 mL of nanopure water. This concentration was chosen to be roughly equivalent to that used for textile washing in the home. Triplicate fabric swatches of ~2 g were cut from each shirt and placed in 250 mL polypropylene bottles with 50 mL of water (with or without detergent) and 5 glass beads (5 mm diameter) for agitation. The bottles and glass beads were acid-washed in 10% nitric acid for at least 24 h and rinsed at least three times with nanopure water between textile-washing experiments. The bottles containing fabric swatches were secured in an end-over-end mixer and rotated at 40 rpm for 30 min. The fabrics were
removed from the bottles, and excess water was squeezed out with tweezers used to extract them. The tweezers were rinsed with nanopure water between uses. The textiles were transferred to a drying oven and dried overnight at 50°C, a temperature similar to household dryers. This was done to remove any excess water from the fabric that might cause extended release and dissolution of Ag particles on the fibers over time. For selected samples, aliquots of wash water were filtered using a 30 kDa centrifugal ultrafilter for 30 min at 5000 g to quantify ionic Ag in wash solutions. The remaining wash solutions were acidified to 2% HNO₃ (for metal preservation) in the 250 mL wash bottles and analyzed by ICP-MS (Thermo X-Series II, Waltham, MA).

Effect of Light Irradiation on Ag Release from Tethered-AgNP Shirts. Passive-release studies were carried out to determine the impact that light exposure has on the release of total silver from the tethered-AgNP fabric at two distinct stages in the exposure cycle: (A) during initial submersion in water, in the absence or presence of irradiation, and (B) in the subsequent washing of the fabric with detergent. Tethered-AgNP textile samples were digested with aqua regia (3 parts trace-metal-grade HCl and 1 part trace-metal-grade HNO₃) both before and after tethered-AgNP shirts were irradiated and washed. This allowed the measurement of the total silver remaining in the fabric and provided a means to calculate a silver-mass balance for each sample using the following equation:

\[
\text{initial fabric } m_{Ag} = \text{irradiation release } m_{Ag} + \text{washing release } m_{Ag} + \text{residual fabric } m_{Ag}
\]

(eqn 1)

A total of 16 samples were cut (~2 in. × 2 in. each) from the as-received tethered-AgNP fabric and weighed (average mass: 0.66 ± 0.02 g) prior to submersion in water. Each sample was then placed in a clear polyethylene terephthalate (PET) jar purchased from SKS Industries (part no. 0618-08) and submerged (to allow collection of released Ag in supernatant) in 50 mL of 3 mM phosphate buffer solution at pH 6.5, prepared as previously described. A total of eight jars were sealed and wrapped in aluminum foil, producing dark-control and exposed) were placed in a homemade light box (Figure S1), which consisted of eight low-profile 8 W fluorescent bulbs (Pegasus Lighting, part no. NULS-8m; spectra in Figures S2 and S3) to provide continuous illumination. Fabric samples were submerged in water, in the absence or presence of irradiation, submersion in water, in the absence or presence of irradiation, and (B) in the subsequent washing of the fabric with detergent. Tethered-AgNP textile samples were digested with aqua regia (3 parts trace-metal-grade HCl and 1 part trace-metal-grade HNO₃) both before and after tethered-AgNP shirts were irradiated and washed. This allowed the measurement of the total silver remaining in the fabric and provided a means to calculate a silver-mass balance for each sample using the following equation:

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\]

(eqn 1)

Toxicity of Wash Water to Zebrafish Embryos. Fabric-wash water aliquots were collected before acidification and used for zebrafish embryo (Danio rerio) exposures, as reported in previous studies. These in vivo assays evaluate a comprehensive battery of developmental end points for chemical hazard via multiple mechanisms of action. Tropical SD wild-type adult zebrafish were housed at an approximate density of 1000 per 100 gallons. Spawning funnels were placed into their tanks the night prior, and embryos were collected and staged. All of the wash water samples were diluted using a 1/2 log series starting at 1× in Nanopure water. The final wash water concentrations tested were 1×, 0.1×, 0.032×, 0.01×, 0.0032×, 0.001×, and 0× (blank) dilutions of the starting wash. Embryos were statically exposed and assessed for toxicity end-point at 24 h postfertilization (hpf).

Toxicity Characteristic Landfill Leachate Procedure on Washed Ag-Textiles. Toxicity characteristic leaching procedure (TCLP) was conducted following the U.S. Environmental Protection Agency (EPA) standard method and a modified method, which was created by adding 2000 ppm of Cl− to the TCLP fluid prepared in accordance to this standard method. A concentration of 2000 ppm of Cl− is representative of reported concentrations found in typical landfill leachates.

**RESULTS AND DISCUSSION**

Silver Nanoparticle Synthesis, Characterization, and Integration into Textiles. As shown in TEM micrographs (Figure S4), the as-prepared AgNPs were 20.0 ± 7.0 nm diameter particles and were nearly spherical in shape. The
particles contained a Tween 20 polymer coating, which aided in their dispersion in water. The Tween 20 AgNPs dispersed well in water, with a mode spICP-MS measured diameter of 18.2 nm (Figure S5) and a hydrodynamic diameter of 31.3 ± 0.8 nm as measured by MP-PALS (Figure S6). The AgNPs resulted in a ζ potential of −16.3 ± 0.5 mV at pH 7.0.

The fabrics manufactured for this study contained 22.8 ± 0.1 μg Ag/g fabric and 1.07 ± 0.01 μg Ag/g fabric for the covalently tethered and electrostatic attachment methods, respectively. Figure S7A shows a scanning electron microscopy image of the tethered-AgNP fabric. Energy dispersive X-ray analysis (EDS) analysis of the observed particles confirmed the presence of Ag (Figure S9).

A pair of additional commercially available, silver-enabled textiles (shirts) were purchased. Vendor information suggested that Polygiene (referred to here as Ag-salt-coated) contains silver chloride particles attached to polyester fabric. The Ag content of the fabric was measured as 16.4 ± 0.1 μg Ag/g fabric. Imaging by STEM (Figure S7B) shows discrete particles, and EDS analysis confirmed the presence of Ag (Figure S10).

The second purchased textile (X-Static, referred to here as Ag0-coated) contained silver-coated fibers woven into the polyester textile as observed by SEM (Figure S7C, S7D), STEM (Figure S8), and EDS (Figures S11 and S12). The silver content of the Ag0-coated textile was 4030 ± 60 μg Ag/g fabric, the highest measured in this study.

Use Phase: Silver Release during Simulated Washing. Amount of Silver Released during Washing Variation by Textile Type. The amount of Ag released from the textiles over multiple washes is presented in Figure 1. The textile swatches were weighed before washing, and the mass of Ag measured in solution by ICP-MS was normalized to each fabric-swatch mass.

Figure 1a shows the extent of release for all four textiles in deionized (DI) water normalized to the initial Ag loading of each one. The Ag0-coated textile, due to its much higher initial loading, released 106 ± 10 μg/g (2.6% of initial loading) total Ag after four washes. The tethered-AgNP textile released 18 ± 3 μg/g (76% of initial) Ag loading compared with 0.79 ± 0.18 μg/g (79%) for the electrostatic-AgNP and 3.1 ± 0.7 μg/g (19%) for the Ag salt-coated textiles. The tethered-AgNP textile was washed an additional two times (six times total) to test whether all or nearly all of the attached Ag could be removed by washing. The two additional washes resulted in an additional 3.4 ± 0.1 μg/g, 14% of initial, for 90% total Ag release over six washes. The amount of release during washing (Figure 1a) clearly increases with increased initial loading, although this does not scale linearly, given the variation seen in release as % of loading (Figure 1b).

Washing experiments were also conducted using AATCC detergent (composition given in Table S1). The Ag release trends observed with detergent (Figure 1c,d) are very similar to those observed in DI water: the Ag0-coated textile released the greatest amount of Ag, 10.1 ± 0.3 μg/g, again followed by tethered-AgNP (13 ± 1 μg/g), Ag-salt-coated (2.9 ± 0.1 μg/g), and electrostatic-AgNP (0.58 ± 0.12 μg/g) (Figure 1c). The Ag released in the detergent washes was slightly lower than that measured in the DI water washes. Single-detergent washes of the Ag0-coated textile released Ag in the range of 0.59%−0.77% per wash, which is similar to observations by Mitrano et al.20 After an Ag0-coated fabric was washed in detergent, their study...
found that less than 1% of the initial Ag loading on this type of textile was released after a single wash.

**Washing with Detergent and Formation of Ag-Containing Particles.** For selected textile wash samples, aliquots of wash water were taken after washing the textiles but before acidification for total [Ag] analysis by ICP-MS. These aliquots were filtered using a 30 kDa centrifugal ultrafilter (3.6 nm pore size) to remove any particulate Ag. The filtrate was acidified to 2% HNO₃ and analyzed for [Ag] by ICP-MS. The results for wash 1 of each textile in DI water and detergent are shown in Figure S13. For each textile, the pair of bars reports the total Ag released (left) and the dissolved Ag released (30 kDa ultrafiltered, right). As shown in the leftmost pair of bars, 80% of Ag released from the Ag²⁻-coated textile when it was washed in DI water was present as dissolved Ag (30 kDa permeate). When washed in detergent, the same textile released 22% of the total Ag as dissolved. Mitrano et al.²⁰ defined dissolved as 10 kDa filterable and measured ~8% of released Ag as dissolved from a Ag²⁻-coated textile washed in detergent. Differences in detergent concentration and composition, the specific textile used, and filter pore size will all affect this measurement, but in general, our results corroborate this previous work. A large percentage of Ag (92%) was measured as dissolved when released from tethered-AgNP textiles washed in DI water. When textiles were washed in detergent, this value dropped to 31%, quite similar to observations for the Ag²⁻ coated textile. It is likely that the Ag released from these textiles is primarily present as Ag⁺, and constituents of the detergent are forming Ag-containing particles via reaction with Cl⁻ or S-containing molecules. The present study did not investigate the exact speciation of Ag as it was not the aim of our work. Previous work by Mitrano et al.²⁰ demonstrated the presence of Ag chlorides and sulfides in wash water, and Lombi et al. demonstrated the presence of varied Ag species on shirts (e.g., Ag⁰, Ag⁺, AgCl, Ag₂S, and Ag-phosphate) even before washing.²¹ For the Ag-salt-coated shirt tested in this study, much less dissolved Ag was released during washing in DI water, 28% of the total Ag, suggesting that most Ag is being released as particles (Figure S13). When washed in detergent, almost all Ag is present as particles, with only 4% measured in the 30 kDa permeate.

**Light Irradiation Reduction of the Amount of Ag Released from Textiles.** Because of well-documented photochemical transformations in nanosilver, we investigated the role that light exposure plays in silver release from textiles upon subsequent washing, swatches of tethered-AgNP fabric were submersed in water and either exposed (light) or not exposed (dark) to light during the initial textile submersion period, and this water was analyzed for Ag⁻⁻ ions (using AgNO₃ solutions) irradiated under the same conditions used on the fabric (Figure S14). In these tests, the quantity of Ag released was independent of the exposure time under a given set of conditions and suggests there is a finite limit on the concentration of Ag that is available for release as a result of either thermodynamic or kinetic limitations.

Following immersion, the light-exposed and nonexposed fabrics were washed once with detergent using the previously established textile washing procedure to investigate the role of initial immersion and irradiation in moderating silver release during subsequent laundering. As shown in Figure 2 (inset, black bars), less silver was released from the fabrics exposed to light, although the extent of Ag released from the tethered-AgNP fabric during washing was independent of submersion time for both exposed and dark samples. Fabric samples exposed to light from two through 6 weeks released an average of 1.1 μg/g Ag; samples kept in the dark for two through 6 weeks released an average of 2.2 μg/g Ag.

The silver mass balance for these fabric samples (silver release during submersion, silver release during subsequent washing, and residual silver on fabric) remained relatively constant for all immersion times regardless of irradiation, with an average measured total silver of 26.1 ± 3.56 μg Ag/g fabric for light-exposed fabric and 26.6 ± 3.89 μg Ag/g without light exposure. This supports the idea that our experimental approach is able to account for all of the Ag initially present in the fabric. In summary, these data show that the extent of silver release into solution and during subsequent washing depends on whether or not the textile is exposed to visible light but is independent of immersion time.

**Textile Retention of Antimicrobial Efficacy after Multiple Washes.** All four silver-containing textiles (Ag²⁻-coated, tethered-AgNP, electrostatic-AgNP, and Ag-salt-coated) plus...
one untreated (no silver present) textile were tested for antimicrobial efficacy. The percent reduction of *E. coli* growth, both before washing and after washing in either DI water or detergent, is shown in Figure 3. Before washing, all four textiles were highly effective, with only the electrostatic-AgNP textile exhibiting less than 99% reduction in *E. coli* growth. After washing, the Ag2-coated textile (4030 μg Ag/g fabric) and tethered-AgNP textile (23 μg Ag/g fabric) still exhibited >99% reduction in *E. coli* growth. The Ag salt-coated textile washed in DI water had reduced effectiveness compared to unwashed textile, but it still showed 94% reduction of bacterial growth. The electrostatic-AgNP textile, not surprisingly due to its low Ag loading, showed the greatest loss in antimicrobial efficacy after some of the initial Ag was removed during washing. Some reduction in bacterial count was seen for untreated textiles washed in detergent, and in this case, it may be attributed to the presence of residual detergent on the fabric. To confirm the role of detergent, we conducted an additional control experiment in which detergent was applied to untreated fabric, dried, and inoculated with bacteria culture. The bacterial growth reduction in this control experiment (81.6%) is comparable with untreated detergent-washed samples (75.1%). Overall, these data demonstrate that silver-containing fabrics can maintain high antimicrobial efficacy even with relatively low (a few ppm) silver content. This is an important result from a life cycle perspective because the largest environmental impact of Ag-containing textiles may result from mining of silver ore, and obtaining the same product quantity of silver, ranging between 4 and 12 μg Ag/g fabric, this leachate represented <0.3% of the total silver contained by the fabric when it was subjected to the TCLP testing (Figure 5). In contrast, the TCLP leaching of silver from the other three fabrics was generally <1 μg Ag/g fabric. Fabrics that had tethered or electrostatically attached nanosilver were a representative nonmicrobial aquatic test organism. This organism has been used previously as a rapid whole-animal-based test organism for nanomaterial toxicity. Although most silver released from textiles during release) is a good example of maximizing the net environmental benefit.

**Toxicity of Silver Textile Wash Water Is Mostly Due to Detergent.** Although most silver released from textiles during washing would presumably be discharged from WWTPs in treated effluent or as runoff from land treated with biosolids, there is a risk for silver washed from textiles to be released directly to surface waters. To test the toxicity of the wash water collected from our washing assay, we used zebrafish (*D. rerio*) embryos as a representative nonmicrobial aquatic test organism. This organism has been used previously as a rapid whole-animal-based test organism for nanomaterial toxicity. Except for the water used to wash the Ag2-coated textiles, almost no mortality was observed for zebrafish embryos when they were exposed to the nondiluted DI-water-wash samples (Figure 4). The Ag2-coated textile had by far the greatest initial loading of Ag, and this resulted in the highest [Ag]aq in the wash, 1366 ± 224 μg/L. It should be noted that the Ag levels in these washes represent a worst-case scenario because during actual use the wash water would become highly diluted upon discharge. The next highest aqueous concentration of Ag released during washing was from the tethered-AgNP textiles, 222 ± 34 μg/L, which resulted in essentially no toxicity in this assay. By comparison, all detergent-wash water samples exhibited toxicity to zebrafish embryos at the concentration of detergent used during textile laundering. This includes a control sample in which no Ag textiles were added to the detergent wash solution, indicating that the detergent was responsible for the toxic effect to zebrafish embryo. To account for possible dilutions in the environment after release, we used diluted washing supernatants (1/2 log series) for toxicity exposures; none of these exhibited significant toxicity to *D. rerio*.

**End-of-Life Disposal and Fate of Ag-Enabled Textiles.** Following the simulated washing experiments, the fabric samples were tested using TCLP protocols. None of the samples exceeded the Resource Conservation and Recovery Act (RCRA) regulatory limit for toxicity characteristic hazardous waste because the leached silver concentration was at least an order of magnitude lower than the 5 mg/L regulatory limit, regardless of the washing process or presence of chloride in the leachate. These results correspond to previously reported findings for TCLP leaching of AgNPs from commercial products. Although the Ag2-coated fabric leached the highest quantity of silver, ranging between 4 and 12 μg Ag/g fabric, this leachate represented <0.3% of the total silver contained by the fabric when it was subjected to the TCLP testing (Figure 5). In contrast, the TCLP leaching of silver from the other three fabrics was generally <1 μg Ag/g fabric. Fabrics that had tethered or electrostatically attached nanosilver were affected by the detergent wash, which consequently caused a greater release of silver during the standard TCLP test. The detergent wash increased silver release by almost an order of magnitude for
these fabrics (tethered-AgNP and electrostatic-AgNP) but only a slight increase for the Ag-salt-coated fabric during standard TCLP testing. For example, the samples with potentially weakest (electrostatic) attachment of silver released 0.04 μg/g Ag (4.2% of initial) in TCLP testing after being washed in DI water; however, the addition of the detergent caused the release to increase to 0.65 μg/g Ag (65% of initial). In contrast, the Ag\textsuperscript{0}-coated fabrics were not significantly affected by the action of the detergent, releasing 4.7 μg/g Ag (DI water washed, 0.12% of initial) and 5.5 μg/g Ag (detergent washed, 0.14% of initial) during TCLP testing, which followed washing. This suggests that detergent may facilitate the leaching of silver from fabrics that have been disposed in a landfill, but this release could be strongly influenced by the AgNP attachment method.

For most fabrics, chloride-modified TCLP testing (TCLP-NaCl) of the DI-water-washed samples released more silver than standard TCLP testing, which was expected considering that previous studies have reported that chloride facilitates the dissolution of AgNPs.\textsuperscript{43} However, chloride addition caused less silver than the standard TCLP test to be leached from the detergent-washed samples with tethered-AgNP. This suggests that chloride addition or strong electrolyte may suppress the dissolution effect induced by the detergent alone in fabrics with chemically secured AgNPs. The importance of this implication is significant considering commercially available fabrics may contain such chemically secured AgNPs. Although not all of the Ag was released from the textiles during testing, this is due to the limited time scale of the TCLP test. In a landfill, we expect that all the Ag remaining in a textile would eventually be released to the environment.

**BALANCING RISKS WITH BENEFITS OF NANOENABLED PRODUCTS**

Overall, we found that each method of attaching Ag to textiles was effective for reducing bacterial growth. Washes in DI water mostly showed the release of ionic Ag, whereas nanoparticulate Ag was primarily detected in the effluent from detergent-based washes, likely due to Ag precipitation. By lowering the initial Ag loading and by tethering AgNPs to textiles, we maintained a high degree of antimicrobial efficacy while releasing less Ag during use phases (e.g., washing). Silver loadings as low as a few parts per million (μg/g) were found to be effective. Excess Ag that is not released during use will continue to leach from garments if disposed of in landfills. Thus, it is possible to reduce the potential impacts across the lifecycle while maintaining desired performance by reducing the amount of Ag used to treat the textile.

In addition to providing critical data for assessing lifecycle impacts of silver-containing textiles, this study aims to broaden the discussion regarding antimicrobial (and other nanoenabled) consumer products to balance potential benefits and product efficacy against design considerations (e.g., methods for attaching Ag) and transformations, fate, and risks associated with Ag textiles. It is important to measure impact and performance together\textsuperscript{43} because this combination offers insight into designs that can minimize the impact per functional unit (i.e., the impact-to-benefit ratio).\textsuperscript{36} This life cycle perspective approach is broader than just textiles and encourages consumers, product manufacturers, and regulators to develop quantitative metrics to compare the net environmental benefits of nanoenabled products to non-nano alternatives.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b06043.

Additional details regarding the additional characterization of free AgNPs and the irradiation of textiles control study. A table showing the composition of aqueous detergent used in washing experiments. Figures showing fabric samples under irradiation, spectral output of light sources, TEM micrograph of the synthesized Tween 20-stabilized AgNPs used for production of tethered-AgNP and electrostatic-AgNP textiles, size distribution of synthesized AgNPs obtained by spICP-MS, size distribution of synthesized AgNPs obtained by MP-PALS, electron micrographs of silver-containing textiles used in this study, STEM image of Ag-coated textile, EDS spectrum corresponding to STEM micrographs and Ag\textsuperscript{0}-coated textile, Ag release from four different textiles in unfiltered and 30 kDa ultrafiltered supernatant from textile-washing experiments, and results of the irradiation control study with duplicate untreated polyester fabric. (PDF)
REFERENCES


(23) Artiaga, G.; Ramos, K.; Ramos, L.; Câmara, C. G.; Gómez-Gómez, M. Migration and characterisation of nanosilver from food containers by AF4-ICP-MS. Food Chem. 2015, 166, 76−85.


