Unraveling the Complexity in the Aging of Nanoenhanced Textiles: A Comprehensive Sequential Study on the Effects of Sunlight and Washing on Silver Nanoparticles

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S Supporting Information

ABSTRACT: The scientific understanding of nanoparticle (NP) release and transformations they undergo during the product life cycle is hampered by the narrow scope of many research endeavors in terms of both breadth of variables and completeness of analytical characterization. We conducted a comprehensive suite of studies to reveal overarching mechanisms and parameters for nanosilver transformations either still adhered to the fabric or when released after washing. Laboratory prepared nanoenhanced fabrics were investigated: three Ag variants and one Au used as an unreactive reference to separate mechanical from chemical releases. Sequential combinations of sunlight irradiation and/or washing in seven different detergent formulations was followed by NP characterization divided into two groups: (1) dissolved and particulate matter in the wash solutions and (2) the fraction that remained on the fabric. Analytical techniques included spICP-MS, XANES, TEM, SEM, and total metals analysis of fabric digests and wash water filtrates. Sunlight irradiation stabilizes metallic Ag upon washing. Detergents containing oxidizing agents assisted with Ag particle release but not Au NPs, inferring additional chemical mechanisms. While particle size played some role, the NP capping agent/fabric binder combination was a key factor in release. When particles were released, little alteration in size was observed. The use of well-controlled fabrics, unreactive reference materials, and a life-cycle based experimental regime are paramount to understanding changes in Ag speciation and release upon use of nanoenhanced textiles.

Life Cycle Thinking: Nano-Textiles
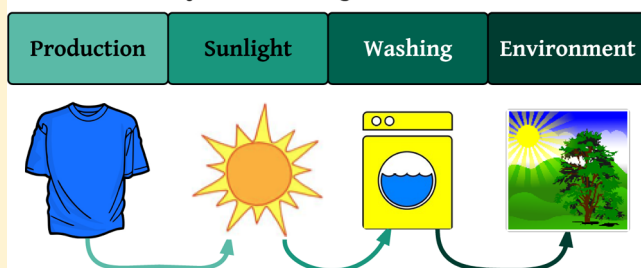
INTRODUCTION

Silver (Ag) and Ag-based compounds have become the most widely represented and studied inorganic antimicrobial agent for use in textiles;[1,2] the efficiency of which depends directly on the concentration of free Ag ions (Ag^+) and/or nanoparticles (Ag NPs) released from the fibers. Within the realm of materials science research, these credentials are being vetted with the hope of bringing additional functionalized textiles to the consumer market.[3] The adoption of Ag NPs over traditional antimicrobial chemical treatments (e.g., metal salts, quaternary ammonium compounds, triclosan, etc.) is supported because while some of the historic compounds met desired antimicrobial demands, they were not acceptable from economical, environmental, or long-term efficiency standpoints. Ag NPs are thus a potential improvement for several reasons: they do not stain the textile like ionic Ag,[4] have negligible impact on fabric breathability and handling,[5] and the use of Ag NPs potentially offers an overall reduced environmental impact.[6,7] However, in the context of environmental health

and safety research, comparably few studies have investigated the speciation and release of Ag from either laboratory prepared or commercial products despite the broad generalizations about average Ag release rates from fabrics and typical transformation of particles.[8,9] While the scientific integrity of these Ag release and characterization studies is sound, the breadth of variables considered and completeness of analytical characterization in most instances limits the overarching conclusions that can be applied to the real world (e.g., commercial textiles, detergents and consumer use patterns). Nevertheless, taken together a history of (nano) Ag application to fabrics and particle release and transformation investigations provides a baseline for factors which are likely to be most important for textiles washed under normal conditions.

A

A wealth of research has been conducted to load textiles with Ag NPs, either by embedding them into synthetic fibers during the spinning process or depositing on the fibers during finishing.[1,3,10] Simultaneous applications of Ag NPs (of all sizes, formed in situ or preformed) and other chemicals (e.g., binders, reducing agents, solvents, etc.) have been applied to both natural and synthetic fibers.[3] While a small amount of Ag NPs is sufficient to provide desired effects, little is known on the amount and form of Ag NP release during realistic use conditions, impacting both the efficacy of the fabrics and subsequent environmental safety. Ag NP releases and (change in) speciation is likely due to both the nature of the textile itself and the form of Ag present in the materials.[9,11] Benn and Westerhoff investigated the release of Ag from commercially available socks, but since the textile was only submerged in water the dynamics and extent of silver release were basically affected by the manufacturing procedure and Ag diffusion from the surface.[12] Increasing complexity, Geranio et al. followed the influence of pH, surfactants, and bleaching agents on silver release from commercial textiles.[13] The authors found that at pH 10 (relevant to conventional washing), little Ag dissolution was evident but the addition of bleaching agents (e.g., hydrogen peroxide, peracetic acid) significantly accelerated dissolution. The extent of Ag NP transformation based on detergent chemistry was further studied by Mitrano et al.,[14] where the authors also determined oxidants in the wash solution to be a driving factor for particle change. Additionally, Mitrano et. al compared the laundering of laboratory textiles with known conventional Ag or nano-Ag treatments to characterize chemical and physical form of material released and determined that all silver-treated textiles, regardless of whether the treatment is "conventional" or "nano", can be a source of Ag NPs when laundering these fabrics.[15] Beginning to tackle the important aspect of following products through their life cycle, Hedberg et al. described sequential exposures of Ag NP to synthetic sweat, laundry detergent solutions, and freshwater to simulate possible transport pathways through different aquatic media;[16] yet the direct link to textiles is tenuous since aqueous transformations of particles may differ from those of particles immobilized on a textile. Silver speciation and release in commercial textiles can also be influenced by washing, which can steer both the performance of the textile and the character and concentration of Ag released.[17−19] Further expanding the life-cycle thinking and estimating the relative importance of different phases over time, the fastness of AgNPs during the use phase (e.g., washing) and end of life stage (e.g., landfilling) of nanotextiles was recently investigated.[20] Most recently, Reed et al. assessed the benefit of nanosilver textiles compared to potential release; investigating multiple silver attachment methods to the fabric, washing scenarios and landfilling.[21]

It quickly becomes clear that not one aspect of the nanotextile production or use conditions alone is responsible for Ag transformation or release, but rather it is a combination of several factors that are important when determining the fastness and functionality of nano-Ag for the fabrics. Influential factors may include the textile fabrication process (including fabric and binder composition), NP size, NP capping agent, and effects occurring during each of the products life cycle stages directed by the consumer (e.g., weathering, use and disposal). Even when previous studies have covered the topic of a given use stage, such as washing, typically only one variant of detergent was used or a textile with undefined properties chosen, which can limit the applicability of predicting a "typical" behavior profile. Other factors, such as the effect of sunlight on NP transformations embedded in textiles and effects on subsequent stages of the life cycle require additional, in-depth investigations since comparatively few studies have taken this approach.[20,21] Systematic controls over these parameters are essential to correlate cause and effects; that is why commercial products are difficult to investigate because the nature of the Ag is variable and it is usually impossible to ascertain precise production methods. Besides the relatively narrow scope of textile variables or use conditions chosen, complete characterization of the system is often missing. To best understand the dynamics of nanoenhanced fabric washing, the concentration, form, and speciation of Ag should be determined both in the wash water and for the fraction that remains on the fabric. While some modeling efforts present a marginal risk or impact to the environmental from Ag NP releases from textiles,[7,22] the situation can change depending on new Ag NP application methods.[23] Furthermore, a better understanding of specific NP release form, transformation and fate is needed from a variety of real world exposure scenarios, which would serve as a basis for materials scientists deriving product design strategies aiming to minimize exposure and for environmental scientists to better understand the varieties of release and transformations possible.

In this study, we aimed to investigate a large matrix of textiles through multiple stages of product wear to provide overarching themes responsible for Ag-NP release and transformation. By studying several different textiles with known additives prepared and aged in the same fashion, we can tease out which factors of NP choice, fabric composition, or use parameter is most responsible for NP transformation and/or release from nanotextiles.

■ MATERIALS AND METHODS

Four different nanoenhanced fabrics were laboratory prepared using NP of various size, capping agent, and metal type. Twenty nm Ag NPs with citrate and PEG coatings and 100 nm Ag NPs with citrate coating served as reactive particles whereas 100 nm Au NPs with citrate coating was used as nonreactive reference to contrast the mechanical release of NPs compared to the (additional) chemical release the detergents may cause the Ag. The fabrics were subjected to sequential combinations of sunlight irradiation and/or washing in seven different commercially available detergent formulas. Characterization was divided into two groups: analysis of dissolved and particulate matter in the wash solutions and analysis of the metallic fraction that remained on the fabrics. Analytical techniques included single particle ICP-MS and TEM of the released particles, total metal analysis after each exposure for both the wash water and fabric swatches, and both SEM and XANES analysis of the textiles for the visual integrity and speciation of Ag, respectively. An overview of the approach and the method used is presented in Figure 1.

Nanoparticles, Textiles, and Detergents. Ionic $AgNO_3$ and Au solutions (1000 mg/L in 0.5 M HNO_3 or HCl, Merck) were diluted as ICP-MS calibration solutions ranging from 0 to 5 mg/L. The roster of test nanomaterials included 100 nm citrate stabilized metallic Ag NPs (Sigma-Aldrich), 20 nm particles (both citrate and PEG coated, synthesized at the University of Birmingham, UK), and 100 nm citrate-stabilized Au NPs (NanoComposix). The latter NPs were used as inert "tracers" in the washing experiments, intended to differentiate between mechanical release of particles and further chemical
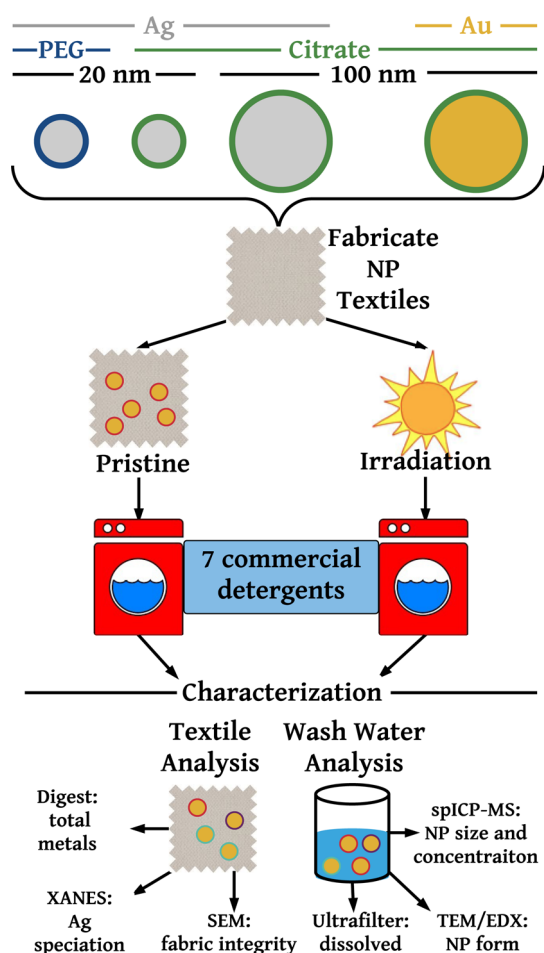
Figure 1. Schematic of NP selection, textile fabrication, exposure, and the analysis/characterization of both the fabric and wash water. The experimental procedures followed in this work combine a comprehensive selection of NP properties (size, capping agent, metal), precise incorporation into laboratory prepared fabric, sequential aging parameters under many conditions (sunlight irradiation, washing with different detergents), and complete characterization of NPs which remain on the textiles and are released into the wash water. Analysis of fabric consisted of SEM analysis to study fabric integrity through the aging process, XANES to understand Ag speciation before and after washing, and total fabric digestion and ICP-MS analysis for loss of Ag during washing. Wash water analysis consisted of spICP-MS to identify the size and concentration of Ag-NPs released from the fabric, TEM/EDX to study the NP form, and speciation and ultrafiltration to measure the dissolved Ag constituent.

release associated with oxidative dissolution of metallic Ag. The particle size of the 100 nm Ag and Au pristine particles used was verified in-house by spICP-MS measurements in DI H_2O (Figure S1). Size distributions were similar to TEM analysis provided by the manufacturer. Twenty nm particles were characterized when produced by the University of Birmingham by dynamic light scattering, UV−vis, zeta potential, TEM (Figure S2), then independently characterized again in-house by TEM measurements (Figure S3). The zeta potential of Ag 20 nm particles were measured at −46 ± 1 and −12 ± 1 mV for citrate and PEG variants, respectively.

Standardized polyester (PET) textiles were prepared from liquors composed of Ag or Au NPs and commercial wetting and binding agents. Further details of materials, fabric preparation, and preparation for analysis are given in the SI.

Seven washing solutions were used in this work, the same as used in the work of Mitrano et al.[14,20] Five were "grocery store brand" detergents from a Swiss store, are commercially available, and intended for use in private homes. Two liquid detergents ("color" and "all purpose" (CL and APL)) and three powder detergents ("color", "all purpose", and "oxi" (CP, APP, and OP)) were chosen. Additionally, two detergents (one liquid, one powder) were acquired from a company producing detergents for industrial-scale laundering, e.g. for hospitals, nursing homes, restaurants, etc. (labeled industrial detergent, IL and IP). For brevity, detergent formulations are hereafter mentioned only by their abbreviations. Further details are provided in the SI.

Fabric Aging and Washing Procedures. Select sheets of fabric were subjected to accelerated aging in the Q-SUN Xe-3 Xenon test chamber (Q-LAB), which is meant to mimic exposure to full spectrum sunlight. Fabrics were exposed for 7 days (168 h; 870.7 kJ/m² total irradiance) in the chamber at 70 °C (black panel) and 40 °C (air, 50% humidity) and 1.44 W/m² at 420 mm. QSUN exposure is represented graphically in all figures by red shading or text throughout the figures and tables. The washing procedure was carried out as described in previous literature and ISO Standard 105-C06:2010, with some modifications for these specific solutions.[13,15,18,24] Each washing experiment was conducted in triplicate, and results are indicative of the average. Complete details can be found in the SI.

Fabric and Washing Solution Analyses. Complete characterization of NPs which remain on the textiles and are released into the wash water have were analyzed by a myriad of analytical techniques, as summarized in Figure 1.

Fabric Analysis. Total Au or Ag concentrations in the textiles were determined by acid digestion followed by ICP-MS analysis; complete methods are given in the SI. Visual inspection of the fabric fibers after treatments were observed by SEM, as shown in the SI. Silver speciation in the textiles was assessed by XANES, as explained in the SI.

Wash Solution Analysis. In each washing solution, ultra-filtration (VIASPIN centrifugal filters, 10 kDa cutoff) with subsequent acidification of the filtered solution to 2% HNO_3 was performed and Ag was quantified by ICP-MS. Additionally, aliquots were taken for spICP-MS after the wash cycle (without acidification). To prevent further particle dissolution or aggregation until analysis, samples intended for spICP-MS analysis were diluted directly in DI water for spICP-MS measurements and stored frozen until analysis. Details about sample preservation and spICP-MS analysis are given in the SI. Particles in the washing solution were further analyzed by scanning transmission electron microcopy (STEM) and EDX, for details see the SI.

■ RESULTS AND DISCUSSION

Washing Induced Releases of NP from Fabrics. The amount of Ag release is not solely dependent on (changes to) the Ag NP chemical structure but also to the morphological and topological properties of the fibers, which influence the Ag mode of binding, adhesion ability, adsorption capacity, and moisture content necessary for Ag release.[1] The physical integrity of the fabric remained intact throughout the different aging tests despite the physical stresses they underwent during simulated sunlight (QSUN) exposure and washing, as assessed by SEM analysis (Figure S4). Visual observations (e.g., removal of Ag staining on the textile) was noted (Figure S5); however

this observation cannot distinguish between detachment of the particle from the textile (release) and dissolution of Ag; and so these visual observation can simply be indicative of Ag transformations during the wash cycle.

Our previous studies concerning the washing of silver containing textiles (both conventional and nano varieties, fabricated with these same conditions) with a standard laboratory detergent (containing no oxidizing agent) approximated the release of silver between 10 and 35%.[15,20] Furthermore, when investigating the behavior of Ag NP in a variety of washing detergents, we concluded that those which contained a higher concentration of oxidizing agent resulted in enhanced oxidative dissolution of the Ag particles over the course of the wash cycle, though no changes to Au particles were observed.[14] Physical incorporation of the NPs with the fabric and the external washing environment (i.e., mechanical abrasion and chemical wear) are both contributing factors to the concentration and form of release.

Total Metal Remaining on Fabric. Because Au is an inert metal, the incorporation of Au NPs onto the textiles served as a measurement for the physical release of NPs associated only with mechanical stress on the fabrics during the washing process or of material which was only weakly bound to the textile surface. Despite the drastically different washing detergent chemistries, a constant amount of Au was retained on the fabrics, with approximately 85−90% of the Au recovered after fabric acid digestion (Figure 2). This suggests a baseline of
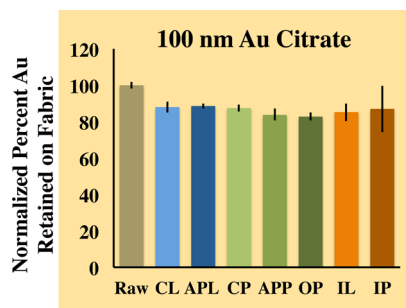
Figure 3. Concentration of Ag remaining on fabric after one wash cycle as determined by aqua regia microwave digestion of fabric and ICP-MS analysis, normalized to unwashed (raw) fabric. Blue bars indicate grocery liquid detergent varieties, green are grocery powder, and orange are industrial detergent. Error bars indicate standard deviation of duplicate fabric digests. Three Ag NP variants are depicted with 20 nm citrate, 20 nm PEG, and 100 nm citrate in plots A, C, and E, respectively. Corresponding sequential aging procedures (sunlight exposure and subsequent washing) are shown in plots B, D, and F. For details on washing detergent composition, see the Materials and Methods section.

Figure 2. Concentration of Au remaining on fabric after one wash cycle as determined by aqua regia microwave digestion of fabric and ICP-MS analysis, normalized to unwashed (raw) fabric. Blue bars indicate grocery liquid detergent varieties, green grocery powder, and orange industrial detergent. Error bars indicate standard deviation of duplicate fabric washes and digests. The amount released in this case represents the mechanical stress of washing and/or mechanical removal or particles by the detergents; i.e. a lower threshold of possible release of NPs from the fabric under these washing conditions.

particulate release from the first wash due to purely mechanical stress, either because the particles were not fully imbedded into the binder during the textile fabrication process and/or because the mechanical abrasion in the washing containers released particles from the textile surface. While it is possible that some chemical factors may have broken down the matrix of the binder and/or textile threads to release Au particles, this is less likely given the very different chemical properties of the various detergents and the evenness with which Au was released across the experimental set.

In contrast to equal release of Au across all washing conditions, variable Ag release was noted with different detergents (Figure 3), ranging from approximately 10 to 25%
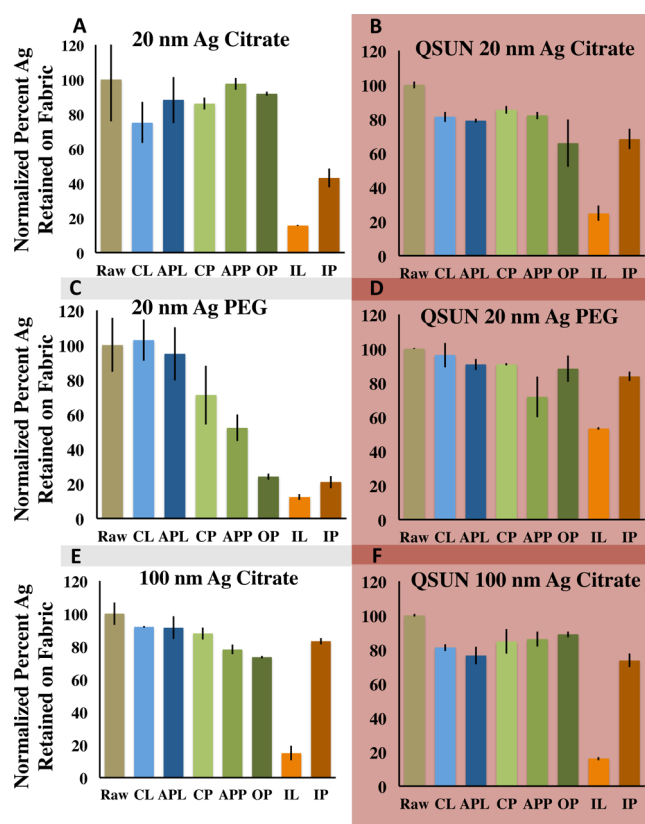
for most detergents to over 75% for the IL detergent. The dominating factor affecting release across all textile treatments was the detergent chemistry where those containing oxidizing agents released more silver (e.g., APP, OP, IL, and IP). Mild detergents, i.e. those containing no oxidizing properties, released similar concentrations of Ag as Au, suggesting predominantly mechanical release was at play in those systems. Severity of oxidant often directly correlated with Ag release, where, for example, in the strongest detergent, IL, only 20% of the Ag remained on the fabric after one wash.

The preferential chemical release of Ag compared to the mechanical release of Au is depicted in Figure 4, where the ratio of the relative gold release to the silver release is shown. A ratio larger than 1 refers to a preferential release of Ag over Au. Detergent chemistry plays a large role in concentrations of Ag released, where those containing oxidizing agents clearly assist in release of Ag particles from Ag NP functionalized textiles (but less so of Au NPs), inferring an additional chemical release reactions specific to Ag. Nevertheless, taken as a whole, the detergent chemistry and (additional) chemical release of Ag compared to Au is of relatively minor influence, expect in a few cases, such as the stronger industrial detergents or Ag capped with PEG.
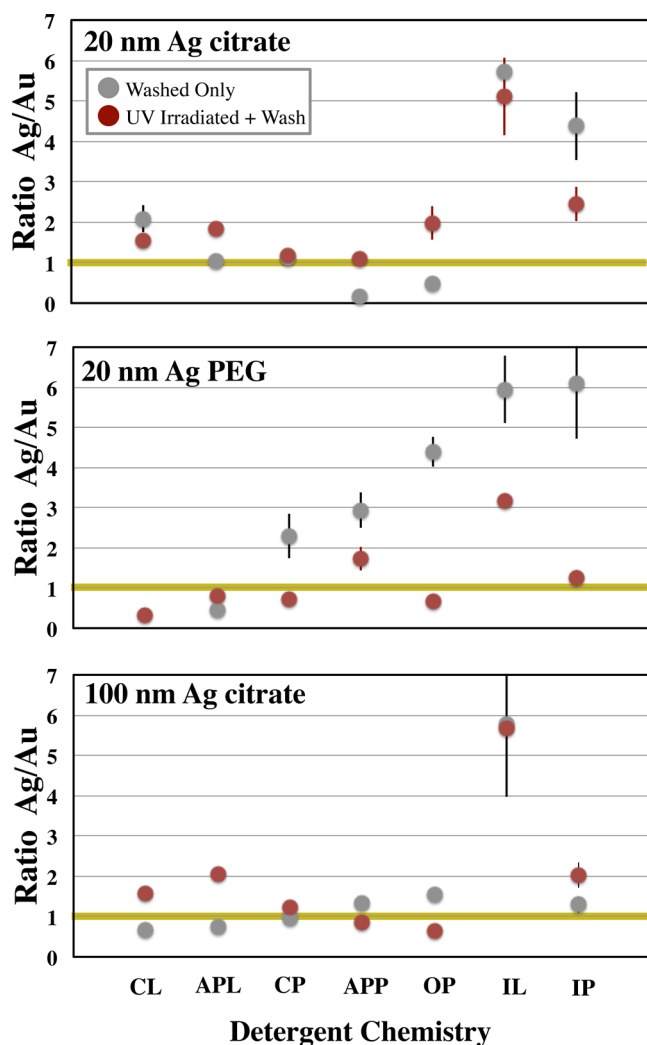
Figure 4. Ratio analysis of preferential chemical release of Ag compared to mechanical release of Au with 20 nm Ag citrate capped NPs, 20 nm Ag PEG capped NPs, and 100 nm Ag citrate capped NPs. The yellow line at one represents the release of Au from fabrics under each washing condition. Gray dots are fabrics only washed, red dots are fabrics with sunlight exposure and subsequently washed.

An additional factor that influenced the concentration of metal that was retained on the fabric after washing was the Ag NP coating composition. Here, 20 and 100 nm citrate capped Ag NP treatments released similar concentrations of metal for the majority of treatments, yet the 20 nm PEG capped Ag NPs released significantly more metal in the wash solutions containing oxidizing agents (Figure 3C). We hypothesize this is due to the interactions of the capping agent and the binder. In this instance, the binder used was a blocked polyisocyanate with cationic ion character; so the citrate capped particles (negative ionic charge) may more strongly bind to the matrix than the PEG capped particles (neutral) in the matrix. This disparity is also noted when compared to the release of Au particles, which were also citrate coated (Figure 4, panel B).

However, when fabrics were first irradiated by the QSUN and then washed (Figure 3 panels B, D, and F), less Ag was released than when washing alone (Figure 3 panels A, C, and E) for some of the detergent types, especially for the PEG coated NP treatment. While the strongest bleaching detergent still leached the most amount of Ag from the fabrics, the overall

chemical influences were reduced as compared to the amount of Au released from the fabrics (Figure 4, red dots). The continuous release of Ag^+ and Ag^0 is only possible if Ag is bound to the fibers through physical sorption;[25] chemical binding of Ag to the fibers may significantly reduce the release of Ag^+ into solution.[26] Therefore, the influence of the QSUN irradiation to inhibit Ag release may be caused by changing the linkages of Ag to the fiber/binder. For example, UV irradiation has been shown to form silver polyacrylate complexes and these species are very stable against reoxidation,[27−29] which would be a limiting step in the further oxidative release of Ag NPs in subsequent washing procedures. Additionally, photoreduction of Ag^+ on the particle surface decreases the amount of oxidized silver available for dissolution and may thus result in a better-crystallized metallic Ag that is less prone to dissolution. Therefore, the main mechanism to inhibit Ag NP release from the textile is either a stronger particle bonding to the fabric or the formation of more binding sites for the Ag that is not dissolved during the washing process, or some combination of both possibilities.

Metal in the Wash Water: Total Metal and Particulate Analysis. Analyzed by spICP-MS, Au recovery from all washing detergent varieties showed no change in particle size distribution compared to the pristine particles (Figure 5). This confirmed that (1) NPs were released directly from the fabrics into the wash water, (2) given the sample preparation scheme (e.g., dilution in DI water, freezing, thawing and analysis by spICP-MS) we achieved reproducible results of particle distributions (i.e., no agglomeration, etc.), and (3) primary Au particle size was not altered in any detergent solution. With the spICP-MS technique, total concentration of metal released can also be estimated and directly compared to releases determined by fabric digestion and total metals analysis (Tables S4 and S5). Although the spICP-MS concentration sometimes overestimated metal concentrations as compared to fabric digest results (especially in liquid detergents) and other times underestimated the concentration, values were in the same order of magnitude, which, given the differences between measurement analyses, we consider this good agreement.

Particulate Ag in the washing solution was measured by spICP-MS for grocery store liquid and powder variants for 100 nm Ag standard textiles and those exposed to simulated sunlight (Figure 6), but particle recovery was not high enough to definitively determine a size distribution for fabrics washed in industrial detergents by this method. The wash water from fabrics containing 20 nm particles were not analyzed because the size (distribution) was too close to the detection limit of spICP-MS. Ag particles washed in grocery liquid detergents did not have a significant change in particle size (Figure 6A) compared to the pristine particles nor did size or surface structure appear different with TEM analysis (Figure 7A). All particles imaged by TEM were found to be metallic Ag as assessed by EDX measurements (Figure S5). While there was a slight downward shift in particle size in the grocery detergent which had the highest amount of oxidizing agent (Figure 6C, oxi powder), the minimal change in particle size is a large contrast to the notable size changes to particles suspended in oxidant containing washing detergent alone in our previous work.[14] At least two factors may contribute to this difference: (1) when fabrics are washed in the detergent, the oxidizing agent also reacts with the textile and so it is less available to interact with the particles on the textile or when particles are released into solution and (2) the particles are, to some extent,
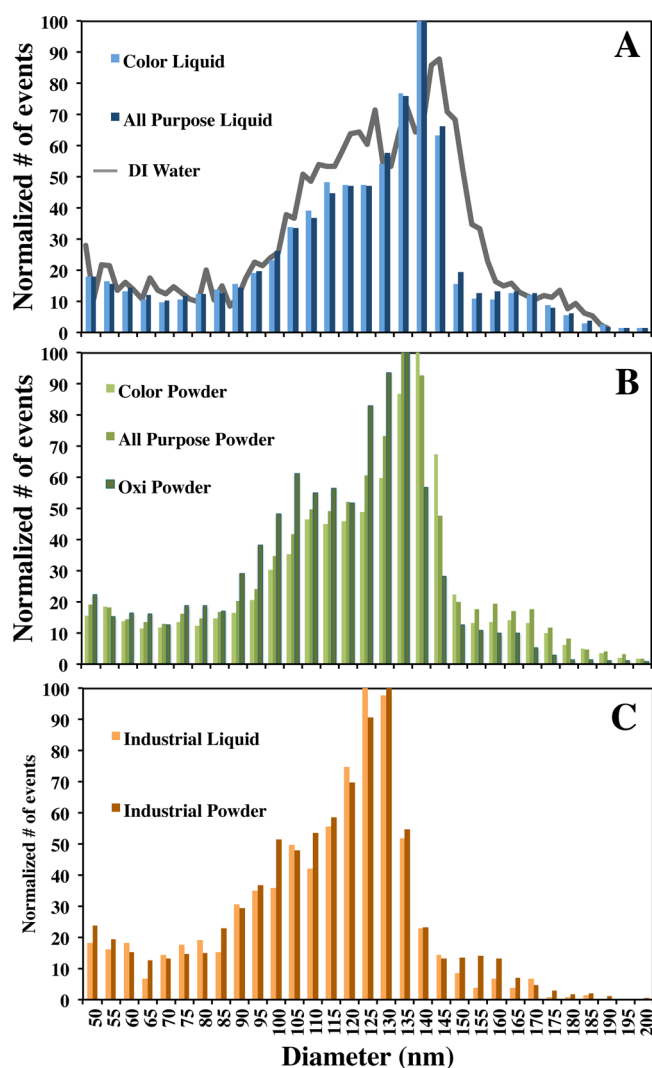
Figure 5. Au NPs released into wash water from fabrics washed in various detergents as determined by spICP-MS. Grocery liquid detergents (panel A, liquid and all purpose variants represented by light and dark blue bars), grocery powder detergents (panel B, color, all purpose and oxi detergents represented by increasingly darker green bars), and industrial detergents (panel C, liquid and powder variants represented by light and dark orange bars) had similar particle release profiles. Each histogram is the average of triplicate measurements, normalized for total particle release after background subtraction. The dark trace in panel A is the 100 nm Au NP size distribution analyzed by spICP-MS in DI water.

physically encapsulated by the binder and are less permeable to oxidative dissolution than pristine particles which remain free in suspension. While no coating was distinctly visible on the NP surface (Figure 7C), the particles appear visually more intact when released from the fabric than when simply suspended in oxi detergent.[14] As with the Au analysis, total released Ag concentration as assessed by spICP-MS was in the same range as the concentrations measured by fabric digest, and only a very small fraction (<1%) was dissolved except in the case of the IL detergent, where approximately 20% was dissolved (Table S4). Likewise, with the 20 nm particles of both capping agents, a minimal concentration of Ag was noted in the ultrafilter analysis except in the stronger industrial detergents (Table S5).

For fabrics which underwent simulated sunlight (QSUN) exposure prior to washing, two discrete particle size

distributions are apparent in the wash solution: the unaltered, primary particle size and smaller particles, i.e. <50 nm; presumably also including particles smaller than the size detection limit of spICP-MS of 30 nm (Figure 6, panels B and D). There does not appear to be differences in the distributions due to the washing detergent, but rather the physical structure of the particles has been altered, as seen by TEM analysis of the particles released into the wash water (Figure 7, panels B and D). As with the nonirradiated samples, all particles imaged in the detergent solution were metallic Ag as evidenced by EDX analysis of particles (Figure S6). The concentration of Ag released after washing is less for the textiles that were exposed to sequential aging as determined by fabric digestion, yet as before the fraction of NPs released when calculated by spICP-MS is overestimated (Table S4).

Silver on the Textiles: Speciation Changes Across Subsequent Treatments. Washing textiles with different detergents resulted in marked changes in Ag-speciation in the textile after washing as assessed by XANES (Table 1, Ag K-edge spectra of standards used in LCF of sample spectra Figure S7). In 100 nm Ag fabrics, the initial Ag speciation was 100% metallic Ag, though for the 20 nm fabrics (both citrate and PEG coated), the composition was closer to 80% metallic Ag and 20% AgCl. While metallic silver was still the largest contributor to the speciation profile for all NP inclusion variants and under all washing conditions, AgCl and Ag_2S species were found to coexist alongside metallic Ag in many instances. No apparent trends in the change of speciation were found based on correlations of either detergent chemistry or NP inclusion. Particle release and transformation from the washing of textiles is naturally diversified due to the complex chemistry of Ag in various detergents. The washing procedure appeared to promote the formation of more stable Ag species (for example, Ag_2S, AgCl) on the textile surface (a phenomena also observed by Lombi et al.[19]) but only metallic Ag was observed in the wash water by TEM/EDX. This may indicate only the more mobile fraction is released from the fabric surface (found in the wash water) and the more stable fraction remains on the textile through the washing process. In many instances TEM observations suggested particles found in the wash water were of similar size and physical form as the pristine particles, yet we cannot exclude the possibility that some of these formed in solution from ionic Ag released from the fabric.[15] A variety of different Ag species coexist after washing which has important implications for the risk assessment of Ag textiles because metallic Ag is only one of the many silver species that need to be considered. Additionally, Ag_2S is unlikely to provide the same efficacy as Ag^0 in terms of antimicrobial properties,[30] which may have ramifications for how effective the textile treatment is after normal washing circumstances.[18] Conversely, AgCl is now the most commonly available form of silver antimicrobial used for commercial textiles treatments and AgCl has similar efficacy to Ag^0 (as AgNP). The efficacy of all Ag antimicrobials is ultimately driven by availability of Ag^+.

The prewashing speciation of the fabrics after sunlight irradiation was entirely (100%) metallic Ag. For the 100 nm Ag textiles, this was no change, but this was a transformation step for the 20 nm Ag treated fabric, where the AgCl was reduced to metallic Ag. This seems to corroborate with the fact that less dissolution is seen in the irradiated material and that photoreduction of the Ag is likely occurring. The postwashing speciation of textiles that were first exposed to the QSUN had a surprisingly different speciation profile than unexposed nano-
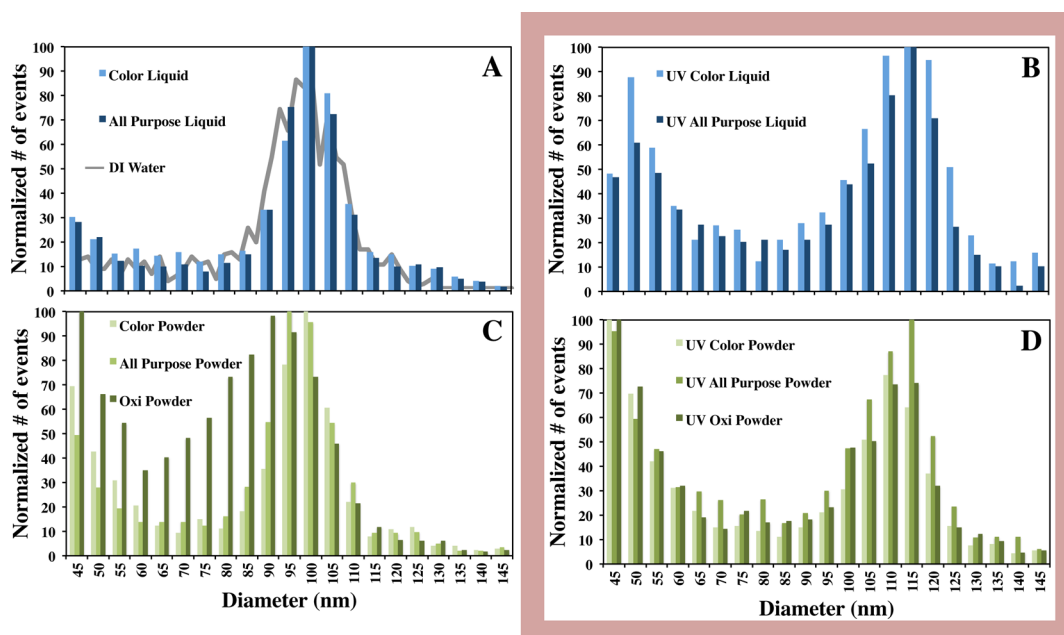
Figure 6. Ag NPs released into wash water from fabrics washed in various detergents as determined by spICP-MS. Grocery liquid detergents (panel A, color and all purpose variants represented by light and dark blue bars) and grocery powder detergents (panel C, color, all purpose and oxi detergents represented by increasingly darker green bars) and sequential aging of fabrics from QSUN solar spectrum then washing in grocery liquid detergents (panel B) and grocery powder detergents (panel D). Each histogram is the average of triplicate measurements, normalized for total particle release after background subtraction. The dark trace in panel A is the 100 nm Ag NP size distribution analyzed by spICP-MS in DI water.
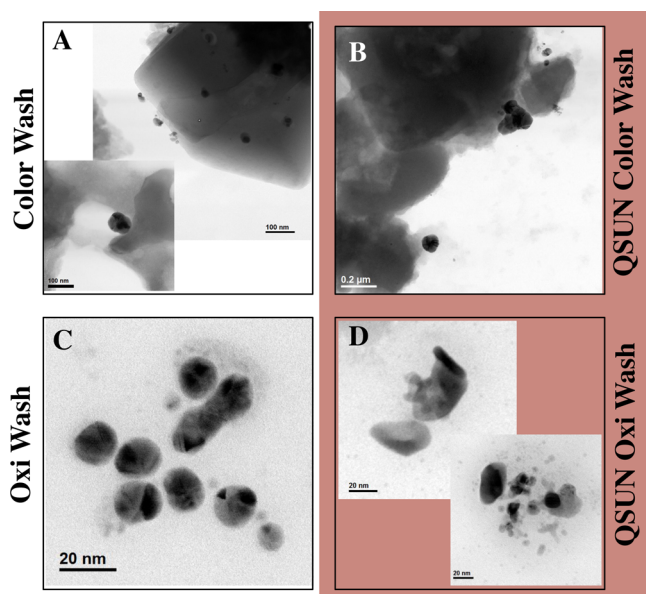

Figure 7. Representative TEM images of Ag particles released from fabrics in wash water in grocery color powder detergent (panel A), UV aging with grocery color powder detergent (panel B), grocery oxi detergent (panel C), and UV aging with grocery oxi detergent (panel D). Particles found were either metallic Ag or Ag with associated Si. Particle size and form varied by detergent, with particles similar to primary particles in the color wash solution, fused particles in the UV and color detergent (but with similar size to primary particles), or particles of varying size which appeared fractured along clearly defined lines in oxi detergents (either with or without the additional UV treatment). Additional images and EDX analysis can be seen in Figure S6.

textiles; with the vast majority of Ag measured as only metallic Ag (Table 1). In the case of the 20 nm particles, which were

initially comprised of both metallic Ag and AgCl, the QSUN irradiation initiated photoreduction of the particles resulting in a transformation of the nanocomposite even without washing. How the irradiation inhibited further chemical changes to the NPs through the washing procedure is not entirely defined, but photoreduction of the Ag likely made the particles more stable, or rather, at least less soluble as noted by the decrease in dissolution after irradiation. However, as to why the particles do not release in their entirety (opposed to oxidative dissolution) is another matter; and this may not necessarily be because of a direct transformation of the particles themselves. For example, prolonged exposure to the simulated sunlight may have also altered the physical and/or chemical properties of the binder, which further physically protected the Ag from detergent solutions and thus inhibited particulate release.

Implications for Nanotextile Risk Assessment. The potential for nanomaterials to be released from consumer goods is not in itself a new topic, but the basis of scientific understanding of released particles and the transformations they may undergo during the products life cycle (e.g., during storage, use, and disposal) is often hampered by the narrow scope of many research endeavors in terms of both the breadth of variables studied and the completeness of characterization using multiple analytical methods. The experimental studies presented in this work are not only representative of real world studies to discern possible environmental risk from the release of Ag and NP fate, but also suggest which factors may adversely affect these nanoenhanced commercial textiles. Some broad generalizations from this study suggest that (1) sunlight irradiation can reduce further changes in speciation upon washing, (2) for nonoxidant containing detergents release of nano-Ag is mainly by mechanical action as evidenced by equal behavior of Ag and Au, (3) more Ag is released from fabrics than Au when the detergent contains a high concentration of oxidant, suggesting additional chemical influences opposed to

Table 1. Best-Fit Ag Speciation As Identified by Linear Combination Fitting (LCF) of K-Edge XANES[a]

100 nm Ag Citrate
Treatment: Washing only

Component	Unwashed	CL	APL	CP	APP	OP	IL	IP
Ag⁰	100 (0)	88 (1.6)	97 (2.5)	99 (0)	73 (2.1)	52 (3.4)	----	77 (9.1)
AgCl		13 (1.5)			13 (2.1)	13 (3.2)	----	
Ag₂S					15 (2.1)	34 (5.9)	----	13 (9.1)
R-Factor	0.00222	0.00388	0.0028259	0.00382	0.0016441	0.00403		0.0067661

20 nm Ag Citrate
Treatment: Washing only

Component	Unwashed	CL	APL	CP	APP	OP	IL	IP
Ag-NP	81 (0.9)	91 (0.9)	57 (2.4)	78 (2.5)	75 (2.5)	79 (1.3)	***	66 (2.1)
AgCl NP	19 (0.8)	9 (0.8)	41 (2.5)				***	34 (2.2)
Ag₂S NP				19 (2.5)	16 (4.3)	22 (1.2)	***	
R-Factor	0.001053	0.0023	0.001	0.0028	0.0034	0.0012999		0.003213

20 nm Ag PEG
Treatment: Washing only

Component	Unwashed	CL	APL	CP	APP	OP	IL	IP
Ag-NP	73 (0.8)	56 (0.9)	78 (0.9)	89 (0.9)	56 (2.8)	75 (2)	***	58 (1.8)
AgCl NP	26 (0.8)	44 (0.9)	22 (0.9)	10 (0.9)	11 (3.1)	26 (1.9)	***	41 (1.7)
Ag₂S NP					26 (9.3)		***	
R-Factor	0.00099	0.0011139	0.001	0.001132	0.0022792	0.0058065		0.004413

100 nm Ag Citrate
Treatment: QSUN then washing

Component	Unwashed	CL	APL	CP	APP	OP	IL	IP
Ag⁰	100 (2.5)	99 (1.6)	81 (2.6)	100 (0)	82.5 (2.6)	95 (2)	----	99 (2)
AgCl							----	
Ag₂S							----	
R-Factor	0.00309	0.003279	0.0179	0.003957	0.0016441	0.002839		0.0056525

20 nm Ag Citrate
Treatment: QSUN then washing

Component	Unwashed	CL	APL	CP	APP	OP	IL	IP
Ag-NP	95 (0.7)	93 (0.8)	***	98 (0.7)	***	95 (1.3)	***	***
AgCl NP		8 (0.8)	***		***		***	***
Ag₂S NP			***		***		***	***
R-Factor	0.000152	0.0009627		0.0007		0.0021744		

20 nm Ag PEG
Treatment: QSUN then washing

Component	Unwashed	CL	APL	CP	APP	OP	IL	IP
Ag-NP	96 (0.6)	84 (0.8)	***	98 (0.8)	***	98 (1)	***	***
AgCl NP			***		***		***	***
Ag₂S NP		13 (0.8)	***		***		***	***
R-Factor	0.0005444	0.0034797		0.0008956		0.0015419		

[a]The bottom set of tables (written in red text) represent the analysis of fabrics with sunlight irradiation prior to washing. Species proportions are presented as percentages with standard deviation of three replicates in brackets. Species with less than 10% of the total were omitted. Goodness of fit is indicated by the R-factor. Cells with dashes (----) indicate measurements that were below the detection limit. Cells with asterisks (****) indicate that no measurement was taken for that variant.

only mechanical release, (4) particle capping agent and binder interactions play an important role in particle stability on the fabric surface, and (5) a large portion of material released from the fabrics are particles with little or no alteration of the primary particle size, though some physical differences to the particle shape and surface can be observed. In a large portion of silver release from textile literature, the incorporation of Ag has not always been in nanoparticulate form. The difference in initial starting material influences the transformation and variations in how the silver transformed when released from the textile (e.g., Lorenz et. al, Lombi et. al).[18,19] Additionally, we know that the chemistry of the detergent plays an important role in particle release and transformation. Therefore, when a different detergent is used, such as the ECE reference detergent in Mitrano et. al and Geranio et. al, we may expect different speciation to occur (e.g., the detergent used in those studies contained phosphate whereas none of the detergents in this scheme did).[13,15] The negligible degradation of Ag NPs in this study compared to those suspended in these same detergents, i.e. in Mitrano et al.,[14] is most likely due to the protection offered by the incorporation into the fabrics themselves, as discussed above. Nevertheless, NP degradation was observed under the harshest of exposure conditions (oxi containing detergent and sunlight irradiation). The drastic difference between the transformations of particles suspended in detergent alone compared to the relatively little changes in released particles from the fabrics highlights the necessity to conduct experiments which represents a real life situation as closely as possible; since simplified systems may not be able to properly predict outcomes of the more complex, truly relevant

real life scenario. This is true in the case of nanoenhanced products, but of course is an equally qualified sentiment across many sectors of environmental and biological effects of nanomaterials.

This work presents the most comprehensive analysis of release and transformation of Ag nanomaterials from textiles to date, it is the first study to analyze the silver fractions and transformations both on the fabric surface and in the washing solution and is one of only a few to implement sequential aging of textiles of any kind. Furthermore, the comparison of known textile formulations, NP compositions, and the extensive matrix of variables undertaken in this work is necessary if we wish to relay "typical" NP transformations or "general" NP release rates when textiles are laundered by consumers; because without this broad foundation of variables, individual, basic case studies do not reflect the breadth of nanoenhanced textiles. Nevertheless, a deeper connection must be made between environmental scientists studying these fabrics for their release of potentially (eco)toxic characteristics and the materials scientists who are producing the myriad of textiles vying for space in the competitive consumer market. Significant work has been undertaken to understand the factors that influence Ag NP deposition (including in situ formation of NPs and surface applications), the chemical and physicochemical activation of fibers before loading Ag NPs to enhance their binding efficiency. In many cases, the bar suggesting a given formulation is a "success" is high. For example, Gorjanc et al. considered their material to have poor laundering durability after antibacterial activity (against several bacterial species) declined after 50 washing cycles.[31] Typical tests involve 10 to 20 washing cycles where the intersection of continued antibacterial efficiency and release of Ag are formulation dependent.[11,25,32−40] In some instances, improved antimicrobial efficiency was noted, which was attributed to possible disaggregation of Ag NPs during washing.[41] We have recently studied the effects of multiple washes (and subsequent landfilling) of the same laboratory prepared fabrics used in this study and found that total metal released varied significantly on washing pattern variants (cycles, detergents) but overall larger releases of NPs from textiles were observed during the use phase of the life-cycle rather than the disposal phase.[20] An additional, more in depth comparison on washing release patters from laboratory prepared textiles can be found in that manuscript. Yet often in environmental literature, the investigation of multiple washing cycles and efficacy tests are significantly more limited and are rarely tied to (known) differences in the material: in short, the scope is often too narrow. This is not to suggest studies to date are not valuable, or inherently incorrect in their conclusions, but rather it is not surprising that simple correlations are difficult to define when so many variables are at play. Especially as formulations of nanoenhanced products (including textiles) continue to rapidly develop, the potential environmental risks of NPs released from these products need to be understood in relation to their precise incorporation into the product. Needless to say, this life cycle thinking and basing environmental risk on feasible, industry-relevant formulations and test cycles of products not only holds true when investigating textiles but naturally extends to all products in which nanomaterials are incorporated.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b01478.

> Additional tables and figures containing the particle size distribution of the pristine 100 nm Ag and Au particles (Figure S1) and the 20 nm Ag particles capped with citrate or PEG size distribution (Figure S2), TEM of primary particles included in the fabric (Figure S3), the washing detergent composition and chemistry (Tables S1 and S2), study on fabric digestion with different acids (Table S3), the physical appearance of textiles before and after washing in different detergents (Figure S4), total Ag and Au measured by fabric digestion and ICP-MS analysis, Ag concentrations in wash water ultrafiltrate, calculation of total particulate matter in the wash solutions as estimated by spICP-MS (Tables S4 and S5), EDX spectra of TEM images of particles in washing detergents (Figure S5), and the XANES spectra of as well as the LCF of experimental textiles (Figure S6) (PDF)

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Notes

The authors declare no competing financial interest.

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