Migration of Ag- and TiO$_2$-(Nano)particles from Textiles into Artificial Sweat under Physical Stress: Experiments and Exposure Modeling

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Supporting Information

ABSTRACT: Engineered nanoparticles (ENP) are increasingly used to functionalize textiles taking advantage, e.g., of the antimicrobial activity of silver (Ag)-ENP or the UV-absorption of titania (TiO$_2$)-ENP. Mobilization and migration of ENPs from the textile into human sweat can result in dermal exposure to these nanoobjects and their aggregates and agglomerates (NOAA). In this study we assessed exposure to NOAA migrating from commercially available textiles to artificial sweat by an experimental setup that simulates wear-and-tear during physical activity. By combining physical stress with incubation in alkaline and acidic artificial sweat solutions we experimentally realized a worst case scenario for wearing functionalized textiles during sports activities. This experimental approach is not limited to NOAA, but can be used for any other textile additive. Out of four investigated textiles, one T-shirt and one pair of trousers with claimed antimicrobial properties were found to release Ag <450 nm in detectable amounts (23–74 μg/g/L). Textiles containing TiO$_2$ for UV protection did not release significant amounts of TiO$_2$ <450 nm, but the antimicrobial T-shirt released both TiO$_2$ and Ag <450 nm. The silver was present in dissolved and particulate form, whereas TiO$_2$ was mainly found as particulate. On the basis of our experimental results we calculated external dermal exposure to Ag and TiO$_2$ for male and female adults per use. For silver, maximal amounts of 17.1 and 8.2 μg/kg body weight were calculated for total and particulate Ag <450 nm, respectively. For TiO$_2$, the exposure levels amount to maximal 11.6 μg/kg body weight for total (mainly particulate) TiO$_2$. In comparison with other human exposure pathways, dermal exposure to NOAA from textiles can be considered comparably minor for TiO$_2$-NOAA, but not for Ag-NOAA.

INTRODUCTION

Engineered nanoparticles (ENP) are increasingly common in functionalized consumer products. Functional textiles rank high by number and potential for consumer exposure, since they are often worn in direct contact with the skin. The ENP that are most frequently added to textiles are silver (Ag) and titania (TiO$_2$), for antimicrobial activity or UV protection, respectively. Both Ag- and TiO$_2$-ENP can release nanoobjects and their agglomerates and aggregates (NOAA) that potentially can be taken up from textiles by the skin, by ingestion, or by inhalation and are under investigation for having toxicological effects after uptake into the human body. By mass, the external exposure to substances in textiles for adults is largest for the skin, since both ingestion and inhalation involve transport from the textile to the intake organ; for children the oral pathway (e.g., sucking of sleeves) may play an additional noteworthy role.

To date, it is still unclear to what extent nanoparticles are taken up by the skin. In some studies nanosized TiO$_2$ and ZnO did not penetrate the deep layers of healthy adult skin, whereas a different study reported that TiO$_2$ penetrates porcine skin (in vitro) and skin of hairless mice (in vivo), and in yet another study excess $^{68}$Zn was detected in the blood of healthy volunteers after exposure to $^{68}$Zn-enriched ZnO ENP. For Ag, dermal uptake has been shown to be relatively low for healthy skin but increased for damaged skin in in vitro studies. Therefore, uptake fractions ranging from 0.1% (realistic case) to 100% (worst case) have been assumed in the risk assessment for Ag-NOAA for consumers wearing Ag-treated textiles.

Until today, dermal external exposure to substances in textiles has not been examined in a rigorous way. For substances in textiles no registration is required in Switzerland, Germany, and many other EU countries, since textiles in the EU are treated as articles. Substances in articles also do not need to be listed on a product label or be evaluated according to their potential for consumer exposure. However, due to concerns about nanoparticle health effects, risk assessments for NOAA are needed that take into account all relevant
Table 1. Description of the Functional Textiles Investigated in this Studya

<table>
<thead>
<tr>
<th>no.</th>
<th>type</th>
<th>composition of fabric</th>
<th>product labeling</th>
<th>mass of textile (g)</th>
<th>Ag content (mg Ag/kg textile)</th>
<th>Ti content (mg Ti/kg textile)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>socks</td>
<td>41% polypropylene, 31% polyamide, 18% cotton, 10% wool</td>
<td>&quot;silver integrated in polyamide fiber&quot;</td>
<td>42 (pair)</td>
<td>18 ± 2</td>
<td>2153 ± 35</td>
</tr>
<tr>
<td>2</td>
<td>shirt</td>
<td>83% polyester, 17% wool</td>
<td>Ag-NP</td>
<td>89/64</td>
<td>183 ± 10</td>
<td>2153 ± 35</td>
</tr>
<tr>
<td>3</td>
<td>shirt</td>
<td>100% polyester</td>
<td>&quot;silver ions&quot;</td>
<td>71</td>
<td>45 ± 8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>trousers</td>
<td>93% polyamide, 7% elasthane</td>
<td>AgCl-NP (200–400 nm)</td>
<td>345/300</td>
<td>41 ± 0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>shirt</td>
<td>80% polyamide, 20% polyester</td>
<td>contains nano-TiO2</td>
<td>203</td>
<td>7149 ± 725</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>pants (children)</td>
<td>82% polyamide, 18% lyra</td>
<td>contains nano-TiO2</td>
<td>68</td>
<td>6772 ± 112</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>long sleeved shirt</td>
<td>46% Lenzing Modalüum (cellulose), 46% cotton, 8% elastane</td>
<td>contains TiO2 (incorporated sunblocker)</td>
<td>176</td>
<td>2983 ± 11</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>long sleeved shirt</td>
<td>91% polyamide, 9% elastane</td>
<td>contains TiO2</td>
<td>187</td>
<td>8543 ± 32</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>long sleeved shirt</td>
<td>53% polyester, 47% polyethylene terephthalate, PBT</td>
<td>contains TiO2</td>
<td>183</td>
<td>4482 ± 98</td>
<td></td>
</tr>
</tbody>
</table>

aData from Lorenz et al.,25 Windler et al.,26 and Windler.45 According to personal communication with manufacturers. "Textile weights for male/female clothes.

Exposure routes, including use of textiles. After earlier demonstrations that silver is present in commercial textiles, a consumer exposure scenario for Ag-nanoparticles in functionalized socks has been proposed recently. This exposure scenario is designed as a ‘worst worst-case’ approach and therefore contains unrealistic assumptions, such as an immediate release of total Ag-content. Such extreme worst cases that are constructed in the absence of appropriate data are useful as a first tier for risk assessment, but they do not establish a basis for decision-making, because the share of one single source in the overall dose is not accessible.

External exposure data for Ag- and TiO2-ENP today are available from studies on single sources. Exposure studies assessed external consumer exposure to Ag-ENP via inhalation of consumer sprays18,19 and TiO2-ENP exposure from ingestion of selected food items.20 Dermal external exposure to ENP has been assessed for TiO2-ENP in sunscreens21,22 and in an aggregate exposure assessment for ENP in personal care products.6

Personal care products are applied onto the skin, which potentially allows direct uptake of ENP. In contrast, ENP in textiles first need physical mobilization by wear-and-tear and/or chemical mobilization by sweat before human exposure can occur. Therefore, to assess the dermal exposure to NOAA released from textiles an experimental setup is needed that accounts for the release of substances into human sweat during wearing. The experimentally determined NOAA concentration in sweat can then be used to estimate external dermal exposure. In a study by Kulthong et al.,2010 silver concentrations after incubation of ENP-containing textiles in artificial sweat solutions were measured. These authors used a static setup that accounts only for chemical mobilization of nanoparticles by the sweat solution. Also, their study did not distinguish between dissolved and particulate silver, which presumably have different uptake parameters. A second study23 used a similar setup involving a textile with a very high content of silver (17%). Both studies, however, did not take into account physical stress acting on the fabric (wear-and-tear), which for substance migration probably will play an important role.

In this study we constructed a more realistic exposure scenario for wearing Ag- and TiO2-ENP-containing textiles. In order to parametrize the model, we designed a migration experiment that simulates physical (wear-and-tear) and chemical mobilization and examined a range of commercial textiles that are functionalized with Ag- and TiO2-ENP. Physical stress is simulated by incubation of the textiles in the ISO standard model washing machines that have previously been used by Geranio et al.17 and in two recent studies25,26 to investigate nanoparticle release from textiles during washing.

During use, the same process of textile parts rubbing against each other takes place as during washing, and this process presumably is responsible for the release of particles and fibres from a textile. Instead of washing solutions, though, we used artificial human sweat. After incubation, we analyzed the fraction <450 nm (that includes nanoparticles, as well as their aggregates and agglomerates that can release nanoparticles on the skin27) and the dissolved fractions in the sweat solutions by ICP-OES and STEM. On the basis of the results of these experiments, we obtained more realistic external exposure estimates for dermal exposure to NOAA from textiles.

MATERIALS AND METHODS

Characteristics of Textile Samples and Fabric Analysis. All textile samples used in this study were commercially available products and intended for sports or outdoor activities. The fabrics are therefore supposed to be in direct skin contact and suffer physical stress at heavy-sweating sites of the body. An overview of the textiles analyzed in this study is provided in Table 1. The samples encompass adult and children products that are either labeled to contain Ag or marketed with UV-sunscreen (corresponding to 3.59 and 14.3 g TiO2 per kg fabric). Textile 2 shows that all samples contained between 18 and 183 mg Ag/kg textile (corresponding to 3.59 and 14.3 g TiO2 per kg fabric). Textile 2 contains both Ag and Ti.

Experimental Setup. The experimental setup is based on the ISO method 105-C06 for “color fastness to domestic and commercial laundering” and employs a model washing machine Washtex-P Roaches (steel vessels: 75 ± 5 mm diameter, 125 ± 10 mm height, 550 ± 50 mL; rotation/motor speed 40 ± 2 rpm) at room temperature and 8 g of fabric. In order to simulate realistic migration from textiles into artificial...
sweat and to reduce background levels of Ag and Ti, the ISO method was adapted as follows:

1. The washing solution was replaced by artificial sweat of either pH 5.5 or pH 8.0 following the ISO method 105-E04 “color fastness to perspiration”.
2. The volume of the liquid phase (i.e., artificial sweat) was reduced from 150 to 120 mL to enhance the textile/sweat ratio. In a pretest, 120 mL was found to be the minimum volume necessary to completely wet the investigated 8.0 ± 0.2 g of fabric.
3. The sweat solutions were not directly filled into the steel vessels of the washing machine but into polyethylene HD (PE-HD) bottles (volume: 300 mL) embedded in the steel vessels to reduce background Ag. For each textile sample and washing cycle, new PE-HD bottles were used.
4. The steel balls that simulate physical stress were replaced by acrylic plastic balls to reduce the silver background.

An exposure time of at least 30 min is needed to establish repeatable average experimental conditions (e.g., number of washing rotations, adjustment of sample to the temperature in the water bath).

**Exposure to Artificial Sweat.** The artificial sweat solutions were prepared as described in the ISO procedure 105-E04 “color fastness to perspiration” by dissolving 5 g NaCl, 2.2 g NaH2PO4·H2O, and 0.5 g 1-histidine-monohydrochloride-monohydrate (C5H4O2N2·HCl·H2O) in 1000 mL of deionized water. The pH was adjusted to 5.5 or 8.0 by adding the respective amount of 0.1 N NaOH.

For each of the sweat exposure experiments, 120 mL of artificial sweat (alkaline or acidic) and 10 acrylic balls were filled into a PE-HD bottle. The bottle was placed inside one of the steel vessels of the washing machine, and 150 mL of water was filled in the space between the steel vessel and the PE-HD bottle to allow heat transfer from the water bath to the artificial sweat. Then, the steel vessels each containing one PE-HD bottle were preheated in the water bath (40 °C) for 45 min. After preheating, one fabric sample of 8.0 ± 0.2 g was added to each of the artificial sweat solutions, and, after thorough closure of the PE-HD bottles, the textile samples were exposed to sweat inside the rotating washing machines for 30 min at 40 °C.

Afterward, the artificial sweat solution was collected in the original plastic bottles. The textile samples were dried horizontally under constant conditions (23 °C, 50% humidity).

In order to evaluate the experimental conditions we varied the incubation time (sweat volume 120 mL: 30, 60, 90, and 120 min) and the volume of the acidic sweat solution (incubation time 30 min: 60, 90, 120, and 180 mL) for one textile that released silver above the limit of detection LOD (textile 4).

**Analysis of Sweat Solutions after the Migration Experiment.** Particulate matter of Ag and Ti in artificial sweat was fractionated by filtering 3 × 10 mL of sweat solution with cellulose nitrate membrane filters (0.45 μm, Sartorius Stedim Biotech). The filtrate was combined and acidified with HNO3 (65%, Fluka), and three replicates were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin-Elmer, OPTIMA 3000) without further processing. The LOD (per g fabric) was 12.5 μg/g/L for TiO2 and Ag, dissolved and <450 nm, and 6.25 μg/g/L for Ag >450 nm, respectively.

In order to determine the fraction of Ag and TiO2 in dissolved form, the remaining filtrate was further fractionated by filtration with centrifugal filters with a cutoff of 30 kDa (Vivaspin 6, 30 000 MWCO, polyether sulfone, centrifugation for 10 min at 13 500 rpm). Triplicates of 2.5 mL of the centrifuged solution were put into plastic tubes, mixed with 1.5 mL of distilled water and 1 mL of HNO3 (65%) and analyzed by ICP-OES. The particulate fraction <450 nm was determined by subtracting the dissolved fraction from the filtrate fraction.

The particulate fraction of Ag >450 nm was determined by acid digestion of the filters as described in Lorenz et al. The particulate fraction of TiO2 >450 nm was calculated by subtracting the fraction <450 nm from the total amount of TiO2 measured by KOH digestion as described in Windler et al. (see also Supporting Information).

For scanning transmission electron microscopy (STEM) analysis, one drop of each filtrate or unfiltered sweat solution was placed on a TEM grid (copper with carbon coating), soaked through with a lint free tissue and analyzed by STEM (Technai F30 ST, FEL, FEG, 300 kV, scanning mode). The electron micrographs were analyzed with the open software ImageJ (ImageJ, 2008). To obtain information on the NOAA size range, the dimensions of all relevant particles identified in the images were measured.

**Speciation Calculations.** The speciation of Ag in the artificial sweat solutions was calculated using ChemEQL. The Ag-chloride complex formation constants were taken from Fritz, the Ag-histidine values from Czoik et al., and the AgCl(I) solubility product from NIST.

**Calculation of Dermal Exposure.** External dermal exposure to Ag and TiO2 was calculated with the exposure model represented by eq 1 that was developed for consumer exposure to substances in textiles. This model describes migration of a nonvolatile substance from textile fabric, i.e., the amount of Ag or TiO2 depositing on the skin surface during a single use. The exposure levels were modeled separately for dissolved and particulate material. In case of Ti, it was assumed that all particulate material is present as TiO2 in sweat, independent of pH. Accordingly, the exposure levels were adapted to the molar mass of TiO2. The parameters and model assumptions are as follows:

\[
E = \frac{m_{\text{textile}} a_{\text{sub}} r_{\text{sweat}} A_{\text{expo}} f_{\text{contact}}}{m_{\text{bw}}} \quad (1)
\]

where \(E\) is the external exposure per use [μg substance/kg body weight], \(m_{\text{textile}}\) is the total weight of textile [g], \(a_{\text{sub}}\) is the released amount of substance from fabric into sweat per gram fabric and mL sweat [μg/g/mL], \(r_{\text{sweat}}\) is the released volume of sweat per time and body surface [mL/min/m²], \(A_{\text{expo}}\) is the exposure time [min], \(f_{\text{contact}}\) is the fraction of textile in close contact with sweat and skin, and \(m_{\text{bw}}\) is the body weight of the consumer [kg body weight].

The exposure \(E\) represents external exposure for an intense sports activity, during which the fabric is completely wetted by sweat and prone to heavy friction for 60 min (e.g., fabric during a tennis match, 60 min linearly extrapolated from 30 min in experiment). The parameter \(m_{\text{textile}}\) was determined by weighing the unwashed and tempered specimen before the sweat release experiments (textile 2, T-shirt: 89/64 g and textile 4, trousers 345/300 g for male/female adult). The release of Ag or Ti per gram of fabric and sweat volume (\(a_{\text{sub}}\)) is assumed to linearly depend on the volume of sweat (as shown by experiments with textile 4 and expected for a continuous source emitting below saturation). The sweat release rates of 1.8 and 1.25 mL/min/m².
Table 2. Release of Ag and TiO₂ into Sweat per Gram of Textile for 30 Minutes of Incubation in 120 Milliliters of Sweat

<table>
<thead>
<tr>
<th>no.</th>
<th>type</th>
<th>element analyzed</th>
<th>substance release into acidic sweat (μg/g/L)</th>
<th>substance release into alkaline sweat (μg/g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>dissolved</td>
<td>particulate &lt;450 nm</td>
</tr>
<tr>
<td>1</td>
<td>socks</td>
<td>Ag</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>2</td>
<td>shirt</td>
<td>Ag</td>
<td>43 ± 1</td>
<td>31 ± 5</td>
</tr>
<tr>
<td>3</td>
<td>shirt</td>
<td>Ag</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>4</td>
<td>trousers</td>
<td>Ag</td>
<td>45 ± 5</td>
<td>nd</td>
</tr>
<tr>
<td>2</td>
<td>shirt</td>
<td>Ti</td>
<td>nd</td>
<td>63 ± 13</td>
</tr>
<tr>
<td>5-9</td>
<td>various, see Table 1</td>
<td>Ti</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

**nd**: under the detection limit of 12.5 μg/g/L for Ti and Ag, 6.25 μg/g/L for Ag >450 nm.

Figure 1. Particles detected with STEM in the sweat solutions of textile 2 with corresponding EDX-measurements. Ag-NP in acidic sweat (I), TiO₂-NP in alkaline sweat (II), TiO₂ particles in acidic sweat (III).

for male and female adult, respectively, are taken from Ichinose-Kuwahara et al. 34 who report sweat rates of trained male and female individuals at high exercise intensity (cycling) that represent maximal values for short-term sweat production. The duration of exposure, i.e., the wearing time for the respective textile, is \( t_{\text{expo}} \). High sweat rates as assumed here solely occur during limited time periods. An exposure time of 60 min
representing a continuous sports event without break is therefore assumed to be a reasonable worst case.

The body area covered by different textiles \( A_{\text{app}} \) was derived by Lorenz\(^3\)\(^5\) from surface areas of body parts as stated in the Exposure Factors Handbook.\(^\text{36}\) For the short-sleeved T-shirt we used 0.98/0.69 m\(^2\) and for trousers 0.83/0.69 for male/female adults, respectively. The factor \( f_{\text{contact}} \) takes into account that some textiles are worn loose, so that only part of the fabric is in contact with the skin. In the case of tight-fitting T-shirts, a factor of 1 was considered as worst case. For the trousers, \( f_{\text{contact}} \) was set to 0.5 because the trousers had a straight cut, implying a fairly loose fit. The exposure \( E \) was normalized to the 50th percentiles of body weights \( (m_{\text{bw}} \text{ for male/female: } 77/62 \text{ kg as recommended in the Exposure Factors Handbook})\(^\text{36}\).

Exposure levels for children were not modeled, because sports clothing functionalized with Ag to our knowledge is solely marketed for adults and the UV-protecting shirts designed for children did not release measurable amounts of Ti during our sweat exposure experiments.

**RESULTS**

**Release of Ag and TiO\(_2\) during Migration Experiment.**

The repeatability of our experimental setup was tested by conducting the whole experiment with three different samples of textile 4 in parallel with 120 mL of artificial sweat solution with pH 5.5. The concentration of Ag after incubation was 0.33 mg/L with a standard deviation for the three independent samples of 0.01 mg/L.

Silver was released from two out of four textiles in detectable amounts, whereas only one textile out of six released Ti in detectable amounts. An overview of the concentrations is provided in Table 2. Under acidic conditions, textile 2 released more dissolved (43 \( \mu \)g/g/L) than particulate Ag <450 nm (31 \( \mu \)g/g/L) and textile 4 released 45 \( \mu \)g/g/L Ag only in dissolved form. Textiles 2 and 4 released similar amounts of dissolved and particulate Ag into alkaline sweat (dissolved/particulate: 31/34 \( \mu \)g/g/L and 25/23 \( \mu \)g/g/L). For both textiles, in alkaline sweat solution a higher concentration of particulate silver <450 nm was observed than in the acidic sweat solution. The mass of Ag particles >450 nm was under the detection limit for all textiles except for textile 2 where 30 \( \mu \)g/g/L were observed in acidic and 11 \( \mu \)g/g/L in alkaline sweat. With STEM we found Ag-containing NOAA of 20–200 nm in the leachate of textile 2 (see Figure 1, Ia, for a representative picture); in the leachate of textile 4 no particles were detected by STEM. The EDX spectrum of the particles released from textile 2 shows peaks for both Cl and Ag (see Figure 1, Ib), suggesting that the detected particles consist of AgCl (no Na was detected in the EDX).

The initial content of Ti in the analyzed fabrics was more than 1000-fold higher than the Ag content. Nevertheless, only textile 2 released measurable amounts of Ti during sweat exposure (Table 2). Independent of pH, only particulate Ti was released, with a higher amount identified in acidic sweat (63 and 38 \( \mu \)g/g/L for Ti <450 nm in acidic and alkaline sweat, respectively). These Ti concentrations correspond to 105 and 63 \( \mu \)g/g/L TiO\(_2\). Particulate Ti >450 nm released by textile 2 was 725 and 188 \( \mu \)g/g/L, respectively.

With STEM, the presence of TiO\(_2\) particles in both alkaline and acidic sweat was confirmed (see Figure 1, II and III). The EDX signals show particles of 150–300 nm that consist of Ti and O only (with traces of NaCl in the background for II).

**Release of Silver under Different Experimental Conditions.** The release of Ag from textile 4 into the sweat solution under physical stress increased linearly with sweat volume, resulting in a constant Ag concentration of about 0.35 mg/L, and was independent of the duration of sweat contact (Figure 2). In order to check whether equilibrium was reached after 30 min of incubation, we performed speciation calculations and could show that at pH 5.5 and pH 8 the total dissolved Ag in equilibrium with AgCl(s) is 2.9 \( \mu \)M (0.31 mg/L). Dissolved Ag–chloro complexes are the major dissolved species due to the high chloride content in the sweat (0.085 M). The Ag–histidine complexes (AgHis and AgHis\(_2\)) only contributed 2% to the dissolved Ag (i.e., 0.06 \( \mu \)M). The solubility limit for Ag\(_3\)PO\(_4\) was not reached, and AgCl(s) was therefore the solubility limiting solid phase. The predicted solubility of Ag in sweat (0.31 mg/L) is therefore matching almost precisely the measured dissolved Ag concentration of 0.33–0.40 mg/L (for 8 g of textile, see also Supporting Information; values in Table 2 are normalized to 1 g of fabric), indicating that for textile 4 equilibrium with AgCl was reached within 30 min for different sweat volumes (see Figure 2).

**Exposure Modeling.** The modeled exposure levels encompassing dissolved and particulates <450 nm were in the range of 3.5–11.6 \( \mu \)g Ag or TiO\(_2\) per kg body weight (see Figure 3). Particles larger than 450 nm were not considered for human exposure because they are assumed not to pass the skin barrier and not to release nanoparticles. For both, Ag and TiO\(_2\),
males are higher exposed than females independent of type of sweat and textile. Assuming that a man wears T-shirt and trousers containing Ag, the exposure to particulate/dissolved Ag per use during physical activity is up to 8.2/8.5 for alkaline and 3.4/13.7 μg/kg body weight for acidic sweat. The corresponding exposure levels for women are approximately half: 4.5/4.3 and 1.6/7.7 μg/kg body weight for alkaline and acidic sweat, respectively.

The exposure to TiO₂ from the investigated shirts is higher in acidic sweat, resulting in the highest modeled exposure levels of 11.6 and 5.2 μg/kg for males and females, respectively.

DISCUSSION

Experimental Setup. The experimental conditions for the sweat release experiments were designed to model a realistic worst-case for textiles with sweat exposure during sports activities. Special attention has been paid to the following criteria:

1. In favor of reproducibility the setup should make use of available standard methods as far as possible.
2. The textile samples should be subject to physical stress that simulates sports activities, i.e., the fabric should be in contact with an adequate amount of sweat over a period of 30–60 min.
3. Artifacts through excess of sweat or unrealistic temperature should be minimized.

Accordingly, our method was adapted from ISO methods.²⁴ For the migration experiments we chose the minimal amount of sweat that was needed to completely wet the fabric and the minimal time needed to ensure good repeatability of the adapted ISO procedure of washing. The amount of sweat of 120 mL is realistic, but worst case (maximal sweat production is 54 mL/m² in 30 min for an adult male, i.e., 108 mL for a total body surface of about 2 m²), and friction and wrinkling are maximized by the dynamic contact with plastic balls inside the vessel. Although the experimental setup has not been tested against real-life exposure, the setup presumably is a better model for real-life situations than the static experiments published to date, since it involves the mechanical component.

Our experimental setup is not specific to NCAA but can be used to assess migration into sweat under wear-and-tear conditions for any other textile additive. Moreover, as it attempts to simulate a ‘realistic worst case’ it can be used in the context of aggregate exposure assessment³⁸ and for source discrimination.⁵⁹,⁶⁰

Migration of Ag and TiO₂ into Artificial Sweat. The investigated textiles that are advertized for their UV protecting properties released TiO₂ below our limit of detection. The TiO₂ particles are firmly incorporated into the fiber, as frequently found for UV-absorbing pigments, which prevents their release. Only for one of these textiles a significantly lower TiO₂-content was measured after 10 ISO washing cycles with washing detergent so that we can safely assume that repeated wearing (and sweating) will not result in any further TiO₂ release.

Textile 2 released TiO₂ in dissolved and particulate form, but this textile also contained silver and did not claim to protect from UV radiation. Presumably in this textile TiO₂ was not contained in the fiber, but used in some kind of coating that allows release. The total silver amount that was released from textiles 2 and 4 in acidic/alkaline sweat was 5/7% and 13/14% of the initial silver content of the textile, respectively. This is higher than found for the maximum release of 3.3% reported for commercial textiles from manufacturers in Thailand.²³ In that study only chemical mobilization into artificial sweat was investigated for six commercial functional textiles, of which only one textile released silver in a considerable amount. Like in the present study the highest release was found for the alkaline sweat solution. The difference suggests that mobilization by physical stress may play an important role for the Ag release.

Another study on mobilization of silver by sweat investigated a commercial fabric with an extremely high metallic silver content of 17%.²⁴ According to the authors the textile is used as an “electromagnetic wave repellent” textile. They found very low release fractions of 0.02–0.05%, corresponding to concentrations of total silver after release of about 0.3 mg/L in alkaline sweat solutions and 0.9 mg/L in acidic sweat of pH 3, including a large number of particles >500 nm.

Dissolved and particulate silver <450 nm was released from textile 2, in contrast to textile 4 that released mainly dissolved Ag (as can be expected for AgCl-NP). This is consistent with the microscopic analysis, as only after the experiment with textile 2 particulate Ag was detected in the artificial sweat. The EDX analysis suggests that AgCl particles were present in sweat that either originate from the textile or were formed by precipitation of dissolved Ag. The latter would mean that the Ag(0) particles, which according to the producer are present in textile 2, have been oxidized in the sweat solution. However, we can also not exclude that Ag(0) particles were indeed present in the solution and precipitated together with AgCl so that we were not able to see them in the STEM. Furthermore, for the Ag(0) content in the textile we rely on information from the producer, which may not be correct for the particular garment investigated, since during the production process the ingredients may have been changed on short notice. However, in the light of the diverging dissolution behavior of textiles 2 and 4, we consider the possibility of AgCl incorporated in textile 2 less likely.

A comparison with washing experiments of the same textiles showed that migration is different for both types of solutions (see Figure 4). Mostly much larger fractions of dissolved Ag are found in sweat compared to washing liquid due to the high chloride concentration in sweat that stabilizes Ag as dissolved Ag–chloro complexes. Release of particulate silver was mostly less than in washing experiments, suggesting either less particulate release in sweat or higher precipitation of released silver in the washing liquids.

Human Exposure. Our model attempts to provide a realistic worst case of exposure to total and particulate Ag and TiO₂ from functional textiles. In our experiments we took into account both chemical and physical mobilization. In the model we assumed that the total amount released into sweat subsequently is deposited on the skin. In reality part of the silver will be redeposited on the textile itself, thereby reducing exposure. Also, the process of drying and wetting of the textile during use will reduce the amount of sweat available for mobilizing silver, likewise resulting in a reduction of exposure. Additionally, showering after sports activities will wash off Ag/TiO₂ from the skin and may significantly reduce exposure. Also, the surface of the textile in contact with the skin can be reduced, e.g., if creases form during use.
The exposure assessment was based only on T-shirt and trousers, because in this study we did not find any migration for particulate and dissolved silver <450 nm from the socks we investigated. However, functional socks potentially can contribute to the overall exposure. We based our exposure calculations on the results of the here reported experiments for a limited number of textiles. We cannot exclude that other types of textiles release higher amounts of silver into artificial sweat. However, by using adjusted release rates new data can easily be introduced into the model.

On this basis we conclude that our experiments and modeling provide reasonable worst case estimations suitable for risk assessment and comparison to other sources of silver for human exposure. Our model calculations show a maximum exposure to total silver (particulate <450 nm plus dissolved Ag) for human exposure. Our model calculations show a maximum exposure to total silver (particulate <450 nm plus dissolved Ag) from wearing both Ag-functionalized trousers and T-shirts of about 1.3 mg/d for males and 0.6 mg/d for females (with standard body weights of 77 and 62 kg, respectively). Other sources for dermal exposure to silver, e.g., include hand creams that sometimes contain up to 0.1% of Ag. Exposure from such a cream for an adult female with realistic (not worst case) assumptions will amount to 4.8 mg/day (for usage on hands and face with each 0.8 g, three times a day), which is 4–8 times higher. Therefore, with respect to total silver exposure of consumers, textiles can be considered a comparably minor source.

The exposure to Ag-ENP, however, is about 0.6 and 0.3 mg/d for males and females, respectively. These exposure values representing a realistic worst case are around 2 orders of magnitude lower compared to the previously discussed “worst worst case for Ag-ENP exposure from textiles” (0.2–4 mg/kg body weight for external exposure, and 6–150 mg/d for a person). Sources of Ag-NOAA for the consumer are to date mainly textiles and, to a lesser extent personal care products (e.g., toothpaste and mouthwash). Oral exposure to Ag dietary supplements can amount to 0.5 mg/d in extreme cases, which is in the same range as our exposure values, but oral absorption is assumed to be much more efficient than dermal absorption. Considering, however, that Ag-NP-treated textiles are on the rise, and presumably only few people take Ag as dietary supplement, dermal exposure from functionalized textiles remains a noteworthy potential pathway for Ag-NOAA. Toxicological thresholds of Ag-NOAA are still under debate, while ionic silver is considered to be toxicologically of low concern.

For TiO$_2$ other consumer products like creams and sunscreens will cause a significantly larger dermal exposure than determined for textiles. In sunscreens also TiO$_2$-NP are used and external exposure to TiO$_2$-NOAA therefore can amount to 1000 mg from one event of sunscreen use alone (calculated from Lorenz et al. for one single event, whole person, female high exposure scenario), making the textiles a comparatively minor source.

Children presumably are even less exposed to nanoparticles from textiles via the sweat-mediated dermal pathway. Apart from the smaller number of ENP-treated products on the market (and less release by these products as demonstrated in our study), children also release less sweat that mobilizes the substances from the textiles. Conversely, mouthing and sucking of sleeves could lead to enhanced exposure, which however is outside the scope of this study.

We conclude from our study that compared to other exposure pathways dermal exposure to NOAA from textiles represents a minor pathway for total human exposure to TiO$_2$-NOAA. For Ag-NOAA, the picture is more complex. The potential dermal exposure to Ag-NOAA from textiles is, by mere amount, comparable in magnitude to the major known source of Ag-ENP, which are dietary supplements. However, due to their much smaller percutaneous uptake rates Ag-NOAA on the skin presumably cause much less internal exposure and thus have far less toxic potential than orally administered Ag-ENP in dietary supplements.

## ASSOCIATED CONTENT

### Supporting Information

Description of the digestion methods, the release data per 8 g of fabric, and a table with model parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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### REFERENCES


