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## Characterization of silver release from commercially available functional (nano)textiles

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### HIGHLIGHTS

- ▶ Eight commercially available silver textiles were investigated.
- ▶ The total silver content ranged from 1.5 to 2925 mg Ag/kg.
- ▶ Only four of the textiles released measurable Ag amounts.
- ▶ AgCl, Ti/Si–AgCl composites, Ag-sulfide and Ag were identified in washing solution.
- ▶ 34–80% of the released Ag was in the form of particles larger than 450 nm.

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### ABSTRACT

Silver, both in the nano as well as in other forms, is used in many applications including antimicrobial textiles. Washing of such textiles has already been identified as an important process that results in the release of silver into wastewater. This study thus investigated the release of silver from eight different commercially available silver-textiles during a washing and rinsing cycle. The silver released was size-fractionated and characterized using electron microscopy. In addition, the antimicrobial functionality of the textiles was tested before and after washing. Three of the textiles contained nanosized silver (labeled or confirmed by manufacturers' information), another used a metallic silver wire and four contained silver in undeclared form. The initial silver content of the textiles was between 1.5 and 2925 mg Ag/kg. Only four of the investigated textiles leached detectable amounts of silver, of which 34–80% was in the form of particles larger than 450 nm. Microscopic analysis of the particles released in the washing solutions identified Ti/Si–AgCl nanocomposites, AgCl nanoparticles, large AgCl particles, nanosilver sulfide and metallic nano-Ag, respectively. The nanoparticles were mainly found in highly agglomerated form. The identified nanotextiles showed the highest antimicrobial activity, whereas some of the other textiles, e.g. the one with a silver wire and the one with the lowest silver content, did not reduce the growth of bacteria at all. The results show that different silver textiles release different forms of silver during washing and that among the textiles investigated AgCl was the most frequently observed chemical form in the washwater.

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### 1. Introduction

Silver is an engineered nanomaterial (ENM) that currently attracts a considerable amount of attention. An increasing number of articles deals with the effects and risks of nano-Ag to humans and the environment (Blaser et al., 2008; Wijnhoven et al., 2009; Johnston et al., 2010; Marambio-Jones and Hoek, 2010; Scheringer

et al., 2010; Tolaymat et al., 2010; Nowack et al., 2011). Silver and nanosilver are used in a variety of consumer products, for example, in textiles to add antimicrobial and anti-odor functionality (Das-tjerdi and Montazer, 2010). The growth of microbes on textiles can be controlled by an antimicrobial finishing of the textile or by incorporating a biocide into synthetic fibers during extrusion (Gao and Cranston, 2008). The production of antimicrobial textiles has been estimated to be 100000 t worldwide in 2000 with a yearly increase in production by more than 15% (Gao and Cranston, 2008). Textiles functionalized with different forms of nanosilver

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have been shown to have long-lasting antimicrobial effects (Matyjas-Zgondek et al., 2008; Ilic et al., 2009).

The environmental effects of nanosilver over the whole life cycle of the textiles are determined by the chemical and physical characteristics of the substance in the consumer product and are also influenced by consumer behavior and the release scenario (Meyer et al., 2011; Walser et al., 2011). Exposure modeling has shown that textiles may indeed be one of the most important sources of Ag nanoparticles in the environment (Mueller and Nowack, 2008; Gottschalk et al., 2009).

The risks associated with human or environmental exposure to ENM are chiefly determined in part by the release and transformation processes that control their environmental fate and transformation (Nowack et al., 2012). These processes act not only on the ENM that might be released directly into the environment but more importantly also on ENM still in consumer products and those that have been released from products (Auffan et al., 2010; Botta et al., 2011).

Only very few studies so far have considered the actual source of ENM in the environment and have therefore directly investigated the release from consumer products (Gottschalk and Nowack, 2011). Among the product types investigated, paints (Kaegi et al., 2008, 2010), textiles (Benn and Westerhoff, 2008; Geranio et al., 2009; Impellitteri et al., 2009; Benn et al., 2010; Kulthong et al., 2010) and sprays (Hagendorfer et al., 2010; Lorenz et al., 2011) account for the majority of the investigations.

The experimental determination of the release of Ag from different textiles has been the topic of a small number of studies: Benn and Westerhoff (2008) have investigated the release of Ag from commercially available nanotextiles into distilled water. They have shown that a large fraction was released as dissolved ionic silver. Geranio et al. (2009) have shown that the majority of Ag released from nanotextiles into washing liquid under conditions relevant for washing is present in the form of particles larger than 450 nm, that only 5–15% are smaller particulates and that the level of Ag dissolved is very low for most textiles. Impellitteri et al. (2009) have shown that bleach has strong effects on the speciation of the silver in the textiles and that significant transformation of elemental Ag to AgCl occurred in the presence of bleach. Benn et al. (2010) have quantified the release of Ag from various textiles into tap water. The majority of the Ag released was able to pass a 20 nm filter, and therefore must have been either in dissolved form or as very small nanoparticles. Farkas et al. (2011) have provided evidence that in the effluent of a washing machine that is releasing Ag into the washwater Ag nanoparticles of about 10 nm diameter are present. These studies have shown that exposure of nanotextiles to aqueous solutions indeed results in the release of silver, but the chemical identity of the released particles remains in most studies unclear.

The aim of this work was to quantify the release of Ag from commercially available silver textiles and to characterize the particles released with regard to size and chemical form. In order to investigate a realistic exposure scenario reflecting the use of textiles in households, we used a washing cycle with detergent followed by a rinsing cycle with tap water. The released particles were size fractionated and also characterized using STEM and TSEM. In addition we tested the antimicrobial activity of the textiles before and after washing to relate silver content and release with the functionality of the textiles.

## 2. Methods

### 2.1. Textiles

Eight commercially available textile samples were included in this study (Table 1). The textile samples differed in various

characteristics such as Ag-content, composition of fibers, fabric density and application type. Concerning the fabric, five textiles were made of artificial fibers, whereas three textiles had a high cotton content. Information about the silver content in the products originated from different sources: one product clearly indicated “nano” silver on the product label. For another four products, silver without any further specification was mentioned on the product description. In two cases, the presence of silver was confirmed by manufacturers (personal communication) and in one case, visible metallic silver wires were integrated in the fabric. For the measurements and experiments the samples were taken either from the same part of the fabric (e.g. always the sole of socks) or from parts with the same color and texture of the fabric.

### 2.2. Ag release during washing and rinsing

The washing experiments were based on the international standard “ISO 105-C06: 1994 (procedure A1S) for color fastness to domestic and commercial laundering (ISO, 1994)”. The tests were performed with a lab washing machine matching this standard (Washtex-P Roaches; motor speed  $40 \pm 2$  rpm, steel vessels ( $75 \pm 5$  mm diameter,  $125 \pm 10$  mm height,  $550 \pm 50$  mL)) and a washing solution of  $4 \pm 0.01$  g L<sup>-1</sup> ECE Color Fastness Test Detergent 77 in distilled water (pH 10.6). The main components of this detergent are LAS (8%), sodium triphosphate (43.8%), sodium and magnesium silicate (9.4%), and sodium sulfate (21%). The chloride content of the washing solution was measured by potentiometric titration to be 8.7 mg L<sup>-1</sup>. To meet the requirements of this study, i.e. the analysis of silver leaching from fabric, the standard method was adapted at some points: First, the ten steel balls normally used to simulate friction during washing were replaced by polyethylene balls ( $\varnothing = 8$  mm). This was necessary to avoid any leaching of silver from the steel balls into the washing solution, as this would have elevated the background signal of silver. The same applied for the vessels made of steel that are normally in direct contact to the washing solution and textile. To avoid this, washing experiments were performed in polyethylene-HD-bottles of 300 mL volume that were introduced inside the normal steel vessels. To allow heat transfer between the heating bath and the washing solution inside the polyethylene-HD-bottles, 150 mL of water were filled in the space between steel vessel and polyethylene-HD-bottle. Between the washing experiments the used polyethylene balls were washed with 2 M HNO<sub>3</sub> during 1 h. Second, the volume of washing solution was reduced from 150 to 120 mL, because the polyethylene-HD-bottles were smaller than the original steel vessels. Third, after each washing cycle, two rinsing cycles with  $20 \pm 0.03$  mL tap water (St. Galler Stadtwerke, water hardness 16°fH/9°dH) were carried out in order to better resemble washing events carried out with commercial washing machines. Fourth, the washing solution was preheated to 40 °C to guarantee that the textile samples were washed from the beginning at 40 °C.

During each washing event, one sample of each textile was treated as follows: first,  $120 \pm 0.15$  mL of washing solution and ten polyethylene balls were added into a polyethylene-HD-bottle and preheated up to 40 °C in the washing machine for  $45 \pm 5$  min. After preheating, a rectangular textile sample of  $8 \pm 0.05$  g was added into the washing solution and washed for 30 min at  $40 \pm 2$  °C. The fabric:water ratio was adapted from the ISO norm and slightly increased while guaranteeing complete wetting of the samples. Then the sample was removed from the washing solution and wrung out into the polyethylene-HD-bottle. Still wet, the sample was then placed into a new polyethylene-HD-bottle filled with  $20 \pm 0.03$  mL of tap water and rinsed for 5 min by running the washing machine. The sample was wrung out and the rinsing procedure repeated with a new bottle and fresh rinsing water. The two collected rinsing solutions were combined. Finally, the sample was

**Table 1**Description of the textiles analyzed in this study and their total Ag content. bdl: below detection limit of 1.25 mg kg<sup>-1</sup>.

Sample number	Product type <sup>a</sup>	Country of origin	Fiber composition	Product labeling concerning Ag particles	Additional information	Total Ag content (mg kg <sup>-1</sup> )
1	Socks	Germany	41% polypropylene, 31% polyamide with Ag, 18% cotton, 10% wool	“Silver integrated” in polyamide fiber	–	18 ± 2
2	Socks	Switzerland	100% polypropylene	“Silver”	–	1.5 ± 0.9
3	Socks	Japan	100% cotton	“Extra thin silver wires”	Silver wires are visible	761 ± 31
4	T-Shirt	Switzerland	83% polyester, 17% wool	“Silver”	Contains Ag nanoparticles	183 ± 10
5	T-Shirt	Switzerland	100% polyester	“Silver ions”	–	45 ± 8.0
6	Socks	UK	80% cotton, 20% elastic yarn	“Nanosize silver particles are incorporated into cotton fibers”	–	2925 ± 19
7	Trousers	Germany	93% polyamide, 7% elastane	–	Contains AgCl nanoparticles	41 ± 0.4
8	Socks	Germany	75% cotton, 23% polyamide, 2% elastane	“Sanitized – silver freshness”	–	bdl

<sup>a</sup> The product names can be obtained upon request by contacting the corresponding author.

dried horizontally without being stretched under controlled conditions (23 °C, 50% humidity).

### 2.3. Fractionation of released Ag

For size fractionation, three replicates of 10 mL were taken from each, the washing and rinsing solution. Each sample was then filtered through a 0.45 µm cellulose-nitrate filter (Sartorius Stedim Biotech). The resulting filters including the washing or rinsing residue (for textile 7 only 2 filters) were digested by the microwave digestion method described in detail under “Ag Analysis by ICP-OES and XRF”. For determining the particulate fraction <0.45 µm, triplicates of 2.5 mL of the washing or rinsing filtrate were transferred to a plastic tube and 1.5 mL distilled water and 1 mL HNO<sub>3</sub> (65%, Fluka) were added. To analyze the dissolved fraction (<30 kDa) of Ag in the washing solution, three replicates of 4 mL of the filtrate (<0.45 µm) were transferred to centrifugal filters <30 kDa (Vivaspin 6, 30'000 MWCO, polyether sulfone). These were centrifuged at 13 500 rpm for 10 min (Hermle Z300) and 2.5 mL of each centrifugate were mixed with 1.5 mL distilled water and 1 mL HNO<sub>3</sub> (65%, Fluka).

### 2.4. Ag analysis by ICP-OES and XRF

In order to be able to determine the silver content of the fabrics or the filters, a microwave acid digestion had to be carried out beforehand. For the fabrics, three replicates of 0.2 ± 0.04 g from each textile were used. The textiles as well as the filters were digested with 3.5 mL HNO<sub>3</sub> (65%, Fluka) and 1 mL H<sub>2</sub>O<sub>2</sub> (30%, Sigma-Aldrich) in a microwave digestion system (MLS 1200 MEGA digestion system, EM-45/A Exhaust Module, Program 2). The digests were filled up to 10 mL with nanopure water (Millipore, 17–18 MΩ cm).

The silver content of the digests and the filtrates was quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES Perkin-Elmer OPTIMA 3000). For the calibration a silver standard solution (silver nitrate in 5 M HNO<sub>3</sub>, 1000 mg L<sup>-1</sup>, Merck) was used. The limit of detection for the ICP-OES was taken as 0.005 mg L<sup>-1</sup>. Blanks for filter digests were 0.003 mg L<sup>-1</sup>, for the filtrates 0.01 mg L<sup>-1</sup> and for digestion of textile samples 0.15 mg kg<sup>-1</sup>.

In order to assess the intrinsic variability in silver contents between pieces of the same textile, three different specimen of textile 1 were digested as described above. The average Ag content was 18 ± 2 mg kg<sup>-1</sup>, indicating that in this case the variations are low.

In addition to ICP-OES, the total Ag content of textile 4 was analyzed by X-ray fluorescence spectrometry (SPECTRO X-LAB 2000,

Spectro, Germany) (in triplicate) because the acid digestion of this textile was found to be incomplete. Quartz crucibles with 1.5 g ± 0.04 g of the textiles were added into a programmable muffle furnace (Nabertherm Tony Güller) at 600 °C for 1:20 min. The incinerated textile samples were pulverized through a zirconium oxide bowl inside a zirconium oxide crucible placed in a lab mill (Retsch MM 200) at 31 s<sup>-1</sup> for 1 min. The remaining powder was then transferred to a plastic bottle and filled up to 4 g with cellulose from spruce (Fluka) in order to have sufficient material to form a pellet. To get a uniform mixture the sample was milled again, together with 0.9 ± 0.02 g of wax (Licowax C micropowder PM, Fluxana HD Elektronis) and two polyethylene balls (24 s<sup>-1</sup> for 1 min) and compacted into pellets. The elemental composition was then analyzed with a Spectro X-Lab 2000 and the results corrected for the dilution of the mass by cellulose.

### 2.5. Electron microscopy

Without further treatment the washing solution samples were applied onto carbon coated copper grids. The liquid was soaked immediately through the grid to minimize aggregation and precipitation artifacts. The grids were then dried and investigated using TSEM and STEM, the elemental composition was determined using EDX (Energy Dispersive X-ray Spectroscopy). TSEM was performed on a FEI Nova NanoSEM 230 with SE detector, STEM on a FEI Technai F30 with a HAADF detector.

### 2.6. Antibacterial activity of textiles

The antibacterial activity of the fabrics was tested according to the ISO 20743:2007 standard method (ISO, 2007) using the Gram-negative bacterium *Klebsiella pneumoniae* (ATCC 4352). The samples were inoculated with 50 µL of inoculum (1.6 × 10<sup>5</sup> cfu mL<sup>-1</sup>) per 100 mg of fabric. The inoculum contained nutrient broth diluted to 0.43 g L<sup>-1</sup> NaCl, 0.15 g L<sup>-1</sup> beef extract, 0.25 g L<sup>-1</sup> peptone, and 0.1% Tween 20 for improved wetting. The incubation was performed at 37 °C for 18 h and activity values (reduction of colony forming units, cfu) were calculated as log<sub>10</sub>(cfu control 18 h) – log<sub>10</sub>(cfu sample 18 h).

## 3. Results

### 3.1. Ag content

The initial silver content of the textiles was between 1.5 and 2925 mg Ag/kg textile (Table 1). Textile 8 did not contain any detectable silver (although the label stated that it contained Ag)

and was thus not further used for the release experiments. The range of Ag concentrations found here is within the range observed in previous studies. Geranio et al. (2009) found between 8 and 2660 mg kg<sup>-1</sup> in nanotextiles, and 21600 mg kg<sup>-1</sup> in a silver coated textile. Benn and Westerhoff (2008) reported Ag concentrations of 0.9 to 1358 mg kg<sup>-1</sup> (and one textile not containing any Ag), Benn et al. (2010) found silver contents of 30–270 mg kg<sup>-1</sup>, and Kulthong et al. (2010) from 0.99 to 15.1 mg kg<sup>-1</sup> (and three textiles without detectable Ag). The range from 1 to more than 1000 mg kg<sup>-1</sup> can therefore be considered normal for silver-containing textiles on the market today.

### 3.2. Ag release

Four out of seven Ag textiles leached a detectable amount of Ag (Fig. 1). Neither the washing nor rinsing solutions of textiles 1–3 contained any silver (i.e. below the ICP-OES detection limit of 0.005 mg L<sup>-1</sup>). In contrast, textiles 4–7 all leached detectable amounts of Ag. The textiles released between 0.32 and 38.5 mg L<sup>-1</sup> into the washing solution (4.5–575 mg kg<sup>-1</sup>) and between 0.36 and 22.7 mg L<sup>-1</sup> into the rinsing solution (1.8–113 mg kg<sup>-1</sup>). Textile 6 leached about 20-times more Ag than the other textiles, which can be explained by the high total Ag amount in the fabric.

The fraction of Ag released in one washing/rinsing cycle compared to the initial amount was 20%, 14.8%, 23.5% and 17.6% for textiles 4–7, respectively. For these samples, Fig. 2 shows the released Ag size fractions in %. Three out of four samples released the largest fraction (up to about 80%) as coarse, particulate material above 0.45 μm. In contrast, one sample (textile 6) released most Ag as material smaller than 0.45 μm (58%). Dissolved silver <30 kDa was detected in the washing solutions of two samples, textiles 6 and 7, at fractions of 8% and 19%, respectively. The ratio of Ag released into washing or rinsing solution varied between the textiles. Textiles 4,5 and 6 released more Ag into the washing solution whereas the opposite was observed for textile 7.

### 3.3. Particle characterization

The washing solutions in which Ag was detected by ICP-OES were additionally investigated using electron microscopy and EDX. In all samples particles in the nano and/or micrometer-range were detected, with silver signals present in the corre-

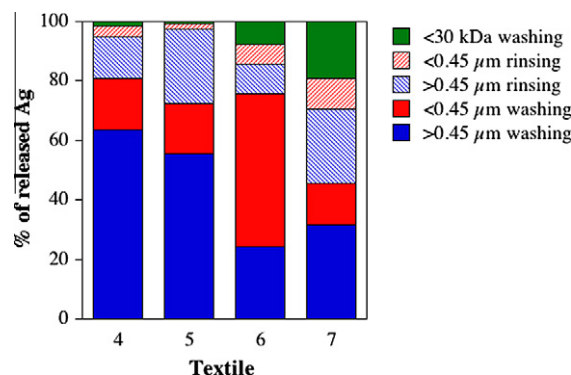


Fig. 2. Relative distribution of the Ag size fractions of textiles 4–7 released during washing and rinsing.

sponding EDX spectra. Fig. 3 shows an electron micrograph with EDX spectra of particles detected in the washing solution of sample 4. A Ti-containing particle with a few 100 nm in diameter was clearly covered with Ag-containing nanoparticles (Fig. 3). Area 3 shows the EDX spectrum of the large particle, indicating that it consists mainly of Ti and Si. The EDX spectra of the small particles in area 1 and 2 show that these particles contain Ag and Cl, indicating that they consist likely of AgCl. The Cu signal in all the spectra originates from the used Cu-grid. Nanocomposites consisting of AgCl and Ti have been described in the literature (Kulthong et al., 2010) and were also used as “nanosilver” for adding antimicrobial activity to cotton (Wasif and Laga, 2009). It is therefore likely that such a composite was used as finishing in textile 4. Whereas the Ti/Si matrix is not in the nanorange, the single AgCl particles clearly are below 100 nm. The fractionation of the Ag in the washwater of this textile showed that only 21% of the Ag was able to pass a 450 nm filter, in agreement with the particles observed by STEM that were on the order of a few 100 nm.

In the washing solution of textile 5 (Fig. 4, top) particles in the range of several 100 nm up to the μm range were observed. These particles were irregularly shaped and the EDX spectra showed that they consist of pure AgCl. The most important fraction in the washing solution was the particulate fraction above 450 nm, which is in agreement with the STEM analysis. In addition the washing solution of textile 5 also contained many nanoparticles of 10–30 nm diameter (Fig. 4, bottom). The EDX spectra of these particles showed the presence of Ag and sulfur. The sulfur signal was not observed in the background and was never found in any other washing sample in significant amounts. It is therefore likely that these nanoparticles consist of Ag-sulfide.

Textile 6 released agglomerates with diameter of several hundred nm. The agglomerates consisted of primary particles well below 100 nm (Fig. 5, top) that contained Ag as shown in the EDX spectrum, indicating the presence of metallic Ag. This textile sample released the 58% of Ag as particles <450 nm into the washwater, however, the particles were strongly agglomerated and single dispersed nanoparticles were not detected. This textile therefore represents the only one that released metallic Ag nanoparticles.

The washwater of textile 7 contained agglomerates of Ag-containing nanoparticles (Fig. 5, bottom). This agrees with the fractionation of the released Ag, which showed that only about 25% of the released Ag was in the fraction smaller than 450 nm. The agglomerates were therefore retained by the filter. The EDX spectrum showed the presence of Ag and Cl, and also traces of Al. This textile contained AgCl according to the manufacturer, which was confirmed by the presence of AgCl in the washwater.

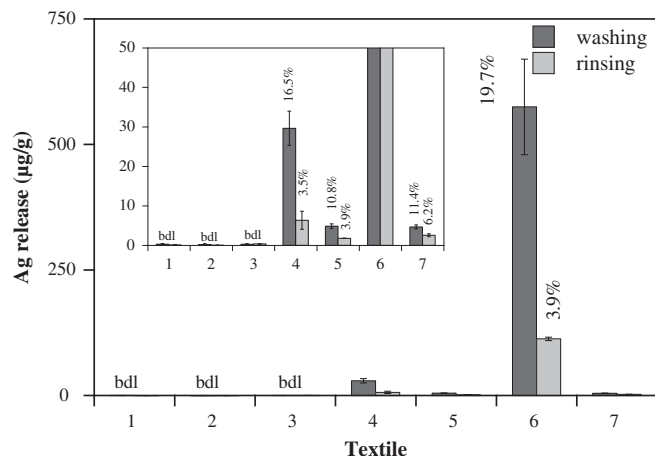


Fig. 1. Amount of silver released from the seven investigated textiles during washing and rinsing. The inset shows an expanded view of the low concentration range. The percentage of total Ag released is shown on top of the columns. bdl: below detection limit.



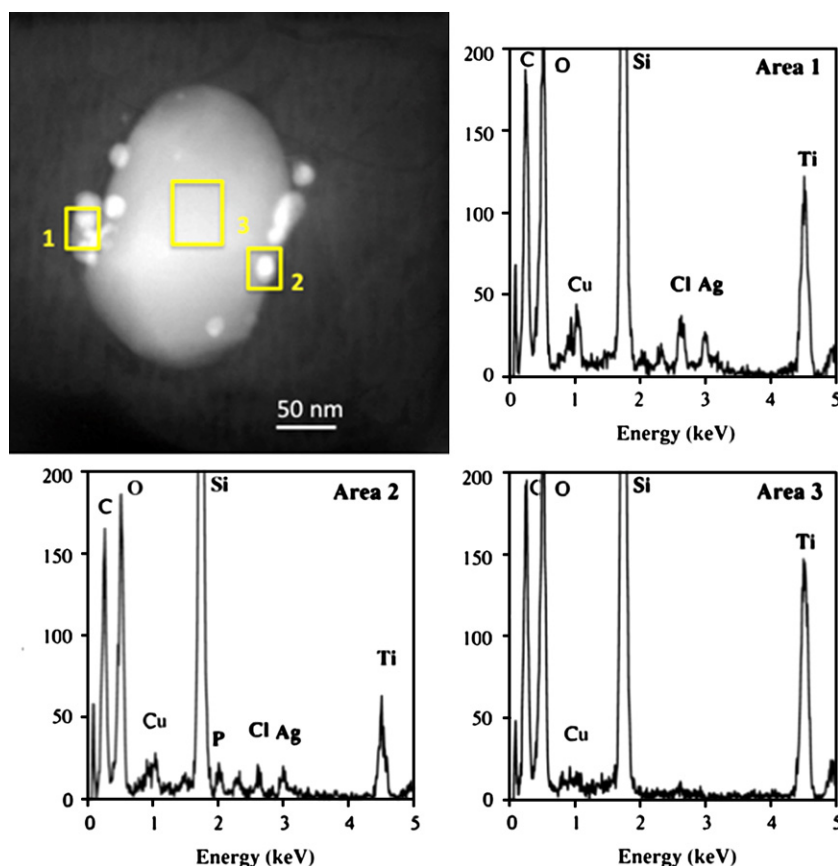


Fig. 3. STEM of Si/Ti containing particle dotted with Ag/Cl-containing nanoparticles in washing solution of textile 4 including EDX analysis of three spots.

#### 3.4. Antimicrobial activity of raw and washed textiles

The effect of the textiles on the growth of the Gram- bacterium *Klebsiella pneumoniae* is shown in Fig. 6. Three of the textiles tested did not have any antibacterial activity (textiles 2, 3 and 8). Textile 8 – which did not contain any measurable Ag – did therefore also not contain any other effective biocide. Of the two other textiles that did not show any effect, textile 2 contained the lowest Ag amount of all textiles ( $1.5 \text{ mg kg}^{-1}$ ) and textile 3 is the one with the silver wires, which obviously had no antibacterial effect despite a very high Ag content of more than  $700 \text{ mg kg}^{-1}$ . Textile 5 showed antibacterial activity (3-log reduction) before washing, but not after washing. We note that this cannot be due to complete loss of silver, as this textile only lost about 15% of its silver content. Textile 1 also had a 3-log reduction in bacterial number before and after washing. A 3-log reduction reflects a biocide concentration equal to the minimal inhibitory concentration but lower than the bactericidal dosage (Egger et al., 2009). Three of the textiles (textiles 4, 6 and 7) exhibited a more than 5-log reduction in bacterial number (complete killing of the inoculum) before and after washing.

#### 4. Discussion

The textile samples used in this paper were commercially available and were either labeled to contain Ag or their manufacturers provided information about their silver content. As found in several other studies, not all commercial products contain what is promised on their packages (Benn and Westerhoff, 2008; Kulthong et al., 2010). In this study, one textile contained no Ag at all in the fabric and another one contained only very low amounts. Only one label explicitly stated nano-Ag (Textile 6), although two more

products were also based on nanoparticles according to information obtained directly from the manufacturer (Textiles 4 and 7). Many so-called “conventional” silver forms are indeed based on nanosilver but labeled in a different way (Nowack et al., 2011). Based on manufacturer labeling alone it is impossible to know which textiles contain what form of silver or if a given textile contains silver at all.

The three textiles that contained silver in the form of nanoparticles (according to the manufacturers) all exhibited a very high antimicrobial activity and clearly outperformed all the other textiles. The use of nanoparticles is therefore coupled to a superior functionality. Many forms of silver can be applied to textiles, but not all show antibacterial activity, which in fact is related to the respective release rates of  $\text{Ag}^+$ . This is especially apparent for the textile with the silver wire, which had no antimicrobial activity, although its Ag content was much higher than that of two of the nanotextiles. Presumably, the silver ion releasing surface was too small to attain potent concentrations, indicating again the much better functionality of nanobased silver-formulations.

The release of Ag from the textiles depends on the one hand on the form and amount of Ag in the textiles but also on the medium that is used for washing. Previous studies have used distilled water (Benn and Westerhoff, 2008), tap water (Benn et al., 2010), and washing solution (Geranio et al., 2009). The main difference caused by different media is clearly the amount of Ag that is released in ionic form. Whereas Benn and Westerhoff (2008) reported up to 86% of the Ag released as dissolved  $\text{Ag}^+$ , the amount found in this work and by Geranio et al. (2009) in washing solution are much lower and the particulate fraction was much more important. A common washing solution has a high pH (10 and above) and contains a variety of other components that may chemically interact with Ag, e.g. chloride ions. For an assessment reflecting the

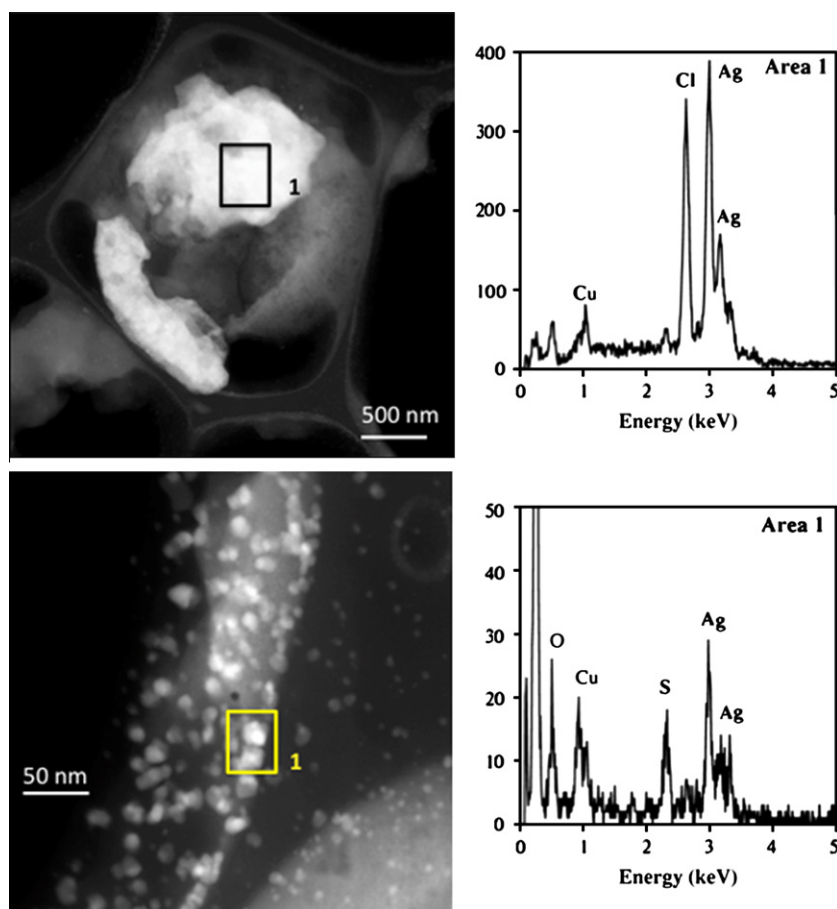


Fig. 4. STEM of different Ag-containing particles released from textile 5 into the washing solution with the EDX-spectra of the particles.

washing of textiles in households, distilled water is surely not the suitable medium. It is also important to note that the detergent used in our study did not contain any bleaching agents, which have been shown to rapidly oxidize nano-Ag and result in a fast release of dissolved  $\text{Ag}^+$  (Geranio et al., 2009). Tap water as used by Benn et al. (2010) and in this study is a suitable extractant because of which the rinsing step during washing also uses tap water.

Of the four textiles that released measurable Ag, three released AgCl particles (Textiles 4, 5 and 7) and only one released metallic Ag nanoparticles (Textile 6). The released AgCl was found in three very different morphological forms: nanocomposites of Ti/Si and nanoparticles, large AgCl particles for a textile labeled to contain “silver ions” and agglomerates of AgCl nanoparticles from a textile where we had the information that it contained AgCl particles. Speciation calculations show that the  $8.7 \text{ mg L}^{-1}$  chloride in the washing solution would be able to precipitate a majority of the total Ag released from textiles 4 and 6 (94 and 70%) if released in ionic form. Secondary formation of AgCl is therefore a possibility and we cannot rule out the possibility that Ag was released as dissolved  $\text{Ag}^+$  that precipitated in the washing solution as AgCl.

In the washing solution of one sample (textile 5) Ag-sulfide containing nanoparticles were detected.  $\text{Ag}_2\text{S}$  is the prevalent silver species found in wastewater and is the result of rapid transformation of all forms of silver including nano-Ag (Kim et al., 2010; Kaegi et al., 2011). Because this Ag-sulfide species was almost never found in any of the other samples, it is unlikely that it was formed in the washing solution. The washing powder used contains 21% of  $\text{Na}_2\text{SO}_4$ , so at least there would be enough sulfur around that could be reduced, although this is rather unlikely given that all

experiments were conducted under oxygenated conditions. This textile also did not retain its antimicrobial activity after washing, although more than 85% of the silver was still present. If the released particles are representative of the particles in or on the textile, the low activity could be explained by low bioavailability of  $\text{Ag}_2\text{S}$  or of large AgCl particles, which have a much slower dissolution rate than small nanoparticles of AgCl.

Only agglomerated nanoparticles were found in the washing solutions during the microscopic investigations except for the silver sulfide particles released from textile 5, showing that even in washing solution with its high concentration of detergents that are known to stabilize Ag-NPs, aggregation is an important process.

Our results show that the restriction of the nano-Ag discussion to metallic nano-Ag may miss an important aspect of nano-Ag use and release: of the eight studied silver textiles, only one released metallic nano-Ag. Two of them instead released nano-AgCl and one nanosilver sulfide. Additionally from one textile larger AgCl particles were released. Because washwater is directly released into wastewater, the further fate of these different forms of Ag during treatment will determine the possible release of nano-Ag to the environment (Nowack, 2010). The research on the behavior and effects of nano-Ag should therefore not focus on metallic nano-Ag alone but should also include studies on nano-AgCl and nano-Ag-sulfides.

Ag-sulfides have a very low bioavailability (Blaser et al., 2008) whereas AgCl and nano-Ag both release silver ions that are known to have antimicrobial activity (Marambio-Jones and Hoek, 2010). In contrast to AgCl, which can release  $\text{Ag}^+$  ions by dissolution, nano-Ag particles first need to be oxidized before  $\text{Ag}^+$  can be released

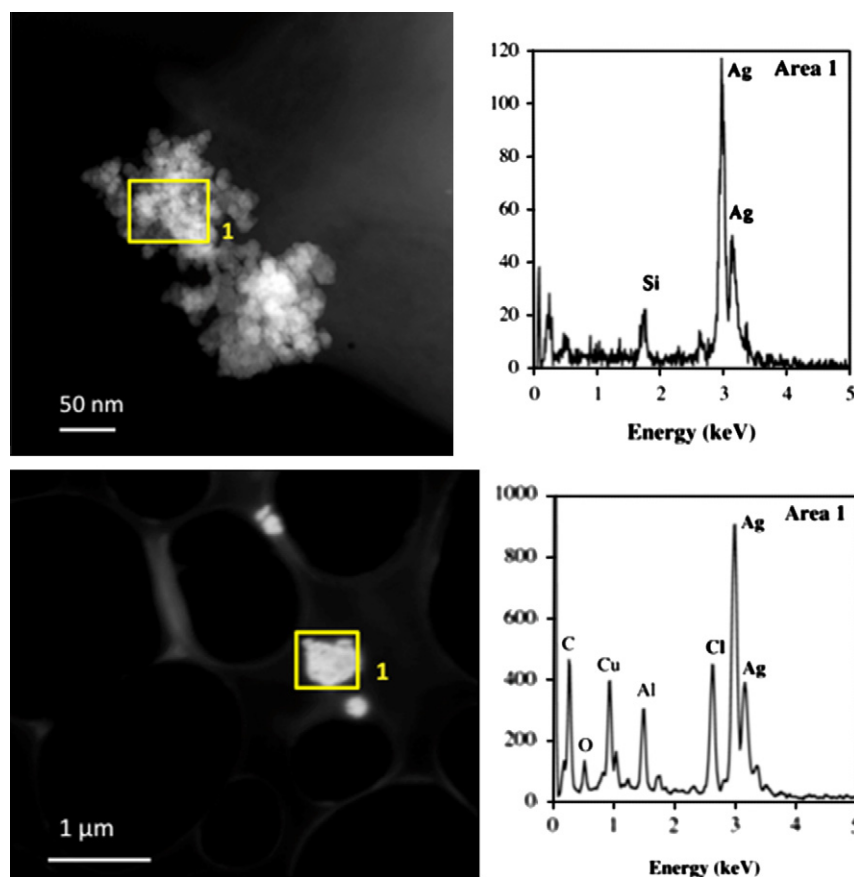


Fig. 5. Electron microscopy of released Ag-containing particles in the washing solution of textile 6 (top) and textile 7 (bottom) with the EDX-spectra of the particles.

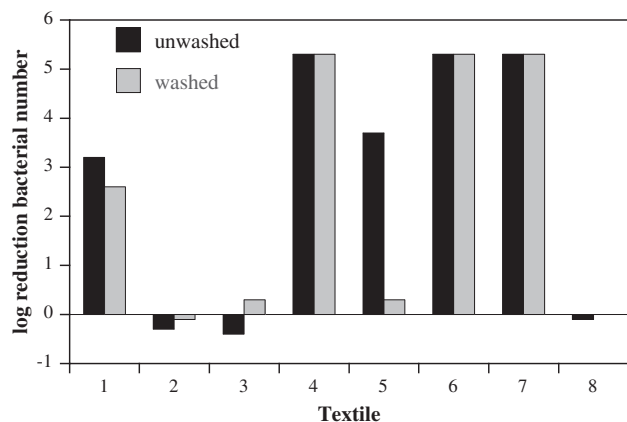


Fig. 6. Antibacterial performance of the investigated textiles: Reduction in bacterial numbers (colony forming units, cfu) on the textiles before and after one washing/rinsing cycle given as  $\log_{10}(\text{cfu control } 18 \text{ h}) - \log_{10}(\text{cfu sample } 18 \text{ h})$ .

into solution. The knowledge on the actually released form of silver is therefore crucial for predicting the further environmental effects of silver.

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