Silver speciation and release in commercial antimicrobial textiles as influenced by washing

Enzo Lombi[a]*, Erica Donner[a,b], Kirk G. Scheckel[c], Ryo Sekine[a], Christiane Lorenz[d,e], Natalie Von Goetz[e] and Bernd Nowack[d]

[a] Centre for Environmental Risk Assessment and Remediation, University of South Australia, Building X, Mawson Lakes Campus, South Australia 5095, Australia

[b] CRC CARE, PO Box 486, Salisbury, South Australia 5106, Australia.

[c] National Risk Management Research Laboratory, US Environmental Protection Agency, 5995 Centre Hill Avenue, Cincinnati, Ohio 45224, USA

[d] Technology and Society Laboratory, Empa – Swiss Federal Laboratories for Materials Science and Technology. Lerchenfeldstrasse 5, CH – 9014 St. Gallen, Switzerland

[e] Institute of Chemical and Bioengineering, ETH Zurich, Vladimir-Prelog-Weg 10, 8093 Zurich, Switzerland

*Corresponding Author: enzo.lombi@unisa.edu.au Tel +61 8 8302 6267

Abstract

The use of nanoscale Ag in textiles is one the most often mentioned uses of nano-Ag. It has previously been shown that significant amounts of the Ag in the textiles are released upon washing. However, the form of Ag present in the textiles remains largely unknown as product labelling is insufficient. The aim of this study was therefore to investigate the solid phase speciation of Ag in original and washed silver textiles using XANES. The original Ag speciation in the textiles was found to vary greatly between different materials with Ag(0), AgCl, Ag_2S, Ag-phosphate, ionic Ag and other species identified. Furthermore, within the same textile a number of different species were found to coexist. This is likely due to a combination of factors such as the synthesis processes at industrial scale and the possible reaction of Ag with atmospheric gases. Washing with two different detergents resulted in marked changes in Ag-speciation. For some textiles the two detergents induced similar transformation, in other textiles they resulted in very different Ag species. This study demonstrates that in functional Ag textiles a variety of different Ag species coexist before and after washing. These results have important implications for the risk assessment of Ag textiles because they show that the metallic Ag is only one of the many silver species that need to be considered.

Introduction

The functionalization of textiles such as cotton, wool and synthetic materials with Ag in order to impart antimicrobial properties to commercial products is an area of intense research and commercial growth (Radetic, 2013). In particular, the use of Ag nanoparticles (Ag-NPs) has been advocated for several reasons including the possibility to avoid discoloration, which occurs when ionic Ag is used (Vigneshwaran et al., 2007), negligible impact on fabric breathability and handling (Wong YWH, 2006) and an overall smaller environmental impact (Windler et al., 2013). Due to the increased production of Ag functionalized textiles, these materials are one of the major sources of Ag-NPs release to the environment (Arvidsson et al., 2011, Gottschalk et al., 2009, MuellerNowack, 2008).

Only a few studies so far have investigated the speciation and release of Ag from Ag-functionalized commercial products. The amount of Ag released, as well as the percentage of total Ag, varies considerably between different functional textiles. For instance, Benn and Westerhoff (2008) reported releases varying between <1% to almost 100% from six commercially available sock fabrics. Similarly, Geranio et al. (2009) and Lorenz et al. (Lorenz et al., 2012) found that Ag released from Ag-functionalised textiles ranged from undetectable to about 45%. The variability in the results within each study is likely due to both the nature of the textile itself and the form of Ag present in the materials. In fact, Geranio et al. (2009) pointed out that mechanical stress is an important factor as about 10% of the textile weight can be lost during the lifetime of a product due to washing (Koehler et al., 2008) and it is reasonable to think that this loss may differ between textiles. Furthermore, it is also reasonable to assume that the speciation of Ag present in the textiles represents a critical parameter controlling Ag release. In the last decade the scientific literature and the number of patents covering methodologies for functionalizing textile materials using Ag, and Ag-NPs in particular, has increased dramatically (Radetic, 2013). For instance, Ag-NPs can be introduced by dipping the materials in suspensions of Ag-NPs, or they can be synthesized *in situ* by immersing the

textiles in solutions of Ag salts and adding a reducing agent (Emam et al., 2013) and references therein). Another standard approach is to incorporate the Ag-NPs into the fiber matrix, therefore reducing release to a great extent (Geranio et al., 2009). These different methodologies most likely result in a number of different Ag species potentially being present in textiles. However, the literature investigating Ag speciation in textiles mainly focuses on laboratory materials and the information on commercial textiles is extremely scant. Impellitteri et al. (2009) used X-ray Absorption Near Edge Structure (XANES) spectroscopy to investigate the speciation of Ag in one antimicrobial sock textile before and after washing and found that Ag was present in a metallic form prior to washing but only accounted for 50% of the remaining Ag after washing with an hypochlorite/detergent solution due to partial conversion to AgCl. Based on results from washing studies, other authors have suggested that both ionic Ag and Ag_2S-NPs may also be present in commercial textiles (Geranio et al., 2009, Lorenz et al., 2012).

Reliable information regarding Ag speciation and release during washing is essential knowledge required to decrease the uncertainties related to environmental exposure assessment of nanomaterials. Models that are being developed to predict environmental concentrations of NPs (Gottschalk et al., 2010, Gottschalk et al., 2013) rely on information regarding input parameters as well as release rates, which are controlled by various factors including speciation. In this study, we aimed to significantly expand the knowledge base regarding Ag speciation in commercial textiles by undertaking XANES analysis of 5 commercial textile products. Clearly this knowledge is also relevant in the context of consumer information as manufacturers often provide limited information on their labels and these may not necessarily be correct. Furthermore, the release of Ag from textiles during two different washing procedures was investigated. Finally, the speciation of the washed textiles was also investigated as this provides information regarding the potential for further release from successive washings.

Materials and Methods

Materials

Five commercially available and Ag-functionalized textile samples, which had previously been investigated for Ag release by Lorenz et al. (2012) were selected for this study (Table 1). While the Lorenz et al. (2012) study focussed on the forms of Ag released during washing, this work focuses on the influence of different washing procedures on Ag release and on the speciation of Ag in the fabric pre- and post-washing. In order to facilitate comparison between these two studies, we have maintained the same sample numbering as that used by Lorenz et al. (2012). The total Ag concentration in the textiles ranged from 18 to 2,925 mg/kg and the materials were comprised of varying proportions of natural fibres, with the exception of two textiles which were completely synthetic. As noted in Table 1, the information provided on the product labels was often generic and Ag-NPs were only mentioned for product 6.

Washing procedure

Two textile washing procedures were utilised in this study. The first one, referred to here as LW (laboratory washing) was described in detail in Lorenz et al. (2012) and was based on the 'ISO 105-IS: 1994 (procedure A1S) for colour fastness to domestic and commercial laundering' (ISO, 1994) using the ECE-2 Colour fastness test detergent. In the second procedure, referred to as MW (machine washing), fabric pieces of 1.5-2.5 g were added to a regular washing cycle to simulate a washing event carried out in an average household by consumers. A 60 min program at 40 °C and 1200 rpm tumbling was applied (washing machine model: V-Zug AG, Unimatic F, type WA-UF) with Persil Megaperls as washing powder (see http://mymsds.henkel.com/ mymsds/DS.do?bu=UW&internet=true for information on composition). Fabric pieces of all five investigated textile samples were washed once, together with 4.5 kg of medium soiled clothes. The

washing experiment was repeated three times (each time including fabric samples of all five textiles). The samples were dried at room temperature and then digested with 3.5 mL of HNO_3 (65%) and 1 mL of H_2O_2 (30%) in a High Performance Microwave (MLS 1200 MEGA digestion system, EM-45/A Echaust Module). The Ag content was quantified by ICP-OES (ICP OES Perkin Elmer OPTIMA 3000).

In order to assess the transformation of species of Ag that are frequently found as a result of washing procedures (Lorenz et al., 2012), Ag-NPs, AgCl-NPs and a zeolite on which Ag was sorbed (as representative of ionic Ag) were subjected to washing procedures similar to those used for the textiles. The Ag-NPs were synthesised by reduction of 1mM silver nitrate ($AgNO_3$) with 2mM sodium borohydride ($NaBH_4$) in the presence of 200 mg/L polyvinylpyrrolidone (PVP). PVP coated AgCl-NPs were prepared according to the method by Kim et al. (2010) in ethylene glycol and were resuspended in water after centrifugation. The NPs were characterised by dynamic light scattering (DLS; NICOMP 380 ZLS, Particle Sizing Systems, FL, USA) and scanning electron microscopy (SEM; Quanta 450 FEG ESEM, FEI Company, OR, USA). The Ag-NPs were polydisperse with the smallest size number-weighted mode at 6.2 ± 0.9 nm, while AgCl-NPs were bimodal with the smaller mode at 79.6 ± 12.3 nm (> 92%, number weighted). SEM images of the NPs are reported in Figure S1 (Supplementary Material). These materials were dispersed in 10 ml of washing liquid at 3.3 mg/L (pre-heated to 40°C), containing 4 g/L of the washing powders described above. The concentration of 3.3 mg/L was derived from an assumed loading of Ag in textiles at 50 mg/kg, which is within the range found and reported by Lorenz et al. (2012) The bottles were then placed on an end-over-end shaker for 30 minutes at 40°C. Subsequently, 9 mL of the solution was frozen immediately and freeze-dried, which also pre-concentrated the Ag, for XAS analysis.

Silver speciation in textiles pre- and post-washing

Silver speciation was assessed by XANES. This technique was chosen as it provides the following advantages: it provides information regarding the overall Ag speciation; it is not limited to the analysis of the textile surface (in contrast to X-ray Photoelectron Spectroscopy, XPS); it does not depend on species crystallinity (in contrast to X-ray Diffraction, XRD); it is not limited to the detection of particles/NPs enriched in Ag (in contrast to electron microscopy). However, it should also be pointed out that definite attribution of Ag to a particular species is not always possible due to the similarity in spectral features of some of the Ag species of interest [especially Ag(I) bound to groups other than thiols].

XANES analysis was performed on all the textile samples pre- and post-washing and a number of Ag standards. The latter include: the pre- and post-washing samples of Ag-NPs, AgCl-NPs and Ag sorbed on zeolite described above; Ag carbonate (Ag_2CO_3), Ag nitrate ($AgNO_3$), Ag phosphate (Ag_3PO_4), Ag oxide (Ag_2O), Ag sulphate (Ag_2SO_4), Ag sulphide nanoparticles (Ag_2S-NPs synthesized by reaction of $AgNO_3$ with elemental sulfur in the presence of PVP) and Ag complexed by cysteine and histidine. These standards were diluted in cellulose to approximately 1,000 mg Ag/kg prior to analysis. The textile samples were folded several times and mounted, using polyimide tape, on a sample holder for analysis.

Silver K-edge XANES of the textiles were collected at the Materials Research Collaborative Access Team (MRCAT) beamline 10-ID, Sector 10 located at the Advanced Photon Source (APS), Argonne National Laboratory (ANL), Argonne, IL. (Segre et al., 2000). The electron storage ring was operating at 7 GeV in top-up mode. A liquid N_2 cooled double crystal Si(111) monochromator was used to select incident photon energies and a platinum-coated mirror was used for harmonic rejection. The monochromator was calibrated by assigning the first derivative inflection point of the absorption K-edge of Ag metal at 25,514 eV and a Ag metal foil spectrum was collected congruently with each sample scan. Powdered samples (not the textile samples) and standards were pressed into pellets and three XANES scans were collected for each sample in transmission and fluorescence mode using

7

a 13 elements Ge detector. Pre- and post-washing samples of Ag-NPs, AgCl-NPs and Ag sorbed on zeolite were collected at the XAS beamline at the Australian synchrotron using a similar setup as described above and a 100 element Ge detector. The same standards were collected independently at the two beamlines. Principal component analysis (PCA) of the normalised sample spectra was used to estimate the likely number of species contained in the samples, whilst target transformation (TT) was used to identify relevant standards for linear combination fitting (LCF) of the sample spectra (ER, 1991). PCA and TT were performed using SixPack (Webb, 2005) while data normalisation and LCF were performed using Athena (RavelNewville, 2005) Fitting range was -30 to +100 eV relative to the Ag K-edge. For each sample, the combination of standards with the lowest residual parameter was chosen as the most likely set of components.

Results

Silver speciation in the unwashed textiles

The Ag K-edge spectra of the standards used in the LCF of the textile sample spectra are reported in Figure S2. The spectrum of Ag-NPs is characterised by significant features with a white line position 15 eV above the absorption edge and two other prominent peaks approximately 36 and 71 eV above the absorption edge. These are well in line with the peak positions reported for reference Ag foils (EXAFS Materials, Danville, USA). The spectrum of AgCl-NPs is also readily distinguishable by the presence of a sharp white line and a second, less intense peak about 16 eV above the white line. A sharp white line, but not the second marked peak, is also evident in the spectra of Ag nitrate, sulphate and Ag sorbed on zeolite. These spectra are in fact similar to each other and this should be considered when interpreting the LCF results. Similarly, the spectra of Ag_2S and Ag bound to cysteine are very similar and this should also be kept in mind when interpreting the LCF results.

By comparing the XANES spectra from the unwashed textiles (Figure 1 and S3) with those from the standards reported in Figure S2, it is immediately evident that Ag is present in the textiles as a mixture of different species/forms. Linear combination fitting indicates that Ag in particulate (metallic) forms dominates the speciation in T4, T5 and T7 (Table 2). In fact, the spectra for T4 and T5 both show the 3 main peaks identified previously for Ag-NPs. However, these spectral features are less marked than in the case of the Ag-NPs standards as a result of the presence of additional Ag species and in particular Ag_2S. In the case of T7, the presence of Ag-NPs is evidenced by the spectral feature which corresponds to the peak observed at 36 eV above the absorption edge for the Ag-NPs standard. Also, the peak observed in the AgCl-NPs standard at 16 eV above the white line is visible in T7. The presence of AgCl-NPs in T7 and of Ag-NPs in T4 was reported by the manufacturers and it is confirmed here, as is the presence of Ag_2S-NPs in T5 which was suggested by Lorenz et al. (2012). In contrast, the two other textiles show Ag XANES spectra that have a much stronger ionic Ag signature. In both cases the presence of a dominant white line peak and the absence of other characteristic features are similar to Ag salts and this is in line with the results from the LCF fitting (Table 2). The results from T6 are not in line with the manufacturer specification which indicates the presence of nanosize Ag particles in this product, but Ag phosphate is found to be dominant here.

Effect of washing on silver speciation of pure compounds

The two washing procedures had significantly different effects on the Ag-NPs and the Ag-zeolite (Figure 2 and Table 3). In contrast, AgCl-NPs were very stable during washing. The MW procedure caused an almost complete conversion of Ag to AgCl whereas LW caused a partial sulfidation of both Ag-NPs and Ag-zeolite, in line with the suggestion by Lorenz et al. (2012). Some of the Ag-zeolite also appeared to be converted to metallic Ag, as evidenced by the appearance of distinctive peaks at approximately 25550eV and 25585eV. Interestingly some trace evidence for Ag phosphate formation was found in the LW treatment but not in the MW treatment. The percentages of Ag phosphate

reported are probably close to the resolution capability of XANES but are nevertheless reported as this finding is in line with the presence of phosphates in the LW detergent (while the MW detergent is P free). The formation of AgCl in the MW treatment cannot be explained on the sole basis of the Cl content in the washing solutions prepared using the two detergents, which is similar - 8.7 mg/l in the phosphate-containing detergent (Lorenz et al., 2012) and 9 mg/l in Persil used in the MW.

Effect of washing on silver speciation of textiles

The relative amounts of Ag released from the textiles during washing is given in Table 1. The data for LW are taken from Lorenz et al. while the MW results are from this study. For T1 and T4 the amounts released are very similar while for T6 and T7 the MW resulted in much higher release. In particular, T7, which only contained 41 mg/kg of silver, released 80% through MW and this is reflected in the poor signal to noise in the XANES spectrum.

A first visual assessment of the XANES spectra reported in Figure 1 indicates that while washing procedures caused considerable changes in Ag speciation in three textiles (T1, T5 and T6) the speciation in T4 and T7 remained fairly constant. Some general trends in changes in speciation caused by washing can be discerned. In the laboratory washed (LW) textiles T1, T4 and T5 the XANES spectra indicate a predominance of metallic Ag. This was present in considerable amount in the unwashed textile of T4 and T5 but not in T1 (Table 1). As the Ag release for T1 was negligible (Table 1), metallic Ag must have been formed in T1 as a consequence of the laboratory washing procedure. This is in line with the finding that spectral features for metallic Ag were found in the samples resulting from the washing of Ag-NPs and Ag-zeolite samples, which suggests that metallic Ag can be retained or formed during LW (Table 2). In T4 and T5 the increase in metallic Ag representation could be due to either removal of Ag species different from Ag-NPs or to their conversion to Ag(0). Another effect of the washing procedure was the formation of Ag oxide in some textiles.

The machine washing (MW) procedure produced a different response, in terms of Ag speciation, in some of the textiles (Table 2 and Figure 1). In particular, the Ag XANES spectra of T1, T5 and T6 for the two washings are significantly different. In all these cases, the AgCl spectral signature was much more evident in the machine washed textiles than in the laboratory washed materials (Figure 1). This is reflected in the results of the LCF (Table 2) and is in line with the results obtained in the washing of Ag-NPs and Ag-zeolite samples that showed an almost complete conversion to AgCl as a consequence of the MW procedure with a commercial detergent. In fact, AgCl represented a much larger proportion of the total Ag across the textiles after machine washing than in the unwashed materials or in the textiles washed under laboratory conditions. These changes in speciation seem to be the result of the transformation of metallic Ag, and Ag phosphate in T6, to AgCl (Table 2). A notable exception is represented by sample T4 (MW). In this case Ag-NPs dominated the spectra after both washing procedures, with significant reduction in the Ag_2S and AgCl content. Given that the Ag release from T4 is similar between LW and MW, it may be that these two are the major components of the released silver. Indeed, AgCl particles were previously found by Lorenz et al. (2012), although Ag_2S was only found in T5.

Discussion

The presence of multiple Ag species/forms in the textiles examined could be due to different causes. Comprehensive investigations of functionalised textiles in the scientific literature have shown that textiles can be functionalised with well-defined NPs under laboratory conditions (Nguyen Khanh et al., 2013, Zhang et al., 2012). However, it is reasonable to assume that upscaling of functionalization methodologies to the industrial level may result in different outcomes from those achievable under well-controlled laboratory conditions. It should also be noted that even in the case of scientific publications, Ag speciation in textiles is generally investigated using XRD and SEM, and less often with the aid of XPS. In fact, in a review on the determination of engineered nanoparticles on textiles,

XANES is not even mentioned (Rezic, 2011). However, as argued above, XANES is possibly the most robust technique available in cases where the overall Ag speciation needs to be assessed. Another possible phase for transformations is during and after incorporation of Ag-NPs into or onto the textile. Some of the processes in the textile industry involve high temperature/extreme pH/high concentrations of other compounds and thus conditions are very different to those used in laboratory settings.

It is also possible that some of the species observed, particularly the Ag_2S, may be the result of processes occurring post-production. Tarnishing of Ag in air is a well-known phenomenon caused by the reaction of Ag with hydrogen sulfide present in air. As this is a surface process it is reasonable to expect that the rate of tarnishing may be accelerated in the case of Ag-NPs as they have a large surface-to-volume ratio. In fact, Mcmahon et al. (2005) showed that the rate of Ag-NPs tarnishing (as nanodisks of 60 nm diameter) was 7.5 times higher than that of bulk Ag under the same conditions. It is therefore not surprising that methods to reduce Ag-NPs tarnishing have been investigated (Chang et al., 2012). Considering the extremely low solubility of Ag_2S, this aspect needs to be further investigated in view of the potential consequences in terms of antimicrobial activity of the functionalized textiles and the release profile of Ag from these materials to the environment (e.g. through wastewater). These processes may occur anywhere during storage, shipment or in homes.

When considering the change in Ag speciation of the textiles caused by washing it should be kept in mind that these changes can be the result of two separate processes: (a) the conversion of some Ag species to others and (b) the preferential release of some Ag species from the textiles. Therefore, the interpretation of the XANES results needs to take into account the Ag release values reported in Table 1. These transformations find some explanation in the complex chemistry of Ag during washing. For instance, it seems that H_2O_2 which is often present during washing can lead to the formation of Ag oxides through Fenton-like reactions involving Ag ions.(JA, 1962) At the same time, North and Bland (1920) reported the reaction of H_2O_2 with Ag_2O to form elemental Ag. In any case, it

is apparent that in all laboratory washed textiles forms of Ag that can be considered more soluble (nitrate, sulphate and Ag-zeolite) were drastically reduced. This is probably the result of combined Ag release during washing and conversion to more insoluble species. This cannot be simply explained on the basis of the initial Ag speciation in the textiles as the Ag XANES spectra for the unwashed T4 and T5 materials was similar but the effect of washing was much more marked for T5 (at least for machine washing) than for T4. These differences also cannot be explained on the basis of different preferential losses of some Ag species in these two textiles as the Ag release during washing was similar and, in both cases, limited.

The two washing procedures tested in this study resulted in different changes in Ag speciation which were textile dependent. In general however, the washing procedures seemed to promote the formation of more stable Ag species. As the changes in Ag speciation were in some cases substantial, it is unlikely that the preferential release of more soluble or less well attached Ag species/forms could be entirely responsible for the changes observed. Rather, chemical reactions are also likely to play a significant role. We cannot explain the different Ag-species formed in some textiles in lab-washing compared to home-washing. The chloride content of the detergent is similar (so we would expect to see similar amounts of AgCl formation). The main difference is that the lab-washing detergent is phosphate-containing while the home washing detergent is based on zeolites. Further controlled lab studies need to elucidate the role that different components of the washing liquid play in silver transformations.

The presence of more insoluble Ag species in laboratory washed textiles, in comparison to the original Ag speciation, could explain the results reported by Geranio et al. (2009); these authors washed nine Ag functionalised textiles two consecutive times (using the same washing procedure employed here) and observed a decrease in the Ag released during the second washing. These results are of interest in relation to the total release of Ag that can be expected as result of multiple washings. Furthermore, a change in Ag speciation as a consequence of washing is also likely to

influence the antibacterial properties of the textiles over time. In fact, Lorenz et al.(Lorenz et al., 2012) reported a reduction in the antimicrobial properties of T1 and T5 in their study but not in the other textiles tested here. However, these results indicate that bulk Ag speciation cannot be used to explain antimicrobial properties of textiles. This is not surprising as the antimicrobial properties are related to the release of Ag^+, a species most likely representing a very small proportion of the total Ag in the textiles (and therefore below the XANES detection capabilities). The toxicity of Ag_2S for example is much lower than that of Ag(0) (Reinsch et al., 2012).

The observed differential reactivity of the Ag associated with the various textiles probably has different causes. It is likely that in addition to the differences in bulk speciation the size, surface functionality and/or passivation of the NPs surface also plays an important role. In addition, interactions between the textiles materials and the washing liquid could also provide an additional source of variability in the response of Ag to the washing procedures. For example, the two polyester based textiles (T4 and T5), whose initial Ag species are also comparable, behave similarly in LW (increase in metallic Ag, decrease in Ag_2S) but are considerably different in MW. It is clear that these variables are interconnected and reveal an additional layer complexity in assessing Ag release.

As the outcome of washing procedures influence the performance of the textiles as well as the profile of Ag released during subsequent washing cycles (which is of environmental importance), these processes need further attention. For instance, the influence of particle properties could be investigated by functionalising different textiles with a number of well characterised Ag-NPs. Such a study would also elucidate the role that textile materials play in Ag transformation. However, this study clearly demonstrate the importance to investigate real-world systems as our work has shown that the speciation of Ag in commercial textiles is far from simple and, for some textiles, there are significant differences in the release and final Ag-speciation between lab-washed and home-washed textiles.

Acknowledgements

Supplementary data

Additional tables and figures containing information about the materials used and the XANES spectra of the standard compounds are available as supporting information. This material is available free of charge via the Internet at http://www.sciencedirect.com.

References

Arvidsson, R., S. Molander, B.A. Sanden and M. Hassellov, 2011. Challenges in Exposure Modeling of Nanoparticles in Aquatic Environments. Hum Ecol Risk Assess 17: 245-262. 10.1080/10807039.2011.538639

Benn, T.M. and P. Westerhoff, 2008. Nanoparticle silver released into water from commercially available sock fabrics. Environ. Sci. Technol. 42: 4133-4139. 10.1021/es7032718

Chang, M., T. Kim, H.-W. Park, M. Kang, E. Reichmanis and H. Yoon, 2012. Imparting Chemical Stability in Nanoparticulate Silver via a Conjugated Polymer Casing Approach. Acs Applied Materials & Interfaces 4: 4357-4365. 10.1021/am3009967

Emam, H.E., A.P. Manian, B. Siorka, H. Duelli, B. Redl, A. Pipal and T. Bechtold, 2013. Treatments to impart antimicrobial activity to clothing and household cellulosic-textiles - why "Nano"-silver? Journal of Cleaner Production 39: 17-23. 10.1016/j.jclepro.2012.08.038

ER, M. 1991. factor analysis in chemistry. New York, John Wiley.

Geranio, L., M. Heuberger and B. Nowack, 2009. The Behavior of Silver Nanotextiles during Washing. Environ. Sci. Technol. 43: 8113-8118. 10.1021/es9018332

Gottschalk, F., T. Sonderer, R.W. Scholz and B. Nowack, 2009. Modeled Environmental Concentrations of Engineered Nanomaterials (TiO2, ZnO, Ag, CNT, Fullerenes) for Different Regions. Environ. Sci. Technol. 43: 9216-9222. 10.1021/es9015553

Gottschalk, F., T. Sonderer, R.W. Scholz and B. Nowack, 2010. POSSIBILITIES AND LIMITATIONS OF MODELING ENVIRONMENTAL EXPOSURE TO ENGINEERED NANOMATERIALS BY PROBABILISTIC MATERIAL FLOW ANALYSIS. Environ. Toxicol. Chem. 29: 1036-1048. 10.1002/etc.135

Gottschalk, F., T. Sun and B. Nowack, 2013. Environmental concentrations of engineered nanomaterials: Review of modeling and analytical studies. Environ. Pollut. 181: 287-300. 10.1016/j.envpol.2013.06.003

Impellitteri, C.A., T.M. Tolaymat and K.G. Scheckel, 2009. The Speciation of Silver Nanoparticles in Antimicrobial Fabric Before and After Exposure to a Hypochlorite/Detergent Solution. J. Environ. Qual. 38: 1528-1530. 10.2134/jeq2008.0390

JA, M., 1962. Higher oxidation states of silver. Chem Rev 62: 65-80.

Kim, S., H. Chung, J.H. Kwon, H.G. Yoon and W. Kim, 2010. Facile Synthesis of Silver Chloride Nanocubes and Their Derivatives. Bull Korean Chem Soc 31: 2918-2922. 10.5012/bkcs.2010.31.10.2918

Koehler, A.R., C. Som, A. Helland and F. Gottschalk, 2008. Studying the potential release of carbon nanotubes throughout the application life cycle. Journal of Cleaner Production 16: 927-937. 10.1016/j.jciepro.2007.04.007

Lorenz, C., L. Windler, N. von Goetz, R.P. Lehmann, M. Schuppler, K. Hungerbuehler, M. Heuberger and B. Nowack, 2012. Characterization of silver release from commercially available functional (nano)textiles. Chemosphere 89: 817-824. 10.1016/j.chemosphere.2012.04.063

McMahon, M., R. Lopez, H.M. Meyer, L.C. Feldman and R.F. Haglund, 2005. Rapid tarnishing of silver nanoparticles in ambient laboratory air. Applied Physics B-Lasers and Optics 80: 915-921. 10.1007/s00340-005-1793-6

Mueller, N.C. and B. Nowack, 2008. Exposure modeling of engineered nanoparticles in the environment. Environ. Sci. Technol. 42: 4447-4453. 10.1021/es7029637

Nguyen Khanh, V., A. Zille, F.R. Oliveira, N. Carneiro and A.P. Souto, 2013. Effect of Particle Size on Silver Nanoparticle Deposition onto Dielectric Barrier Discharge (DBD) Plasma Functionalized Polyamide Fabric. Plasma Processes and Polymers 10: 285-296. 10.1002/ppap.201200089

North B, B.N. 1920. Cambridge, University Press.

Radetic, M., 2013. Functionalization of textile materials with silver nanoparticles. Journal of Materials Science 48: 95-107. 10.1007/s10853-012-6677-7

Ravel, B. and M. Newville, 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. Journal of Synchrotron Radiation 12: 537-541. 10.1107/s0909049505012719

Reinsch, B.C., C. Levard, Z. Li, R. Ma, A. Wise, K.B. Gregory, G.E. Brown, Jr. and G.V. Lowry, 2012. Sulfidation of Silver Nanoparticles Decreases Escherichia coli Growth Inhibition. Environ. Sci. Technol. 46: 6992-7000. 10.1021/es203732x

Rezic, I., 2011. Determination of engineered nanoparticles on textiles and in textile wastewaters. Trac-Trends in Analytical Chemistry 30: 1159-1167. 10.1016/j.trac.2011.02.017

Segre, C.U., N.E. Leyarovska, L.D. Chapman, W.M. Lavender, P.W. Plag, A.S. King, A.J. Kropf, B.A. Bunker, K.M. Kemner, P. Dutta, R.S. Duran and J. Kaduk 2000. The MRCAT insertion device beamline at the Advanced Photon Source. Synchrotron Radiation Instrumentation. P. Pianetta, J. Arthur and S. Brennan. 521**:** 419-422.

Vigneshwaran, N., A.A. Kathe, P.V. Varadarajan, R.P. Nachane and R.H. Balasubramanya, 2007. Functional finishing of cotton fabrics using silver nanoparticles. Journal of Nanoscience and Nanotechnology 7: 1893-1897. 10.1166/jnn.2007.737

Webb, S.M., 2005. SIXpack: a graphical user interface for XAS analysis using IFEFFIT. Phys Scr T115: 1011-1014.

Windler, L., M. Height and B. Nowack, 2013. Comparative evaluation of antimicrobials for textile applications. Environ. Int. 53: 62-73. 10.1016/j.envint.2012.12.010

Wong YWH, Y.C., Leung MYS, Ku SKA, LAM HLI, 2006. Selecetd applications of nanotechnology in textiles. AUTEX Research Journal 6: 1-8.

Zhang, D., G.W. Toh, H. Lin and Y. Chen, 2012. In situ synthesis of silver nanoparticles on silk fabric with PNP for antibacterial finishing. Journal of Materials Science 47: 5721-5728. 10.1007/s10853-012-6462-7

Table 1. Textile composition, Ag labelling information, total Ag and Ag released during the washing procedure. All data (except release during machine washing which was measured in this study) are taken from Lorenz et al. (Lorenz et al., 2012).

Sample	Fibre composition	Product labelling regarding Ag	Total Ag (mg/kg)	Ag release from washing (%)	
				Lab washing	Machine washing
T1	41% polypropylene, 31% polyamide, 18% cotton, 10% wool	'Silver integrated' in polyamide	18 ± 2	0	5
T4	83% polyester, 17% wool	'Silver'	183 ± 10	20	22
T5	100% polyester	'Silver ions'	45 ± 8	14.8	n.a.
T6	80% cotton, 20% elastic yarn	'Nanosize silver particles are incorporated in cotton fibers'	2925 ± 10	23.5	60
T7	93% polyamide, 7% elastane	-	41 ± 0.4	17.6	80

Table 2. Best fit Ag speciation as identified by Linear Combination Fitting (LCF) of K-edge XANES. Species proportions are presented as percentages and the values in brackets show the percentage variation in the calculated values. Goodness of fit is indicated by the R-factor.

Textile	Ag-NPs	AgCl-NPs	Ag$_2$S-NPs	Ag oxide	Ag phos.	Ag nitr.	Ag sulf.	Ag-zeolite	R factor
Unwashed									
T1			16 (1.6)			52 (0.7)	14 (0.7)	18 (1.3)	0.0005
T4	55 (1.7)	11 (3)	32 (5)						0.0001
T5	43 (1.5)	17 (3)	35 (3)	5 (0.8)					0.0001
T6	12 (3)		16 (5)		67 (6)			5 (0.5)	
T7	36 (1.7)	36 (3)	14 (2)				14 (1.7)		0.0005
Lab washed (LW)									
T1	60 (2)		29 (6)		5 (4)			6 (3)	0.0002
T4	87 (2)		7 (4)	3 (3)					0.0002
T5	65 (2)	14 (5)	9 (3)	11 (3)					0.0003
T6	8 (3)		42 (4)		50 (3)				0.0004
T7	23 (2)	33 (4)	28 (3)	15 (2)					0.0002
Machine washed (MW)									
T1		25 (6)	35 (8)			10 (4)	19 (5)		0.0005
T4	92 (3)		4 (4)						0.0005
T5		32 (9)	24 (4)			27 (6)	15 (6)		0.0006
T6		59 (10)	20 (3)		14 (3)		7 (3)		0.0006
T7	7 (4)	42 (8)	38 (6)		9 (6)				0.0007

Table 3. Best fit Ag speciation in Ag-NPs, AgCl-NPs and Ag sorbed on zeolite washed in phosphate-containing detergent (used in the lab washing) and Persil (used in the machine washing) as identified by Linear Combination Fitting (LCF) of k-edge XANES. Species proportions are presented as percentages and the values in brackets show the percentage variation in the calculated values. Goodness of fit is indicated by the R-factor.

Ag form	Ag-NP	AgCl-NP	Ag_2S-NP	Ag phos.	R factor
Lab washed (LW)					
Ag-NPs	62 (5)		27 (1.5)	10 (1.2)	0.00003
AgCl-NPs		94 (1.4)	4 (0.8)	2 (1.1)	0.00005
Ag-zeolite	31 (0.7)	47 (2)	18 (1)	3 (1.3)	0.00006
Machine washed (MW)					
Ag-NPs		92 (1.8)	7 (0.9)		0.00005
AgCl-NPs		98 (0.6)	2 (0.6)		0.00004
Ag-zeolite		93 (1.5)	5 (0.9)		0.00009

Figure 1. Normalised Ag K-edge XANES spectra of unwashed and washed textiles. Dotted red lines show the best 4-component linear combination fit of reference spectra as documented in Table 2.
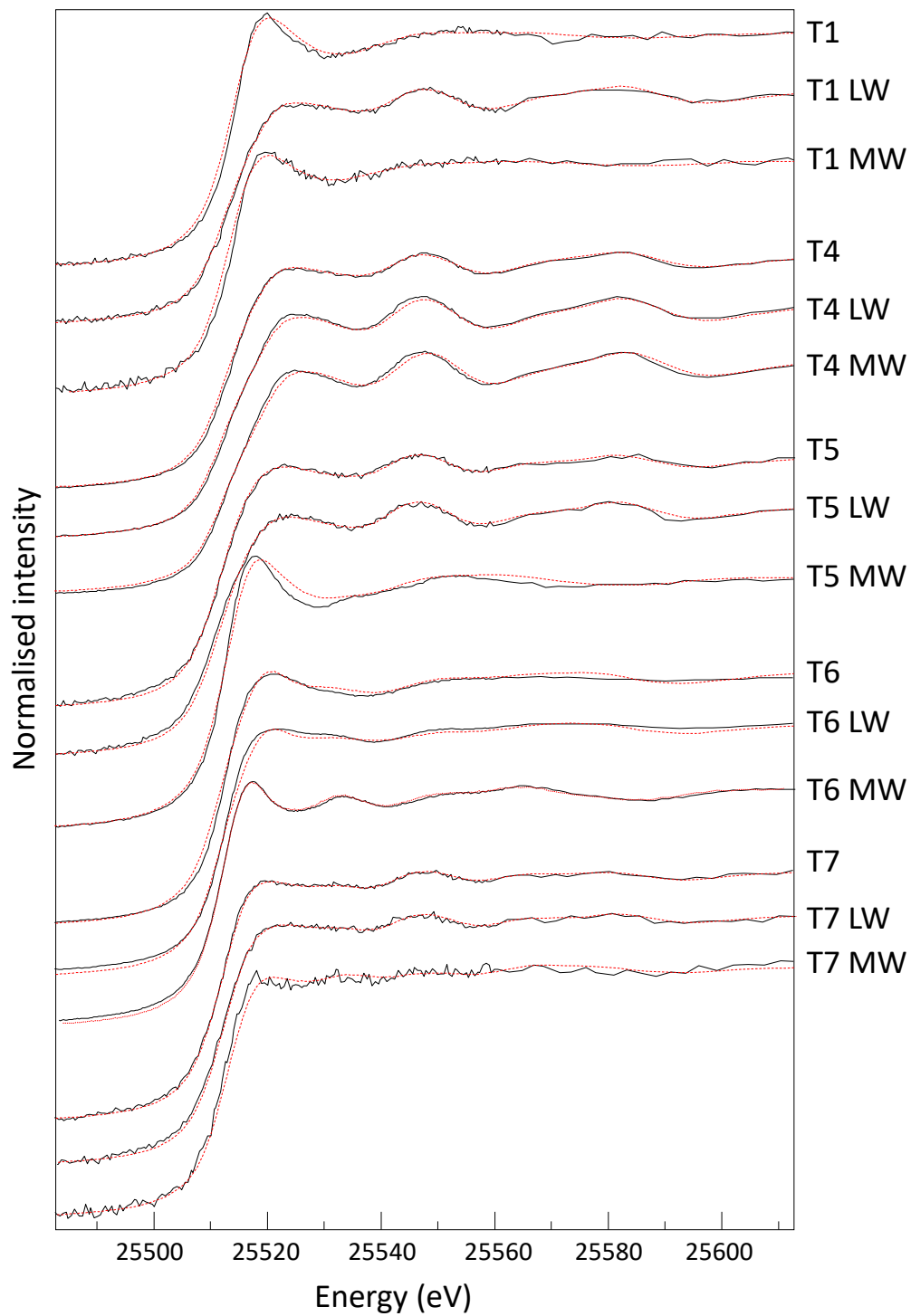
Figure 2. Normalised Ag K-edge XANES spectra of unwashed and washed Ag-NPs, AgCl-NPs and Ag-sorbed zeolite. Dotted red lines show the best 4-component linear combination fit of reference spectra as documented in Table 3.