

## Chemical forms of silver nanoparticles and silver in antimicrobial fabrics in soil

The increased use of silver (Ag)- and silver nanoparticle (AgNP)-containing products has raised concerns about their effect on the environment. Owing to their bacteriocidal properties, Ag and increasingly AgNPs are being employed in a wide range of commercial products, but the fate and behavior of Ag released into the environment are poorly understood. It has been demonstrated that Ag in sock textiles can dissolve as ionic and colloidal forms under household washing condition [1]. As a result of various effluent pathways, one of the largest sinks of Ag generated in municipal areas may be wastewater treatment plants and landfill. The soil is also a potential sink for Ag in the environment. Synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy is a technique that provides information on the oxidation state and coordination environment of metals in the solid phases of soil. Few studies are available on Ag speciation with regard to how AgNPs undergo phase transformations (e.g., sulfidation, complexation and adsorption) in the soil. Similarly, little is known about the solubility and speciation of Ag embedded in fabrics being disposed in landfill sites.

### Transformation of AgNP in soil

Silver *K*-edge extended X-ray absorption fine structure (EXAFS) spectroscopy was performed at SPing-8 BL01B1 [2]. Soil spiked with manufactured AgNPs was incubated under aerobic (slightly wet) and anaerobic (flooded) conditions for 30 days. Possible Ag species in the soil were determined by linear combination fitting (LCF) of the EXAFS spectra using known reference compounds and by a shell fit of Fourier transformed (FT) EXAFS spectra. The EXAFS spectrum of Ag in the aerobic soil was very similar to that of metallic Ag. The LCF indicated that metallic Ag was the primary species, accounting for 88% of the total Ag in the aerobic soil spiked with AgNP, indicating that the majority of AgNPs remained persistently in the aerobic soil. This is in agreement with the result of the shell fit of the FT-EXAFS spectrum, showing Ag–Ag coordination in the first shell (Fig. 1). In contrast, in the anaerobic soil, 83% of AgNPs were transformed into Ag<sub>2</sub>S, accompanied by significant decreases in water- and acid-extractable Ag concentrations. The shell fit of the FT-EXAFS spectrum determined the Ag–S and Ag–Ag coordination in the first and second shells, respectively. Our study suggests that the transformation of AgNPs in soil depends on the redox condition, and an important consequence of

the reaction of AgNPs with S is the reduced solubility and potential toxicity of Ag in the environment.

### Ag species in textiles

To examine the situation in that Ag-containing fabrics are disposed of as landfill, we investigated how the solubility and speciation of Ag in sock textiles are changed in soil. The microscale distribution and speciation of Ag at the interface between socks and soil particles were investigated using micro-X-ray fluorescence ( $\mu$ -XRF), and Ag speciation was determined by micro-X-ray absorption near edge structure ( $\mu$ -XANES) spectroscopy at SPing-8 BL37XU [3]. Pieces of Ag-containing sock fabric were added to soil with different water contents. After 60 days, a portion of the soil including the sock fabric was freeze-dried and embedded with epoxy resin. A soil thin section of soil with 80  $\mu$ m thickness was sliced

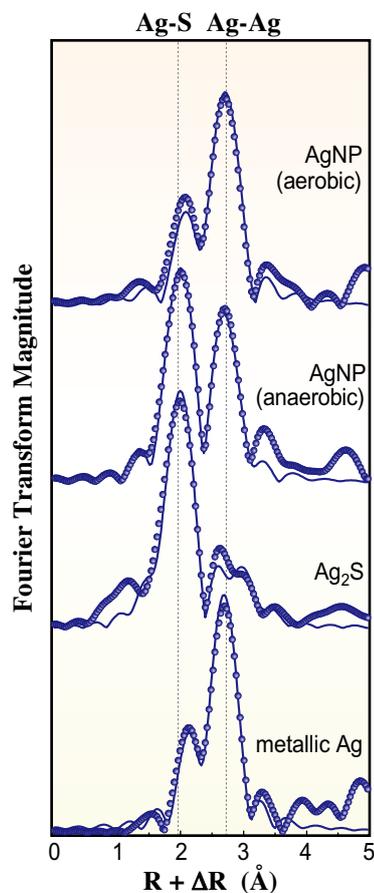


Fig. 1. Experimental (circles) and fitted (solid lines) data for Fourier transformed EXAFS spectra of Ag reference compounds and AgNPs added to aerobic and anaerobic soils. Vertical lines are included as a guide to the eye.

using a microtome (Leica, SP1600) and analyzed by  $\mu$ -XRF and  $\mu$ -XANES.

The result of  $\mu$ -XRF showed that Ag is enriched in the fabric and can also be found in the soil matrix  $\sim 10 \mu\text{m}$  from the edge of the fabric, attesting to the possible dissolution of Ag from the fabric at the microscale. As points of interest (POIs), we selected Ag-accumulating spots on the  $\mu$ -XRF maps and performed  $\mu$ -XANES analysis followed by LCF using Ag reference spectra. A light-microscope image and  $\mu$ -XRF element maps of the sock sample incubated under anaerobic conditions are shown in Fig. 2. The silver at the selected spots was mainly present as metallic Ag (51-89%) and  $\text{Ag}_2\text{S}$  (17-32%), depending

on the location in the soil matrix (Fig. 2). At a  $10 \mu\text{m}$  distance from the fabric (POIs #4 and #5), 25% and 32% of the Ag in the fabric were found to be  $\text{Ag}_2\text{S}$ , which was also found at POI #3,  $20 \mu\text{m}$  away from the edge of the fabric. Part of the Ag at POIs #1 and #2, located  $\sim 20 \mu\text{m}$  from the edge of the fabric, was bound to soil clay minerals. XRD determined that the Ag in sock fabric was present in the form of metallic Ag and  $\text{Ag}_2\text{S}$ , suggesting that these Ag species in the sock fabric remained persistently without notable phase transformations in the soil but associated with the soil minerals to some extent. A long-term study on the transformation of Ag species in fabrics is essential to elucidate the environmental fate of Ag.

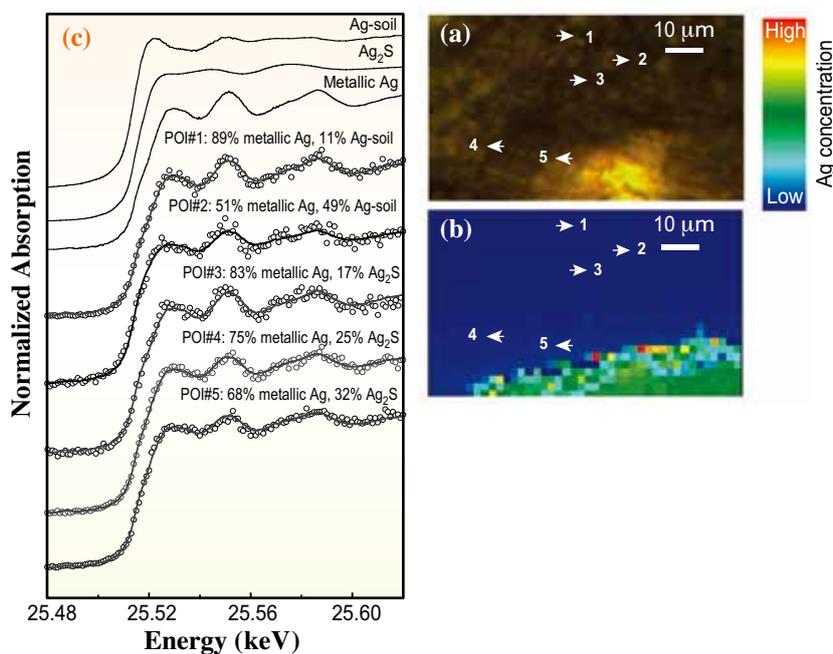


Fig. 2. Thin sections of soils with added Ag-embedded fabrics analyzed by a light microscope (panel a) and micro-XRF for Ag mapping (panel b), and normalized Ag K-edge XANES spectra of selected reference compounds. Also shown are points of interest (POIs) on the thin soil sections with their best component fit by LCF (solid lines). “Ag-soil” is a reference Ag sorbed with kaolinite. “Metallic Ag” is an Ag foil reference.

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