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Chemical speciation and enzymatic impact of silver in antimicrobial fabric buried in soil

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HIGHLIGHTS

- Soil enzymes in relation to Ag speciation in antimicrobial fabric were investigated.
- Ag in sock (metallic Ag and Ag_2S) did not undergo phase transformation in soils.
- Ag in the sock fabric has little detrimental impacts on enzyme activity.

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ABSTRACT

This study investigated the impact of Ag in antibacterial fabric on soil enzymes in relation to solubility and speciation of Ag. Sections of Ag-containing sock fabric (1.0–1.5 cm^2) were incubated in soils with aerobic and anaerobic conditions and periodically determined activity of arylsulfatase, dehydrogenase and urease. Microscale distribution and speciation of Ag at the interface between socks and soil particles were investigated using micro-focused X-ray fluorescence (μ-XRF), and Ag speciation was determined using micro-focused X-ray absorption near edge structure (μ-XANES) spectroscopy. Results showed that the sock fabric consisted of elemental Ag and Ag_2S. After 60-day exposure to soil, majority (50–90%) of Ag in sock did not undergo phase transformation and present as elemental Ag and Ag_2S in aerobic and anaerobic conditions. A part of Ag in sock fabric was bound with soil colloids (<15%), depending on the distance from the edge of sock fabric. Soil enzyme activities were overall unaffected by Ag in sock textile after 60 days of incubation, although a significant decrease in arylsulfatase activity was found only in the initial stage of soil incubation. Silver in the sock fabric is relatively stable and has little detrimental impacts on enzyme activity in ordinary soil conditions.

1. Introduction

Potential impacts of silver (Ag) on the environment have recently been concerned due to the increased use of Ag-containing products. Because of bactericidal properties, Ag has long been used in various commercial products, and the recent development of Ag nanoparticles expanded the use of Ag-containing products. Recent studies using sock fabrics impregnated with Ag or Ag nanoparticles confirmed bactericidal and fungicidal effects [1,2]. Blaser et al. [3] reported that Ag-containing textiles and plastics are the main sources of Ag in the environment. However, few studies have investigated the solubility and environmental fate of Ag in the commercial products. Benn and Westerhoff [4] reported the leaching of Ag from six commercially available sock fabrics, and found that Ag was dissolved from the sock as ionic and colloidal forms. Impellitteri et al. [5] demonstrated that Ag in sock textiles can dissolve in a household washing condition. The dissolved Ag in household effluents accumulates eventually in biosolids at sewage treatments [4]. According to an exposure modeling of Ag nanoparticles, the major sinks of Ag nanoparticles are sewage treatment plants (3.27 t $year^{-1}$) and landfill (0.14 t $year^{-1}$) [6]. Recent increased use of sewage sludge for soil amendments suggests the significance of study investigating environmental impacts of Ag in antibacterial products buried in soil.

Some studies have investigated the speciation and release of Ag from Ag-functionalized textiles in the washing process [5,7], but little is known about the behavior of Ag-containing fabrics being

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disposed in a landfill site. To evaluate environmental risk of metals in soils, it is essential to determine the chemical species of metals and their transformations. It has been reported that Ag reacts readily with sulfur groups (e.g., Ag_2S) in soil humus [8], and toxicity of sulfur-bound Ag compounds is expected to be reduced since the solubility product of Ag_2S, for example, is very low [9]. Hashimoto et al. [10] also reported that solubility and phase transformation of AgNP and Ag salts in soil depend highly on the redox status. The study using X-ray absorption fine structure (XAFS) found that 83% of the AgNP to the anaerobic soil was transformed into Ag_2S, but in the aerobic soil, 88% of the spiked AgNP remained persistent after 30 days of incubation. This study suggests that the solubility and phase transformation of Ag in textiles may differ between aerobic and anaerobic soil conditions. In addition to soil chemical perspectives, toxicity assessment of Ag in fabrics is important to elucidate the effect on soil biological functions. Soil enzyme assays have been widely used to evaluate microbial toxicity of metals [11–13]. This is because some soil enzymes have a high sensitivity to metals, and the method is rapid and simple [13]. Van Gestel and Hensbergen [14] stated that toxicity of metals is related to chemical and physicochemical interactions with soil constituents, suggesting that it is reasonable to employ biological assessments in combination with chemical speciation of Ag in fabrics being added to soils.

The objective of this study was to investigate the impact of Ag in sock textiles on soil enzymes in relation to solubility and speciation of Ag. To allow comparisons of phase transformations of Ag in different redox conditions, we conducted soil incubation study under aerobic and anaerobic conditions. Microscale distribution and speciation of Ag at the interface between socks and soil particles were investigated using micro-focused X-ray fluorescence (μ-XRF), and Ag speciation was determined using micro-focused X-ray absorption near edge structure (μ-XANES) spectroscopy. For biological assessment of Ag-containing sock in the soil, activity of enzymes including arylsulfatase, dehydrogenase and urease were determined.

2. Materials and methods

2.1. Experiment setup

Soil was collected from a paddy field of Field Science Center of Tokyo University of Agriculture and Technology (Fuchu, Tokyo). The soil was air-dried and passed through a 2-mm sieve and used for the following incubation study. Basic soil properties including soil texture, pH, total carbon, water extractable anions, ammonium acetate extractable cations, acid ammonium oxalate Fe and Mn (Fe_{ox}, Mn_{ox}) and dithionite-citrate extractable Fe and Mn (Fe_d, Mn_d) were determined by standard procedures. The soil consisted of 51.9% sand, 22.5% silt and 25.6% clay. Detailed soil properties and analytical procedures are shown in Table S1, Supporting Information (SI). All chemicals used in this study were a special grade (>99% purity) purchased from Wako Pure Chemical Industries Ltd., Japan, unless otherwise noted.

A commercially available sock containing Ag fabrics was examined for the soil incubation study. Weighed sock samples (0.10 g) were digested using a block digester with 5 mL of concentrated HNO_3 and 6 mL of H_2O_2 at 150 °C for 12 h. After digestion, the solution was filtered, diluted with deionized water, and analyzed for Ag by atomic absorption spectrometry. Silver was interweaved with cotton fabrics only in the toe part of the sock (2417 mg kg^{-1}), but other parts of sock little contained Ag with below-detectable levels (<0.05 mg L^{-1}). The XRD determined that Ag in sock fabric was present as a form of elemental Ag and Ag_2S (Fig. S1). Acanthite (Ag_2S) is reported to be a primary corrosion product of metallic Ag [15]. Sections of Ag-containing sock fabric (1.0–1.5 cm^2) were added to 200 g of soil to achieve the soil Ag concentration of 100 mg kg^{-1}. A similar size of sections was also clipped from the sock fabric without Ag, and mixed with the soil. To compare the solubility and speciation of Ag in different redox gradients, the soils were incubated in a 450-mL polypropylene container for 60 days at 25 °C under anaerobic and aerobic conditions by adding different amounts of water. The soil without sock materials (soil only) was defined as control. For the aerobic and anaerobic treatments, the soils were wetted periodically to maintain 50% and 90% water contents during the incubation period, respectively. The redox potential (Eh) of anaerobic soils was periodically measured using platinum electrode and a Ag/AgCl reference electrode (see SI).

2.2. Soil enzyme and chemical analyses

Soil samples were collected at 2, 30, and 60 days after starting the incubation for determination of the activity of three soil enzymes. The activity was analyzed colorimetrically by a spectrophotometer. Arylsulfatase activity was determined by referring to the method proposed by Tabatabai [16]. One gram of soil was exposed to 0.25 mL of toluene, 4 mL of acetate buffer (pH 5.8), and 1 mL of *p*-nitrophenyl sulfate solution for 1 h at 37 °C and admixed with 1 mL of 0.5 mol L^{-1} calcium chloride and 4 mL of 0.5 mol L^{-1} sodium hydroxide. The concentration of *p*-nitrophenol in soil extracts was determined at a wavelength of 400 nm. Dehydrogenase activity was determined by referring to the method proposed by Tabatabai [16]. One gram of soil was exposed to 1 mL of Tris buffer (pH 7), 50 μL of glucose solution (10 g L^{-1}), and 0.2 mL of TTC (2, 3, 5-triphenyltetrazolium chloride) for 3 h at 37 °C in the dark. The soil was admixed with 10 mL of methanol, and the concentration of triphenyl formazan in soil extracts was determined at a wavelength of 485 nm. Urease activity was determined by the method proposed by Kandeler and Gerber [17] with slight modifications. Two grams of soil was exposed to 1 mL of urea (0.48%) and 8 mL of borate buffer (pH 10) for 2 h at 37 °C and admixed with 1 mol L^{-1} KCl solution by shaking for 1 h. The concentration of NH_4 in soil extracts was determined by a modified indophenol-blue reaction at 667 nm. Each enzyme analysis was performed with triplicate samples from each soil.

Soil samples collected at day 60th were used for Ag analyses. A modified Toxicity Characteristic Leaching Procedure [18] was performed for each soil to extract Ag (TCLP-Ag). The TCLP solution (pH 2.88) was prepared by diluting 5.7 mL glacial acetic acid to 1 L with deionized water. Twenty-five (25) mL of TCLP solution was added to 2.5 g of soil and samples were equilibrated for 24 h on a shaker. The supernatant was separated from the solid by centrifugation and analyzed for Ag. Total soil Ag was determined by digesting the soil with HNO_3, H_2O_2, and HF on a heat block-digester. The concentration of Ag in each extract was analyzed by atomic absorption spectroscopy (Hitachi High-Technologies Corp., Japan).

2.3. Distribution and speciation of Ag in the vicinity of the sock by μ-XRF and μ-XANES

Distribution and speciation of Ag at the interface between the sock and soil particles were determined using μ-XRF and μ-XANES spectroscopy. After 60 days of incubation, the soil was immediately frozen by liquid nitrogen. The frozen soil blocks were freeze-dried and embedded with epoxy resins. The center of the soil block was cut out by a diamond saw to include the sock fabric. A thin section with 80-μm thick was sliced by using a microtome (Leica, SP1600) and analyzed for μ-XRF and μ-XANES at the beamline BL37XU at SPring-8 in Hyogo, Japan.

In order to find the area of Ag accumulation around the sock, the elemental distribution of Ag and Fe on the soil thin section was