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Trophic transfer of citrate, PVP coated silver nanomaterials, and silver ions in a paddy microcosm☆

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ABSTRACT

We used replicated paddy microcosm systems to estimate the tropic transfer of citrate-coated silver nanoparticles (AgNP citrate), polyvinylpyrrolidone (PVP)-coated AgNP (AgNP PVP), and silver ions ($AgNO_3$) for 14 days under two exposure regimes (a single high-dose exposure; 60 $\mu g\,L^{-1}$ and a sequential low-dose exposure at 1 h, 4 days and 9 days; 20 $\mu g\,L^{-1} \times 3 = 60\ \mu g\,L^{-1}$). Most Ag ions from $AgNO_3$ had dispersed in the water and precipitated partly on the sediment, whereas the two Ag NPs rapidly coagulated and precipitated on the sediment. The bioconcentration factors (BCFs) of Ag from AgNPs and $AgNO_3$ in Chinese muddy loaches and biofilms were higher than those of river snails in both exposure conditions. These BCFs were more prominent for 14 days exposure (7.30 for Chinese muddy loach; 4.48 for biofilm) in the low-dose group than in the single high-dose group. Their retention of AgNPs and Ag ions differed between the two exposure conditions, and uptake and elimination kinetics of Ag significantly differed between AgNP citrate and AgNP PVP in the sequential low-dose exposure. Stable isotopes analyses indicated that the trophic levels between Chinese muddy loaches and biofilms and between river snails and biofilms were 2.37 and 2.27, respectively. The biomagnification factors (BMFs) of AgNPs and $AgNO_3$ between Chinese muddy loaches and biofilms were significantly higher than those between river snails and biofilms under both exposure settings. The BMFs of AgNP citrate and $AgNO_3$ between Chinese muddy loaches and biofilms were greater than those of AgNP PVP for 14 days in the single high-dose group, whereas the BMFs of AgNP PVP were greater than those of AgNP citrate and $AgNO_3$ in the sequential low-dose group. These microcosm data suggest that AgNPs have the potential to impact on ecological receptors and food chains.

1. Introduction

Silver nanoparticles (AgNPs) are used as antibacterial agents, biosensors, and solar cells, and are used in surface enhanced Raman scattering (SERS) and drug delivery (Ren et al., 2005; Kim et al., 2007; Anandhakumar et al., 2012; Xiu et al., 2012; Lu et al., 2013; Shi et al., 2013). A recent trend has broadened the applications of AgNPs to the agricultural sector (Kumar et al., 2012; Velmurugan et al., 2013; Yokesh Babu et al., 2014; Ibrahim, 2015), including in photosynthetic pigments (chlorophylls and carotenoids) (Najafi et al., 2014) and in antimicrobial and insecticidal agents (Sekhon, 2014; Prasad, 2014; Choi and Park, 2015; Park and Yeo, 2016). These extensive applications of AgNPs may cause AgNPs to release and ultimately end up in the environment, with soils/sediments being considered a major sink for NPs. In Korea, AgNPs and Ag ion are used widely in the agricultural sector against plant pathogenic fungi on cucumber, pumpkin, and perennial ryegrass without any regulation (Jo et al., 2009; Lamsal et al., 2011; Kim et al., 2012); these NPs as non-point source pollutants have thus been discharged in aquatic ecosystems. Given the potential entry of NPs into the environment, their environmental fate and trophic transfer

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throughout the food chain should be regarded with great concern (Yeo and Nam, 2013; Bouwmeester et al., 2014; Kim et al., 2016).

Ionic forms of Ag are highly toxic to bacteria (Sharma et al., 2014) and aquatic organisms due to the induction of highly reactive oxygen species and interaction with enzymes, proteins, and cell membranes (Chae et al., 2009; Yeo and Yoon, 2009; Bilberg et al., 2010; Wise et al., 2010; Asghari et al., 2012; Angel et al., 2013; Ribeiro et al., 2014; Tsyusko et al., 2012; Ahn et al., 2014). Several studies have indicated that AgNPs can accumulate inside the internal organs of some aquatic organisms (Cleveland et al., 2012; Boenigk et al., 2014; Buffet et al., 2014; Colman et al., 2014; Furtado et al., 2014; Ribeiro et al., 2014; Wang and Wang, 2014; Bone et al., 2015), and several microcosm studies are available to investigate trophic transfer and bioaccumulation of AgNPs with replicate microcosm including water and sediment with various biota (Cleveland et al., 2012; Doiron et al., 2012; Bone et al., 2015).

Our previous studies revealed that, in agricultural fields based on a Korean rice paddy ecosystem model, TiO_2 NPs showed their trophic transfer to the aquatic organisms (Yeo and Nam, 2013; Kim et al., 2016). However, limited information is available on the quantitative trophic transfer of AgNPs in a paddy field. The paddy field is a common type of farmland for rice and dropwort where the aquatic environment supports both lower (e.g., snails and small fishes) and higher trophic organisms (e.g., predators, including humans). In the present study, we created several microcosm environments using the Korean rice paddy as a model, and we investigated the distribution, physicochemical behaviors, and trophic transfer of two types of AgNPs (AgNP citrate, AgNP PVP) and Ag ions (as $AgNO_3$) in a simplified microcosm environment.

Stable isotope compositions ($\delta^{13}C$ and $\delta^{15}N$) from the environmental media (freshwater, sandy loam sediment) and various trophic level organisms (aquatic plants, biofilms, river snails, and Chinese muddy loaches) were quantified to evaluate the relationships between trophic transfer and biomagnification rates in artificially designed microcosm environments. We also explored whether AgNPs exposure regimes (a single high-dose versus sequential low-dose exposures) can affect bioconcentration and biomagnification through simplified food chains. Uptake and retention dynamics between AgNP citrate and polyvinylpyrrolidone (PVP) were also assessed in the aquatic test organisms.

2. Materials and methods

2.1. Physicochemical properties of AgNPs and Ag ions

We purchased two types of AgNPs used as surface-coating materials, AgNP citrate (AGS-WM1000SC; 5% citric acid in water, Nano High Tech Co., Korea) and AgNP PVP (AGS-WM1000; 0.5% PVP in water, Nano High Tech Co., Korea), and prepared Ag ions with 2.5% (w/v) $AgNO_3$ (Sigma-Aldrich Co., USA) in H_2O. The structures and sizes of the AgNPs were verified using a field emission transmission electron microscope (FE-TEM; model JEM-2100F, JEOL, USA) equipped with an energy dispersive X-ray analyzer (EDS; model Genesis 2000, EDAX, USA) (Fig. S1B). In addition, the structures of AgNPs were analyzed using X-ray diffraction (XRD; D8 Advance, Bruker, Germany) (Fig. S1A). A nickel filter and Cu*K* radiation (30 kV, 30 mA) were used, and the analysis was performed within a 5–80° range at a 2θ value at a scan rate of 10°/min. The material distribution characteristics and zeta-potential were measured using a particle size analyzer (ELS-Z2, Otsukael, Japan). Analytical samples were diluted with distilled water, and the physical conditions were as follows: water temperature, 25 °C; refractive index, 1.3328; and viscosity, 0.8878 (centipoise, cP).

2.2. Microcosm designs

Experimental microcosm systems (Fig. S2) were prepared according to a previously validated design by Yeo and Nam (2013) with some modifications. Briefly, a greenhouse (33.058 m^2) was installed in the premises of the Technical College of Kyung-Hee University, Korea. The windows on two sides of the greenhouse were used for controlling the air flow, and the interior was maintained at a constant temperature (28 ± 1 °C). Then, two microcosm environments were created, including a paddy microcosm in an acrylic plastic container (370 × 220 × 250 mm) and a water tank (260 × 185 × 138 mm) with a submerged pump (10 W) (Fig. 2A). The pump (10 W) ensured the maintenance of a constant water level during the stabilization period for the microcosms.

Continuous circulation in the water tank was ensured by operating the motor pump (model HJ-750; 10 W, AC 220V/60Hz, Samho Corp., China) with a semi-static daily circulation plan of 8 cycles of 2-h operation and 1-h break. A 40-μm mesh (cell strainer; BD Falcon, USA) was used to prevent the leakage of suspended soil particles or small organisms into the water tank. The sediment was harvested from a paddy field in Seocheon-Dong (37°14 39.770′ N, 127°04 30.080′ E), Young-in, Korea. Analysis was performed on the harvested sediment by using the United States Department of Agriculture (USDA) soil survey manual (Soil Survey Division Staff, 1993), and the sediment was identified as sandy loam with the following physicochemical properties: pH, 6.75; oxidation-reduction potential (ORP), 22.4 mV; electrical conductivity (EC), 48.33 μS cm^{-1}; and total organic carbon (TOC), 48.33 mg L^{-1}. The water used for the microcosms was prepared by dechlorinating tap water collected in a 300-L water tank for at least two days by semi-static circulation with a submerged pump. The composition of the water used in the microcosm was as follows: pH, 7.1; chloride concentration, 0.8 mg L^{-1}; ionic strength, 2.2×10^{-5} M; and TOC, 0.9 mg L^{-1}.

The biota generated in the microcosms included a water dropwort (*Oenanthe javanica DC*) as the producer (prey), a river snail (*Cipangopaludina chinensis*), and the Chinese muddy loach (*Misgurnus mizolepis*). The river snail is an invertebrate consumer and the Chinese muddy loach is a vertebrate consumer (predators). The water dropwort was planted after filling the microcosm container with 10 cm of sediment and 10 cm of water (7 L) and maintained until the beginning of the exposure experiments. Six river snails and six Chinese muddy loaches were placed into the container and left unfed during a stabilization period.

In order to harvest the biofilms expected to develop during microcosm stabilization, a transparent polypropylene board was installed on each side of the experimental container (4 boards; total area, 1,180–1,120 cm^2), along with perforated straws (12 straws, 1 cm in diameter; total area, 750–755 cm^2).

2.3. Single-dose versus sequential multi-dose exposures

Exposure groups of AgNP citrate, AgNP PVP, and $AgNO_3$ were tested under a single-dose exposure and three sequential multi-dose exposure conditions over a period of 14 days. The experiments were performed in the greenhouse using the control group and exposure groups. The container was shielded from light by a foil during the experimental period. Each AgNP type was prepared in diluted concentrations of 60 μg L^{-1} for a single high-dose exposure and 20 μg L^{-1} for three sequential low-dose exposures (1 h, 4 days, and 9 days).

In order to observe the fate and transport of the test materials (AgNP citrate, AgNP PVP, and $AgNO_3$) within the environmental media (water and sediment), we selected a single-dose exposure of 2 mg L^{-1} AgNPs under the same circulation conditions without