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Harmful effect of nanoparticles on the functions of freshwater ecosystems: Insight into nanoZnO-polluted stream

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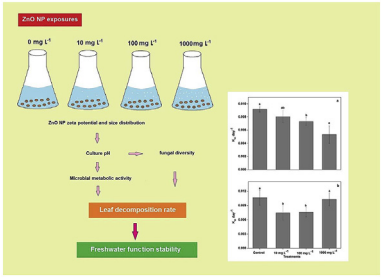
HIGHLIGHTS

- Concentration-and time-dependent effects of ZnO NP on freshwater functions was observed.
- Variability of decomposition rates was detected in 10 and 1000 mg L^{-1} ZnO NPs.
- ZnO NP exposure led to significant reduction of culture pH.
- Microbial metabolic activity was inhibited by 1000 mg L^{-1} ZnO NPs.
- Fungal diversity was negatively related to stability of decomposition rate.

GRAPHICAL ABSTRACT



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ABSTRACT

ZnO nanoparticle toxicity on aquatic organisms has been extensively studied, but its concentration-and time-dependent effects on ecosystem functioning are remain uncertain. Here we assessed the harmful effects of nano-ZnO (10, 100, 1000 mg L^{-1}) on the stream functioning by using a microcosm system simulating poplar leaf decomposition for 50 days. The 100 mg L^{-1} ZnO nanoparticles had significantly and stably inhibitory effect on the litter decomposition during the exposure period. The inhibition was not detected in the 10 mg L^{-1} treatment until 43 d. In contrast, the significant and continuous inhibition started to disappear from 43 d in the 1000 mg L^{-1} treatment. The varied consequences on litter decomposition might be directly affected by the different ZnO nanoparticle homogeneity of the different treatments. ZnO nanoparticles led to significant decreases in pH value of the decomposition environment, which had significant and positive relationships to the activities of dehydrogenase, glycine-aminopeptidase, N-acetylglucosaminidase, and acid phosphatase. Besides, 10 and 1000 mg L^{-1} ZnO nanoparticles led to lower fungal diversity, which was negatively related to the variability of decomposition. In conclusion, fungal decomposers showed different responses to the different concentrations of ZnO nanoparticle, and ultimately affected the stability of ecosystem functions.

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1. Introduction

With the rapid development of nanotechnology, nanomaterials have been widely applied in many commercial products including

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paints, cosmetics, sunscreens, glass, batteries, and stain-resistant clothing (Kahru and Dubourguier, 2010). Among the prevalent nanomaterials, zinc oxide nanoparticles (ZnO NPs) rank in the top three metal nanoparticles used in consumer products, with an estimated global production in the range of 550 to 33,400 tons annually (Bondarenko et al., 2013). Due to the dramatically increased production and usage of these nanomaterials, their potential release into the environment has caused great concerns to government regulatory bodies on their harmful effects on human health and environment (Cattaneo et al., 2010; Engeman et al., 2012; Windler et al., 2012). Their toxicities on aquatic organisms will be influenced by the solubility, stability, as well as the transformation in aquatic ecosystems (Wang et al., 2016).

The harmful effect of ZnO NPs has been assessed in various aquatic species, such as algae (Aravantinou et al., 2015; Hazeem et al., 2016), *Daphnia* (Xiao et al., 2015), *Thamnocephalus* (Blinova et al., 2010), zebrafish (Zhao et al., 2016), and carp (Chupani et al., 2018). The toxic action of ZnO NPs is potentially involved in three modes: (1) dissolution of the nanoparticles to Zn ion, (2) particle-induced reactive oxygen species (ROS) formation, and (3) photocatalytic ROS generation (Ma et al., 2013). However, these studies can not reflect the complexity of a natural system or the response at the ecosystem level to ZnO NPs. Therefore, it is crucial to use a comprehensive method to assess the harmful effect of ZnO NPs on the functions of freshwater ecosystems.

Leaf litter decomposition is a fundamental process in forest headwater streams, which links riparian plants, microbes, invertebrates, and the environmental quality (Young et al., 2008). Changes in environmental conditions can affect the rate of litter decomposition by altering community structures and degrading activities of the microbial and invertebrate decomposers (Webster and Benfield, 1986). The potential effect of NPs on leaf litter decomposition has been the focus of increasing research in ecotoxicology (Bour et al., 2015; Gessner and Tlili, 2016). Pradhan et al. (2011) were the first to show significant reductions in litter decomposition rate when Alder leaves were exposed to CuO NPs and Ag NPs in freshwater ecosystems. Fungi, a functional community in freshwater ecosystem, are suggested to be the primary decomposer of leaves in streams (Suberkropp, 1991, 2001). So, the responses of fungal community structure to NPs can be used to estimate NP effects on fungal functions in streams. However, few studies have focused on fungal community assays when explore the potential effect of NPs on leaf litter decomposition (Tlili et al., 2017).

The estimated concentrations of ZnO NPs were 0.01 and 0.43 $\mu g\ L^{-1}$ in the natural surface water and the treated wastewater, respectively (Gottschalk et al., 2009). Based on the estimates from Gottschalk et al. (2013), many studies on freshwater ecosystems chose the concentrations of NPs in low level. For example, Tlili et al. (2017) designed a leaf decomposition experiment involved three levels of AgNP addition (0, 0.05, and 0.5 μM). Colman et al. (2014) conducted a wetland mesocosm experiment involved two sizes of AgNP addition (12 and 49 nm) at a concentration of 2.5 mg Ag L^{-1}. Given that the environmental level is expected to increase continually due to the widespread application of these nanomaterials, it is necessary to investigate the harmful effect of NPs at higher concentrations related to certain pollution incidents in freshwater ecosystems (e.g. spill scenarios).

Although previous studies had evaluated the effects of CuO NPs and Ag NPs at higher concentrations (hundreds of milligrams per liter) on the litter decomposition in streams (Pradhan et al., 2011, 2015), as one of the most used NPs, ZnO NP effects have not yet been tested. The aim of the present study was to explore the potential effects of ZnO NP (10, 100, and 1000 mg L^{-1}) on stream fungal communities and microbial metabolic activities and to assess the consequences of these effects at the ecosystem level. We hypothesized that ZnO NPs with different concentrations would differentially affect microbial functions and fungal community structures and therefore have different impacts on the rate of litter decomposition. For the purpose, we selected a suite of functional and structural endpoints specifically targeting microbial functions (dehydrogenase activity, extracellular enzyme activities, fungal community structure, decomposition rate, and litter nutrient contents) in stream microcosms to answer the following specific questions: (i) do the concentrations affect the chemical properties of ZnO NPs in stream water; (ii) what are the consequence of ZnO NP exposures on microbial metabolic activities and fungal community structures; (iii) do any effects on microbial functions and fungal community structures have consequences for litter decomposition?

2. Materials and methods

2.1. Poplar leaf conditioning

Populus nigra L. (Poplar) leaves were collected in a forest (34°56′24.73″N, 112°25′56.15″E, 134.5 m altitude, Jiyuan, China) along the Tiannv stream (1–3 m width, 0.5–1 m depth) belong to the Yanwa River. The leaves were soaked in deionized water, cut into discs (diameter of 12 mm), which were subsequently dried at 40 °C to a constant weight. Sets of the leaf discs (0.3 ± 0.03 g) were enclosed in fine mesh (0.5 mm mesh size) nylon mesh bags (N = 63, 15 × 20 cm), which were placed into a bamboo cage and then immersed in the stream for microbial colonization. All the litter bags were retrieved, placed into a cool box with stream water, and returned to the laboratory after two weeks. During the period of microbial colonization, the physicochemical parameters of the stream water was monitored each 2 d in situ by a HQ Series Portable Meter (ProPlus, YSI, USA), which were shown in Table S1. The stream water (25 L) was collected and stored at −20 °C for water renewal throughout the whole experiment.

2.2. Preparation of ZnO NP stock suspension

ZnO NPs (≤50 nm) were purchased as an aqueous suspension (40 wt% in H_2O) from Aladdin Industrial Inc. (Shanghai, China). The stock suspension (60 g L^{-1}) was prepared in deionized water by sonication at 40 kHz in a sonication bath (KQ-500DE, ShuMei®, Kunshan, China) for 30 min in dark before use. Characterization by transmission electron microscopy (TEM) at 200 kV (JEM-2010, JEOL, Tokyo, Japan) showed that size of the ZnO NPs in the stock suspension ranged from 9 to 20 nm as shown in Fig. S1 and the average diameter was 14.9 ± 4.5 nm.

2.3. Microcosm experiments

All leaf discs from each litter bag were gently rinsed with deionized water to remove the sediment and were each placed into 150 mL sterile Erlenmeyer flasks (N = 63) with 60 mL of filtered (Whatman®, 1.2 μm pore size) and sterilized (121 °C, 30 min) stream waters. Three microcosms were used for assessing the initial value of all parameters. Stream water was supplemented with increasing nominal concentrations of ZnO NPs as followed: 0, 10, 100 and 1000 mg L^{-1}, respectively. All microcosms were kept under shaking (150 r min^{-1}) with a 12 h light: 12 h dark photoperiod at 16 ± 0.8 °C. The light was supplemented by fluorescent lamps with an intensity of 28 W m^{-2} (400–750 nm). The stream water and the ZnO NPs were renewed each 7 d. After 0, 5, 15, 33, 43 and 50 d of exposure, a set of 12 microcosms (three replicates for each treatment per sampling time) was taken to measure the leaf mass