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Distribution and bioavailability of ceria nanoparticles in an aquatic ecosystem model

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HIGHLIGHTS

- ▶ We simulated a freshwater ecosystem in laboratory.
- ▶ A radiotracer technique was used as the quantitative method.
- ▶ Distribution and fate of ceria NPs in the aquatic ecosystem model were studied.
- ▶ Hornworts, snails and fish quickly accumulated and desorbed the ceria NPs.
- ▶ Sediments were found to be the ultimate sink of ceria NPs.

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ABSTRACT

Along with the increasing utilization of engineered nanoparticles, there is a growing concern for the potential environmental and health effects of exposure to these newly designed materials. Understanding the behavior of nanoparticles in the environment is a basic need. The present study aims to investigate the distribution and fate of ceria nanoparticles in an aquatic system model which consists of sediments, water, hornworts, fish and snails, using a radiotracer technique. Concentrations of ceria in the samples at regular time intervals were measured. Ceria nanoparticles were readily removed from the water column and partitioned between different organisms. Both snail and fish have fast absorption and clearance abilities. Hornwort has the highest bioaccumulation factors. At the end of the experiment, sediments accumulated most of the nanoparticles with a recovery of 75.7 ± 27.3% of total ceria nanoparticles, suggesting that sediments are major sinks of ceria nanoparticles.

1. Introduction

Engineered nanoparticles (ENPs), which are defined as anthropogenic materials less than 100 nm in at least one dimension, have been manufactured in a large scale and found applications in various areas, such as electronics, biomedicine, textile, cosmetics and environmental remediation, due to their unique properties different from their molecular and bulk counterparts (Masui et al., 2000; Ahn et al., 2006). As a result, the deliberate and accidental release of ENPs into the environment is inevitable and concerns over the potential impacts that their release may have on human health and the environment are increasing (Biswas and Wu, 2005). The aquatic system, as an essential part of the environment, is particularly at risk of exposure to ENPs, as it acts as the ultimate repository of most contaminants such as industrial water and urban waste sewage which may contain industrial nanoscale products or by-products (Hardman, 2006). Consequently, unforeseen chemical and biological consequences may occur. It is therefore necessary to research on the toxicological and ecotoxicological risk of nanomaterials in the aquatic environment.

Recently, many reports on the behavior of ENPs in the aquatic environment emerged and factors influencing the behavior of ENPs in water were also studied. Once ENPs are in the water/sediment environment, their form, distribution between media, and fate will be very complicated and dependent on a variety of physicochemical and biological influences (Weinberg et al., 2011). The potential behavior and fate of ENPs in an aquatic system may include dissolution, agglomeration, sedimentation, association, reaction and decomposition (Hardman, 2006). For example, divalent cations and anions (e.g., Ca^{2+} and SO_4^{2-}) can compress the double electrical layer on the surface of nanoparticles and destabilize the particulates suspension and cause subsequent sedimentation (Zhang et al., 2009a). This may cause poor mobility and long-time retention of nanoparticles in the environment. On the other hand, nanoparticles can absorb natural organic matter (NOM), which will

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significantly reduce their aggregation in the aquatic environment (Kennedy et al., 2008). Ceria NPs were found to be stabilized significantly by Suwannee River NOM and Bihain NOM in both water and algae medium (Quik et al., 2010). It can be predicted that if nanoparticles are stabilized by adhering contaminants resembling NOM, it will result in a long time maintenance of both nanoparticles and contaminants in the water column. In addition, influenced by physicochemical or biological factors, reaction (e.g., photolysis, oxidation) and decomposition (e.g., biodegradation) of ENPs may occur and produce toxic substances (Derfus et al., 2004). Subsequentely, the fate and behavior of ENPs may also be affected.

The above studies have deepened our understanding of the behavior of NPs in the aquatic environment. However, these investigations were limited to simple water systems and available reports on the behavior and fate of ENPs in complex natural aquatic ecosystems were very scarce. Ferry et al. (2009) found that gold nanorods could partition between different organisms in laboratory-constructed estuarine mesocosms, suggesting that gold nanorods can readily pass through the water column to marine food webs. Nanoscale TiO_2 can also transfer from daphnia to zebrafish by dietary exposure in a simplified freshwater food chain (Zhu et al., 2010). These few studies indicate that ENPs will distribute between different environmental organisms and may transfer from low to high trophic level, which present the possibility of biomagnifications in the food chain and a long term residue in the environment. Therefore, it is imperative to focus ongoing studies on the behavior and fate of ENPs in the aquatic environment, which is critical to the risk assessment of nanomaterials. In general terms, there are two main reasons accounting for the poor studies of the behavior and fate of ENPs in the aquatic environment. Firstly, influenced by their physicochemical properties (e.g., size, agglomeration and surface charge), ENPs will associate with environment components and their fate will be very complicated, varying significantly across aquatic systems and between materials (Diegoli et al., 2008; Weinberg et al., 2011). Secondly, quantifying ENPs in the aquatic environment has always been a challenge. That is because the aquatic environment is a huge and complex system containing large amounts of natural nano-sized particles. These natural backgrounds cause a great difficulty in monitoring the target ENPs, especially in the aspect of quantitative measurement (Howard, 2010). Comparing with the conventional analytical methods, radiotracer techniques can effectively distinguish between the extraneous and endogenous sources of target elements and will be well suited for tracing of ENPs in the complex environment matrix (Zhang et al., 2009b; 2011b).

Ceria nanoparticles are increasingly being used in various areas due to their unique properties (Yabe and Momose, 1998; Dawson, 2008). It is also an important member of the metal oxide nanomaterials on the OECD (Organization for Economic Cooperation and Development) list requiring immediate testing. Recently, reports on the toxicity of ceria NPs to different organisms are constantly emerging (Thill et al., 2006; Hoecke et al., 2009; Zhang et al., 2011a). In this work, we selected ceria as the model NPs to study the distribution and bioavailability of metal oxide nanomaterials in aquatic ecosystems using a radiotracer technique. This article sets out to provide direct quantitative data on the environment behavior and fate of ENPs for the nanosafety assessment.

2. Materials and methods

2.1. Synthesis of radioactive ceria NPs

The radioisotope cerium-141 was produced by $^{140}Ce(n,\gamma)^{141}Ce$ reaction. Stable ceria was bombarded with thermal neutrons at a flux of 2×10^{13} n/cm^2 s in a swimming pool reactor for 12 h at China Institute of Atomic Energy. The obtained radioactive ceria was then transformed into $^{141}Ce(NO_3)_3$ by adding H_2O_2 and HNO_3.

Radioactive ceria NPs were synthesized by the same method as the stable ones using the obtained $^{141}Ce(NO_3)_3$ as the starting material. A 0.05 M hexamethylenetetramine (HMT) solution and a 0.0375 M $^{141}Ce(NO_3)_3$ solution were prepared and stirred separately for 30 min. Then the two solutions were mixed together and kept being stirred for 3 h at 75 °C. Then precipitates were separated by centrifugation and washed with deionized water for three times. Stable ceria NPs were also prepared for characterization. Transmission electron microscopy (JEM 200CX, Japan) was applied to characterize the morphology and average size of ceria NPs. The X-ray powder diffraction was recorded on a diffractometer (X'Pert PRO MPD, Holland) in the 2θ range of 10–90°. Zeta potential and hydrodynamic size of ceria NPs in both deionized water and aquarium water were measured using dynamic light scattering (DLS) technique (90 Plus, Brookhaven, New York, USA). Zeta potential in deionized water at different pH was also measured to obtain the point of zero charge (PZC). The BET surface area of ceria nanoparticles was measured by N_2 adsorption with the single-point method.

2.2. Aquatic ecosystem model

Three replicates of an aquatic ecosystem model composed of water, sediments, fish, hornworts and snails were used as laboratories for our study. Fish (*Pseudorasbora parva*, 4–5 cm in length) and snails (*Bellamya purificata*, about 1.5 g in weight) were purchased from an aquatic market in Beijing. Hornworts (*Ceratophyllum demersum L.*) were collected from a lake in Beijing Botanical Garden. Sediments were collected from a reservoir in Beijing.

Three glass tanks with the size of 60 cm × 30 cm × 40 cm (L × W × H) were used as aquariums (Fig. 1). Sediments of 6 cm thickness were placed smoothly on the bottom of each aquarium, and 50 L of deionized water was added. For minimizing the disturbance when sampling, fish were kept in 3 nylon wire cages suspended in water. One hundred grams of hornworts were added into the water. In order to facilitate the sampling process, 30 segments with the length of about 5 cm were cut off from the top of hornwort shoots. Thirty snails were seeded in the water and 30 fish were put into each cage.

2.3. Distribution and bioavailability studies

After ten days of equilibration, all systems were in a good condition and no overt mortality was found. Then the experiment was

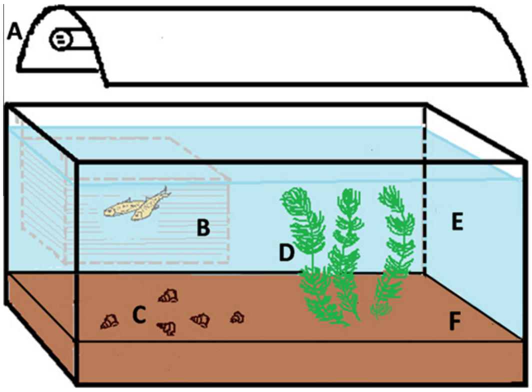

Fig. 1. Structure and composition of the aquatic system model (A) fluorescent lamp; (B) fish in the nylon cage; (C) snails; (D) hornworts; (E) water; (F) sediment. Conductivity and total salinity of the aquarium water were 1.156 ms/cm and 700 mg/L, respectively. Biological oxygen demand (BOD) was 7.5 mg/L and the pH was 7.84 ± 0.05.