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Bioaccumulation and toxic effects of decabromodiphenyl ether in the presence of nanoscale zero-valent iron in an earthworm–soil system

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HIGHLIGHTS

- We carried out multibiomarker risk assessment of BDE209 in the presence of nZVI in earthworms.
- Coexistence of high levels of BDE209 and nZVI caused intestinal damages in earthworms.
- The addition of high levels of nZVI decreased BDE209 bioaccumulation in earthworms.
- Degradation pathways of BDE209 in earthworms are proposed.

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ABSTRACT

In this study, the bioaccumulation and toxic effects of decabromodiphenyl ether (BDE209) (1 and 10 mg kg^{-1}) were investigated in the earthworm *Eisenia fetida* in the presence of different levels of nanoscale zero-valent iron (nZVI) (100, 500, and 1000 mg kg^{-1}) in an earthworm–soil system. The results demonstrated that compared to single BDE209 exposure, the addition of high levels of nZVI significantly ($P < 0.05$) inhibited growth and respiration, while increased the avoidance response of earthworms. The perturbations of antioxidant enzyme activities (superoxide dismutase (SOD) and catalase (CAT)) and the malondialdehyde (MDA) content clearly revealed that oxidative stress was induced by the two chemicals. The histopathological observations of the body wall of earthworms under a combined exposure of 10 mg kg^{-1} BDE209 with 500 or 1000 mg kg^{-1} nZVI illustrated the presence of a serious injury in the intestinal tissues after a 28-day exposure. Additionally, a gas chromatography–mass spectrometry analysis revealed that the coexistence of high level of nZVI significantly ($P < 0.05$) decreased the bioaccumulation of BDE209 in earthworms; BDE208 and BDE206 were the predominant congeners of debrominated metabolites, and 4,6-dibromobenzene-1,2,3,5-tetraol along with benzene-1,2,4,5-tetraol were determined as the two main intermediates. The possible degradation pathways were proposed on the basis of the identified products. This work provides useful information on the biological effects of BDE209 and nZVI.

1. Introduction

In recent decades, electrical and electronic waste (e-waste) pollution worldwide has garnered much attention. E-waste contains an enormous quantity of persistent organic pollutants (POPs) such as polybrominated diphenyl ethers (PBDEs). High concentrations of PBDEs (average = 2283 ng g^{-1} dw (dry weight)) were determined in e-waste dismantling site soils, and decabromodiphenyl ether (BDE209) accounted for 93% of the total concentration (Nie et al., 2015). The highly lipophilic and persistent characteristics (Garcia-Reyero et al., 2014) have made BDE209 prone to accumulate in organisms through the food chain, further

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inducing various toxic effects (Chen et al., 2012; Noyes et al., 2013).

Nanoparticles (NPs) have unique chemical and physical properties such as nanometer scale and large surface area. Increased production of NPs globally will likely increase their release into the environmental matrices (Lankadurai et al., 2015). Among NPs, nanoscale zero-valent iron (nZVI) has been extensively used in in situ remediation (i.e., soil and groundwater) and is likely to interact with other materials. Some studies have focused on the nZVI application for the remediation of BDE209-contaminated soil (Xie et al., 2014; Wu et al., 2016a, 2016b). Furthermore, there have been several studies measuring the toxicity of nZVI on biota ranging from bacteria to organisms (Lee et al., 2008; Li et al., 2015a). However, there exists insufficient information to assess the bioavailability and toxicity associated with exposure to nZVI and BDE209. Additionally, most of the nanotoxicological research studies were conducted under ideal conditions, e.g., sandy loam soil (El-Temsah and Joner, 2012, 2013), and only a few experiments have been performed in a natural soil matrix (Xie et al., 2016).

Earthworm *Eisenia fetida* (*E. fetida*), among various soil organisms, is widespread and abundant in the ecological system, and most importantly, it possesses the ability to accumulate contaminants. Furthermore, *E. fetida* could change the soil properties, improve aeration, and render contaminants available for microbial degradation through its burrowing activity (Rodriguez-Campos et al., 2014). Therefore, *E. fetida* has been commonly used in the laboratory experiment and is considered as a typical organism for understanding the effects of toxicants because of its high sensitivity (OECD, 1984).

The objectives of this paper are to quantify the potential effects of BDE209 in the presence of nZVI in *E. fetida*. First, we investigated the effects of both chemicals on avoidance, growth, and respiration of earthworms; second, superoxide dismutase (SOD) and catalase (CAT) activities as well as malondialdehyde (MDA) content were determined in earthworms to verify biochemical responses induced by the two chemicals; third, the epidermis and intestinal tissues were assessed by histological examinations; and finally, we investigated the accumulation of BDE209 in the presence of nZVI, and explored the possible degradation pathway of BDE209 in earthworms. These results and the related findings would establish a more integrated understanding of ecological risk assessment of NPs and POPs in soils.

2. Materials and methods

2.1. Experimental chemicals

BDE209 (purity > 98%) was purchased from J&K Scientific Ltd., Shanghai, China. nZVI (purity = 99.9%) was purchased from Chaowei Nanotechnology Co., Ltd., Shanghai, China; it was coated with a 1-nm passivation layer, and the specific surface area was 23 $m^2 g^{-1}$. All other reagents used in this study were of analytical grade and obtained from the Sinopharm Chemical Reagent Co., Ltd.

The characterization of nZVI was conducted by transmission electron microscopy (TEM, JEOL JEM-1400). The particle size of nZVI ranged from 50 to 100 nm, confirming the information provided by the manufacturer. The X-ray diffraction (XRD) analysis of nZVI was obtained by RIGAKU D/MAX-2550 VB/PC at 40 kV and 100 mA. The detailed data are shown in Fig. S1, supporting information (SI).

2.2. Soil and earthworm collection

Soil samples were collected from the surface layer (0–20 cm) in the center of the East China University of Science and Technology, Shanghai, China. The soil was air-dried and sieved to 2 mm. The properties of soils were summarized as follows: silty clay loam; pH 7.3; and organic matter 6.5%.

Mature earthworms were purchased from Yonghe Earthworm Culture Farm (Shanghai, China) and cultured in natural soils with cattle manure at room temperature (20 ± 1 °C) for about 28 days. The weights of earthworms were 0.52 ± 0.08 g. One hundred acclimatized earthworms were depurated for 24 h to void their gut before the addition. The container with earthworms was kept under the constant conditions (20 ± 1 °C, 12/12 h day/dark). Additionally, water was added regularly to maintain the soil moisture to 65% of the total water holding capacity.

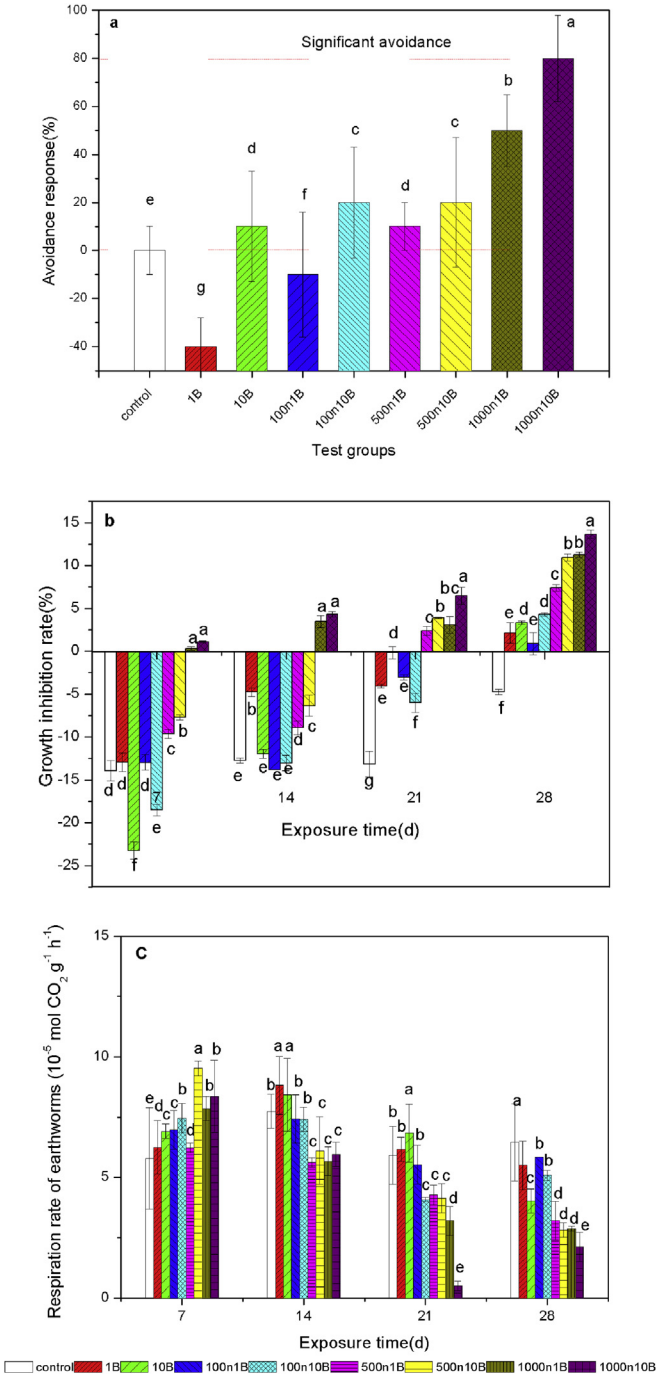

Fig. 1. Avoidance (**a**), growth (**b**), and respiration (**c**) responses of *E. fetida* exposed to various concentrations of nZVI and BDE209 after indicated incubation. The data are presented as mean ± SD (n = 3). Values indicated by different letters (a–g) were significantly different from each other ($P < 0.05$).