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Effects of decabromodiphenyl ether on lead mobility and microbial toxicity in soil

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HIGHLIGHTS

- Pb gradually transformed to stable forms over time during the entire incubation.
- An appropriate amount of BDE209 supply can facilitate the form transformation of Pb.
- The BDE209 addition can affect microbial toxicity of Pb in soil.
- Significant correlations between EXCH/MF and SBR, C_{mic} or qCO_2 were clearly observed.

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ABSTRACT

Lead (Pb) and decabromodiphenyl ether (BDE209) are the main pollutants at e-waste recycling sites (EWRSs). Focus on joint toxicological effects of the two chemicals has increasingly gained a great amount of interest. Therefore, the lab study was performed to determine the Pb mobility and microbial toxicity in a Pb-polluted soil in the presence of BDE209 for the first time. The results showed that BDE209 was barely degraded and could elicit the combined effects with Pb exposure during the entire incubation period. The exchangeable (EXCH) and carbonates fractions of Pb were transformed to organic, Fe/Mn oxides and residual fractions, and the addition of an appropriate amount (100 mg kg^{-1}) of BDE209 facilitated the transformation compared with Pb alone. In addition, soil microbial biomass C (C_{mic}), soil basal respiration (SBR) and metabolic quotient (qCO_2) increased in the beginning of the experiment and then declined with the incubation period extension, and BDE209 addition might cause notable different response relative to the control. Significant correlations between EXCH or mobility factor (MF) of Pb and SBR, C_{mic}, or qCO_2 in soil treated with BDE209 can be clearly observed. Results of the observations provide a better understanding of ecotoxicological effects of Pb and BDE209 joint exposure on indigenous microorganisms in soil at EWRSs.

1. Introduction

Electronic waste (e-waste) contamination has increasingly received emerging attention in recent years with the boost of public awareness of environmental issues, especially in developing countries. In China, over one million tons of e-wastes are flooding every year because of the cheaper labor and the loose enforcement of the environmental laws (Li et al., 2006). It is reported that by illegal imports and domestic generation, substantial e-wastes have been swarmed into Taizhou, Zhejiang Province, which is one of the most well-known e-waste dismantling center in southeast China (Gu et al., 2010).

Whereas, the techniques, including circuit board baking, acid bathing and open burning, applied in recycling process are primitive in most regions, consequently resulting in numerous releases of hazardous materials into the surrounding environment, such as lead, cadmium, beryllium, mercury, polychlorinated biphenyls and brominated flame retardants (Söderström and Marklund, 2002; Wong et al., 2007).

Lead (Pb) and decabromodiphenyl ether (BDE209) are of particular concern for the high detected level and potential toxicity to human and environmental health. For example, Pb concentration ranged from 81.3 to 2374.1 mg kg^{-1} at Taizhou (Tang et al., 2010). Another soil investigation showed that BDE209 concentrations of farmland soils from an e-waste recycling workshop were

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69.1–6319 ng g^{-1} (Luo et al., 2009). All these and other similar reports have exposed the risk to the environment and public health caused by the serious pollution of those contaminants (Zhang et al., 2011a,b; Dong et al., 2014; Zhang et al., 2014).

Soil is a dynamic and complicated ecosystem. Soil microorganisms are the predominant component for the participation of biological activity (Zeng et al., 2006; Zhou et al., 2011; Chen et al., 2014), such as the biogeochemical cycling of carbon, nitrogen and other nutrients, the control of animal and plant pests, the degradation of noxious chemicals, and the maintenance of soil structure (Filip, 2002; Vargas et al., 2011). Much evidence indicated that soil microbes were more sensitive to pollutants than plants or animals growing on the same soil (Cao et al., 2008). Soil microorganisms could respond rapidly by microbial activity (i.e. soil respiration, microbial biomass, and metabolic quotient) to soil contamination (Lu et al., 2013; Zielezny et al., 2006). Additionally, soil microbial activity could adversely impact the pollutants, which reflected the interactions between microorganisms and pollutants (Jiang et al., 2003; Suhadolc et al., 2004).

Total heavy metal concentration was important to indicate pollution risks. However, the toxic effects of heavy metal on the environment would associate with some forms rather than the total concentration of heavy metal (He et al., 2009). Therefore, the changes in metal mobility and soil microbial activity could provide a better insight into the interactive mechanism between microorganisms and pollutants.

In the areas of e-waste recycling sites (EWRSs), Pb and BDE209 were the main contaminants, and the coexistence of the two chemicals was a normalcy. However, the studies on their interaction role and combined effects on soil microorganisms are very scarce. Therefore, the research of this indoor experiment was to assess the effects of BDE209 on Pb mobility and microbial toxicity in soil. That is, Pb speciation in soil, the soil basal respiration (SBR), microbial biomass C (C_{mic}), and metabolic quotient (qCO_2) were investigated, which would be effective information for the risk managements of the combined contamination of Pb and BDE209 in soil at EWRSs.

2. Material and methods

2.1. Chemicals

BDE209 (purity > 98.0%) was obtained from J&K Scientific Ltd., Shanghai, China. Lead (II) nitrate ($Pb(NO_3)_2$) and other reagents were analytical grade and obtained from Shanghai Lingfeng Chemical Co., Ltd., Shanghai, China.

2.2. Experimental set-up

The soil (0–20 cm) used in this experiment (silty clay loam, 6.5% organic matter, pH 7.69) was collected from Taizhou EWRSs in Zhejiang province, China. The test soil was obtained by combining soil samples from five separate sites across the field. In the laboratory, the soil was air-dried and fully mixed, pebbles and large plant residues were removed, and then the soil was sieved using a 2-mm sieve. BDE209 stock solution was prepared by dissolving the BDE209 powder in *n*-hexane, and then treated the soil samples with the stock solution in order to achieve the final concentration levels (1, 10 and 100 mg kg^{-1} BDE209) in different test groups. Prior to the incubation, the background levels of Pb and BDE209 in pristine soil were determined, and the results were 160.25 mg kg^{-1} and 11.8 ng g^{-1}, respectively. Therefore, the BDE209 background concentration was far below the spiked ones and could be neglected. The contaminant/dose pairings of the two chemicals in the treatment groups were represented by control (0 mg kg^{-1} BDE209 + 160.25 mg kg^{-1} Pb), 1B (1 mg kg^{-1} BDE209 + 160.25 mg kg^{-1} Pb), 10B (10 mg kg^{-1} BDE209 + 160.25 mg kg^{-1} Pb) and 100B (100 mg kg^{-1} BDE209 + 160.25 mg kg^{-1} Pb).

All the treatments were incubated at room temperature, and kept in complete darkness. Three runs of each treatment were conducted. During the experiment, the moisture concentration of the soil was regularly adjusted to 65% of the total WHC (water holding capacity) with deionized water. Soil samples were collected for further analysis at 0, 7, 14 and 30 d after the incubation.

2.3. Analytical methods

Soil pH was measured in a 1:5 (W/V) ratio of soil to water by a glass electrode pH meter.

C_{mic} was determined with the classical chloroform fumigation–extraction method (Vance et al., 1987). Moist soil (20 g dry weight) were taken from each sample, and then split into two portions, one for fumigation, whereas the other was left un-fumigated, and both were incubated in the dark for 24 h at a temperature of 25 °C. After chloroform removal, soils samples were extracted with 40 mL 0.5 M K_2SO_4 on a shaker for 30 min at 25 °C. Organic C in the filtered extracts was measured using an automated TOC Analyser (Shimazu, TOC-500, Japan). C_{mic} was calculated by the formula: Microbial biomass C = Ec/k_{EC}, of which Ec = (organic C extracted from fumigated samples) − (organic C extracted from un-fumigated samples) and k_{EC} = 0.45 (Wu et al., 1990).

SBR was determined based on the CO_2 concentration change during 24 h of dark incubation. This was done by putting fresh soil (equivalent to 20 g dw) at 25 °C in 250 ml airtight jars with two vessels inside, where one containing 10 mL water, and the other containing 10 mL 0.5 M NaOH solution to capture the released CO_2. Which was quantified by titration with standardized 0.5 M HCl, after the CO_3^{2-} precipitated by adding 3 M barium chloride ($BaCl_2$) to the absorbed solution, using the phenolphthalein indicator solution (Lu, 1999). qCO_2 was calculated with the ratio of basal respiration to microbial biomass C (Anderson and Domsch, 1989).

Fractions of Pb were determined using the sequential extraction procedure of Tessier et al. (1979). Soil sample (1 g dry weight) was extracted by shaking in different solvents according to the steps below:

(1) *Exchangeable (EXCH):* the soil was extracted with 8 mL of 1.0 M $MgCl_2$ solution (pH 7.0) with agitation at 25 °C.
(2) *Bound to Carbonates (CAR):* the residue from (1) was extracted with 8 mL of 1.0 M NaOAc solution (pH 5.0) with agitation at 25 °C.
(3) *Bound to Fe–Mn Oxides (FeMnOX):* the residue from (2) was extracted with 20 mL of 0.04 M NH_2OH–HCl solution in 25% HOAc (v/v) in water bath with occasional agitation for 6 h at 96 °C.
(4) *Bound to Organic Matter (OMB):* the residue from (3) was extracted with 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 (pH 2.0) for 5 h at 85 °C with occasional agitation. A second 3 mL aliquot of 30% H_2O_2 (pH 2.0 with HNO_3) was then added and the sample was heated again to 85 °C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M NH_4OAc in 20% HNO_3 (v/v) was added and agitated for 30 min at 25 °C.
(5) *Residual (RES):* the residue from (4) was digested by HF–HNO_3–$HClO_4$ mixture.

Between each extraction, after the centrifugation (5000 rpm for 30 min) and filtration, the supernatant from each extraction was analyzed by atomic absorption spectrometry (AAS).

The mobility factor (MF) was an important indicator to determine the mobility of heavy metal (Ettler et al., 2005). The definition of MF was described below: