The effect of zerovalent iron on the microbial degradation of hexabromocyclododecane

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HIGHLIGHTS

- The influence of MZVI on the biodegradation of HBCD was first characterized.
- A microcosm from sediment degraded HBCD through non-debromination process.
- Co-incubation with MZVI inhibited the biodegradation ability of the microcosm.
- The addition of MZVI altered water chemistry and microbial composition.
- The negative effect of MZVI on microbial degradation of HBCD was observed.

GRAPHICAL ABSTRACT
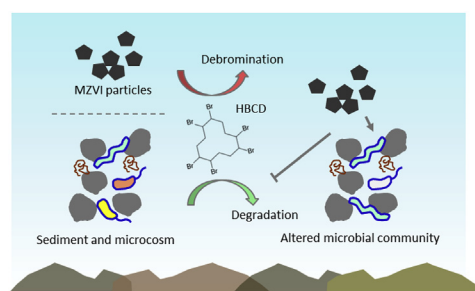
ABSTRACT

Hexabromocyclododecane (HBCD), a commonly used brominated flame retardant (BFR), has been listed as a persistent organic pollutant (POP). In order to remediate HBCD in the environment, the influence of microscale zerovalent iron (MZVI) on the HBCD degrading microcosm was evaluated. In the acclimated microcosm collected from river sediment, 49% of HBCD was initially removed through adsorption and then 30% of HBCD was biodegraded through non-debromination processes. In contrast to MZVI only, over 60% of HBCD was gradually degraded by MZVI through a debromination reaction. In the microcosm-MZVI combined system, the biodegradation ability of the microcosm was inhibited. The aqueous chemistry was changed by the addition of MZVI, which led to the alteration of microbial composition and biodegradation ability. These better understandings can facilitate an evaluation of the impact of MZVI on HBCD biodegradation when ZVI was used to remediate this BFR.

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1. Introduction

Brominated flame retardants (BFRs) have been widely used in many industrial products for decades, such as in electrical equipment, furniture, and textiles. Hexabromocyclododecane (HBCD), a brominated aliphatic cyclic hydrocarbon, is one of the most commonly used BFRs in expanded and extruded polystyrene foams. With its consistent and increasing usage, HBCD has been

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detected in increasing amounts in various environmental and human samples (Law et al., 2014; Marvin et al., 2011; Qu et al., 2007; Ryan and Rawn, 2014). HBCD is an endocrine disruptor and shows toxicity to the liver, nervous, and immune systems in humans and other animals (Darnerud, 2003; Deng et al., 2009; Dorosh et al., 2011; Palace et al., 2008; Saegusa et al., 2009). The biological mechanisms for HBCD-mediated toxicity are the alteration of enzyme expressions, the increase of hormone turn over, the inhibition of the function of enzymes and hormones, the formation of reactive oxygen species (ROS), and the induction of apoptosis (Al-Mousa and Michelangeli, 2012; Du et al., 2015; Zhang et al., 2008; Zou et al., 2013). Due to its long-term persistence, high bioaccumulability, and potential toxicity, HBCD has been added into the list of persistent organic pollutants (POPs) by the Stockholm Convention. Therefore, the regulation and remediation of this emerging contaminant is of serious concern (Koch et al., 2015; Marvin et al., 2011).

Several physical and chemical treatments have been reported for depleting HBCD. By means of pyrolysis, about 75% of HBCD was debrominated; the rest of the compound was transformed into bromo-organic compounds, which are also high-risk pollutants for the environment (Barontini et al., 2001). Photodegradation can mineralize HBCD into carbon dioxide and water by irradiation with sunlight in the presence of Fe(III)-carboxylate complexes; however, this novel method is still under development (Zhou et al., 2014). Nanoscale zerovalent iron (NZVI) sequentially debrominated HBCD under anaerobic conditions, with the formation of a double-bond between the adjacent carbon atoms (Tso and Shih, 2014); the major concern for this material is its impact on ecosystems and the cost.

Biotransformation provides an alternative choice for non-intrusive remediation toward emerging contaminants; in addition, it is eco-friendly and low cost. The biodegradation of HBCD has been reported in various environmental samples and biota (Davis et al., 2005, 2006; Gerecke et al., 2006; Szabo et al., 2010; Zegers et al., 2005). HBCD was sequentially debrominated by anaerobic microcosms or pure strains with half-lives ranging from 0.7 to 9.6 days (Gerecke et al., 2006; Peng et al., 2015a). In contrast, the HBCD degradation rate was slower in aerobic environmental samples with half-lives ranging from 11 to 63 days (Davis et al., 2005). Recently, several enzymes responsible for the aerobic transformation of HBCD have been identified. The cytochrome enzymes in liver converted HBCD into hydroxylated derivatives, which facilitated the detoxification and elimination of the hazardous compounds (Esslinger et al., 2011; Szabo et al., 2010; Zegers et al., 2005). Two hexachlorocyclohexane (HCH)-converting enzymes, LinA2 and LinB, have been assessed for their HBCD transformation abilities: the dehydrochlorinase LinA2 eliminated one hydrogen bromide from HBCD (Heeb et al., 2014) and the haloalkane dehalogenase LinB eliminated two bromine atoms through hydrolysis (Heeb et al., 2012). Naturally evolved biodegradation mechanisms are diverse; however their transformation efficiencies are limited. In addition, some metabolic intermediates could also be toxic. Therefore, combining physical/chemical treatments with biodegradation mechanisms could enhance both the degradation rate and transformation efficiency of BFRs (Peng and Shih, 2013).

Zero-valent iron (ZVI) has a high reduction ability and has been applied in pollutant remediation (Fu et al., 2014). Combining this material with biodegradation mechanisms lead to a synergistic effect on degrading some emerging contaminants (Shih et al., 2012; Xu et al., 2014). ZVI previously transformed recalcitrant compounds into less toxic or more labile by-products, which facilitated further biodegradation reactions (Kim et al., 2012; Oh et al., 2005; Xu et al., 2014). The corrosion of ZVI also led to a low redox environment,

which was suitable for some halorespiring microorganisms (Kocur et al., 2015; Lee et al., 2001; Rosenthal et al., 2004). Besides, uptaking or reducing of iron ions by microorganisms limited the formation of iron oxide precipitations and prolonged the reactive status of ZVI. Generally, NZVI displays more reactivity than micro-scale ZVI (MZVI) because of its larger surface area (Shih and Tai, 2010; Yan et al., 2013). However, NZVI showed bactericidal effect due to the generation of ROS and the interruption of energy transduction (Lee et al., 2008). It also impeded the biodegradation activity through inhibiting the expression of specific enzymes (Xiu et al., 2010). Therefore, MZVI has less impact on the ecosystems than NZVI.

The influence of MZVI on the biodegradation toward HBCD has not yet been investigated. The aim of this study is to evaluate the effect of MZVI on microbial degradation of HBCD. An acclimatized microcosm from river sediment was used to investigate the biodegradation ability; two dosages of MZVI were chosen to degrade HBCD alone or co-incubated with the microcosm. The influence of MZVI was assessed according to the degradation kinetics, the generation of bromide ions, the characteristics of water chemistry, and the microbial composition and abundance.

2. Materials and methods

2.1. Chemicals

Technical HBCD was purchased from Sigma-Aldrich (95% purity, Milwaukee, WI, USA). Reduced iron particles (purity >90%, 325 mesh) were obtained from Hayashi Pure Chemical Ind., Ltd. (Osaka, Japan). Ultra residue analysis grade of methanol, dimethyl sulfoxide (DMSO), and ethyl acetate (EA) were purchased from Burdick & Jackson (Muskegon, MI, USA). The stock solution of HBCD was prepared in DMSO. Pure water was double-distilled and deionized with a Milli-Q water purification system (Millipore, Temecula, CA, USA).

2.2. Microcosm set-up

Samples were taken from the river-bank of Hsin-Dian Creek, Taipei, Taiwan. Anaerobic sediment was collected from an anoxic zone below the sediment–water interface. The texture, pH, and element composition (carbon, hydrogen, nitrogen, sulfur, and oxygen) of the sediment were analyzed (Peng et al., 2015b). The content of basal salt medium (BSM) was according to our previous report (Peng et al., 2015b); the medium was prepared anaerobically by boiling, purged with N_2 during cooling, and sterilized by autoclaving at 121 °C for 30 min. Eight grams of sediment was acclimatized with 50 mL of anoxic BSM medium containing 10 mg L^{-1} HBCD. The non-inoculated medium was used as a blank control; for sterilized control, the microcosm was autoclaved at 121 °C for 30 min. The concentration of HBCD in the medium after acclimatizing for around 1 month was measured. The cultures and all of the following experimental settings were handled in an anaerobic chamber, placed in amber bottles, sealed, and incubated at 30 °C.

2.3. Degradation kinetics analysis

The removal kinetics of HBCD by the acclimatized microcosm, MZVI, and the co-incubated system was investigated. The microcosm was washed once with anoxic BSM medium and then cultured with the same medium (100 mL) containing 10 mg L^{-1} HBCD. This spiked HBCD concentration was higher than the 0.43−4.2 pg/L concentration found in the Great Lakes surface water (Venier et al., 2014) and the 0.03−31.6 ng g^{-1} concentration in the