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Biochar accelerates microbial reductive debromination of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) in anaerobic mangrove sediments

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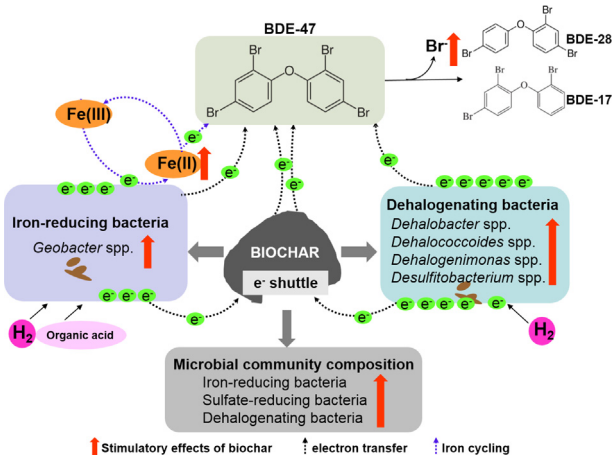
HIGHLIGHTS

- Biochar enhanced anaerobic reductive debromination of BDE-47 in mangrove sediment.
- The stimulatory effect of biochar on BDE-47 debromination was dosage-dependent.
- Bacterial iron-reducing process was promoted by biochar amendment.
- Biochar amendment increased the abundances of dehalogenating bacteria.
- Biochar selectively enriched microbial communities involved in PBDE degradation.

GRAPHICAL ABSTRACT



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ABSTRACT

A common congener of polybrominated diphenyl ethers, 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), is a prevalent, persistent and toxic pollutant. It could be removed by reduction debromination by microorganisms but the rate is often slow. The study hypothesized that spent mushroom substrate derived biochar amendment could accelerate the microbial reductive debromination of BDE-47 in anaerobic mangrove sediment slurries and evaluated the mechanisms behind. At the end of 20-week experiment, percentages of residual BDE-47 in slurries amended with biochar were significantly lower but debromination products were higher than those without biochar. Such stimulatory effect on debromination was dosage-dependent, and debromination was coupled with iron (Fe) reduction. Biochar amendment significantly enhanced the Fe(II):Fe(III) ratio, Fe(III) reduction rate and the abundance of iron-reducing bacteria in genus *Geobacter*, thus promoting bacterial iron-reducing process. The abundances of dehalogenating bacteria in genera *Dehalobacter*, *Dehalococcoides*, *Dehalogenimonas* and *Desulfitobacterium* were also stimulated by biochar. Biochar as an electron shuttle might increase electron transfer from iron-reducing and dehalogenating bacteria to PBDEs for their reductive debromination. More, biochar shifted microbial

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community composition in sediment, particularly the enrichment of potential PBDE-degrading bacteria including organohalide-respiring and sulfate-reducing bacteria, which in turn facilitated the reductive debromination of BDE-47 in anaerobic mangrove sediment slurries.

1. Introduction

Biochar, a carbon-rich material produced by oxygen-limited pyrolysis of biomass, improves soil fertility, enhances nutrient availability, mitigates climate change and remedies environmental pollution [1]. Biochar particles have large internal surface areas and high aromatic nature thus enhancing the sorption of organic contaminants to their surfaces and reducing the mobility and bioavailability of pollutants [2–4]. So far, the applications of biochar on organic pollutant removal have been extensively reported [1,5], but most of these studies focused on the capability of biochar to adsorb contaminants. Researches on the roles of biochar in degrading pollutants are very limited and even less on the mechanisms behind. Microbial degradation is a major natural attenuation process controlling the fate of organic pollutants in contaminated soils [6–8]. The stimulatory effects of biochar on microbial transformation and removal of pentachlorophenol (PCP) [9,10] have been reported previously. On the contrary, inhibitory effects of biochar on the microbial degradation rate of organic pesticides were also found [5]. Given these inconsistent results, the biochar effects on the microbial degradation of organic pollutants and the mechanisms behind must be further researched prior to its application as a soil amendment strategy for the remediation of contaminated sites.

Polybrominated diphenyl ethers (PBDEs), a class of brominated flame retardants, are ubiquitous environmental pollutants because of their extreme persistence and adverse effects on ecosystem and human health [11,12]. Because of the strong hydrophobicity, PBDEs tend to retain and accumulate in soil/sediment [2]. High concentrations of PBDEs have been detected in soils/sediments around the world, especially in the coastal and estuarine areas near electronic wastes recycling sites [11,13]. Along tropical and subtropical coastlines, mangroves are important intertidal wetlands with close proximity to human activities, and mangrove sediments have been reported to be contaminated with PBDEs [2]. Due to frequent tidal flooding, mangrove sediments, except the surface few centimeters, are often anaerobic [8,14]. In anaerobic environment, microbial reductive dehalogenation was the predominant process responsible for the degradation of halogenated organic pollutants, such as polychlorinated biphenyls (PCBs) [15], PCP [9] and PBDEs [11,16,17]. During the reductive dehalogenation process, strictly anaerobic organohalide-respiring bacteria (OHRB), including dehalogenating bacteria and some iron-reducing bacteria, transformed highly halogenated pollutants to less halogenated end-products [6,18]. Anaerobic reductive debromination of PBDEs by dehalogenating bacterial consortia/isolates has been reported by previous study [7,11]. The intrinsic potential of mangrove sediments to reductively debrominate BDE-153 was found to be higher than that in marine and freshwater pond sediments, probably because mangrove sediment harbored more diverse and special microbial groups to degrade organic pollutants [8]. However, the intrinsic degradation of PBDEs is still slow [11], thus new explorations for accelerating the microbial degradation of PBDEs are needed. Chen et al. [17] reported that the enhanced abundances of dehalogenating bacteria (*Dehalobacter* spp. and *Dehalococcoides* spp.) in PBDE-contaminated mangrove sediments added by nitrogen (N), and such biostimulation increased PBDE reductive debromination. Not only nutrient addition, it is possible that biochar may also stimulate the PBDE-degrading bacteria and the microbial reductive debromination of PBDEs in anaerobic mangrove sediment, similar to the positive effect of biochar on the biodegradation efficiency of PAHs and PCP mentioned above.

The present study aims to investigate the effect of spent mushroom substrate (SMS) derived biochar on microbial reductive debromination of PBDEs in anaerobic mangrove sediment slurries spiked with 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47). The study also attempts to explore the mechanisms behind the biochar-induced effect on microbial reductive debromination. SMS as a bulky waste byproduct of commercial mushroom industry has been extensively used for the bioremediation of soils contaminated with organic pollutants [19]. BDE-47 was selected as the model PBDE congener because it was one of the most toxic and prevalent congeners [2,17].

2. Materials and methods

2.1. Sediment and biochar preparation

Subsurface sediment (5–20 cm) was freshly collected from the middle part of the mature mangrove forest in Mai Po (22°29′N to 22°31′N and 113°59′E to 114°03′E), a typical mangrove swamp located in the northwestern Hong Kong SAR. The sediment characteristics were measured according to the previous methods [20] and showed in Supporting Information (SI) Table S1. The fresh sediment was mixed homogenously and passed through an 8 mm sieve to remove large sand grains and plant debris before use.

The biochar was produced by charring SMS, sourced from a mushroom industry in Zhangzhou, Fujian, China, at 500 °C for 4 h in a muffle furnace (Isotemp, Fisher Scientific, USA) under oxygen-limited conditions using nitrogen gas (N_2) as the medium gas. The biochar was then allowed to naturally cool to room temperature, gently ground, and homogenized to pass a 250 μm sieve. The pH of the biochar was 9.65. The biochar was washed with 0.1 M HCl followed by distilled water till neutral pH [9], then oven-dried at 105 °C for 24 h. Only HCl was used to remove the metal salts from the biochar in this study, instead of HCl-HF to remove heavy metals, SiO_2 and other soluble salts, as the main objective of the present study was to investigate the effect of biochar on the microbial degradation of BDE-47, not the adsorption dynamics of BDE-47 on biochar surface. However, as trace heavy metals in biochar are known to pose threats to microorganisms in sediment [21], while SiO_2, as one of the most important components of environment matrix, has been widely reported to be non-toxic to microorganisms [22,23], so only heavy metals need to be removed by washing the biochar with HCl. The washing of biochar only with HCl prior to their experiments was the same procedure as described by previous studies [9,24]. The basic properties and element composition of the biochar were determined with previously described methods [9,20] and the mean values of 9 replicates are shown in Table S1.