



# Formation of brominated phenolic contaminants from natural manganese oxides-catalyzed oxidation of phenol in the presence of Br<sup>-</sup>



Kunde Lin <sup>a, b, \*</sup>, Lianghui Song <sup>b</sup>, Shiyang Zhou <sup>b</sup>, Da Chen <sup>c</sup>, Jay Gan <sup>d</sup>

<sup>a</sup> State Key Laboratory of Marine Environmental Science, Key Laboratory of the Ministry of Education for Coastal and Wetland Ecosystem, College of the Environment and Ecology, Xiamen University, Xiamen 361005, China

<sup>b</sup> College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, China

<sup>c</sup> Cooperative Wildlife Research Laboratory and Department of Zoology, Southern Illinois University, Carbondale, IL 62901, USA

<sup>d</sup> Department of Environmental Sciences, University of California, Riverside, CA 92521, USA

## HIGHLIGHTS

- BPCs are produced from MnO<sub>x</sub>-catalyzed oxidation of phenol in the presence of bromide.
- The formation pathways were proposed.
- BPCs production increased with increasing concentrations of Br<sup>-</sup> or phenol.
- MnO<sub>x</sub>-mediated oxidation may play a role on the natural production of BPCs.

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## ABSTRACT

Brominated phenolic compounds (BPCs) are a class of persistent and potentially toxic compounds ubiquitously present in the aquatic environment. However, the origin of BPCs is not clearly understood. In this study, we investigated the formation of BPCs from natural manganese oxides (MnO<sub>x</sub>)-catalyzed oxidation of phenol in the presence of Br<sup>-</sup>. Experiments at ambient temperature clearly demonstrated that BPCs were readily produced via the oxidation of phenol by MnO<sub>x</sub> in the presence of Br<sup>-</sup>. In the reaction of MnO<sub>x</sub> sand with 0.213 μmol/L phenol and 0.34 mmol/L Br<sup>-</sup> for 10 min, more than 60% of phenol and 56% of Br<sup>-</sup> were consumed to form BPCs. The yield of BPCs increased with increasing concentrations of phenol and Br<sup>-</sup>. Overall, a total of 14 BPCs including simple bromophenols (4-bromophenol, 2,4-dibromophenol, and 2,4,6-tribromophenol), hydroxylated polybrominated diphenyl ethers (OH-PBDEs), and hydroxylated polybrominated biphenyls (OH-PBBs) were identified. The production of BPCs increased with increasing concentrations of Br<sup>-</sup> or phenol. It was deduced that Br<sup>-</sup> was first oxidized to form active bromine, leading to the subsequent bromination of phenol to form bromophenols. The further oxidation of bromophenols by MnO<sub>x</sub> resulted in the formation of OH-PBDEs and OH-PBBs. In view of the ubiquity of phenol, Br<sup>-</sup>, and MnO<sub>x</sub> in the environment, MnO<sub>x</sub>-mediated oxidation may play a role on the natural production of BPCs.

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## 1. Introduction

Brominated phenolic contaminants (BPCs) including simple

bromophenols, hydroxylated polybrominated diphenyl ethers (OH-PBDEs), and hydroxylated polybrominated biphenyls (OH-PBBs) are a class of organobromine compounds widely present in the environment (Gribble, 2010). Simple bromophenols such as 4-bromophenol (**1**), 2,4-dibromophenol (**2**), and 2,4,6-tribromophenol (**3**) are found to occur ubiquitously in air, water, and sediment, and their origin is thought to be both natural and anthropogenic (WHO, 2005). In contrast, OH-PBDEs and OH-PBBs

\* Corresponding author. College of the Environment and Ecology, Xiamen University, Xiamen 361102, China.

E-mail address: [link@xmu.edu.cn](mailto:link@xmu.edu.cn) (K. Lin).

are not originally man-made chemicals and are traditionally recognized as metabolites of the brominated flame retardants PBDEs and PBBs, respectively (Safe et al., 1978; Stapleton et al., 2009). However, the detection of 6-hydroxy-2,2',3,4,4',5-hexaBDE (6-OH-BDE137) and 2,2'-hydroxy-3,3',5,5'-tetrabrominated biphenyl (2,2'-diOH-BB80, **4**) in marine biota could not be adequately explained by the anthropogenic route, suggesting the existence of natural formation pathways (Malmvarn et al., 2005; Marsh et al., 2005).

Previous studies have shown that OH-PBDEs and OH-PBBs may originate from biotic and abiotic processes in natural or engineered environments (Von Gunten, 2003; Zhai and Zhang, 2011; Agarwal et al., 2014, 2015; Lin et al., 2014a, b). Agarwal et al. (2014) reported marine bacteria as producers of OH-PBDEs/PBBs and for the first time established a genetic and molecular foundation for their production. Based on the proposed bacterial biosyntheses of OH-PBDEs, Agarwal et al. (2015) recently identified new structural classes of OH-PBDEs in marine sponges. Our previous study showed that bromoperoxidase isolated from the red alga *Corallina officinalis* catalyzed the dimerization of bromophenols **2** and **3** in the presence of Br<sup>-</sup> to form 2'-hydroxylated-2,3',4,5',6-pentaBDE (2'-OH-BDE121) and 4'-OH-BDE121 (Lin et al., 2014a). In addition to enzymatic processes, OH-PBDEs/PBBs have been found as byproducts of oxidation during treatment of water containing Br<sup>-</sup>. Br<sup>-</sup> is a ubiquitous component of natural waters, with typical concentrations of 0.6–2.5 μmol/L in sources of drinking water and ~1.0 mmol/L in seawater (Flury and Papritz, 1993; Westerhoff et al., 1994). When contacting with oxidative disinfectants such as chlorine, ozone, and chlorine dioxide, Br<sup>-</sup> in water may be quickly oxidized to hypobromous acid (HOBr), which may subsequently react with natural organic matter (NOM) to yield various BPCs (Von Gunten, 2003; Zhai and Zhang, 2011). For example, Zhai and Zhang (2011) reported the formation and decomposition of some BPCs during chlorination of simulated raw water containing 3.0 mg C/L Suwannee River humic acid and 25 μmol/L Br<sup>-</sup>. These studies collectively suggest that Br<sup>-</sup> may serve as an important precursor for the biotic/abiotic formation of BPCs.

Leri et al. (2010) probed Br distribution and speciation in estuarine and marine sediments using *in situ* X-ray spectroscopy and spectromicroscopy and found that organobromine compounds were prevalent throughout diverse sedimentary environments, and that their occurrence was correlated with organic carbon and metals such as Fe and Mn. The authors speculated that the formation of organobromine compounds was likely due to interactions between metal cations and NOM. However, it is unclear whether manganese oxides (MnO<sub>x</sub>) are responsible for the conversion of Br<sup>-</sup> to organobromine compounds. Manganese oxides are among the most important naturally occurring oxidants in sediments, particularly in marine sediments (Post, 1999). Manganese oxides readily participate in a wide variety of environmental redox processes and influence the environmental fate of organic contaminants (Borch et al., 2010). For example, the transformation of bromophenols **1–3** by δ-MnO<sub>2</sub> led to the formation of OH-PBDEs and OH-PBBs (Lin et al., 2014b). However, it is unknown whether MnO<sub>x</sub>-catalyzed oxidation of organic compounds would be coupled with simultaneous oxidation of Br<sup>-</sup> to produce BPCs.

The objective of this study was to explore the formation of BPCs through MnO<sub>x</sub>-catalyzed oxidation of phenol in the presence of Br<sup>-</sup>. The experiments were carried out with natural MnO<sub>x</sub> sand commonly found in the environment and phenol was used as a model substrate. The formed BPCs were identified and possible reaction pathways were proposed. The effects of Br<sup>-</sup> and phenol concentrations on the reaction were also evaluated.

## 2. Materials and methods

### 2.1. Chemicals

Technical standards of **1** (>99%), **2** (>95%) and **3** (>98%), phenol (>99.5%), potassium bromide (>99%), and tetrabutylammonium hydroxide solution (1.0 M in methanol) were purchased from Sigma-Aldrich (St. Louis, MO). Iodomethane (>98%) was purchased from Chengdu Aikeda Chemical Reagent (Chengdu, Sichuan, China). Authentic standards of 2'-hydroxy-2,3',4,5'-tetraBDE (2'-OH-BDE-68, **5**) was purchased from AccuStandard (New Haven, CT). Reagent water (18.2 MΩ·cm resistivity) was prepared using a Millipore water purification system (Millipore S.A.S., Molsheim, France). Other chemicals used were of analytical or high performance liquid chromatography (HPLC) grade. All solutions were stored at 4 °C before use.

6'-Hydroxy-2,3',4-triBDE (6'-OH-BDE-25, **6**) was prepared by Baeyer-Villiger oxidation followed by acid-catalyzed hydrolysis of 4-bromo-2-(2,4-dibromophenoxy)benzaldehyde according to a modified method from Marsh et al. (2003). The intermediate 4-bromo-2-(2,4-dibromophenoxy)benzaldehyde was prepared by the coupling of 2,4-dibromophenol with 4-bromine-2-fluorobenzaldehyde. Compound **4** was synthesized by tetrabromination of 2,2'-biphenyldiol using benzyltrimethylammonium tribromide (Marsh et al., 2005). Both crude products were purified on a semipreparative C18 column. The synthetic standards were characterized by <sup>1</sup>H NMR and gas chromatograph (GC) coupled with mass spectrometer (MS). The analytical data are given in Table S1 in Supplementary data.

The MnO<sub>x</sub> sand was a common material used for drinking water treatment and purchased from Kaiyuan Ceramic Materials (Dengfeng, Henan, China). The MnO<sub>x</sub> sand was passed through a 60-mesh mesh prior to use and analyzed with X-ray diffraction spectrometer (PANalytical X'Pert PRO, 40 kV and 40 mA, Cu Ka, λ = 0.154 nm), X-ray photoelectron spectroscopy (Kratos AXIS Ultra DLD, Shimadzu), and energy dispersive spectroscopy (Shimadzu, Kyoto, Japan). The analytical results showed that Mn, Fe, Al, Si, O, K, and C were the main elements and MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, α-Fe<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> were the main oxides in the MnO<sub>x</sub> sand. The surface area of the MnO<sub>x</sub> sand was determined to be 28.2 m<sup>2</sup>/g by Brunauer-Emmett Teller adsorption (ASAP 2020, Micromeritics Instrument, Norcross, GA).

### 2.2. Experimental procedure

All experiments were conducted in 30-mL amber glass vials. Briefly, the reaction was initiated by the addition of 1 mL of aqueous mixture of phenol and KBr at different concentrations to vials containing 2.0 g of MnO<sub>x</sub> sand. The vials were sealed to prevent volatilization of phenol and the closed vials were incubated at 25 ± 1 °C in the dark. The pH of reaction solution was near 7.0 without pH adjustment. The pH was measured before and after reaction and showed a negligible change, likely due to the release of H<sup>+</sup> in the subsequent reaction of Br<sub>2</sub> with phenol. The effect of Br<sup>-</sup> on the reaction products was evaluated by changing the initial Br<sup>-</sup> concentration (0, 0.034, 0.34, and 3.4 mmol/L) while keeping phenol concentration fixed at 2.13 μmol/L. The effect of phenol on the reaction was assessed by changing the phenol concentration (0, 0.213, 2.13, 21.3, and 213 μmol/L) while keeping the Br<sup>-</sup> concentration fixed at 0.34 mmol/L. At designated time intervals (0, 5, 10, 20, 40, 80, 160 min), six samples were collected and subjected to the subsequent analysis. Three of the samples were used for the characterization and analysis of BPCs, and the other samples were used to determine the remaining concentrations of phenol, Mn(II) and Br<sup>-</sup>.

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