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Biologically mediated abiotic degradation (BMAD) of bisphenol A by manganese-oxidizing bacteria

Nusrat Shobnam [a,1], Yanchen Sun [b,c], Maheen Mahmood [a], Frank E. Löffler [b,c,d,e,f], Jeongdae Im [a,*]

[a] Department of Civil Engineering, Kansas State University, Manhattan, KS 66506, USA
[b] Department of Civil and Environmental Engineering, University of Tennessee, Knoxville, TN 37996, USA
[c] Center for Environmental Biotechnology, University of Tennessee, Knoxville, TN 37996, USA
[d] Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[e] Department of Microbiology, University of Tennessee, Knoxville, TN 37996, USA
[f] Department of Biosystems Engineering and Soil Science, University of Tennessee, Knoxville, TN 37996, USA

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ABSTRACT

Bisphenol A (BPA), a chemical of environmental concern, is recalcitrant under anoxic conditions, but is susceptible to oxidative degradation by manganese(IV)-oxide (MnO_2). Microbial Mn(II)-oxidation generates $MnO_{2\text{-bio}}$; however, BPA degradation in cultures of Mn(II)-oxidizing bacteria has not been explored. We assessed $MnO_{2\text{-bio}}$-mediated BPA degradation using three Mn(II)-oxidizing bacteria, *Roseobacter* sp. AzwK-3b, *Erythrobacter* sp. SD-21, and *Pseudomonas putida* GB-1. In cultures of all three strains, enhanced BPA degradation was evident in the presence of Mn(II) compared to replicate incubations without Mn(II), suggesting $MnO_{2\text{-bio}}$ mediated BPA degradation. Increased Mn(II) concentrations up to 100 μM resulted in more $MnO_{2\text{-bio}}$ formation but the highest BPA degradation rates were observed with 10 μM Mn(II). Compared to abiotic BPA degradation with 10 μM synthetic MnO_2, live cultures of strain GB-1 amended with 10 μM Mn(II) consumed 9-fold more BPA at about 5-fold higher rates. Growth of strain AzwK-3b was sensitive to BPA and the organism showed increased tolerance against BPA in the presence of Mn(II), suggesting $MnO_{2\text{-bio}}$ alleviated the inhibition by mediating BPA degradation. The findings demonstrate that Mn(II)-oxidizing bacteria contribute to BPA degradation but organism-specific differences exist, and for biologically-mediated-abiotic-degradation (BMAD), Mn-flux, rather than the absolute amount of $MnO_{2\text{-bio}}$, is the key determinant for oxidation activity.

1. Introduction

Bisphenol A (BPA) is a high production volume chemical for the manufacture of polycarbonate plastic and epoxy resins (Staples et al., 1998; Crain et al., 2007; Rochester, 2013). The global demand of BPA exceeded 7.7 million tons in 2015 and is predicted to grow (Industry Experts, 2017). Low concentrations of BPA detected in sediment and surface waters (Bolz et al., 2001; Heemken et al., 2001; Klečka et al., 2009) and possible risks of human exposure (Hengstler et al., 2011; Sekizawa, 2008) triggered substantial efforts exploring the environmental fate of BPA (Staples et al., 1998; Im and Löffler, 2016). With a K_{OW} of 3.42, BPA is susceptible to adsorption by suspended solids and solid matrices (e.g., sediments) (Staples et al., 1998). Diverse taxa of bacteria, fungi, algae, and plants have been demonstrated to degrade BPA under oxic conditions (Staples et al., 1998; Im and Löffler, 2016; Zhang et al., 2013). Under anoxic conditions, several studies concluded that BPA is recalcitrant (Kang and Kondo, 2002, 2005; Voordeckers et al., 2002; Im et al., 2014a), until recent efforts demonstrated that chemically synthesized manganese dioxide ($MnO_{2\text{-syn}}$) mediated BPA transformation and mineralization without oxygen requirement (Lin et al., 2009, 2013; Im et al., 2015; Balgooyen et al., 2017; Huang et al., 2018; Saroyan et al., 2019). GC/MS analysis detected a number of transformation products (Lin et al., 2009), and hydroxycumyl alcohol (HCA) was identified as a major intermediate (Im et al., 2015, 2014b; Balgooyen et al., 2017; Wang et al., 2018).

MnO_2 is a naturally occurring, strong oxidant, abundant in anoxic

* Correspondence to: Kansas State University, Department of Civil Engineering, 1701C Platt ST, Manhattan, KS 66506, USA.
E-mail address: jeongdaei@ksu.edu (J. Im).
[1] Present address: Govind Development, LLC, 9510 Leopard St., Corpus Christi, TX 78410, USA.

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soils as well as marine and freshwater sediments (Vandieken et al., 2012; Sigg et al., 1987). Therefore, its efficacy to oxidize organic (e.g., antibacterial agents, pesticides, endocrine disruptors, and heterocyclic compounds) (Remucal and Ginder-Vogel, 2014; Sochacki et al., 2018; Zhang et al., 2017) and inorganic (e.g., HS^-, heavy metals) (Miyata et al., 2007; Hennebel et al., 2009; Villalobos et al., 2005) contaminants has been widely investigated. The formation of MnO_2 mineral phases is not fully understood, but it is believed to be mainly attributed to microbial activities (Tebo et al., 2004; Learman et al., 2011). Biologically produced reactive mineral phases have attracted attention for their roles in the degradation of priority pollutants in subsurface environments, and biologically-mediated abiotic degradation (BMAD) has drawn attention as a sustainable remediation approach (Im et al., 2014b; He et al., 2015; Niedźwiecka and Finneran, 2015; Kwon et al., 2011; Perreault et al., 2012). Many microorganisms, including bacteria and fungi, are known to catalyze Mn(II) oxidation leading to the formation of MnO_2 in natural and engineered environments (Tebo et al., 2004). The few studies that examined the role of Mn(II)-oxidizing bacteria (MOB) controlling the environmental fate of contaminants used either purified, cell-free $MnO_{2\text{-bio}}$ (Kim et al., 2012; Forrez et al., 2010, 2011; Tran et al., 2018) or mixed cultures (Sochacki et al., 2018; Forrez et al., 2009; Zhang et al., 2015). A recent study demonstrated the degradation of cylindrospermopsin, an alkaloid cyanotoxin, using Mn(II)-oxidizing bacterial isolates in the presence of exogenous Mn(II) (Martínez-Ruiz et al., 2020b, 2020a). Although BPA degradation by $MnO_{2\text{-syn}}$ has been extensively studied (Im and Löffler, 2016; Remucal and Ginder-Vogel, 2014), the potential impact of microbial Mn(II) oxidation (i.e., BMAD) on BPA is uncertain.

To assess the validity of the BMAD principle, we assessed BPA degradation in cultures of the three extensively studied MOB including *Roseobacter* sp. strain AzwK-3b, *Erythrobacter* sp. strain SD-21, and *Pseudomonas putida* strain GB-1. These MOB species were selected on the basis of distinct Mn(II) oxidation mechanisms. Strain AzwK-3b oxidizes Mn(II) indirectly through the enzymatic formation of extracellular reactive oxygen species (ROS), specifically superoxide radicals (Learman et al., 2011). Strain SD-21 utilizes a Ca^{2+}-binding heme peroxidase (Anderson et al., 2009), and strain GB-1 employs multicopper oxidases and peroxidase cyclooxygenases (also referred to as animal heme peroxidases) to oxidize Mn(II) (Geszvain et al., 2016). The findings imply that Mn flux, rather than the absolute amount of $MnO_{2\text{-bio}}$, is a key determinant for BMAD activity, and highlight that oxic-anoxic transition zones with active Mn cycling are potential hotspots for MnO_2-mediated BPA degradation.

2. Materials and methods

2.1. Chemicals and preparation of $MnO_{2\text{-syn}}$

BPA (> 99% purity), $MnCl_2 \times 4H_2O$ (> 98% purity), leucoberbelin blue (LBB, 65% dye content), and L-ascorbic acid were purchased from Sigma-Aldrich (St. Louis, MO). Metyrapone [2-methyl-1,2-di-(3-pyridyl)−1-propanone] was purchased from Cayman Chemical Company (Ann Arbor, MI). $MnO_{2\text{-syn}}$ was prepared according to established procedures (see Supplementary Material) (Kostka and Nealson, 1998), and HCA (> 95% purity confirmed by NMR) was synthesized as previously described (Im et al., 2015). TraceMetal grade HNO_3 (67–70%, wt/wt) was purchased from Fischer Scientific (Hampton, NH).

2.2. Strains and culturing conditions

Strain AzwK-3b and strain SD-21 were maintained in an organic-rich K-medium (2 g L^{-1} peptone, 0.5 g L^{-1} yeast extract, 20 mM HEPES buffer, pH 7.5) prepared with 75% (vol/vol) artificial seawater (K-ASW) (Learman et al., 2011). Strain GB-1 was grown in Lept medium (0.5 g L^{-1} yeast extract, 0.5 g L^{-1} casamino acids, 5 mM glucose, 0.48 mM calcium chloride, 0.83 mM magnesium sulfate, 3.7 μM iron (III) chloride, trace metal solution containing: 0.04 μM copper sulfate, 0.15 μM zinc sulfate, 0.08 μM cobalt chloride, 0.06 μM sodium molybdate and 10 mM HEPES buffer pH 7.5) (Banh et al., 2013). Culture vessels (250-mL Erlenmeyer flasks) containing 100 mL of medium were capped with aluminum foil and incubated at 30 °C and on a rotary shaker (120 rpm) in the dark.

2.3. $MnO_{2\text{-bio}}$ formation and BPA degradation

Typical levels of Mn(II) in freshwater range from 0.02 to 4 μM and Mn(II) concentrations up to 200 μM have been reported (USEPA, 2004). To determine the effect of Mn(II) concentrations on $MnO_{2\text{-bio}}$ formation, cultures of strain AzwK-3b, strain SD-21 and strain GB-1 received 0, 10, 100, and 500 μM Mn(II) in the absence of BPA. Replicate experiments tested the effects of Mn(II) concentrations on BPA degradation in strain SD-21 and strain GB-1 cultures that received 18 μM BPA. Strain AzwK-3b cultures received a lower BPA concentration as we determined inhibitory effects on growth when at concentrations exceeding 9 μM. Potential inhibition of BPA on the growth of each bacterial species was assessed in K-ASW-medium with 0, 9, 18 and 44 μM BPA in the absence of Mn(II). The effect of Mn(II) on BPA inhibition observed in strain AzwK-3b cultures was examined with 18 μM BPA in the absence or presence of 100 μM Mn(II). BPA was added before sterilization of the culture medium and Mn(II) was added from sterile 100 mM $MnCl_2$ stock solutions. Uninoculated (sterile) medium incubations served as negative controls. All experiments were performed in triplicate. Pseudo-first order kinetics were assumed based on the linearity observed during the initial stage of incubation (Im et al., 2015; Forrez et al., 2010; Tran et al., 2018; Liao et al., 2016). The pseudo-first-order rate constants (k) were obtained by plotting the natural log of BPA concentrations as a function of time (i.e., $k = -\Delta(\ln C_t)\ \Delta t^{-1}$) using three early time points, where linear relationships were observed. The standard deviation of the slope was determined using the LINEST function in Excel 2016 (Microsoft Corp., Redmond, WA). To verify that adsorption was negligible even at the highest observed OD_{600} value for each strain, a validated methanol extraction procedure (Im et al., 2016) was employed, which confirmed that sorptive losses of BPA were marginal. Briefly, each strain grown to stationary phase in the absence of BPA and Mn(II) was centrifuged for 10 min at 10,000*g* and resuspended in fresh medium containing 18 μM BPA. After 1-min incubation, triplicate 0.75-mL aliquots of cell suspension were centrifuged, and the supernatant was collected for aqueous phase BPA analysis. The total BPA concentrations were obtained by a methanol extraction procedure (Im et al., 2016). Therefore, for quantification of BPA and HCA in live cultures, 1-mL aliquots of culture suspensions were centrifuged for 10 min at 10,000*g* without methanol extraction, and the supernatant was subjected to HPLC analysis.

2.4. Abiotic BPA degradation by $MnO_{2\text{-syn}}$

To compare the BPA degradation efficiency of $MnO_{2\text{-syn}}$ and $MnO_{2\text{-bio}}$, abiotic BPA degradation kinetics were determined under sterile conditions using 10 μM $MnO_{2\text{-syn}}$ (nominal concentration) as previously described (Im et al., 2015), and the degradation rates and extents were compared with those from biological incubation of strain GB-1 amended with 10 μM Mn(II). Briefly, experiments performed in triplicate were conducted in 160-mL glass serum bottles with a total volume of 100 mL containing 18 μM BPA in 5 mM potassium phosphate buffer at pH 7. BPA degradation was initiated by adding $MnO_{2\text{-syn}}$ from a 0.4 M sterile stock suspension to achieve a final nominal concentration of 10 μM. Aliquots (0.5 mL) of the reaction mixture were collected periodically and transferred to 2-mL glass HPLC vials containing 20 μL of L-ascorbic acid solution (50 mg mL^{-1}) and immediately vortexed for 5 s. L-ascorbic acid quenches the reaction by converting any remaining $MnO_{2\text{-syn}}$ to soluble Mn(II), which liberates any sorbed BPA (Im et al., 2015).

2.5. BPA degradation in the absence of Mn(II)

Cytochrome P450 monooxygenase systems can contribute to BPA degradation and demonstrated in *Sphingomonas* sp. strain AO1 (Sasaki et al., 2005b). Both strain AzwK-3b and strain SD-21 possess genes encoding putative cytochrome P450s enzyme systems. To examine if cytochrome P450 contributes to cometabolic BPA degradation, metyrapone, a known cytochrome P450 inhibitor, was used. Strain AzwK-3b and strain SD-21 were incubated in K-ASW-medium in the presence and absence of 0.5 mM metyrapone (Kolvenbach et al., 2007). To confirm that traces of Mn(II) in yeast extract did not impact BPA degradation by strain AzwK-3b and strain SD-21 in the absence of exogenous Mn(II), additional experiments were performed using a Mn (II)-free defined mineral salt medium. Strain AzwK-3b and strain SD-21 were incubated in a J-Acetate medium consisting of 10 mM sodium acetate, 10 mL L^{-1} Wolfe's vitamin supplement (Wolin et al., 1963), 1.5 mM NH_4Cl, 2 mM $KHCO_3$, 73 μM KH_2PO_4, 3.6 μM $FeSO_4 \times 7H_2O$ complexed with 78 μM nitrilotriacetic acid, 20 mM HEPES (pH 7.6), and prepared with 50% (vol/vol) artificial seawater (Estes et al., 2017).

2.6. Analytical procedures

An Agilent 1100 Series HPLC system equipped with a fluorescence detector (FLD) was used for the detection and quantification of BPA and HCA. A reversed-phase Agilent Eclipse XDB C18 column (4.6 mm × 150 mm, 5 μm) was used for isocratic separation with an acetonitrile-water (50:50, vol/vol) eluent at a flow rate of 1 mL min^{-1} (Im et al., 2015). MnO_2 was quantified using a colorimetric LBB assay (Krumbein and Altmann, 1973) relative to a standard curve prepared with $KMnO_4$. For standard curve preparation, 30 μL of $KMnO_4$ dilutions spanning a concentration range from 7 to 100 μM were aliquoted into empty wells of a 96-well microtiter plate followed by the addition of 270 μL LBB solution (40 mg LBB in 100 mL 45 mM acetic acid). For $MnO_{2\text{-bio}}$ quantification in live cultures, 50 μL samples were collected in 2-mL microcentrifuge tubes and mixed with 450 μL LBB solution. Samples of $MnO_{2\text{-syn}}$ were diluted and mixed with LBB solution at a ratio of 1:10. All samples were incubated at room temperature for 15 min in the dark, centrifuged for 1 min at 10,000*g* to pellet solids, and 300 μL of the supernatant was transferred to a flat bottom 96-well microtiter plate. Absorbance was measured at 618 nm using an Epoch 2 microplate spectrophotometer (BioTek Instruments, Inc., Winooski, VT). Growth of the strains was monitored by measuring absorbance of live cultures at 600 nm using the same instrument. To dissolve $MnO_{2\text{-bio}}$ and prevent any interferences with the growth measurements, L-ascorbic acid (12 μL of a 50 mg mL^{-1} stock solution) was added to individual wells. The total Mn(II) concentrations were measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The samples (5 mL) were filtered through a 0.45-μm nitrocellulose membrane filter (Millipore Corp., Bedford, MA) and acidified with 30 μL HNO_3 (67–70%, wt/wt). A Students' *t*-test was performed to test the significance of any difference between the means and a p-value < 0.05 value was considered to be statistically significant.

3. Results and discussion

3.1. Effect of Mn(II) on $MnO_{2\text{-bio}}$ formation

In cultures of all three bacterial species tested, the maximum nominal $MnO_{2\text{-bio}}$ concentrations increased with increasing Mn(II) concentrations up to 100 μM. At the highest Mn(II) concentration tested (500 μM), lower $MnO_{2\text{-bio}}$ concentrations were observed in cultures of strain SD-21 and strain GB-1 or did not result in a further increase of $MnO_{2\text{-bio}}$ (strain AzwK-3b; $P > 0.1$) (Fig. 1 and Fig. S1a–c). The observation that elevated Mn(II) concentrations negatively affect MnO_2 formation is not unprecedented and has been reported for *Leptothrix discophora* and *Pseudomonas putida* strains MB1, MB6, and MB29 at Mn(II)

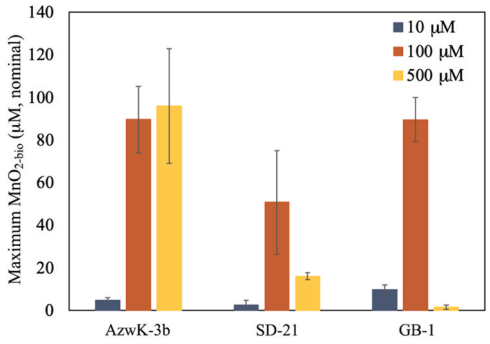

Fig. 1. Effects of Mn(II) concentrations on $MnO_{2\text{-bio}}$ formation in the absence of BPA. Error bars represent the standard deviations of triplicate samples of triplicate cultures.

concentrations higher than 100 μM (Sabirova et al., 2008). The inhibitory effects of Mn(II) on MnO_2-mediated contaminant degradation have been attributed to the passivation of the MnO_2 surface (Lin et al., 2009, 2013), but a detailed mechanistic understanding of the inhibition of Mn (II) oxidation by excess Mn(II) has not been attained.

3.2. Enhanced BPA degradation in the presence of Mn(II)

To evaluate the effect of Mn(II) on BPA degradation, each culture was first incubated with BPA in the absence of Mn(II). BPA degradation was observed in cultures of strain AzwK-3b and strain SD-21, but not in cultures of strain GB-1 (Fig. 2). For all three MOB cultures, enhanced BPA degradation was evident in the presence of Mn(II) compared to replicate incubations without Mn(II) (Fig. 3a–c and Fig. S2a–f), suggesting that MOB produced $MnO_{2\text{-bio}}$, which subsequently mediated abiotic BPA degradation (i.e., the BMAD process). Interestingly, the amount of $MnO_{2\text{-bio}}$ produced in the different cultures did not correlate with the observed BPA degradation rates. The highest amounts of $MnO_{2\text{-bio}}$ were observed in incubations with 100 μM Mn(II) for all three species, but the Mn(II) concentrations that resulted in the highest observed BPA degradation rates were lower. For strain AzwK-3b and strain GB-1, the highest BPA degradation rates of 0.44 ± 0.09 and 0.23 ± 0.02 day^{-1}, respectively, were observed with 10 μM Mn(II), even though about 10-times lower amounts of $MnO_{2\text{-bio}}$ were generated compared to incubations with 100 μM Mn(II) (Fig. 3a, c; Fig. S2a, b, e, f). Strain SD-21 consumed BPA at rates of 1.33 ± 0.52 day^{-1} with 100 μM Mn(II) (Fig. 3b, Fig. S2c, d), and a similar rate of 0.92 ± 0.42 day^{-1} was measured in cultures with 10 μM Mn (II) ($P > 0.1$) although 10-times

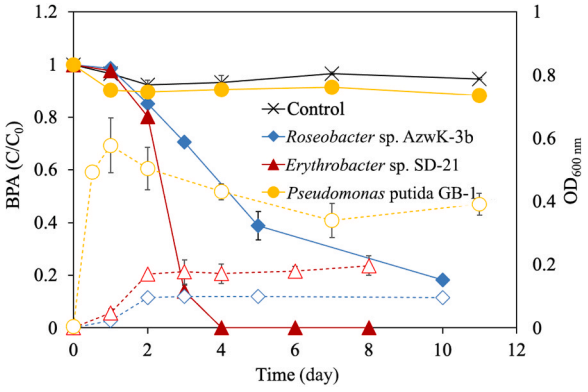

Fig. 2. Growth and co-metabolic degradation of BPA by strain AzwK-3b, strain SD-21, and strain GB-1 in the absence of Mn(II). The solid lines represent C/C_0 BPA concentrations, and the dashed lines show the cell growth based on OD_{600} nm absorbance measurements. Error bars represent the standard deviations of triplicate samples. Error bars smaller than the symbol size are not depicted.

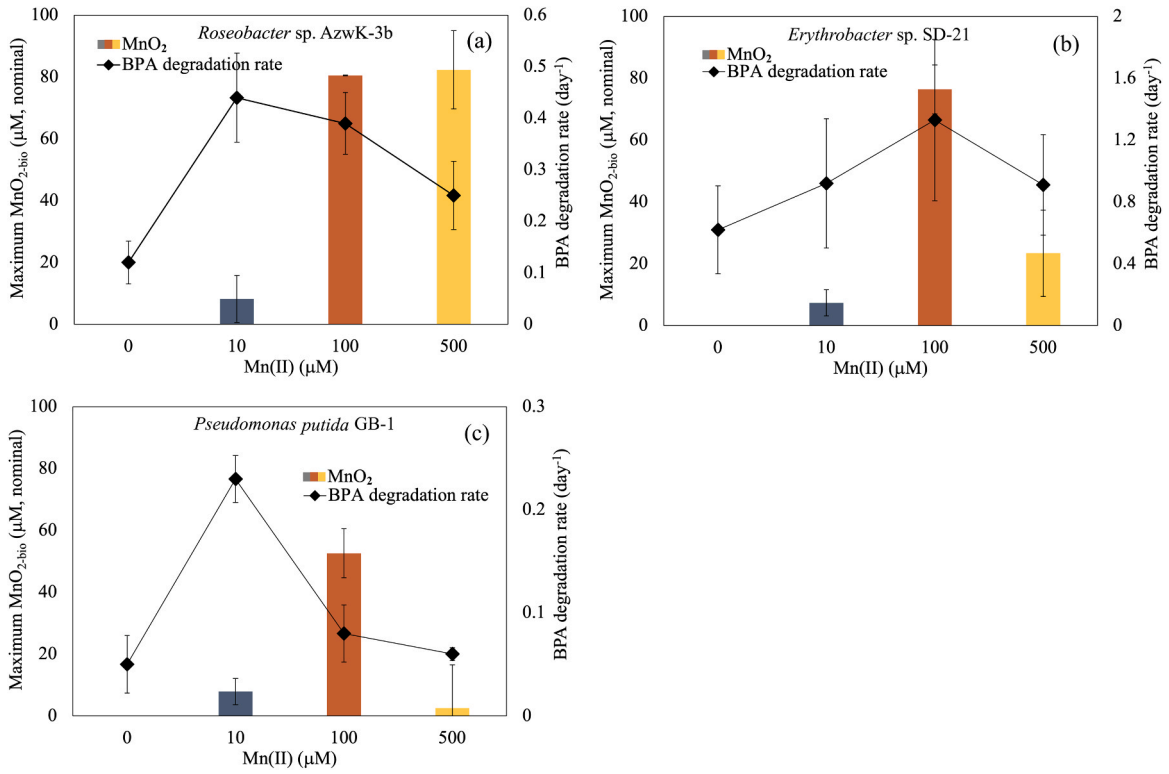

Fig. 3. BPA degradation and MnO_2 formation in cultures of Mn(II)-oxidizing bacteria amended with different Mn(II) concentrations. The columns show maximum nominal $MnO_{2\text{-bio}}$ concentrations, and the diamonds show BPA degradation rates. Panels (a), (b) and (c) show MnO_2 formation and BPA degradation rates in cultures of strain AzwK-3b, strain SD-21, and strain GB-1, respectively. Error bars represent the standard deviations of triplicate cultures.

more $MnO_{2\text{-bio}}$ was formed in vessels with 100 μM Mn(II) (Fig. S2d). Similar observations were made with *Leptothrix discophora* strain SS-1 and *Pseudomonas putida* strains MB1, MB6, and MB29; i.e., increasing amounts of $MnO_{2\text{-bio}}$ were generated but the rates of 17α-ethinylestradiol degradation did not increase in the presence of elevated concentrations of Mn(II) (Sabirova et al., 2008). Several studies also demonstrated that the removal of organic contaminants was significantly lower or came to a complete halt when microbial activity was precluded by heat treatment or sodium azide additions (Sochacki et al., 2018; Tran et al., 2018; Meerburg et al., 2012). These findings emphasize the relevance of BMAD for contaminant turnover, and suggest that Mn flux, rather than the absolute amount of $MnO_{2\text{-bio}}$, is the relevant metric and a potentially useful measure to gauge the $MnO_{2\text{-bio}}$-mediated contaminant transformation activity. Unfortunately, robust tools to determine in situ Mn(II) fluxes in environmental systems are not available.

In sterile abiotic experiments with $MnO_{2\text{-syn}}$, 10 μM $MnO_{2\text{-syn}}$ degraded 2.1 ± 0.3 μM BPA at a rate of 0.06 ± 0.0.03 day^{-1}. In live cultures of strain GB-1 amended with 10 μM Mn(II), about 5-fold higher BPA degradation rate of 0.30 ± 0.07 day^{-1} was observed and 9-fold more BPA (18.5 ± 0.4 μM) was consumed (Fig. 4). These findings suggest that Mn cycling and regeneration of $MnO_{2\text{-bio}}$ occurred in the live cultures, resulting in more effective BPA degradation. Microbial Mn(II) oxidation coupled with Mn(IV)-mediated BPA degradation constitutes an efficient cycle, and a small amount of Mn can turnover a substantial amount of BPA (Fig. 5). A recent study demonstrated light-driven Mn(II) oxidation in microbial biofilms in the absence of O_2 (Daye et al., 2019), suggesting that BMAD processes that act on BPA are not limited to oxic-anoxic transition zones but can also be expected in the photic zones of anoxic water bodies.

Strain AzwK-3b cultures that received 100 μM or 500 μM Mn(II) produced similar amounts of $MnO_{2\text{-bio}}$ (80.5 ± 0.4 μM versus 82.4 ± 0.3 μM, respectively), but BPA degradation rates decreased from

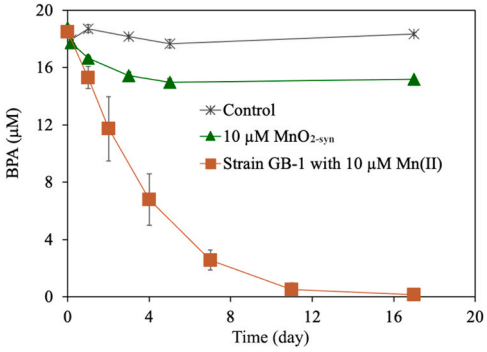

Fig. 4. Degradation of BPA in abiotic incubations with 10 μM of $MnO_{2\text{-syn}}$ versus biotic incubations with 10 μM of Mn(II). No more than 2.1 ± 0.3 μM BPA was degraded in sterile abiotic incubations with 10 μM of $MnO_{2\text{-syn}}$ over a 17-day incubation period. In incubations with 10 μM Mn(II) inoculated with *Pseudomonas putida* strain GB-1, the initial amount of 18 μM BPA was completely consumed. Error bars represent the standard deviations of triplicate samples of triplicate cultures. Error bars smaller than the symbol size are not depicted.

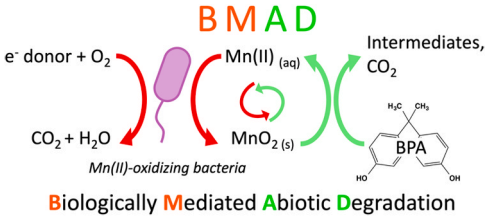

Fig. 5. Schematic illustration of biologically mediated abiotic degradation of BPA.

0.39 ± 0.10 to 0.25 ± 0.06 day^{-1} (Fig. 3a). A plausible explanation is sorption of excess Mn(II) to solid phase MnO_2, which impacted the reactivity of $MnO_{2\text{-bio}}$. MnO_2 has been reported to have high adsorption capacities for metal ions, and suppression of BPA degradation by $MnO_{2\text{-syn}}$ has been reported in the presence of Mn(II) (Lin et al., 2009, 2013).

3.3. Inhibitory effect of BPA on strain AzwK-3b and relief of inhibition by $MnO_{2\text{-bio}}$

In the absence of Mn(II), BPA concentrations of up to 9 μM had no effect on growth of strain AzwK-3b and similar growth rates ranging between 2.77 ± 0.32 day^{-1} and 3.2 ± 0.43 day^{-1} were measured ($P > 0.1$). At BPA concentrations of 18 μM and higher, inhibition was observed ($P < 0.05$) and the first order growth rate declined to 1.68 ± 0.37 day^{-1} in the presence of 18 μM BPA and to 0.75 ± 0.23 day^{-1} in the presence of 44 μM BPA. The maximum growth yield as indicated by $OD_{600\ nm}$ measurements decreased by approximately 20% and 67% in the presence of 18 and 44 μM BPA, respectively. The addition of 100 μM Mn(II) relieved the inhibitory effect of BPA, and the growth yields recovered (Fig. S3), suggesting $MnO_{2\text{-bio}}$-mediated BPA degradation alleviated the observed growth inhibition. Apparently, the formation of $MnO_{2\text{-bio}}$ protected strain AzwK-3b from BPA toxicity, and the formation of $MnO_{2\text{-bio}}$ formation is a defense response to toxins susceptible to MnO_2-mediated oxidation and degradation. Indeed, Mn(II) oxidation and $MnO_{2\text{-bio}}$ formation have been proposed to protect bacterial cells from toxic metals and reactive oxygen species (Tebo et al., 2004; Ghiorse, 1984). For strain SD-21 and strain GB-1, no apparent growth inhibition was observed with BPA concentrations up to 44 μM (Fig. S4a and b).

3.4. BPA degradation intermediates

HCA has been detected as the major intermediate of BPA degradation mediated by $MnO_{2\text{-syn}}$ (Lin et al., 2009; Im et al., 2015; Balgooyen et al., 2017, 2019). Because an in vitro estrogen receptor binding assay suggested that HCA has a 100-fold higher binding affinity than BPA (Nakamura et al., 2011), the formation of HCA is of concern. In the presence of Mn(II), HCA was detected as a degradation intermediate in the cultures of all three bacterial species. BPA-to-HCA conversion efficiency was calculated by dividing the amount (μmol) HCA formed by the amount BPA removed, assuming one mol of BPA will produce one mol of HCA (Im et al., 2015). For strain AzwK-3b and strain GB-1, BPA-to-HCA conversion efficiencies were in a similar range to that of $MnO_{2\text{-syn}}$-mediated BPA degradation (i.e., 50–64%) (Fig. 6), suggesting that $MnO_{2\text{-bio}}$ and $MnO_{2\text{-syn}}$ are functionally equivalent and/or HCA was not readily consumed by both strains. For strain SD-21, a much lower BPA-to-HCA conversion efficiency of 20% was determined (Fig. 6), suggesting that HCA was (co-)metabolically degraded as it was formed, which is plausible given the high BPA degradation rate observed in this strain in the absence of Mn(II) (Fig. 2).

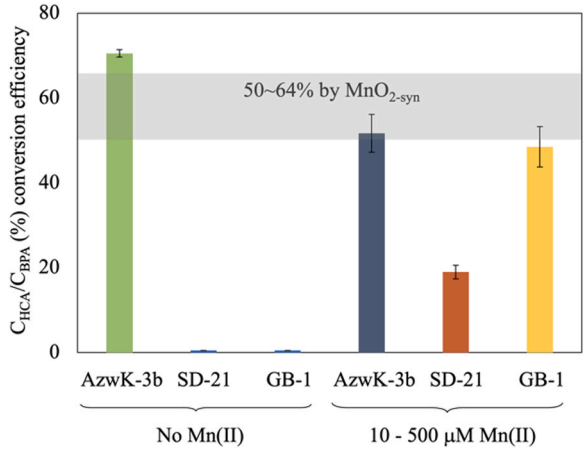

Fig. 6. Conversion efficiency of BPA to HCA in the absence or presence of Mn (II). The gray shaded area indicates the BPA-to-HCA conversion efficiency observed in $MnO_{2\text{-syn}}$-mediated BPA degradation experiments reported previously (Im et al., 2015). Error bars represent the standard deviations of triplicate samples of triplicate cultures.

3.5. Effect of trace Mn in peptone and yeast extract on BPA degradation in the absence of exogenous Mn(II)

Strain AzwK-3b and strain SD-21 degraded BPA in the absence of exogenous Mn(II) in organic rich K-ASW-medium containing 2.0 g L^{-1} peptone and 0.5 g L^{-1} yeast extract (Fig. 1) (Learman et al., 2011). Peptone and yeast extract are commonly used as carbon and nitrogen sources as well as supplements to provide essential nutrients such as vitamins and amino acids. Both peptone and yeast extract contain trace metals, and Mn up to 3.2 μg g^{-1} (dry weight) has been reported for yeast extract (Grant and Pramer, 1962). Indeed, ICP-MS determined that K-ASW-medium contained 0.3 μM Mn(II), suggesting that $MnO_{2\text{-bio}}$-mediated BPA degradation could occur without exogenous Mn(II) supply. Additional experiments using Mn-free, defined mineral salt medium with acetate as the sole carbon source (J-Acetate medium) still supported BPA degradation by strain AzwK-3b (Fig. S5). Mn(II) was not detected in J-Acetate medium by ICP-MS (data not shown), indicating co-metabolic BPA degradation rather than mediated by MnO_2. The Mn (II) detection limit as calculated by 3σ/S, where σ is the standard deviation of five blank injections and S is the slope of the calibration curve (Long and Winefordner, 1983), was 20.0 ± 4.4 nM. Strain SD-21 did not grow in J-Acetate medium and the contribution of trace Mn(II) in yeast extract on BPA degradation could not be examined; however, the high BPA degradation rates observed in strain SD-21 cultures without Mn(II) suggest that this bacterium can (co-)metabolize BPA (Fig. 1).

3.6. BPA degradation in the absence of Mn

As of 2020, 24 genera, including *Pseudomonas*, have been reported to harbor species capable of aerobic BPA degradation (Im and Löffler, 2016; de Santana et al., 2019; Heidari et al., 2017), but BPA degradation has not been linked to the genera *Roseobacter* and *Erythrobacter*. When *Roseobacter* sp. strain AzwK-3b and *Erythrobacter* sp. strain SD-21 were incubated with 9 μM BPA (2 mg L^{-1}) and 18 μM BPA (4 mg L^{-1}), respectively, in the absence of Mn(II), BPA was consumed (Fig. 2). In strain AzwK-3b cultures, BPA consumption occurred at a rate of 0.12 ± 0.04 day^{-1}, but complete degradation was not achieved even after an extended incubation period of 20 days (data not shown). Strain SD-21 completely consumed 18 μM BPA in 4 days at a rate of 0.62 ± 0.28 day^{-1}. Efforts to grow strain AzwK-3b and strain SD-21 in defined mineral salt medium (Im et al., 2014b) with 9 and 18 μM BPA as the sole carbon source, respectively, were not successful and BPA was not degraded (data not shown), suggesting that partial BPA consumption observed in rich media was co-metabolic. For strain AzwK-3b, HCA was detected during BPA degradation in the absence of Mn(II) (Fig. 6), suggesting that this strain may have an oxidative pathway through radical coupling, similar to $MnO_{2\text{-syn}}$-mediated BPA degradation (Lin et al., 2009). Enzymatic radical coupling has been proposed as a microbial co-metabolic degradation mechanism for pesticides (Bollag, 1991) and lignin (Brown and Chang, 2014; Kirk and Farrell, 1987). In *Erythrobacter* sp. strain SD-21 cultures, BPA was readily degraded in the absence of Mn(II) but HCA was not detected (Fig. 6), suggesting that the strain may have a different degradation pathway circumventing the formation of HCA or the intermediate was readily turned over thereby evading detection.

Many aerobic bacteria and fungi possess genes encoding cytochrome P450s. These heme-containing monooxygenase enzyme systems have broad substrate specificity and attack on BPA has been documented

(Sasaki et al., 2005b; Kolvenbach et al., 2007). Metyrapone, a cytochrome P450 inhibitor, is widely used to demonstrate the involvement of cytochrome P450, and the addition of metyrapone repressed BPA degradation activity in *Sphingomonas* sp. strain AO1 (Sasaki et al., 2005a). Both strain AzwK-3b and strain SD-21 possess P450 genes, and consumed some BPA without Mn(II) additions to the medium; however, BPA consumption still occurred in the presence of metyrapone (Fig. S6) suggesting that cytochrome P450 was not involved.

Many *Pseudomonas* isolates are known to aerobically degrade BPA (Im and Löffler, 2016) and degradation rates as high as 82.9 day^{-1} have been reported in *P. monteilii* strain N-502; (Masuda et al., 2007) however, no disappearance of BPA was observed in the incubations of *Pseudomonas* putida strain GB-1. The inability of *Pseudomonas putida* strain GB-1 to degrade BPA was unexpected because the strain has been reported to possess cytochrome P450 enzyme systems (De Vrind et al., 1998). Further, many other *Pseudomonas putida* strains have been reported to produce laccase and co-metabolize various organic compounds, including BPA (Kuddus et al., 2013; Liu et al., 2016; Mandic et al., 2019; Telke et al., 2009).

Due to the hydrophobic nature of BPA (log K_{ow} of 2.2–3.82) (Staples et al., 1998), adsorption of BPA onto hydrophobic cell surface components has been reported (Im et al., 2016; Endo et al., 2007). The OD_{600nm} in cultures of strain AzwK-3b, strain SD-21, and strain GB-1 that reached early stationary phase in the absence of BPA were 0.096 ± 0.002, 0.197 ± 0.031, and 0.578 ± 0.086, respectively. The BPA concentrations in the aqueous phase of strain AzwK-3b, strain SD-21, and strain GB-1were 17.5 ± 0.2, 17.2 ± 0.2, 17.1 ± 0.3 μM, respectively, and the total BPA concentrations were 17.4 ± 0.2, 17.4 ± 0.3, and 17.3 ± 0.2 μM, respectively, indicating that adsorption to biomass cannot explain the observed BPA disappearance.

4. Environmental implications

BPA is commonly present in anoxic sediments (Bolz et al., 2001; Heemken et al., 2001), but a number of studies concluded that BPA is recalcitrant to microbial degradation under anoxic conditions (Kang and Kondo, 2002, 2005; Voordeckers et al., 2002; Im et al., 2014a). The incubation of BPA with the MOB in the presence of Mn(II) demonstrated that (i) exogenous Mn(II) enhanced or induced BPA degradation by producing $MnO_{2\text{-bio}}$, and (ii) Mn flux, rather than the absolute amount of $MnO_{2\text{-bio}}$, was relevant for effective BPA degradation. Manganese is the second most abundant transition metal in the Earth's crust, and many phylogenetically distinct Mn(II)-oxidizing bacteria and fungi have been identified in soil, sediment, and aquatic environments (Im and Löffler, 2016). The new findings, combined with previous $MnO_{2\text{-syn}}$ studies, suggest that Mn(II) oxidation and $MnO_{2\text{-bio}}$ formation may play relevant roles in controlling the fate and longevity of BPA in the environment. A future research focus should be on the interplay between microbial Mn (II) oxidation and mineral phase-mediated contaminant degradation under simulated in situ conditions, which can lead to innovative engineering approaches that capitalize on the BMAD concept.

CRediT authorship contribution statement

Nusrat Shobnam: Conceptualization, Methodology, Validation, Investigation, Data curation, Writing - original draft. **Yanchen Sun**: Conceptualization, Methodology. **Maheen Mahmood**: Investigation, Data curation. **Frank E. Löffler**: Conceptualization, Methodology, Validation, Writing - review & editing, Supervision, Funding acquisition, Project administration. **Jeongdae Im**: Conceptualization, Methodology, Validation, Investigation, Data curation, Writing - original draft, Writing - review & editing, Supervision, Funding acquisition, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.125987.

References

Anderson, C.R., Johnson, H.A., Caputo, N., Davis, R.E., Torpey, J.W., Tebo, B.M., 2009. Mn(II) oxidation is catalyzed by heme peroxidases in "*Aurantimonas manganoxydans*" strain SI85-9A1 and *Erythrobacter* sp. strain SD-21. Appl. Environ. Microbiol. 75 (12), 4130–4138.

Balgooyen, S., Alaimo, P.J., Remucal, C.K., Ginder-Vogel, M., 2017. Structural transformation of MnO_2 during the oxidation of bisphenol A. Environ. Sci. Technol. 51 (11), 6053–6062.

Balgooyen, S., Campagnola, G., Remucal, C.K., Ginder-Vogel, M., 2019. Impact of bisphenol A influent concentration and reaction time on MnO_2 transformation in a stirred flow reactor. Environ. Sci. Process. Impacts 21 (1), 19–27.

Banh, A., Chavez, V., Doi, J., Nguyen, A., Hernandez, S., Ha, V., Jimenez, P., Espinoza, F., Johnson, H.A., 2013. Manganese (Mn) oxidation increases intracellular Mn in *Pseudomonas putida* GB-1. PLoS One 8 (10), e77835.

Bollag, J.-M., 1991. Enzymatic binding of pesticide degradation products to soil organic matter and their possible release. In: Somasundaram, L., Coats, J.R. (Eds.), Pesticide Transformation Products: Fate and Significance in the Environment. American Chemical Society, pp. 122–132.

Bolz, U., Hagenmaier, H., Körner, W., 2001. Phenolic xenoestrogens in surface water, sediments, and sewage sludge from Baden-Württemberg, south-west Germany. Environ. Pollut. 115 (2), 291–301.

Brown, M.E., Chang, M.C.Y., 2014. Exploring bacterial lignin degradation. Curr. Opin. Chem. Biol. 19 (1), 1–7.

Crain, D.A., Eriksen, M., Iguchi, T., Jobling, S., Laufer, H., LeBlanc, G.A., Guillette, L.J., 2007. An ecological assessment of bisphenol-A: evidence from comparative biology. Reprod. Toxicol. 24 (2), 225–239.

Daye, M., Klepac-Ceraj, V., Pajusalu, M., Rowland, S., Farrell-Sherman, A., Beukes, N., Tamura, N., Fournier, G., Bosak, T., 2019. Light-driven anaerobic microbial oxidation of manganese. Nature 576 (7786), 311–314.

De Vrind, J.P.M., Brouwers, G.J., Corstjens, P.L.A.M., Den Dulk, J., De Vrind-De Jong, E. W., 1998. The cytochrome c maturation operon is involved in manganese oxidation in *Pseudomonas putida* GB-1. Appl. Environ. Microbiol. 64 (10), 3556–3562.

Endo, Y., Kimura, N., Ikeda, I., Fujimoto, K., Kimoto, H., 2007. Adsorption of bisphenol A by lactic acid bacteria, *Lactococcus* strains. Appl. Microbiol. Biotechnol. 74 (1), 202–207.

Estes, E.R., Andeer, P.F., Nordlund, D., Wankel, S.D., Hansel, C.M., 2017. Biogenic manganese oxides as reservoirs of organic carbon and proteins in terrestrial and marine environments. Geobiology 15 (1), 158–172.

Forrez, I., Carballa, M., Noppe, H., De Brabander, H., Boon, N., Verstraete, W., 2009. Influence of manganese and ammonium oxidation on the removal of 17α-ethinylestradiol (EE2). Water Res. 43 (1), 77–86.

Forrez, I., Carballa, M., Verbeken, K., Vanhaecke, L., Michael Schlüsener, M.S., Ternes, T., Boon, N., Verstraete, W., 2010. Diclofenac oxidation by biogenic manganese oxides. Environ. Sci. Technol. 44 (9), 3449–3454.

Forrez, I., Carballa, M., Fink, G., Wick, A., Hennebel, T., Vanhaecke, L., Ternes, T., Boon, N., Verstraete, W., 2011. Biogenic metals for the oxidative and reductive removal of pharmaceuticals, biocides and iodinated contrast media in a polishing membrane bioreactor. Water Res. 45 (4), 1763–1773.

Geszvain, K., Smesrud, L., Tebo, B.M., 2016. Identification of a third Mn(II) oxidase enzyme in *Pseudomonas putida* GB-1. Appl. Environ. Microbiol. 82 (13), 3774–3782.

Ghiorse, W.C., 1984. Biology of iron- and manganese-depositing bacteria. Annu. Rev. Microbiol. 38 (1), 515–550.

Grant, C.L., Pramer, D., 1962. Minor element composition of yeast extract. J. Bacteriol. 84, 869–870.

He, Y.T., Wilson, J.T., Su, C., Wilkin, R.T., 2015. Review of abiotic degradation of chlorinated solvents by reactive iron minerals in aquifers. Groundw. Monit. Remediat. 35 (3), 57–75.

Heemken, O., Reincke, H., Stachel, B., Theobald, N., 2001. The occurrence of xenoestrogens in the Elbe river and the North Sea. Chemosphere 45 (3), 245–259.
Heidari, H., Sedighi, M., Zamir, S.M., Shojaosadati, S.A., 2017. Bisphenol A degradation by *Ralstonia eutropha* in the absence and presence of phenol. Int. Biodeterior. Biodegrad. 119, 37–42.
Hengstler, J.G., Foth, H., Gebel, T., Kramer, P.-J., Lilienblum, W., Schweinfurth, H., Völkel, W., Wollin, K.-M., Gundert-Remy, U., 2011. Critical evaluation of key evidence on the human health hazards of exposure to bisphenol A. Crit. Rev. Toxicol. 41 (4), 263–291.
Hennebel, T., De Gusseme, B., Boon, N., Verstraete, W., 2009. Biogenic metals in advanced water treatment. Trends Biotechnol. 27 (2), 90–98.
Huang, J., Zhong, S., Dai, Y., Liu, C.-C., Zhang, H., 2018. Effect of MnO_2 phase structure on the oxidative reactivity toward bisphenol A degradation. Environ. Sci. Technol. 52 (19), 11309–11318.
Im, J., Löffler, F.E., 2016. Fate of bisphenol A in terrestrial and aquatic environments. Environ. Sci. Technol. 50 (16), 8403–8416.
Im, J., Prevatte, C.W., Lee, H.G., Campagna, S.R., Löffler, F.E., 2014a. 4-Methylphenol produced in freshwater sediment microcosms is not a bisphenol A metabolite. Chemosphere 117C (1), 521–526.
Im, J., Walshe-langford, G.E., Moon, J., Löffler, F.E., 2014b. Environmental fate of the next generation refrigerant 2,3,3,3-tetrafluoropropene (HFO-1234yf). Environ. Sci. Technol. 48 (22), 13181–13187.
Im, J., Prevatte, C.W., Campagna, S.R., Löffler, F.E., 2015. Identification of 4-hydroxy-cumyl alcohol as the major MnO_2-mediated Bisphenol A transformation product and evaluation of its environmental fate. Environ. Sci. Technol. 49 (10), 6214–6221.
Im, J., Yip, D., Lee, J., Löffler, F.E., 2016. Simplified extraction of bisphenols from bacterial culture suspensions and solid matrices. J. Microbiol. Methods 126, 35–37.
Industry Experts, 2017. Bisphenol A - Global Market Overview. ⟨https://industry-experts.com/verticals/files/articles/cp021-bisphenol-a-a-global-market-overview.pdf⟩.
Kang, J.-H., Kondo, F., 2002. Bisphenol A degradation by bacteria isolated from river water. Arch. Environ. Contam. Toxicol. 43 (3), 265–269.
Kang, J.-H.H., Kondo, F., 2005. Bisphenol A degradation in seawater is different from that in river water. Chemosphere 60 (9), 1288–1292.
Kim, D.G., Jiang, S., Jeong, K., Ko, S.O., 2012. Removal of 17α-ethinylestradiol by biogenic manganese oxides produced by the *Pseudomonas putida* strain MnB1. Water Air Soil Pollut. 223 (2), 837–846.
Kirk, T.K., Farrell, R.L., 1987. Enzymatic "combustion": the microbial degradation of lignin. Annu. Rev. Microbiol. 41 (1), 465–501.
Klečka, G.M., Staples, C.A., Clark, K.E., van der Hoeven, N., Thomas, D.E., Hentges, S.G., 2009. Exposure analysis of bisphenol A in surface water systems in North America and Europe. Environ. Sci. Technol. 43 (16), 6145–6150.
Kolvenbach, B., Schlaich, N., Raoui, Z., Prell, J., Zühlke, S., Schäffer, A., Guengerich, F. P., Corvini, P.F.X., 2007. Degradation pathway of bisphenol A: does *ipso* substitution apply to phenols containing a quaternary α-carbon structure in the para position? Appl. Environ. Microbiol. 73 (15), 4776–4784.
Kostka, J., Nealson, K., 1998. Isolation, cultivation and characterization of iron- and manganese-reducing bacteria. In: Burlage, R.S. (Ed.), Techniques in Microbial Ecology. Oxford University Press, New York, p. 468.
Krumbein, W.E., Altmann, H.J., 1973. A new method for the detection and enumeration of manganese oxidizing and reducing microorganisms. Helgol. Wiss. Meeresunters. 25 (2–3), 347–356.
Kuddus, M., Joseph, B., Wasudev Ramteke, P., 2013. Production of laccase from newly isolated *Pseudomonas putida* and its application in bioremediation of synthetic dyes and industrial effluents. Biocatal. Agric. Biotechnol. 2 (4), 333–338.
Kwon, M.J., O'Loughlin, E.J., Antonopoulos, D.A., Finneran, K.T., 2011. Geochemical and microbiological processes contributing to the transformation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in contaminated aquifer material. Chemosphere 84 (9), 1223–1230.
Learman, D.R., Voelker, B.M., Vazquez-Rodriguez, A.I., Hansel, C.M., 2011. Formation of manganese oxides by bacterially generated superoxide. Nat. Geosci. 4 (2), 95–98.
Liao, X., Zhang, C., Liu, Y., Luo, Y., Wu, S., Yuan, S., Zhu, Z., 2016. Abiotic degradation of methyl parathion by manganese dioxide: kinetics and transformation pathway. Chemosphere 150, 90–96.
Lin, K., Liu, W., Gan, J., Gant, J., Gan, J., 2009. Oxidative removal of bisphenol A by manganese dioxide: efficacy, products, and pathways. Environ. Sci. Technol. 43 (10), 3860–3864.
Lin, K., Peng, Y., Huang, X., Ding, J., 2013. Transformation of bisphenol A by manganese oxide-coated sand. Environ. Sci. Pollut. Res. Int. 20 (3), 1461–1467.
Liu, J., Tan, L., Wang, J., Wang, Z., Ni, H., Li, L., 2016. Complete biodegradation of chlorpyrifos by engineered *Pseudomonas putida* cells expressing surface-immobilized laccases. Chemosphere 157, 200–207.
Long, G.L., Winefordner, J.D., 1983. Limit of detection a closer look at the IUPAC definition. Anal. Chem. 55 (07), 712–724.
Mandic, M., Djokic, L., Nikolaivits, E., Prodanovic, R., O'Connor, K., Jeremic, S., Topakas, E., Nikodinovic-Runic, J., 2019. Identification and characterization of new laccase biocatalysts from *Pseudomonas* species suitable for degradation of synthetic textile dyes. Catalysts 9 (7), 629.
Martínez-Ruiz, E.B., Cooper, M., Fastner, J., Szewzyk, U., 2020a. Manganese-oxidizing bacteria isolated from natural and technical systems remove cylindrospermopsin. Chemosphere 238, 124625.
Martínez-Ruiz, E.B., Cooper, M., Al-Zeer, M.A., Kurreck, J., Adrian, L., Szewzyk, U., 2020b. Manganese-oxidizing bacteria form multiple cylindrospermopsin transformation products with reduced human liver cell toxicity. Sci. Total Environ. 729, 138924.
Masuda, M., Yamasaki, Y., Ueno, S., Inoue, A., 2007. Isolation of bisphenol A-tolerant/degrading *Pseudomonas monteilii* strain N-502. Extremophiles 11 (2), 355–362.
Meerburg, F., Hennebel, T., Vanhaecke, L., Verstraete, W., Boon, N., 2012. Diclofenac and 2-anilinophenylacetate degradation by combined activity of biogenic manganese oxides and silver. Microb. Biotechnol. 5 (3), 388–395.
Miyata, N., Tani, Y., Sakata, M., Iwahori, K., 2007. Microbial manganese oxide formation and interaction with toxic metal ions. J. Biosci. Bioeng. 104 (1), 1–8.
Nakamura, S., Tezuka, Y., Ushiyama, A., Kawashima, C., Kitagawara, Y., Takahashi, K., Ohta, S., Mashino, T., 2011. *Ipso* substitution of bisphenol A catalyzed by microsomal cytochrome P450 and enhancement of estrogenic activity. Toxicol. Lett. 203 (1), 92–95.
Niedźwiecka, J.B., Finneran, K.T., 2015. Combined biological and abiotic reactions with iron and Fe(III)-reducing microorganisms for remediation of explosives and insensitive munitions (IM). Environ. Sci. Water Res. Technol. 1 (1), 34–39.
Perreault, N.N., Crocker, F.H., Indest, K.J., Hawari, J., 2012. Involvement of cytochrome c CymA in the anaerobic metabolism of RDX by *Shewanella oneidensis* MR-1. Can. J. Microbiol. 58 (2), 124–131.
Remucal, C.K., Ginder-Vogel, M., 2014. A critical review of the reactivity of manganese oxides with organic contaminants. Environ. Sci. Process. Impacts 16 (6), 1247–1266.
Rochester, J.R., 2013. Bisphenol A and human health: a review of the literature. Reprod. Toxicol. 42, 132–155.
Sabirova, J.S., Cloetens, L.F.F., Vanhaecke, L., Forrez, I., Verstraete, W., Boon, N., 2008. Manganese-oxidizing bacteria mediate the degradation of 17α-ethinylestradiol. Microb. Biotechnol. 1 (6), 507–512.
de Santana, F.S., Gracioso, L.H., Karolski, B., dos Passos Galluzzi Baltazar, M., Mendes, M.A., do Nascimento, C.A.O., Perpetuo, E.A., 2019. Isolation of bisphenol A-tolerating/degrading *Shewanella haliotis* strain MH137742 from an estuarine environment. Appl. Biochem. Biotechnol. 189 (1), 103–115.
Saroyan, H.S., Bele, S., Giannakoudakis, D.A., Samanidou, V.F., Bandosz, T.J., Deliyanni, E.A., 2019. Degradation of endocrine disruptor, bisphenol-A, on an mixed oxidation state manganese oxide/modified graphite oxide composite: a role of carbonaceous phase. J. Colloid Interface Sci. 539, 516–524.
Sasaki, M., Maki, J., Oshiman, K., Matsumura, Y., Tsuchido, T., 2005a. Biodegradation of bisphenol A by cells and cell lysate from *Sphingomonas* sp. strain AO1. Biodegradation 16 (5), 449–459.
Sasaki, M., Akahira, A., Oshiman, K.I., Tsuchido, T., Matsumura, Y., 2005b. Purification of cytochrome P450 and ferredoxin, involved in bisphenol A degradation, from *Sphingomonas* sp. strain AO1. Appl. Environ. Microbiol. 71 (12), 8024–8030.
Sekizawa, J., 2008. Low-dose effects of bisphenol A: a serious threat to human health? J. Toxicol. Sci. 33 (4), 389–403.
Sigg, L., Sturm, M., Kistler, D., 1987. Vertical transport of heavy metals by settling particles in Lake Zurich. Limnol. Oceanogr. 32 (l), 112–130.
Sochacki, A., Felis, E., Bajkacz, S., Kalka, J., Michalska, J.K., 2018. Removal and transformation of benzotriazole in manganese-oxide biofilters with Mn(II) feeding. Chemosphere 212, 143–151.
Staples, C.A., Dome, P.B., Klecka, G.M., Sandra, O.T., Harris, L.R., 1998. A review of the environmental fate, effects, and exposures of bisphenol A. Chemosphere 36 (10), 2149–2173.
Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, D., Verity, R., Webb, S.M., 2004. Biogenic manganese oxides: properties and mechanisms of formation. Annu. Rev. Earth Planet. Sci. 32 (1), 287–328.
Telke, A.A., Kalyani, D.C., Jadhav, U.U., Parshetti, G.K., Govindwar, S.P., 2009. Purification and characterization of an extracellular laccase from a *Pseudomonas* sp. LBC1 and its application for the removal of bisphenol A. J. Mol. Catal. B Enzym. 61 (3–4), 252–260.
Tran, T.N., Kim, D.G., Ko, S.O., 2018. Synergistic effects of biogenic manganese oxide and Mn(II)-oxidizing bacterium *Pseudomonas putida* strain MnB1 on the degradation of 17α-ethinylestradiol. J. Hazard. Mater. 344, 350–359.
USEPA, 2004. Drinking Water Health Advisory for Manganese.
Vandieken, V., Pester, M., Finke, N., Hyun, J.-H., Friedrich, M.W., Loy, A., Thamdrup, B., 2012. Three manganese oxide-rich marine sediments harbor similar communities of acetate-oxidizing manganese-reducing bacteria. ISME J. 6 (11), 2078–2090.
Villalobos, M., Bargar, J., Sposito, G., 2005. Mechanisms of Pb(II) sorption on a biogenic manganese oxide. Environ. Sci. Technol. 39 (2), 569–576.
Voordeckers, J.W., Fennell, D.E., Jones, K., Häggblom, M.M., 2002. Anaerobic biotransformation of tetrabromobisphenol A, tetrachlorobisphenol A, and bisphenol A in estuarine sediments. Environ. Sci. Technol. 36 (4), 696–701.
Wang, L., Jiang, J., Pang, S.Y., Zhou, Y., Li, J., Sun, S., Gao, Y., Jiang, C., 2018. Oxidation of bisphenol A by nonradical activation of peroxymonosulfate in the presence of amorphous manganese dioxide. Chem. Eng. J. 352 (July), 1004–1013.
Wolin, F.A., Wolin, M.J., Wolfe, R.S., 1963. Formation of methane by bacterial extracts. J. Biol. Chem. 238, 2882–2886.
Zhang, W., Yin, K., Chen, L., 2013. Bacteria-mediated bisphenol A degradation. Appl. Microbiol. Biotechnol. 97 (13), 5681–5689.
Zhang, Y., Zhu, H., Szewzyk, U., Geissen, S.U., 2015. Removal of pharmaceuticals in aerated biofilters with manganese feeding. Water Res. 72, 218–226.
Zhang, Y., Zhu, H., Szewzyk, U., Lübbecke, S., Uwe Geissen, S., 2017. Removal of emerging organic contaminants with a pilot-scale biofilter packed with natural manganese oxides. Chem. Eng. J. 317, 454–460.