5 Persistence, Toxicity, and Strategies for Remediation of Brominated Flame Retardants in Soil and Sedimentation in Aquatic Matrices Under Aerobic and Anaerobic Conditions

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Contents

Abstract

Novel brominated flame retardants (NBFRs) and legacy BFRs have been used in industrial and home applications to reduce the risk of ignition. However, the use of flame retardants is of particular concern due to the likelihood of being found in

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high concentrations, persistence in the environment, and for bioaccumulation in the environment. BFRs are of interest due to the potential toxicity to humans and endocrine-disrupting properties. To adress toxicity and persistence of BFRs, new or novel BFRs (NFBRs) have been introduced as a replacement. However, NBFRs have similar chemical properties and environmental fates as legacy BFRs. This chapter discusses various methods of abiotic and biotic degradation of BFRs, culturing conditions, potential microorganisms, and enzymes that can biodegrade BFRs from various environmental sources. We include the proposed mechanisms of biodegradation and persistence in the environment for several congeners. Water matrices are also discussed as an environmental source since BFRs in sedimentation are not well known and pose an essential factor in assessing the amount of BFRs present in the environment. The presence of BFRs in our environment have been concerning as they have been linked by various studies to the decline of sperm counts and fertility issues of both genders as well as contribute to cognitive and developmental problems in children.

Keywords

Brominated flame retardants · Bioremediation · Halogenated · Endocrine disruptor · Polybrominated diphenyl ethers (PBDEs) · Neurotoxicity · Decabrominated diphenyl ether (BDE-209) · Decabromodiphenyl ethane (DBDPE) · New brominated flame retardants · Tetrabromobisphenol A (TBBPA) · Minimal salts media (MSM) · Hexabromocyclododecanes (HBDC)

5.1 Introduction

Epoxy resins are widely used for many products but are highly combustible. Furthermore, the amount of heat created and the toxic gases released once ignited are significant causes of deaths and property damage. For this reason, flame retardants (FRs) have been developed to mitigate this problem (Waaijers and Parsons 2016). BFRs represent various chemicals applied to many products, including plastics, polymers, textiles, wood, or other ignitable objects, to prevent combustion. During the process of combustion, free radicals are formed. Halogens, namely bromine, are good at detaining free radicals and lowering the decomposition temperature (Kodavanti et al. 2017). Approximately one-quarter of the world's flame retardants are brominated (Andersson et al. 2006). There are three main groups of BFRs used. These are decabrominated diphenyl ether (BDE-209), tetrabromobisphenol A (TBBPA), and hexabromocyclododecane (HBCD) (Andersson et al. 2006).

BFRs, also known as organohalogens, comprise a group of chemicals that use flame retardants, which is concerning due to their toxicity, bioaccumulation, and environmental accumulation. NBFRs have been cited as being neurotoxic in children who are still developing (Roze et al. 2009). Due to bioaccumulation and toxicity, BFRs have been banned in various countries, and novel BFRs are being

used as an alternative to BFRs. However, novel BFRs have been shown to accumulate in aquatic matrices, air, sediment, and sludge and bioaccumulate in animals (Xiong et al. 2019). In this review, we will also focus on water matrices as sedimentation is a part of land management that is often overlooked and often harbors pollutants that are harmful to aquatic ecosystems (Bakker et al. 2008).

5.2 Toxicity of BFRS

The toxicity of BFRs has been cited in many publications. BFRs are lipophilic and are stored in adipose tissue, and have the ability to biomagnify in the food chain. This is a potential risk considering that the animals humans consume have been shown to harbor BFRs. Evidence shows that DBDPE was found to induce oxidative stress, changes in morphology, and transcriptomics in white rot fungus *P. ostreatus* (Wang et al. 2022a). This study observed a decrease in fungal biomass in concentrations from 1 to 50 mg L^{-1} DBDPE. A decrease in superoxide dismutase, catalase, and glutathione was also observed. This is significant since all three are crucial in the detoxification process. Most significant was the role in the downregulation of genes involved in metabolisms such as oxidative phosphorylation, TCA cycle, and carbon metabolism. This study highlights transcriptomics as an essential tool in molecular biology for understanding the mechanisms of toxicity after exposure to pollutants. Moreover, a multi-omics approach can accurately map the pathways in response to pollutant exposure, thus revealing the mechanisms of toxicity for organisms (Li et al. 2022).

Kidney miRNAs from grass carp were found to be significantly changed after exposure to BFR and DBDPE (Gan et al. 2016). The study found that five kidney miRNAs were significantly downregulated, while 36 kidney miRNAs were significantly upregulated. Interestingly, miR-155, miR-205, and most miR-10 family members were upregulated. miR-155 is known to regulate immune response, miR-205 is linked to nephropathy, and dysregulation of miR-10 family members is associated with various cancers (Gan et al. 2016). The study proposes using miRNAs as biomarkers for evidence of environmental toxicity. This could be a useful tool to determine the extent of toxicity in organisms.

Sun et al. (2020) found that exposure to DBDPE and BDE-209 was linked to hepatoxicity, liver pathology, and changes in the morphology of the liver. These changes also included an increase in liver weight, with an abnormal liver/body ratio. The study also found that BDE-209 and DBDPE could induce inflammation and oxidative stress, increase serum glucose levels, and interfere with metabolic pathways through the downregulation of enzymes in rats. A recent publication found similar results with DBDPE and BDE-209. Jing et al. (2019) linked BDE-209 to morphological and structural changes in the heart. The study on male rats also found that decabromodiphenyl ethane (DBDPE) and BDE-209 increased inflammatory markers, interleukin-1 beta (IL-1 b), as well as IL6 and IL10. The results of the study also indicated that BDE-209 had stronger toxic effects and could cause oxidative stress, inflammation, and heart damage. DBDPE also caused

oxidative stress, lipid peroxidation, genetic toxicity, and DNA damage in the earthworm, *Eisenia fetida* (Zhao et al. 2020). Lipid peroxidation and enzyme inhibition were also found in a study by Feng et al. (2013) in *Carassius auratus*. These findings present severe implications for public health as chronic exposure and high concentrations of DBDPE lead to heart and liver disease, lipid peroxidation, and possibly DNA damage.

Ji et al. (2014) discovered gender-specific responses to TBBPA. The physiological effects on the model organism, *Mytilus galloprovincialis*, were determined using iTRAQ-based proteome analysis. TBBPA exposure may cause a variety of physiological responses, including apoptosis, signal transduction, immunological and oxidative stress, and energy disturbance. More importantly, the study revealed gender-specific responses and encouraged inclusion of both genders when investigating the effects of environmental toxicity of BFRs. Several articles highlight a cocktail of pollutants, including BFRs that may be responsible for the declining sperm counts and semen quality within the past few decades (Ingle et al. 2018; Yu et al. 2018). In addition, BFRs were cited as causing fertility problems in both genders as well as developmental problems in children (Kodavanti et al. 2022).

5.3 Persistence of BFRs in the Environment

Polybrominated diphenyl ethers (PBDEs) are ubiquitous in the environment as they are present in air, soil, and water. PBDEs, penta-PBDE, octa-PBDE, and deca-PBDEs, have been on the persistent organic pollutants (POPs) list since 2017 (Jing et al. 2019; Ezechiáš et al. 2014). Altogether, there are 209 different congeners. Since PBDEs are not bound to other chemicals, they can be easily added to furniture or textiles. In addition, they are volatile and quickly released into the air (Webster et al. 2009). For this reason, household dust and indoor air have a higher concentration of PBDEs than outdoors. Novel PBDEs have been used as a replacement for legacy PBDEs however, they are also persistent in the environment and are toxic and biomagnified in the food chain (Ezechiáš et al. 2014).

Due to various physiological properties such as low vapor pressure, low Henry's law constant, low solubility, and low octanol-water partition, legacy BFRs such as TBBPA can quickly be deposited onto the soil, sediments, and particles in the atmosphere (Dong et al. 2022; Sunday et al. 2022). The majority of BFRs are additives. They are added and mixed as the polymer is being made but are not usually bound to the polymer covalently (Yu et al. 2016). Therefore, PBDEs are considered additives, allowing them to easily volatilize away from the original product they were added to and subsequently enter the environment (Yang et al. 2018). More concerning is that little is known about the toxicity of partially degraded BFRs or lower brominated BFRs as a result of natural environmental processes. Moreover, assessing the amount of BFRs trapped in sedimentation is difficult. Figure 5.1 illustrates the broad distribution of BFRs in soil and sedimentation in Europe, Asia, and the USA. Lao et al. (2023) found that the amounts of BFRs, especially PBDEs, present in sediment were significantly correlated with the amount

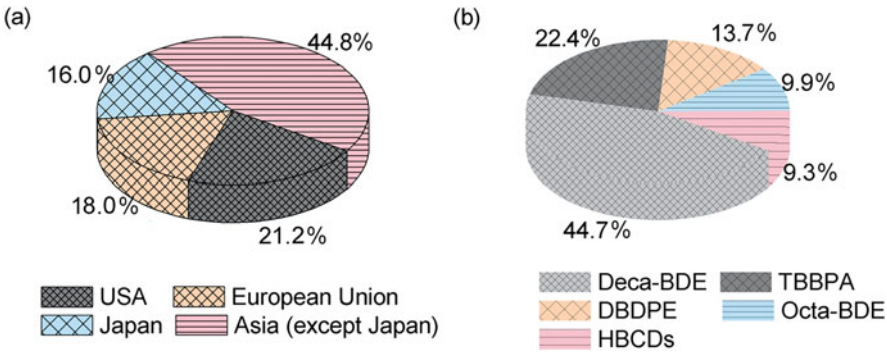

Fig. 5.1 BFR consumption and distribution in soil and sediment. [Retrieved from Yu et al. (2016)]

of industrialization and output of the surrounding geographical areas along the Pearl River Delta (Lao et al. 2023). Figure 5.1 shows the distribution of various BFRs in Asia, Europe, the USA, and Japan in soil and sediment.

5.3.1 Potential Exposure to Legacy BFRs and NBFRs in Indoor and Outdoor Settings

The persistence of legacy BFRs in indoor settings poses a health risk for humans, and the same may be expected of NBFRs. Four main routes of toxicity were identified. These are ingestion of indoor dust, absorption through the skin, inhalation of BFRs in indoor dust, and ingestion of BFRs in food (Zuiderveen et al. 2020). Reche et al. (2019) collected samples of outdoor ambient air, indoor workplace ambient air, and indoor dust across Spain to determine concentrations and trends for each. The study found that high concentrations of outdoor PBDE ranging from 1.18 to 28.6 pg m^{-3} were correlated to outdoor landfills and recycling centers. In addition, high dechlorane plus (DP) concentrations in indoor air at concentrations of 2.90–42.6 pg m^{-3} were strongly correlated to new electronic devices.

A similar study by McGrath et al. (2018) conducted in Melbourne, Australia, tested 51 dust samples from homes, offices, and vehicles to identify prominent BFRs in each setting. The BFRs tested were eight PBDEs (−28, −47, −99, −100, −153, −154, −183, and −209) and seven NBFRs (PBT, PBEB, HBB, EH-TBB, BEH-TEBP, BTBPE, and DBDP) identified using selective pressurized liquid extraction (S-PLE) and gas chromatography coupled to tandem mass spectrometry (GC-MSMS). The study also found that legacy and NBFRs were linked to specific areas, such as offices with the highest concentrations of penta-BDE. At the same time, homes and vehicles contained higher levels of EH-TBB and BDE 209. In addition, toddlers were more at risk by up to 2 orders of magnitude than adults for exposure to PBDEs and NBFRs. This is especially concerning since evidence suggests that BFRs are neurotoxic to children (Roze et al. 2009).

Ingestion of BFRs has been found to vary with different foods and locations close to e-waste recycling areas. Various studies have found the presence of PBDEs in fish and meat products in China (Shi et al. 2018). Sun et al. (2014) found that daily consumption of PBDEs in the coastal regions of South China ranged from 1.42 to 5.91 ng d^{-1}. HBCDs were ubiquitous in human milk and food products of animal origin in China despite that HBCD has been restricted since 2016 (Shi et al. 2018). The implications of this are that HBCD and relevant congeners are likely airborne, and contaminated dust is being ingested and tends to persist in the environment and biomagnify in the food chain.

5.4 Biodegradation of BFRs in Soils and Sedimentation Under Anaerobic and Aerobic Conditions

The kinetic rates for the biodegradation of BFRs in both anaerobic and aerobic soils differ. Generally, degradation kinetics are faster in aerobic soils (Nyholm et al. 2010). However, biodegradation is much more substantial and efficient under anaerobic conditions (Gerecke et al. 2006). During the anaerobic digestion of organic micropollutants, four main stages occur. These consist of methanogenesis, hydrolysis, acidogenesis, and acetogenesis (Carneiro et al. 2020). These processes are also influenced by microorganisms and cometabolite biotransformation (Arias et al. 2018).

Biodegradation of other BFRs, such as tetrabromobisphenol A (TBBPA), was found to be influenced by the complexity of the carbon source. Complex sources such as wastewater, as opposed to glucose, were biodegraded slower (Macêdo et al. 2022). This was further corroborated by Balaban et al. (2021) demonstrating that the addition of a vitamin source delayed bacterial growth and, as a result, reduced TBNPA and DBNPG biodegradation. Moreover, the study concluded that concentrations higher than 0.5 mg L^{-1} inhibited biodegradation in *Clostridium* spp. This is in agreement with Wang et al. (2022b), who stated that higher concentrations of DBDPE inhibit biodegradation. Concentrations higher than 50 mg L^{-1} were too toxic for the organisms.

Clostridium spp. has also proven to be effective in the biodegradation of HBCD (Li et al. 2020). In this study, both *Bacillus* spp. and *Clostridium* spp. were capable of biodegradation of up to 70% and 77% from cell suspensions taken from Chiang Chung soil and riverbank soil, respectively. The biodegradation was conducted under aerobic conditions. The biodegradation kinetics was slower in soil than in soil suspension for this study.

Huang et al. utilized a system of maize plants and *P. aeruginosa* strain HS9 to remove HBCD from the soil. The optimal temperature and pH reported were 30 °C at pH8, respectively, for the increased degradation rate of hexabromocyclododecane (HBCD). The study reported that the HS9 strain could remove 69% of the 1.7 mg L^{-1} of HBCDs (α-, β-, and γ-HBCD) in 14 days. The addition of HS9 was also found to stimulate plant growth by removing HBCDs from the soil. Further, adding HS9 enriched the number of microbes in rhizospheric soil. This included

fungal microbes, an essential part of soil microbial ecosystems. Peng et al. (2015) reported degradation of HBCD and a-HBCD to 90% under similar culturing conditions of 30 °C and pH 7 using the bacterial strain *Achromobacter* sp. Stepwise increasing additions of HBCD were added to culturing conditions to optimize the ability to biodegrade α-, β-, and γ-HBCD in a study by Geng et al. (2019). The biodegradation of HBCD was under aerobic conditions using a *Pseudomonas* sp. strain GJY at 30 °C at pH 7. Soil samples were collected from Ziya e-waste recycling centers in Tianjin, China. The strains were derived from the soil samples using extinction-dilution techniques. The degradation of each isomer was conducted in MSM with each diastereoisomer. After 8 days, the results showed degradation efficiencies of 85.38%, 82.64%, and 75.5% for α-, β-, and γ-HBCD, respectively.

Another synergistic application for degradation was applied to degrade BDE-209. Chang et al. (2021) utilized a novel bio-slurry bioreactor (NBB), which consisted of UVA LED irradiation coupled with biodegradation by microbes in a Ca-montmorillonite clay slurry. The NBB coupled UV-resistant bacteria, *Stenotrophomonas* sp., *Pseudomonas* sp., and *Microbacterium* sp., and UV photolysis was carried out in a clay slurry under anaerobic conditions. Quantification of debromination was done by measuring Br^- using ion chromatography. Biodegradation was done by using BDE-209 as the sole source of carbon. The degradation kinetics were most efficient with the coupled system than either alone.

Yan et al. (2018) reported using soil columns under anaerobic conditions to degrade pentabromodiphenyl ether (BDE-91). The study replaced oxygen with sulfate as the final electron acceptor in columns filled with soil to remediate contaminated reclaimed water to recharge groundwater. Interestingly, this study used sulfate-reducing bacteria and archaea for the biodegradation of BDE-91. Elevated levels of sulfate were found to enhance the biodegradation of BDE-91.

Anaerobic conditions were utilized in a study by Ramaswamy et al. (2021). *Dehalococcoides mccartyi* strain CG1 debrominated tetrabromobisphenol A (TBBPA) ultimately into BPA in 10 days. *Dehalococcoides mccartyi* strain CG1 was able to utilize TBBPA as a sole source of carbon. Furthermore, a proteomic analysis revealed that the reductive dehalogenase, PcbA1, was responsible for debromination of TBBPA. Therefore, the acceleration of biodegradation of TBBPA was interpreted as metabolic utilization of TBBPA. Furthermore, a 92-fold increase in cell density of *D. mccartyi* strain CG1 demonstrated further evidence of this.

BDE-209 and other polybrominated diphenyl ethers can be broken down by coupling a Fenton system with persulfate (Wu et al. 2020). This abiotic approach can remove BDE-209 from soils or other hard surfaces. The study reported degradation efficiency ranging from 73.4 to 95.8%. The addition of persulfate resulted in the generation of SO_4. The SO_4 was believed to make a nucleophilic attack on BDE-209, resulting in debromination to lower brominated constituents and pentabromophenol (Wu et al. 2020). The mechanism was achieved through the cleavage of C–O bonds and subsequent replacement with OH groups (Wu et al. 2020). The resulting products, nona-BDEs and pentabromophenols, were vulnerable

to further transformation. The study presents this data as a cost-effective solution for removing BDE-209 from soils in an aerobic environment.

Larger eukaryote organisms are potential solutions to removing BFRs from the soil. Earthworms were used in a study by Qiao et al. (2022) for the potential removal of BFRs: BDE 209, PBT, DBDPE, BTBPE, and HBB. The removal of these BFRs varied with each BFR. BFRs with similar molecular weights and chemical structures had similar enrichment and removal results. The study also demonstrated the potential for secondary pollution from worm castings that were not retained in the earthworm. The use of earthworms could remove BDE-209 and DBDPE from the soil. The removal of the other BFRs could have been more efficient.

5.5 Biodegradation of Contaminated Water and Sediment Matrices

Systematic surveillance of BFRs in wastewater treatment plants (WWTPs) is crucial for understanding efficient methods of removal and contamination. Moreover, little is known about certain BFRs, such as 1,2-dibromo-4-(1,2-bromomethyl) cyclohexane (TBECH), in aqueous environments. Anaerobic digestion is a well-studied aspect of wastewater treatment. Hydrolysis is essential in this process and facilitates the enzymatic breakdown of larger molecules into monomers (Macêdo et al. 2022). Carneiro et al. (2020) found that hydrolysis and acidogenesis were crucial steps in removing organic micropollutants from wastewater. Wastewater treatment plants could detoxify wastewater by coupling bioremediation methods with regular treatments. Ruan et al. (2019) discovered that BFRs were prevalent in influent water sampled from various WWTPs in Hong Kong. This work emphasized the need to monitor the enantiomer-specific behavior of chiral BFRs in the various treatments used in WWTPs. The study also discovered that biological treatment resulted in more efficient BFR elimination and enantiomer-specific degradation of chiral BFRs.

A novel approach of combining an upflow anaerobic sludge blanket bioreactor (UASB) and integrated fixed film/activated sludge (IFAS) system can increase the efficiency of organic micropollutant removal as was done in a study by Arias et al. (2018). This innovative approach reduced nitrogen by using methane as an electron donor. The study reported that the system consisting of methanotrophs and heterotrophic denitrifiers removed 93% of chemical oxygen demand and dissolved methane in the UASB effluent. The purpose of the system was to increase microbial diversity to achieve more efficient removal of organic micropollutants. However, different culturing conditions, which will be discussed further, are essential for achieving this goal.

In a study by Balaban et al. (2021), a four-strain consortium was used to degrade both TBNPA and DBNPG. Table 5.1 lists the genera, GenBank accession number, and species in the consortium that biodegraded both TBNPA and DBNPG. Interestingly, the study reported that both compounds were degraded at similar rates. The authors hypothesized that this might be due to similar enzymes and metabolic

Table 5.1 Table showing the genera, species, and GenBank accession numbers of the four-strain consortium with initial densities of each strain

ID	Strain (highest similarity, 99%)	GenBank accession number	OD 600 (initial density CFU mL^{-1})
DB2	*Pseudomonas citronellolis*	KY229738	0.001 (1.10×10^5)
DB3	*Gordonia sihwensis*	KY229739	0.001 (1.70×10^5)
DB4	*Shinella zoogloeoides*	KY229740	0.004 (4.90×10^5)
DB5	*Microbacterium oxydans*	KY229741	0.027 (3.00×10^6)
TB1	*Pseudomonas aeruginosa*	KY229734	
TB2	*Delftia tsuruhatensis*	KY229735	
TB3	*Pseudomonas citronellolis*	KY229736	
TB4	*Sphingobacterium siyangense*	KY229752	
TB5	*Microbacterium paraoxydans*	KY229753	

The species listed are capable of biodegradation of TBNPA and DBNPG. Retrieved from Balaban et al. (2021)

pathways of degradation for both. The study proposed a monooxygenase pathway for degradation. When both TBNPA and DBNPG were added, the degradation kinetics were almost twice as long (from 3–4 days to 7 days). Bacterial growth was determined to be the limiting factor, and a carbon source was needed for biodegradation. Yeast extract and glucose significantly enhanced biodegradation (3–7 days), while the vitamin mix slowed degradation kinetics (1–2 months).

Liang et al. (2019a) found that efficient removal of typical BFR, 2,4,6-tribromophenol (TBP), was possible using *Bacillus* sp. GZT. This study also identified genes and enzymes corresponding to the bioremediation of TBP and proposed an enzymatic pathway (pictured below in Fig. 5.2) for biodegradation. Interestingly, the study proposed the possibility of biodegradation enhancement and tolerance with recombinant strains containing the genes: tbpA, tbpB, tbpC, tbpD, and tbpE.

Lin et al. (2021) used a microbial fuel cell to bioremediate and detoxify wastewater. Microbial fuel cells (MFCs) have been used more recently to biodegrade various organic compounds and recover energy by increasing the electron transfer rate and biodegradation efficiency (Hassan et al. 2018). The efficiency of using MFCs is evident with a less toxic final product of bioremediation and energy recovery through bioelectrochemical processes (Hassan et al. 2018). Lin et al. used different genera of bacteria for dehalogenation (*Pseudomonas*), electroactive bacteria (*Desulfovibrio*), and aromatic ring-cleaving bacteria (*Geobacter*) in the MFC for further biodegradation than bisphenol A.

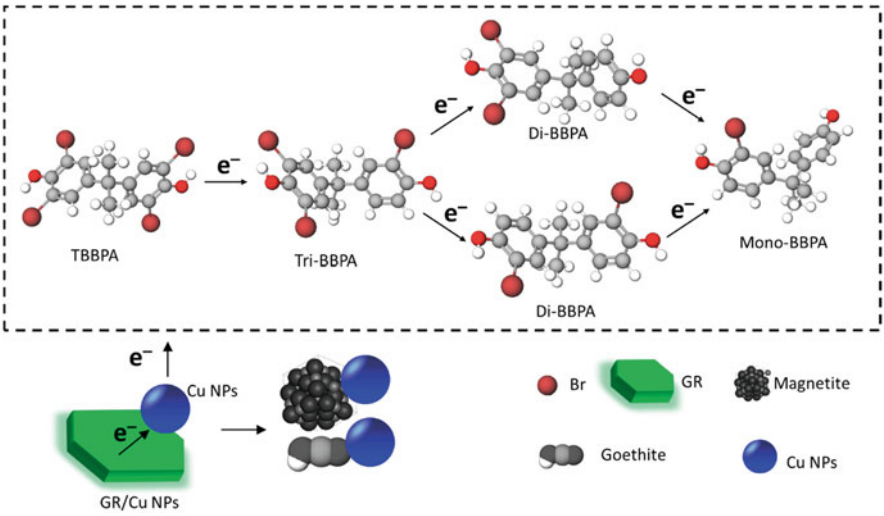

Fig. 5.2 Proposed mechanism of reduction by GR-Cu NPs. The reduction of TBBPA occurs on the surface of Cu NPs, and electrons from GR are transferred to the active sites of Cu NPs. GR(Cl) is transformed into two byproducts, goethite and magnetite, after TBBPA is reduced. [Retrieved from Fang et al. (2019)]

5.6 Catalytic Methods of Degradation and Reduction of BFRs in Wastewater, Aquatic Matrices, and Sediment

The presence of BFRs in sedimentation from a temporospatial aspect needs to be better studied and understood. In a study by Vauclin et al. (2021), sediment cores were taken along the backwater areas along the Rhône River. An age-depth model was established to find how the concentrations of BFRs and other pollutants were prevalent for each period. The findings were consistent with phasing out certain pollutants, such as polychlorinated biphenyls, which showed lower concentrations after phasing out. The study also found that novel and legacy BFRs reached peak concentrations in the early 2000s and have remained stable since the 2010s. The study highlighted the importance of sediment cores for determining spatiotemporal trends in both legacy and novel BFRs. Due to the hydrophobicity of BFRs, sedimentation often becomes a sink, and high concentrations of BFRs can be found in river sedimentation near e-waste sights (Yu et al. 2016). Xiong et al. (2017) proposed bioaugmentation with *Bacillus* sp. GZT for TBP removal from river water/sediment. This is in addition to the phyla isolated from sediments. These were Firmicutes, Actinobacteria, Proteobacteria, and Bacteroidetes. In this study, the biodegradation of TBP was enhanced by supplementation with NaCl, glucose, yeast extract, sodium propionate, and humic acids.

Catalytic methods of removing BFRs from wastewater have been explored in various studies. These methods include photocatalytic, electrocatalytic, and plasma catalytic degradation and reduction. Sedimentation can reduce and debrominate BFRs through microorganisms or reductive catalysis. Green rust (GR), which consists of layers of sedimentation with Fe(II) and high amounts of Fe^{2+}–O–Fe^{3+} in the iron hydroxide layer, is capable of reductive catalysis (O'Loughlin and Burris 2004). Figure 5.2 illustrates the proposed mechanism of reduction by GR-CuNPs, which primarily occurs on the surface of the GR. O'Loughlin and Burris (2004) demonstrated that the addition of Cu and Ag significantly enhanced the reducing capabilities of GR on halogenated organic compounds. Fang et al. (2019) also confirmed that adding Cu nanoparticles (Cu NP) to GR enhanced the reduction of TBBPA. The GR was interlayered with Cl^-, SO_4^{2-}, and CO_3^{2-}. The GR(Cl)-Cu NP obtained the greatest degradation efficiency at 92.11%.

Enhanced heterogeneous photo-Fenton catalytic photodegradation was utilized by Huang et al. (2020). An efficient degradation rate of 97.4% was achieved by coupling bio-template synthesized ceria with natural ferrihydrites in a novel heterogeneous photo-Fenton system. Furthermore, adding bio-template synthesized ceria with natural ferrihydrites resulted in the regeneration of Fe^{2+} and the production of photoelectrons, which is often a limiting factor.

Natural organic matter is an environmentally friendly alternative for use in photocatalytic degradation. Soluble organic matter can form active free radicals such as OH when hit with visible light that, in turn, can oxidize BFRs (Dong et al. 2022). Natural organic matter such as humic acids and carboxylate ions in the environment has proven to be a promising solution to BFRs. Humic acids can form reactive oxygen species or photochemically produced reactive intermediates capable of degrading persistent organic pollutants (Dong et al. 2022). For example, Son et al. (2019) used Aldrich humic acid to photodegrade HBCD and its three diastereoisomers in simulated solar light. Likewise, Zhang et al. (2018) found that dissolved organic matter could photodegrade novel BFR, 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), in simulated light with the addition of chlorine.

5.7 Mechanisms of Biodegradation

The debromination of BFRs is the most important step in the biodegradation of BFRs since it allows for complete mineralization (Segev et al. 2009a). In general, the more bromines in a BFR, the slower the biodegradation rate. Typically, the arrangement and amount of bromines or halogens are also inversely proportional to biodegradation kinetics. Under anaerobic conditions, biodegradation of PBDEs favors reductive bromination or reduces the number of bromines (Zhao et al. 2018). In aerobic degradation, cleavage of the aromatic ring occurred first, followed by debromination and hydroxylation (Zhao et al. 2018). It is important to note that reductive removal of the halogen or debromination forming a halide anion is crucial

in reducing the toxicity of the compound in question (Hug et al. 2013). This outlines the importance of organohalide respiration, which refers to the respiration process where anaerobic bacteria use halogenated hydrocarbons as a final electron acceptor (Hug et al. 2013).

The fate and intermediate lower brominated BFRs, such as in PBDEs, can often be even more environmentally toxic than the parental species (Pan et al. 2016). Therefore, it is important to understand the fate, mechanisms, and degradation kinetics of both novel and legacy BFRs undergoing natural photodegradation (Zhang et al. 2018). Pan et al. (2016) reviewed the fate of PBDEs in various environmental matrices, including aqueous, organic, solid, gas, and Ti–O_2-mediated phases, to understand the natural photodegradation of PBDE congeners.

In some instances, the method of degradation influenced the resulting congeners. For example, Wang et al. (2019) investigated the debromination of 2,2′,4,4′--tetrabromodiphenyl ether (BDE-47), which had preferential debromination at the para-bromine in the H-transfer system to generate BDE-17, while the preference was ortho-bromine in an electron transfer system to generate BDE-28. Both methods were part of a nanoscale zerovalent iron (n-ZVI) system and six n-ZVI-based bimetallic systems (Fe/Cu, Fe/Ni, Fe/Pd, Fe/Ag, Fe/Pt, and Fe/Au). Interestingly, the metals Pd, Pt, Ni, Cu, and Au use hydrogen gas to debrominated PBDEs. The study determined that bimetallic and NaBH4, Fe/Pt, Fe/Ni, and Fe/Pd preferred H-transfer mechanisms, while e-transfer mechanisms preferred Fe/Ag. Conversely, Fe/Cu and Fe/Au preferentially debrominate equally under e-transfer and H-transfer mechanisms. The mechanism for debromination of halogenated compounds has been divided into two hypotheses. The first hypothesis has been to attribute dehalogenation to electron transfer, where the difference in corrosion potential between Fe and the additive metal allowed for more current and, thus, more electron transfer (Yan et al. 2010; Wang et al. 2019). The other hypothesis is that the additive's ability to absorb hydrogen would dictate the speed of hydrogen transfer and, thus, dehalogenation (Chun et al. 2010; Wang et al. 2019). Chun et al. (2010) also concluded that the size and distribution of the metal additives on the surface of Fe were the most important variable. Hydrogen transfer in a palladized zerovalent zinc (Pd/ZVZ) system is also pH dependent, as illustrated in a study by Xu et al. (2020).

As previously mentioned, Geng et al. (2019) conducted biodegradation studies using *Pseudomonas* strain GJY. The study also proposed a mechanism of biodegradation of the three diastereoisomers of HBCD. In addition, they tracked subsequent metabolites using ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MSMS). The study proposed that the pathway for HBCD biodegradation consisted of ring opening, hydroxyl substitution, and debromination. This pathway differs from other biotransformation studies of HBCD and highlights that microorganisms influence how HBCD isomers are distributed in environmental settings. Figure 5.3 highlights a proposed pathway of debromination of HBCD-contaminated soil from Chiang Chun (Li et al. 2020).

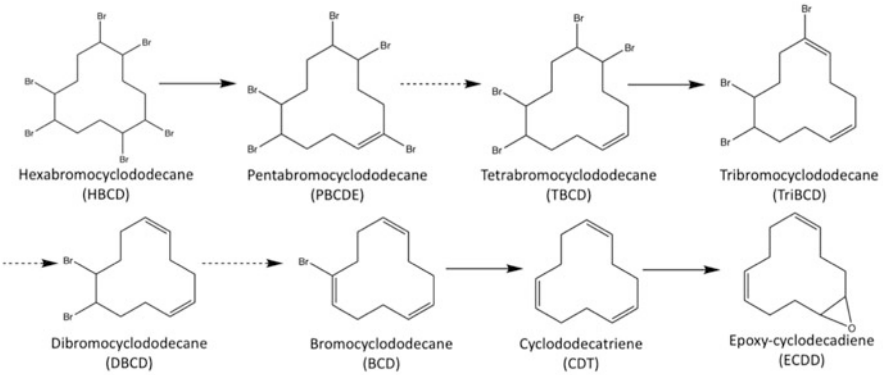

Fig. 5.3 The proposed pathway of HBCD biodegradation through the process of debromination from soils collected from Chiang Chun. The metabolites were identified via gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). [Retrieved from Li et al. (2020)]

5.8 Genes and Enzymes Involved in the Biodegradation of BFRs

Genome annotations and identification of enzymes involved in biodegradation pathways are crucial for successful biodegradation of BFRs and other pollutants. Liu et al. (2015) overexpressed tbbpa A for biodegradation studies of TBBPA. This gene was identified due to upregulation when exposed to TBBPA. Whole-genome sequencing of *Ochrobactrum* sp. strain T was compared to the NCBI database for identification of potential TBBPA-degrading genes. Gene tbbpa A was identified and cloned into an expression vector. The constructed strain was able to degrade TBBPA and removed bromine with 78% efficiency and demineralization at 37.8% efficiency in 96 h. This was observed to be very similar to the parental strain. These results demonstrated the possibility of creating constructs for the purpose of biodegradation of POPs. Culturing conditions were aerobic in mineral medium at 37 °C at pH 7. Table 5.2 lists the genes and enzymes that have been identified as capable of degradation and mineralization of BFRs. Some enzymes may be capable of biodegradation of multiple BFRs with similar structures.

Whole-genome sequencing of microorganisms capable of debromination as well as biodegradation is another important step in deducing the molecular mechanisms involved in bioremediation of BFRs (Shah et al. 2018; Liang et al. 2019a). Genes encoding enzymes that play an important role in the biodegradation of BFRs are ideal targets for genomic analysis when considering potential candidates for biodegradation. Wang et al. (2022b) isolated extracellular enzymes, MnP, Lip, Lac, and cytochrome P450, which aided in the biodegradation of DBDPE. The most important extracellular enzyme for degradation was Lac. The study also noted that

Table 5.2 Genes and enzymes experimentally shown to biodegrade BFRs

Genes/enzymes	BFRs or congener degraded	References
C12O, C23O, C34O, Nid A, and Rf	Aromatic hydrocarbons, can facilitate oxidative cleavage of catechol and LBN PBDE congeners	Chou et al. (2016)
Dehalogenases: RdhA and Rdases Dioxygenases: C23O, RF, and ARHD	BDE-209	Chang et al. (2021)
Genes: tbpA, *tbpB*, *tbpC*, *tbpD,* and *tbpE*	TBP	Liang et al. (2019b)
Monooxygenase	TBNPA and DBNPG	Balaban et al. (2021)
Dehalogenase: PcbA1	TBBPA	Ramaswamy et al. (2021)
Gene: tbbpa A encoding for bromophenol dehalogenase	TBBPA	Liang et al. (2019a)
LinA2 and LinB: haloalkane dehalogenases	HBCD	Heeb et al. (2014)
Laccase	Bromophenols	Uhnáková et al. (2009)
Enzymes: MnP, LiP, Lac, and cytochrome P450	DBDPE	Wang et al. (2022b)
P. aeruginosa LY11 Crude enzyme extract	BDE-209	Liu et al. (2015)

antioxidant enzymes CAT and SOD were important for reducing the toxicity of *P. ostreatus.*

Enzymes have a potential to degrade BFRs more efficiently and rapidly than the organism itself. This was illustrated in a study by Liu et al. (2015). Crude enzyme extract was isolated from *P. aeruginosa* LY11. This strain is known for biodegradation of BDE-209. The crude enzyme was extracted through sonication, centrifugation, and finally filtration through a 0.22 μm filter. The resulting filtrate is what was considered crude enzyme extract. In this study, the crude enzyme was able to degrade BDE-209 in a shorter time period of 5 h and more efficiently at 92.77%. This study provides insight into the possibility of using crude enzyme extract from other microorganisms previously known to biodegrade specific BFRs. The potential to mass produce crude enzyme extract through over-expression systems may be a more efficient means of bioremediation of BFRs.

5.9 Culturing Conditions in Bioremediation Strategies

The culturing conditions for many degradation systems varied with each type of BFR. Some were cultured in aerobic or anaerobic conditions where temperature, pH, and culture supplementation varied with each organism. For some, supplementation was necessary for bioremediation, while other studies used the BFR as the sole carbon source. Table 5.3 summarizes the culturing conditions for various BFRs from optimized protocols for degradation and mineralization.

Table 5.3 Microorganisms capable of bioremediation of various BFRs and the culturing conditions for optimal mineralization

Microorganism or abiotic system	BFR degraded	Culturing aspects	References
Enterobacter and Clostridium	TBBPA	The addition of noncomplicated carbon sources such as glucose	Macêdo et al. (2022)
Bacterial consortium containing the dominant genera: *Sphingopyxis* spp.	Dibromoneopentyl glycol (DBNPG) and tribromoneopentyl alcohol (TBNPA)	Aerobic with added yeast extract for substrate and bacterial growth stimulation	Segev et al. (2009b)
P. ostreatus	DBDPE	Addition of glucose increased degradation rates	Wang et al. (2022b)
Bacterial consortium predominantly *Pseudomonas* spp.	Decabromodiphenyl ether (DBDE)	Aerobic and micro-aerobic soil slurry microcosm	Chou et al. (2016)
P. aeruginosa strain HS9	Hexabromocyclododecane (HBCD)	HBCD-contaminated soil plant/HS9 system	Huang et al. (2019)
HBCD-1 and HBCD-2 *Achromobacter* sp.	HBCD, α-HBCD	Aerobic culture with minimal salts medium (MSM) at 30 °C at pH 7	Peng et al. (2015)
R. palustris YSC3	HBCD	Modified van Niel medium at 35 °C at pH 9. Cells degraded faster at late log-phase inoculum of 1 ppm γ-HBCD	Chang et al. (2021)
Bacteria: *Thiobacillus*, *Sphingomonas*, *Geothrix*, *Paenibacillus*, *Desulforhabdus* Archaea: *Methanobrevibacter*, *Methanomethylovorans*, *Candidatus* DHVEG-6, *Candidatus, Nitrososphaera, and Methanosphaera*	Pentabromodiphenyl ether (BDE-91)	Anaerobic soil columns with microbial community of sulfate-reducing bacteria and archaea	Yan et al. (2018)
Clostridium spp. and *Bacillus* spp.	HBCD	Aerobic culturing of microbes found in the soil of Chiang Chun and riverbank soil	Li et al. (2020)
Stenotrophomonas sp., *Pseudomonas* sp., and *Microbacterium* sp.	BDE-209	Aerobic UV photolysis biodegradation in clay slurries	Chang et al. (2021)
Dehalococcoides mccartyi strain CG_1	TBBPA	Anaerobic in 100 mL of sodium bicarbonate supplemented with reductants. TBBPA was used as a sole source of carbon for screening	Ramaswamy et al. (2021)

(continued)

Table 5.3 (continued)

Microorganism or abiotic system	BFR degraded	Culturing aspects	References
Pseudomonas sp. GJY	α-, β-, γ-HBCD	Aerobic conditions in MSM with HBCD and each diastereoisomer at 30 °C and at pH 7 for 8 days	Geng et al. (2019)
Bacillus cereus JP12	BDE-209	BDE-209 was used as the sole source of carbon in MSM at 30 °C at a pH of 6	Lu et al. (2013)
Bacillus cereus HBCD-sjtu	HBCD	MSM with .5 mm HBCD at 30 °C, pH 7	Shah et al. (2018)
Sphingomonas sp. *PH-07*	PBDE selected congeners	Pre-grown with diphenyl ether as the sole source of carbon under aerobic conditions. Subsequently grown in MSM with selected PBDE congener	Kim et al. (2007)
Trametes versicolor	2-Bromophenol, 4-bromophenol, 2,4-dibromophenol, tetrabromobisphenol A, 2,6-dibromophenol, and 2,4,6-tribromophenol	Modified from Van der Merwe (2002) at 30 °C at pH 5.5	Uhnáková et al. (2009)
Bacterial genera: *Brevundimonas*, *Rummeliibacillus*, *Lysinibacillus*, and *Clostridium* *Archaea: Halalkalicoccus, Methanobacterium, Methanosarcina, and Methanocorpusculum*	BDE-209 and BDE-28	Anaerobic medium in the dark for 2 years at 30 °C, pH 7, with the reducing agent titanium citrate	Yang et al. (2017)
Geobacter, Dehalobacter, Dehalogenimonas, Desulfitobacterium, and Dehalococcoides	2,2′,4,4′-Tetrabromodiphenyl ether (BDE-47)	Sediment slurry microcosm containing MSM, spent mushroom substrate biochar, and BDE-47 incubated in an anaerobic chamber at 25 °C	Chen et al. (2018)
Bacillus sp. GZT bioaugmentation with *Firmicutes*, *Actinobacteria, Proteobacteria, Bacteroidetes*	TBP	Mineral medium and growth medium for culturing of *Bacillus* sp. GZT at pH 7. Supplementation of MSM with NaCl, glucose, yeast extract, sodium propionate, and humic acids enhanced biodegradation	Xiong et al. (2017)

Tokarz et al. (2008) reported that adding vitamin B12 enhanced the debromination kinetics. Other studies showed enhancements with the addition of glucose or other carbohydrates (Wang et al. 2022b). However, some additions for one strain may enhance degradation and inhibit others. This was evident when adding a vitamin mix slowed the degradation rate of BFRs (Balaban et al. 2021). Some bacterial strains are capable of biodegradation when the BFR is the sole source of carbon. This was observed for the *Bacillus cereus* JP12 strain (Lu et al. 2013), where BDE-209 was added to MSM at 30 °C, pH 6. Degradation efficiency was enhanced by adding other carbon sources, surfactants, and metals Cu^{2+} and Zn^{2+}. Similarly, zerovalent iron enhanced the biodegradation of BDE-209 and BDE-28 (Yang et al. 2017). Shah et al. (2018) also used *Bacillus cereus* for successful biodegradation of HBCD with another strain called HBCD-sjtu at a higher pH of 7 at 30 °C. This demonstrates that physiological conditions were as important as culturing and media for the biodegradation of certain BFRs. It also demonstrated that despite using the same genus and species of bacteria, the BFR degradation influenced the culturing conditions. Optimal temperatures ranged from 30 °C at pH 7 (Peng et al. 2015) to 35 °C at pH 9 (Chang et al. 2021), depending on the bacterial strain. Changes in pH and temperature resulted in less biodegradation efficiency and was dependent on the BFR.

5.10 Conclusion and Future Direction

The possibility of phasing out NBFRs and using bio-sustainable organobromine BFRs is a promising solution to the problem of BFR environmental contamination. Sequencing genomes of microorganisms capable of biodegradation of BFRs is essential for understanding the molecular mechanisms of biodegradation. The potential for isolating genes and enzymes that biodegrade BFRs is high when microorganisms are collected from e-waste sites or near industrial facilities where BFRs are present. There have been many different genera and species of bacteria that have demonstrated the ability to biodegrade various BFRs. However, culturing conditions vary with each species of microbes used.

Another important consideration is the possibility that microorganisms that can remove chloride from hexachlorocyclohexanes may also debrominate BFRs, especially when the chemical structures are similar. Various studies, as previously mentioned, demonstrated that bacterial strains with dehalogenases may also remove halogens from different compounds, thus implying that microorganisms can bioremediate a variety of POPs.

The strategies presented here include various methods to address emerging BFR pollutants from different environmental sources. Catalysis is a proven method for efficient mineralization and biodegradation in abiotic methods. Using natural organic matter is an environmentally friendly way to oxidize BFRs and a promising way to address environmental pollution. One example discussed is humic acids, which form free radicals when exposed to light. In biotic methods, several organisms and systems have been presented. The supplementation and culturing conditions

varied with each BFR and organism. The addition of enzymes proved essential for biodegradation and highlights the possibility of engineering enzymes for the degradation of BFRs or in synergy with microorganisms.

The urgent need to remove POPs has never been more evident. Several publications have identified various pollutants including BFRs as being responsible for declining sperm counts over the past few decades. The exposure to BFRs through ingestion, inhalation, and absorption through the skin has taken their toll on the fertility of both genders as well as developmental consequences for children. This exposure to BFRs is most prevalent in indoor settings, e-waste recycling centers, and other industrial locations where BFRs are manufactured. Therefore, the best strategy moving forward is to bioremediate BFRs from wastewater treatment plants before they are released into the surrounding environment.

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