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Review Article

Brominated Flame Retardants (BFRs) in China: Wastewater Sources and Treatment Methods

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Submitted: 10 May, 2016

Accepted: 08 June, 2016

Published: 09 June, 2016

ISSN: 2333-7141

Keywords

- Brominated flame retardants (BFRs)
- Hexabromocyclododecanes (HBCDs)
- Polybrominated diphenyl ethers (PBDEs)
- Tetrabromobisphenol A (TBBPA)
- Emission source
- Treatment method

Abstract

China is one of the largest producers and users of brominated flame retardants (BFRs) in the world. This has led to ubiquitous environmental occurrence of the main BFRs commercially available in China, namely polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and tetrabromobisphenol A (TBBPA). Wastewater from BFR manufacturing, manufacturing of BFR-based products, and e-waste recycling processes is an important contributor to BFR pollution. While conventional wastewater treatment methods may reduce BFRs in wastewater streams, treatment limitations and sludge disposal remain important concerns. Specialized treatment methods for BFR removal from wastewater should be used where influent BFR concentrations are high, particularly in waste streams originating from the main BFR emission sources in China.

ABBREVIATIONS

BFRs: Brominated Flame Retardants; HBCDs: Hexabromocyclododecanes; PBDEs: Polybrominated Diphenyl Ethers; TBBPA: Tetrabromobisphenol A

INTRODUCTION

Brominated flame retardants (BFRs) are chemicals used in plastics, textiles, electronics, and construction materials to reduce flammability [1]. Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and tetrabromobisphenol A (TBBPA) are the most important high production volume and current use BFRs in China [2]. TBBPA is predominantly used as a reactive flame retardant and is chemically bound in polymers, while PBDEs and HBCD are additives that are not chemically bound and may readily separate from products into the environment [1]. The main commercial formulations of PBDEs are penta-, octa-, and deca-BDE [3], while commercial mixtures of HBCDs contain α-HBCD, β-HBCD, and γ-HBCD [4]. China is the largest producer and user of HBCDs in the world [5] and has a large number of facilities manufacturing PBDEs and TBBPA [6,7]. In 2006 the most widely produced BFRs in China were deca-BDE (36,000 tonnes), TBBPA (18,000 tonnes), octa-BDE (8,000 tonnes), and HBCDs (7,500 tonnes) [2]. The 2004 estimated consumption of BFRs in Asia (except Japan) was 140,000 tonnes.

High production and usage of BFRs in China has resulted in ubiquitous occurrence in the Chinese environment [2,7,8]. Due to their hydrophobic nature, BFRs tend to be bound to solid phase particles in soil, sediment, and sewage sludge [4,9]. Exceptionally high levels of PBDEs (191-9,156 ng/g dry weight (dw)) and TBBPA (1.64-7,758 ng/g dw) were measured in soils at an e-waste recycling area in Qingyuan, Guangdong [10] and a BFR manufacturing site in Shouguang, Shandong [11]. High levels of PBDEs (1.3-1,800 ng/g dw) were also found in sediment from Laizhou Bay, Shandong near a BFR manufacturing area [6]. Numerous other studies show occurrence of PBDEs, HBCDs, and TBBPA in water [12,13], air [5,14,15] dust [16,17], and remote areas [18] of China. The extensive environmental occurrence of BFRs is concerning because of increased exposure and potential health risks to humans and biota. PBDEs, HBCDs, and TBBPA are suspected endocrine disruptors [19], with *in vivo* studies showing changes in hormone activity of humans [6,20] and rats [21] after exposure. Negative effects on growth and reproduction have been observed in plants [22], aquatic species [23], and birds [24].

There is currently no restrictive use on HBCDs or TBBPA in China [7,25]. Usage of penta-BDE and octa-BDE were officially banned in China in 2006 [26] and PBDEs added to the list of banned chemicals included in the Stockholm Convention on Persistent Organic Pollutants in [8]. Since this time, reduced temporal trends have been observed in some parts of China [2]. HBCD was listed in 2013 [5], and TBBPA registered under the Registration, Evaluation, Authorization and Restriction of Chemical substances (REACH) in Europe in 2010 [27] and the Toxic Substances Control Act (TSCA) Work Plan list in the USA in 2014 [28].

Sources of BFRs in Wastewater

The main emission sources of BFRs in China are BFR

Cite this article: *Malkoske T, Tang Y, Xu W, Yu S (2016) Brominated Flame Retardants (BFRs) in China: Wastewater Sources and Treatment Methods. JSM Environ Sci Ecol 4(2): 1027.*

manufacturing sites, sites manufacturing BFR-based products, and electronic waste (e-waste) recycling and disposal [8,7]. Shouguang municipality, Shandong is located in a region with abundant bromine and has been the largest BFR manufacturing center in China since the early 2000's [11]. Jiangsu, Zhejiang, and Guangdong provinces are important in manufacturing of BFR-based products [6,8,29] where PBDEs are mainly used in furniture, textiles, and electronics [8,30], HBCDs in expanded and extruded polystyrene foams [4], and TBBPA in printed circuit boards [7] and plastics [9]. China still receives international shipments of e-waste and is likely the largest e-waste dumping site in the world [31]. Domestic production of e-waste is also increasing and was expected to reach 8 million tonnes in 2015 [29]. Guiyu and Qingyuan, Guangdong and Taizhou, Zhejiang are well-known e-waste recycling areas [29].

Information on wastewater production volumes and occurrence of BFRs in wastewater from emission sources in China and around the world is very limited. BFR manufacturing processes that produce the greatest volumes of wastewater include in situ washing of BFR solids separated by centrifuge and rinse water equipment washing [32]. In BFR-based product manufacturing, textile production requires comparatively large volumes of water. Wastewater mainly originates from used process bath water and rinsing residues from emptying containers and pipes from batch production [33] found that 3,500 tonnes/day of rinse water was produced at a printed circuit board manufacturing facility in Shanghai. TBBPA concentrations in the wastewater ranged from approximately 28.3 to 174.3 ng/L. In a life cycle assessment of e-waste treatment in China with and without waste disposal after processing, wastewater was an important pollutant release pathway for both scenarios [34]. At formal e-waste recycling facilities, electrodialysis and precious metal refining processes produce wastewater. While an increasing amount of China's e-waste is being processed at formal or licensed recyclers, most licensed recyclers cannot achieve high recycling rates and low emissions [31]. More information is needed on wastewater production and BFR occurrence in wastewater from the main emission sources.

Treatment of BFR containing wastewater

Numerous recent studies have recommended urgent steps be taken to address BFR pollution in China [2,5,7,8] . Effective treatment of BFR containing wastewater could be significant in reducing the release of BFRs to the environment. Where treatment is ineffective, elevated levels of BFRs have been found in surface water downstream of WWTP outfalls [35,36].

Studies on BFR removal by conventional wastewater treatment methods show varying degrees of effectiveness. At four wastewater treatment plants (WWTPs) in Hong Kong, influent concentrations of PBDE (1-254 ng/L) were not significantly reduced in treated effluent (20-53%) [37]. Higher reduction was reported at a WWTP near the Detroit River, USA, where influent PBDE (265 ng/L) was reduced 91% in an activated sludge treatment process [38]. In a study of twelve WWTPs treating municipal and industrial wastewater in the Yodo River Basin, Japan, HBCD (16-400 ng/L) was reduced by 80-99% [39]. Potvin et al., [40] found high removal efficiency of TBBPA (41 ng/L to 0.7 ng/L) by conventional activated sludge at a WWTP in Canada. TBBPA in wastewater from printed circuit board manufacturing in Shanghai was significantly reduced in treated effluent (3.21 ng/L) at an on-site WWTP, though the treatment method not specified [33]. Inconsistency in removal rates may require implementation of specialized treatment methods for BFRs. Derden and Huybrechts [30] reported that significant reductions in emissions of Deca-BDE from textile wastewater could be realized by processing at an external specialized processing plant. More information is needed on BFR removal efficiency at WWTPs in China, specifically those receiving wastewater from main emission sources.

Due to their hydrophobicity, BFRs tend to sorbs to suspended particulate matter and accumulate in sludge [4,25]. Final disposal of sludge is an important consideration, with land application, landfilling, and incineration common methods. Where sludge treatment is not practiced, land application may result in soil contamination [41]. Leaching tests done on solid powder waste from the printed circuit board manufacturing facility in Shanghai showed low leachability for TBBPA, with an estimated leach-out portion of 0.0007 to 0.006% [33]. This indicates in some cases land filling may be appropriate for final disposal. Stiborova et al., [42] found 11 PBDE congeners in WWTP sludge were reduced by 62 to 78% after 11 months of cultivation under aerobic conditions. Degradation constants of BDE 209, the most common congener, were 2.77×10^{-3} d^{-1} and 3.79×10^{-3} d^{-1} with half-life from 6 to 8.2 months. Anaerobic digestion degradation half-life of DecaBDE (7×10^2 d) was comparatively longer, while TBBPA (0.59 d) and HBCD (0.66 d) were significantly shorter [43]. Despite concerns about dioxin emissions from incineration, Mark et al., [44] found near total destruction of HBCD after incineration of polystyrene foam, with minimal impact on air emissions.

There are numerous lab studies on treatment methods for BFR removal from water, including anaerobic degradation, ozonation, adsorption, and oxidation [45-49]. The main treatment processes studied for PBDE degradation are photolysis, zerovalent iron, and TiO_2 photocatalysis [50]. In a review of these processes, Santos et al., [50] found TiO_2 photocatalysis most suitable due to higher debromination and mineralization, which avoids the formation of lower brominated PBDE congeners. Debromination was found to be the main degradation mechanism, though other reductive and oxidative processes may also occur. Huang et al., [45] achieved 96% removal of BDE-209 by oxidative reduction using TiO_2 photocatalysis. Photocatalysis under visible light irradiation has gained research interest as a low energy alternative to photocatalysis using UV. Zhou et al., [46] found that HBCD could effectively undergo photodegradation in the presence of Fe(III)-carboxylate complexes under simulated sunlight. Using biological treatment, Peng et al., [47] optimized anaerobic co-metabolic degradation to achieve a TBBPA degradation rate of 96.2% with a half-life of 4.1 days. The mechanism involved simultaneous degradation of TBBPA in the presence of different nitrogen sources. Higher degradation rates were achieved using non-biological treatment methods, including 99.3% degradation after 25 minutes ozonation [51] and 98% removal after 40 minutes by sorption with fly-ash supported nanostructured γ-MnO_2 [49]. Besides specialized treatment, process-integrated measures can also be used for reducing the amount of BFRs in wastewater. One example is reuse of rinse water from process baths in textile manufacturing [29].

CONCLUSION

Brominated flame retardants are ubiquitous in the Chinese environment, raising concerns about human and ecological health risks. Conventional wastewater treatment shows some ability in reducing BFRs in wastewater, but may not be suitable for wastewater originating from the main BFR emission sources in China. Implementing specialized treatment for BFR removal in wastewater from emission sources could significantly reduce the release of BFRs to the environment. Where BFRs are transferred from wastewater to sludge, aerobic/anaerobic digestion and incineration may be suitable sludge treatment methods. More information is needed on wastewater production and BFR occurrence in wastewater from the main emission sources in China.

ACKNOWLEDGEMENTS

This work was supported by Natural Science Foundation of China (21546005) and National Water Pollution Control and Treatment Key Technologies RD Program (2015ZX07406-001).

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Cite this article

Malkoske T, Tang Y, Xu W, Yu S (2016) Brominated Flame Retardants (BFRs) in China: Wastewater Sources and Treatment Methods. JSM Environ Sci Ecol 4(2): 1027.