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Brominated Flame Retardants in Wastes – Aspects Related to Treatment and Recycling

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ABSTRACT

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Brominated flame retardants (BFRs) are chemical compounds that are added to various products to increase flame resistance as a safety measure. These compounds are generally toxic and known as persistent organic pollutants. To this day, there are many articles, studies and researchers dedicated towards study of brominated flame retardants, however they generally lack circular economy aspect of their lifecycle. This work aims to gather literature about BFRs behavior, presence, legislation and treatment options and then analyze them altogether. In result, several study cases indicate not only presence of BFRs in waste streams, specifically electronic waste (e-waste) streams, but also evidence of the leakage of BFR compounds into the recycled products. Several treatment methods were described, such as pyrolysis, thermal degradation. Overall, with proper monitoring and treatment, BFRs have potential to be re-moved from the recycled products and isolated from the e-waste streams as well. Legislation aspect of the brominated flame retardants is handled well in European Union by United Nation Environment Programme (UNEP), RoHS directive and REACH regulation. Asian-Pacific countries also partly follow regulations made by UNEP. When it comes to USA, regulations are handled state by state, which could be improved by applying federal regulations.

CONTENTS

ABBREVIATIONS AND TERMS

BFRs	brominated flame retardants
PBDEs	polybrominated diphenyl ethers
HBCDs	hexabromocyclododecane
TBBPA	tetrabromobisphenol A
PBBs	polybrominated biphenyls
POP	persistent organic pollutant
e-waste	electronic waste
WEEE	waste from electrical and electronic equipment
UNEP	United Nations Environment Programme
RoHS	Restriction of Hazardous Substances Directive
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals

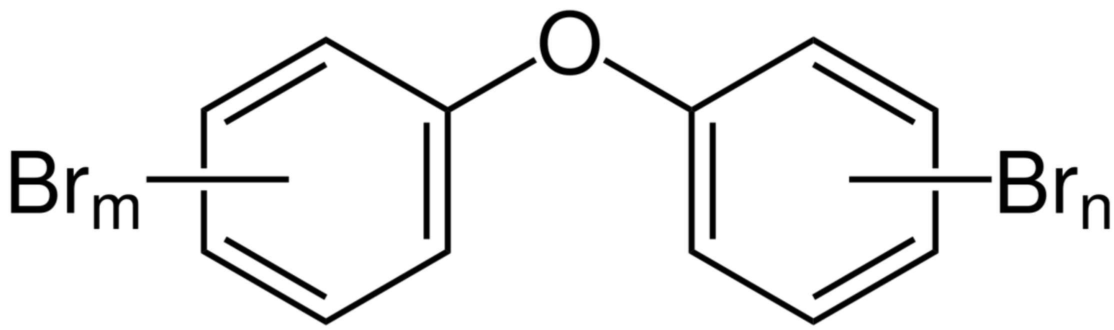
1 INTRODUCTION

1.1 Brominated flame retardants (BFRs)

Brominated flame retardants is a cluster of chemical compounds that are commonly used to enhance fire resistance of various materials. These compounds contain bromine atoms and are added to products such as electronics, textiles, and furniture to reduce the risk of ignition and slow down the spread of fire. BFRs work by interfering with the combustion process, making it more difficult for materials to catch fire. BFRs can be categorized into different groups based on their chemical structures and compositions. One major group includes polybrominated diphenyl ethers (PBDEs), which were widely used in various consumer products. Another group consists of tetrabromobisphenol A (TBBPA), commonly used as a flame retardant in electronic equipment. Hexabromocyclododecane (HBCD) forms another category and is often found in insulation materials. (Barceló et al. 2011)

1.2 Polybrominated diphenyl ethers (PBDEs)

PBDEs are a subgroup of BFRs widely used in various products globally. Historically, PBDEs have been employed as flame retardants in items such as electronics, textiles, plastics, and foam-based materials. The production of PBDEs involves the synthesis of brominated compounds, typically through chemical processes that introduce bromine atoms into diphenyl ethers. (Zota et al. 2011)

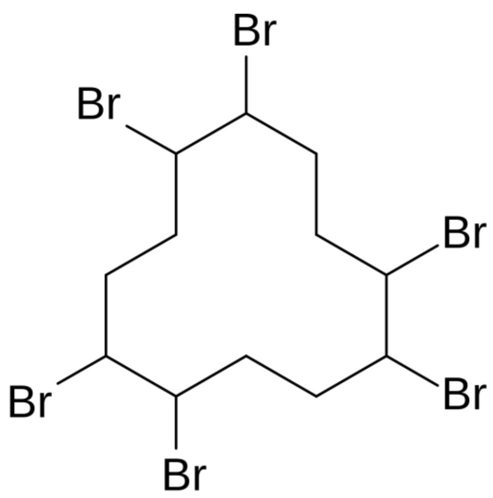


PICTURE1. PBDEs chemical structure. (Wikipedia, 2023)

Certain PBDEs are listed under the Stockholm Convention on Persistent Organic Pollutants (POPs). The specific PBDEs listed under the Stockholm Convention include commercial octa-BDE, penta-BDE, and deca-BDE formulations (Sharkey et al., 2020)

1.3 Hexabromocyclododecane (HBCDs)

HBCDs are a flame retardant belonging to the class of brominated compounds, and it has been utilized in a variety of applications worldwide. HBCDs have found use in construction materials, textiles, and polystyrene foam insulation. The global demand for HBCDs has been substantial, reflecting their efficacy in enhancing fire resistance in diverse products. The production of HBCDs involves chemical processes wherein bromine atoms are introduced into cyclic compounds. The synthesis of HBCDs typically employs a series of reactions to achieve the desired bromination pattern. (Covaci et al. 2006)

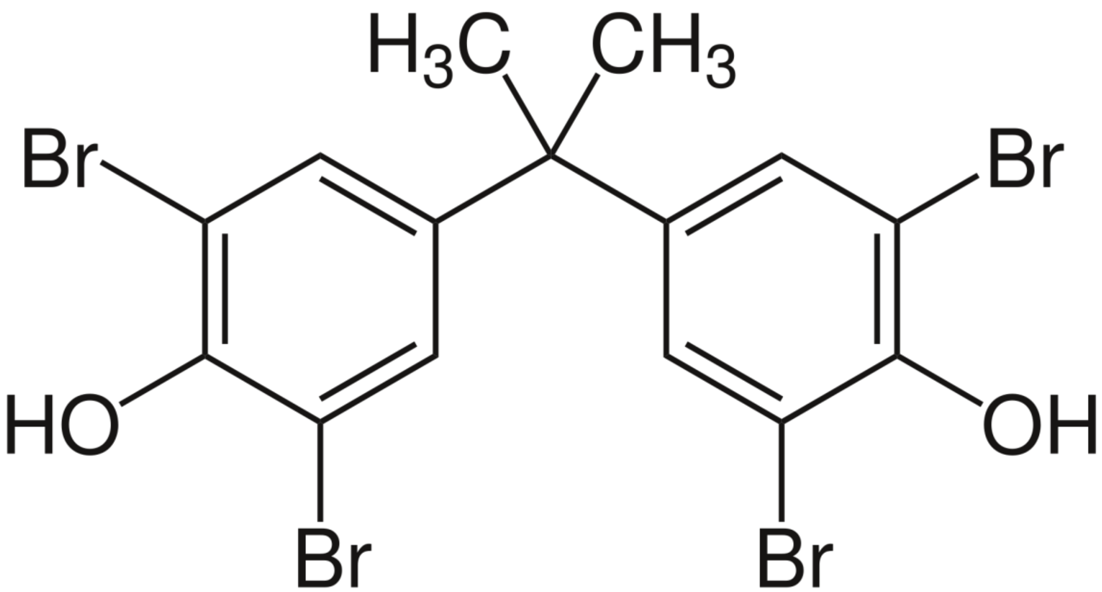


PICTURE 2. HBCD chemical structure (Wikipedia, 2023)

HBCD has faced regulatory restrictions. The compound was also listed as a POP under the Stockholm Convention, prompting global efforts to restrict its production and use. Many countries have implemented measures to limit or phase out HBCD in various products, particularly in construction materials and insulation, in an effort to reduce its environmental impact and potential health risks. Specific regulations can vary by country. (Sharkey et al., 2020)

1.4 Tetrabromobisphenol A (TBBPA)

TBBPA is a flame retardant widely utilized in various applications such as electronics, plastics, and textiles. TBBPA is synthesized through a chemical process involving the bromination of bisphenol A (BPA). Starting with BPA, bromine atoms are introduced through a bromination reaction, resulting in the tetrabromination of the BPA structure. This produces TBBPA, characterized by the addition of four bromine atoms to the phenol groups. The synthesis is followed by purification steps to remove impurities, yielding the final TBBPA product—a white or off-white powder. (Zhou et al. 2020)

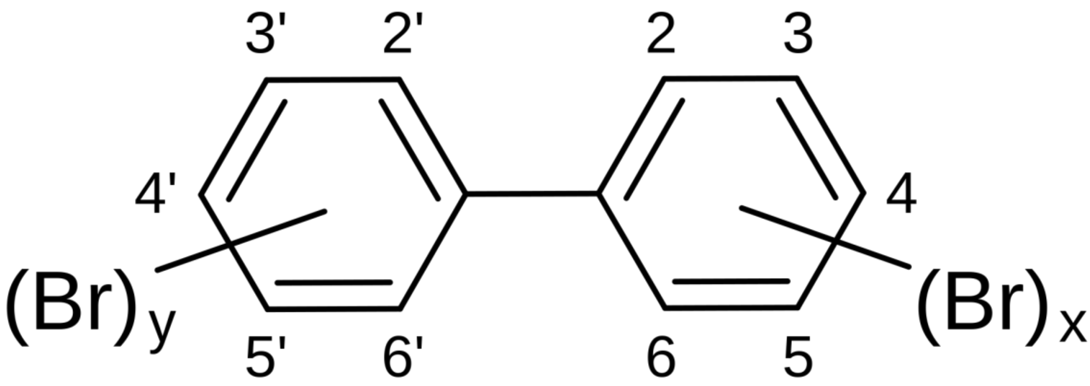


PICTURE 3. TBBPA chemical structure. (Wikipedia, 2023)

TBBPA has been subject to scrutiny within the context of the Stockholm Convention. While it is not currently listed as a POP under the convention, TBBPA has been under consideration, and discussions have taken place regarding its potential environmental persistence and health impacts. (Sharkey et al., 2020)

1.5 Polybrominated Biphenyls (PBBs)

Polybrominated biphenyls were commonly applied to plastics, textiles, and electronic components to reduce flammability. PBBs gained popularity in the mid-20th century. PBBs are synthetic chemicals that are produced through chemical processes involving biphenyl compounds and bromine. The synthesis typically starts with biphenyl, a compound composed of two benzene rings. Bromine atoms are then introduced into the biphenyl structure through bromination reactions. The specific bromination pattern and the number of bromine atoms added can vary, resulting in different forms of PBBs. The reaction typically involves the use of bromine gas or brominating agents to replace hydrogen atoms in the biphenyl structure with bromine atoms. The choice of reaction conditions, including temperature and the presence of catalysts, influences the outcome of the bromination process. (Hanari et al. 2006)



PICTURE 4. PBBs chemical structure. (Wikipedia, 2023)

However, their use has diminished over the years due to reasons stated before. PBBs are not explicitly listed under the Stockholm Convention on POPs, but their production and usage have been regulated in many countries. (Sharkey et al., 2020)

1.6 Toxicity of BFRs

BFRs have raised concerns about their potential toxicity to both the environment and human health. Their persistence and ability to bioaccumulate have become significant issues. In the environment, BFRs can accumulate in air, water, soil, and wildlife, posing risks to ecosystems. Additionally, certain BFRs have been found to be endocrine disruptors, potentially interfering with hormonal systems in humans and animals. Some studies have linked exposure to certain BFRs to adverse health effects, including developmental and reproductive issues. As a result, there's a growing emphasis on researching alternative flame retardants that maintain fire safety standards while minimizing the potential environmental and health risks associated with traditional BFRs. (Lyche et al. 2014)

1.7 Need of research

BFRs continues to be a subject of concern. Regulatory measures are in place in many regions to manage the production and usage of specific BFRs, however information on topic of BFRs is thoroughly dispersed. Most articles focus on handling singular aspect of BFR’s lifecycle, with the need of a complementary source of information, covering multiple aspects of BFRs at the same time. Those aspects would include evidence of BFRs presence, their persistency, treatment methos and legislation coverage.

2 SCOPE

This study intends to collect information concerning BFRs in 3 aspects, their presence in the environment, possible treatment methods and legislation concerning BFRs. BFRs have been studied multiple years and this study aims to collect information from several sources into one. Collective information might be a useful lead painting a clear picture about the magnitude of the issue and possibilities to solve or at very least maintain and monitor the problem. This also could help to better understand whole lifecycle of the BFRs.

3 METHOD

A comprehensive approach was taken to gather relevant information. Multiple articles and studies were collected for a thorough analysis using the scientific databases available from the TAMK library, ScienceDirect and American Chemical Society Journals.

The gathered data was then organized into distinct chapters: presence, leakage, treatment, and legislation of BFRs.

The presence chapter focused on the occurrence of BFRs in the waste streams, sample analysis and mean values of the BFRs. Second chapter describes evidence of BFRs leakage into the recycled products from the waste streams. The treatment chapter describes methods for possible treatment of BFRs in waste streams. Thae last chapter legislation contains the way how those compounds are being handled worldwide, based on region.

4 RESULTS AND DISCUSSION

4.1 Studies on the presence of BRFs in waste streams

Several studies were reviewed to examine the presence of BFRs. While the majority focused on BFRs in waste streams, Ling et al. (2021) research specifically analyzed sediment samples from an e-waste dismantling region and Ma et al. (2023) focused on dust samples inside and outside of UK e-waste recycling facilities.

Reference	Number of samples	BFRs presence in samples	Number of samples with BFRs	BFRs mean value	Country
Honkala I. (2018)	37	P	21	3’911 µg/g	Finland
Yunakovskiy A. (2019)	150	P	48	ND	Finland
Vogt J. (2019)	49	P	39	727 µg/g	Finland
Pivnenko et al. (2017)	20	P	15	17,8 µg/g	Denmark
Drage et al. (2017)	538	P	153	59.53 µg/g	Ireland
Ma et al. (2023)	36	P	36	2.15 µg/g	UK
Sun et al. (2016)	2	P	2	40’238 µg/g	China
Yu et al. (2017)	19	P	19	5.03 µg/g	China
Li et al. (2019)	19	P	19	50.89 µg/g	China
Ling et al. (2021)	50	P	49	7.38 µg/g	China

TABLE1. Appearance of BFRs in different cases.

P- present

ND – not described

As a result, all investigations detected the presence of BFRs in the samples, with concentrations ranging from 2 µg/g to approximately 40,000 µg/g. The highest concentration of BFR particles was identified in a CRT monitor sourced from electronic waste in China, which was manufactured in 1994. (Sun et al. 2016)

Furthermore, the Finnish cases specifically centered on HBCD, indicating that despite the global ban imposed by the Stockholm Convention, HBCDs persist in waste streams as of today. (Sharkey et al. 2020)

4.2 Leaching of BFRs from waste streams

Some cases indicate that there is a problem of BFRs leaching from e-waste streams.

The research conducted by Li et al. (2019) has examined the transfer of BFRs from e-waste to recycled plastics. The study underscores a visible transference of POP-BFRs from e-waste to new products, even those not inherently flameproof, through recycling processes. Within the spectrum of dismantled e-waste categories, TVs emerge as pivotal carriers of PBDEs, exhibiting a high contamination potential within waste streams. Recycling, acting as a bridge between consumption and reutilization, facilitates the passage of POP-BFRs from their original applications to everyday-use plastic items. Results from extrusion experiments indicate that partial amount of HBCDs and PBDEs is present persistently in treated plastics after recycling, 39% and 77% accordingly. Considering the transfer rates and the recycling landscape of e-waste plastics in China, an estimated 687.81 tons of PBDEs annually enter the downstream flow, ensuring their enduring and extensive presence, leading to widespread cross-contamination in daily-use products. In light of the imperative for effective management of POP-BFRs to comply with the obligations of the Stockholm Convention, heightened attention to e-waste recycling is warranted. Strengthening measures are essential to control the outflow of recycled materials containing PBDEs and HBCD, ensuring sound management practices in line with international agreements. (Li et al. 2019)

In many developing nations, waste disposal practices commonly involve the dumping of unsegregated waste in open landfills lacking proper safety against environmental contamination. To investigate how BFRs leach from discarded consumer products in these landfill settings, an extensive landfill lysimeter experiment has been underway since 2006. This study aimed to replicate three specific landfill conditions typical of developing countries: aerobic, semiaerobic, and anaerobic. All four targeted BFRs were identified in both the combined waste sample and the waste plastic sample. Polybrominated diphenyl ethers and tetrabromobisphenol A were of the largest quantities. Less than a single percent of the total value of BFRs was outflowing from the lysimeters over the whole period of this project, which was held for 3 and a half years. The study also suggests that BFRs were partially trapped inside lysimeters. The leaching rate under aerobic conditions was lower compared to anaerobic conditions, suggesting a slower elution of BFRs under aerobic conditions, with faster biodegradation once they are released into the leachate. While atmospheric contamination due to BFR volatilization from waste has not been extensively studied, continuous monitoring of BFR emission from the lysimeters and assessing their extraction behaviour over extended durations is essential. (Kajiwara et al. 2014)

4.3 Treatment for BFRs

As of today, there are several existing methods upon treatment and recycling waste containing BFRs.

4.3.1 Mechanochemical dehalogenation of brominated flame retardants

A study investigated the use of mechanochemical pre-treatment technology as a dehalogenation method to eliminate BFRs. With the usage of chemical compound called Silica and aluminum, mechanochemical method was used for the HBCD treatment in plastic waste. The findings demonstrated effective degradation of HBCD through mechanochemical treatment with the assistance of Si-Al-based additives. The optimal conditions were determined as a SiO_2/Al ratio of 7:2 with a reagent ratio of 15:1. This optimized mechanochemical method was then applied to treat waste plastics containing BFRs. It appears that dehalogenation process is happening simultaneously with the mechanochemical destruction process. The initial experimental findings from the MC treatment of ABS and PP/PE waste plastics with low concentrations of BFRs reveal bromine elimination conversions ranging between 30% and 55%. The efficiency of BFR degradation through MC is notably influenced by disposal time and inherent plastic matrix properties, including particle size and its reactivity in the MC reaction. Furthermore, a proposed mechanism outlines the destruction of HBCD through MC treatment, with debromination and fragmentation identified as the primary degradation pathways. It is crucial to note that this study remains confined to laboratory-scale testing, and for future industrial applications, pilot tests should be conducted. (Lu et al. 2023)

4.3.2 Thermal pyrolysis

Pyrolysis, a thermal degradation process in the absence of oxygen, decomposes organic waste into carbonaceous char, oil, and combustible gases. This study explores pyrolysis of BFR-containing plastics, specifically Br-HIPS and Br-ABS, under different conditions. The results highlight variations in bromine elimination conversions, with Br-HIPS exhibiting higher oil yields than Br-ABS. Different pyrolysis methods, including conventional, fast, and slow, impact product compositions. Fast pyrolysis proves advantageous for Br-ABS recycling, while slow pyrolysis of Br-HIPS generates valuable products. The study emphasizes the importance of bromine content in pyrolysis oils, with efforts needed to meet commercial standards for environmental sustainability. (Ma et al. 2016)

4.3.3 Hydrothermal treatment

The thermal treatment of WEEE plastics can be an effective technology if it not only degrades organobromine compounds but also safely removes bromine and antimony constituents from the oil products. Supercritical fluid technology, a novel technique, offers promising prospects for the chemical recycling of waste plastics. Supercritical fluids, such as supercritical water, provide optimal conditions for various chemical reactions, including depolymerization and dehydrogenation. Hydrothermal treatment in supercritical fluids has shown high efficiency in feedstock recovery from waste, with significant bromine removal achieved. The process involves in situ neutralization of corrosive inorganic bromine species and minimizes the formation of hazardous organohalogen compounds. The use of supercritical fluids for treating BFR-containing plastics, such as Br-HIPS and Br-ABS, has demonstrated effective debromination and removal of bromine and antimony constituents. Challenges include selecting appropriate supercritical fluids, optimizing operating parameters, and addressing energy consumption and equipment cost considerations in the hydrothermal recycling of BFR-plastics. (Yao et al. 2015)

4.3.4 Biomass/Coal

This approach involves co-pyrolysis of WEEE with waste biomass. This innovative method, results in significantly higher oil yields compared to the pyrolysis of individual feedstocks. The interaction between WEEE and biomass during co-pyrolysis leads to improved thermal conversion efficiency, demonstrating potential for high-grade pyrolysis oil production and minimizing environmental impact. Although co-pyrolysis of e-waste plastics and biomass is a promising chemical recycling option, research on this topic remains limited. (Abnisa et al. 2014)

4.3.5 Catalytic hydrodebromination

Catalytic hydroprocessing, specifically catalytic hydrodehalogenation (HDH), is emerging as another way of the treatment. Researchers have explored gas and liquid phase catalytic hydroprocessing for the in-situ dehalogenation of waste compounds, achieving the recovery of valuable raw materials without generating additional hazardous byproducts. Novel processes integrating pyrolysis with catalytic hydrodebromination have been introduced to obtain high-quality bromine-free oils. This two-step process involves pyrolyzing BFR plastics and catalytically upgrading the pyrolysis products, offering both online and offline catalytic upgrading options. (Su et al. 2022)

4.4 Legislation about the BFRs

4.4.1 UNEP and Stockholm convention

The Stockholm Convention is an international treaty initiated by UNEP in 1995 to protect human health and the environment from persistent organic pollutants. These pollutants, including certain hazardous chemicals like PBBs, PBDEs, and HBCD, pose significant risks due to their long environmental persistence, bioaccumulation, and toxicity. The Convention, based on the precautionary approach, initially listed 12 POPs, with provisions for adding more based on scientific evidence. Parties to the Convention commit to taking legal and administrative actions to reduce or eliminate the production and use of listed POPs, control import/export, and report specific exemptions. Exemptions, such as those for recycling or specific applications, come with expiration dates. (Drage et al. 2017)

4.4.2 EU regulations on BFRs

Within the European Union, regulations govern persistent organic pollutants, including legacy BFRs. The POPs regulation, RoHS directive, and REACH legislation collectively address the restriction, use, and disposal of hazardous substances, including BFRs, in consumer articles. Concentration limits for these BFRs are outlined, both for substances entering the market and those entering the waste stream. The regulations also consider unintentional trace contaminants and define disposal methods for waste containing BFRs. The interaction between POPs, RoHS, and REACH regulations is emphasized, along with their collective impact on reducing BFR concentrations in consumer articles and waste within the EU. (European Commission. 2004; 2006; 2011; 2019)

4.4.3 BFRs legislation outside EU

The seven largest producers of e-waste are the EU, China, USA, Japan, India, Brazil, and Indonesia. Similarly, major textile producers and waste generators include China, the EU, USA, and India. While these countries are signatories to the Stockholm Convention (except the USA), the EU is the only one to have comprehensive provisions on all persistent POP-BFRs concerning waste and recycling. In North and South America, Brazil uses exemptions for certain BFRs until

2030, while the United States lacks federal regulations. However, thirteen U.S. states have implemented restrictions on BFRs in commercial goods, varying in scope and stringency. Notably, Maine has extensive restrictions, prohibiting the sale of goods with any BFR quantity and imposing limits on residential upholstered furniture containing BFRs above 0.1%. The absence of a federal mandate results in significant differences in the scope of regulations among states. (Sharkey et al. 2020)

4.4.4 Asia-Pacific legislation concerning BFRs

In the Asia-Pacific Region, major e-waste and textile producers have generally adopted the Stockholm Convention annexes related to persistent organic pollutant POP-BFRs. India, while not adopting all annexes, has implemented a ban on the trade, use, import, and export of specific BFRs and set concentration limits on certain electrical equipment, aligning with the EU's RoHS Directive(Chetry, 2018). Indonesia has ratified the annexes but lacks specific regulations on concentration limits. China has banned certain BFRs and established concentration limits for PBDEs in electronic information products. Japan, with no history of HBB production, has restrictions on PBBs and PBDEs in electrical equipment. Both China and Japan follow Stockholm Convention provisions, with China having exemptions for specific uses of HBCD, and Japan monitoring HBCD use and seeking alternatives. (Sharkey et al. 2020)

5 CONCLUSIONS

As of today, BFRs are still persistent in the environment and will be around in the foreseeable future. Leakage of BFRs from the waste streams into the recycled products has also been detected. With currently available tools, it is possible to maintain, monitor and treat BFRs from the waste streams. As of today, there is no comparison study upon methods of BFRs treatment, suggesting one should be carried out to advance with the topic further

Legislation-wise, there are many regulations, though they are not properly followed all around the globe. While EU and countries within UN try to contribute towards global handling of the BFRs, their regulations are only being partially applied in Asian and USA regions, meanwhile USA lacks federal laws upon the matter. With proper monitoring and treatment, BFRs have potential to be removed from the recycled products and isolated from the e-waste streams as well. Alternatives methods to BFRs are constantly being studied and researched. Awareness of the issue should also be expanded.

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