

Review

Chemicals from Brominated Flame Retardants: Analytical Methods, Occurrence, Transport and Risks

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Abstract: Brominated flame retardants (BFRs) are synthetic chemicals widely used to reduce the flammability of consumer products, including electronics, textiles, and furniture. Despite their effectiveness in fire prevention, BFRs pose significant environmental and health risks due to their persistence, bioaccumulation, and potential toxicity. This review provides a comprehensive examination of BFRs, focusing on recent advancements in analytical methods for their detection and quantification in environmental and biological samples. The study explored the physicochemical properties that influence BFR distribution and transport in various matrices, including soil, water, air, sediments, and biota. The review also summarizes current knowledge on the occurrence and environmental fate of BFRs, highlighting their mobility and long-range transport. Furthermore, the study discusses the health risks associated with BFR exposure, emphasizing their endocrine-disrupting effects and impact on reproductive and neurological functions. By integrating findings from recent studies, this review aims to enhance the understanding of BFR behavior and inform regulatory strategies to mitigate their adverse effects on human health and the environment.

Keywords: analytical methods; environmental occurrence; transport mechanisms; health risks; endocrine disruption; bioaccumulation; toxicity



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1. Introduction

Brominated Flame Retardants (BFRs) are a group of chemicals widely used to reduce the flammability of various materials, including plastics, textiles, and electronics [1]. Their use has been of great societal benefit in improving fire safety. In 2011, 390,000 tons of BFRs were sold, representing 19.7% of the flame retardant market [2]. BFRs encompass a variety of synthetically produced compounds with diverse chemical properties. The main groups include polybrominated diphenyl ethers (PBDEs), such as DecaBDE, OctaBDE (no longer manufactured), and PentaBDE (no longer manufactured, first commercialized in the 1950s); polybrominated biphenyls (PBBs) (no longer manufactured); brominated cyclohydrocarbons; and other brominated flame retardants with various properties and mechanisms [3,4]. Novel BFRs (NBFRs) have surfaced after the prohibition on PBDEs and HBCDD [5]. Emerging contaminants, or NBFRs, are relatively new to the market, present in products, and have the potential to enter the environment. Because of their diverse physico-chemical characteristics, these “novel”, “emerging”, or “new” BFRs have a wide variety of applications in goods including plastics, foams, textiles, furniture, and electrical devices [6]. Research points to possible hazards to human health and the environment from NBFR exposure [7].

BFR-treated items pollute the air, land, and water when they are used or disposed of. These pollutants can then make their way up the food chain, where they are mostly found in foods that come from animals, such as milk, fish, meat, and derivatives [8]. There are emerging concerns due to their persistence, bioaccumulation, and potential adverse effects on human health and the environment which have been demonstrated in studies. Jarosiewicz et al. [9] investigated the mechanism by which brominated flame retardants (BFRs) affect proteins, using human serum albumin (HSA) as a model system. They examined interactions between selected BFRs—tetrabromobisphenol A (TBBPA), tetrabromobisphenol S (TBBPS), 2,4-dibromophenol (2,4-DBP), 2,4,6-tribromophenol (2,4,6-TBP), and pentabromophenol (PBP)—and HSA by measuring intrinsic tryptophan fluorescence and circular dichroism (CD) absorbance. Additionally, to understand the potential effects of these compounds in their native environment, the impact of BFRs on membrane proteins of human erythrocytes (red blood cells, RBCs) was assessed. The study revealed that among the bromophenols, PBP exhibited the strongest oxidative effect on RBC membranes, whereas 2,4-DBP demonstrated the weakest fluorescence-quenching effect on both membrane tryptophan and HSA. In contrast to PBP, both 2,4-DBP and 2,4,6-TBP induced spatial changes in HSA. Notably, TBBPA was found to cause the most significant oxidation of RBC membrane proteins and the model HSA protein, leading to a reduction in tryptophan fluorescence. TBBPA also altered the conformational properties of albumin, impairing the α -helix structure. These findings highlight the differential impact of various BFRs on protein structure and function, with TBBPA showing the most pronounced effects.

Due to insufficient information on incidence and toxicity, the European Food Safety Authority (EFSA) was unable to conduct risk assessments for newly developed and novel brominated flame retardants (NBFRs) in food, even after publishing a scientific paper on the topic [4]. In response, the European Commission issued recommendations (Directive 2014/118/EU) for detecting BFR residues in food, including NBFRs such as 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB) [10]. This limitation stems from the lack of comprehensive studies and information on analytical techniques. Therefore, this review focuses on the analytical methods used for the detection and quantification of BFRs, their occurrence in various environmental matrices, their transport mechanisms, and the associated risks.

Analytical methods play a crucial role in the assessment of BFR contamination [11,12]. Various techniques, such as gas chromatography-mass spectrometry (GC-MS), liquid chromatography-mass spectrometry (LC-MS), and high-resolution mass spectrometry (HRMS), have been developed for the analysis of BFRs in environmental samples. These methods provide sensitive and selective detection, allowing for the identification of BFRs at trace levels in complex matrices.

The occurrence of BFRs has been reported in air, water, soil, sediment, biota, and indoor dust [13–15]. Their widespread presence in the environment is attributed to their extensive use and the persistence of some BFR congeners. BFRs can enter the environment during the manufacturing, use, and disposal of products containing these chemicals. Once released, they can undergo various transport processes, including atmospheric dispersion, surface water transport, and soil sorption, leading to their distribution in different environmental compartments. The risks associated with BFRs stem from their toxicity, bioaccumulation potential, and ability to persist in the environment. Some BFRs have been identified as persistent organic pollutants (POPs) and are subject to international regulations [11]. Human exposure to BFRs can occur through ingestion, inhalation, and dermal contact, with potential health effects including endocrine disruption, neurotoxicity, and carcinogenicity.

The objective of this review is to comprehensively examine the analytical methods used for the detection and quantification of brominated flame retardants (BFRs), explore their occurrence and distribution in various environmental matrices, elucidate their transport mechanisms, and assess the associated environmental and health risks. This review aims to synthesize current knowledge, identify gaps in research, and provide insights into the future direction of studies on BFRs and their impact on the environment and human health.

By understanding the analytical methods for detecting BFRs, their occurrence in the environment, transport mechanisms, and associated risks is essential for assessing and mitigating the environmental and human health impacts of these chemicals. This review aims to provide a comprehensive overview of the current knowledge on BFRs, highlighting the importance of continued research in this field.

2. Analytical Methods for the Detection of BFRs in Environmental and Biological Samples

BFRs display a wide range of physicochemical properties depending on their molecular structure and weight. The large variety in molecular weight, polarity, vapor pressure, and log K_{ow} displayed by different classes of BFRs is associated with varying degrees of environmental mobility, long-range transport, persistence, bioaccumulation, and toxicity [16]. Understanding the physicochemical properties of pollutants is pivotal to studying their fate and behavior in both biotic and abiotic media [17]. The physicochemical properties have led to the development of a wide variety of analytical approaches for sample collection, preparation, and instrumental analysis [18]. Recent reviews on analysis methods for BFRs applied worldwide are available in the literature [11,12,19,20] and are part of the scope of analytical methods mentioned in this paper. The following sections summarize the analytical methods used for the determination of BFRs in recent years (from 2020–2024), including sample collection and extraction techniques, clean-up techniques, detection techniques, and general comments from an analytical quality assurance perspective.

2.1. Sample Collection and Extraction Methods

The collection of BFRs presents a multifaceted challenge requiring interdisciplinary approaches and methodological rigor. The different methods used for the collection and extraction of brominated flame retardants (BFRs) in various environmental matrices depend on the type of samples.

2.1.1. Biotic Samples

Humans and Animal Tissues

Due to their lipophilic nature, BFRs tend to accumulate in various animal tissues such as adipose tissue, liver tissue, blood plasma, breast milk, muscle tissue, brain tissue, reproductive organs (ovaries and testes), and bone tissue. The analysis of BFRs in animal tissues can vary depending on factors such as species, habitat, diet, and exposure levels. Solvent extraction by liquid-liquid extraction (LLE) and Soxhlet extraction were the main methods used for the extraction of BFRs in tissue [21]. Alternative methods for the extraction of BFRs from tissues include Ultrasound-Assisted Extraction (UAE) [22] and Microwave-Assisted Extraction (MAE) [23]. Further methods include accelerated Solvent Extraction (ASE), Solid-Phase Extraction (SPE) [24], and Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) [25]. QuEChERS is a robust and versatile sample preparation technique designed to efficiently isolate analytes from complex matrices. This multi-step process, encompassing extraction, partitioning, and cleanup, is optimized to yield a final extract that is highly suitable for chromatographic analysis. Shortly after PBDE restrictions were implemented in Europe, some researchers in Denmark measured for the presence of novel brominated flame retardants (NBFRs), hexabromocyclododecanes (HBCDDs), PBDEs, and dechlorane in samples of human breast milk [26]. The samples were collected manually using a breast milk pump, dried with diatomaceous earth, and extracted using Soxhlet with hexane:acetone (4:1). The clean-up of the samples was accomplished in a multilayer column containing activated aluminum oxide, sulfuric acid-impregnated silica, and some Na_2SO_4 , eluted with hexane and analyzed by GC-ECNI-MS. Although MAE has been used mainly for the extraction of solid samples like sediments and soil, Dvoršćak et al. [23] described extraction of PBDEs from human milk samples using MAE. Using a Mars X microwave extraction system, they optimized a MAE extraction method [which involved 5 g of freeze-dried milk + 10 mL water + HCOOH + 2-propanol + 40 mL n-hexane:acetone

(1:1, *v/v*); and extraction with MAE at 105 °C for 20 min], cleaned up the extract using 1 multilayer (2 + 6) g SPE column with 20 mL n-hexane:dichloromethane (4:1, *v/v*) elution solvent, and used GC- μ ECD or GC-MS/MS for detection. Employing ultrasound extraction (UAE) coupled with dispersive solid-phase extraction (d-SPE) as a cleanup procedure, Santini et al. [22] compared UAE extraction to conventional SE techniques, revealing significant improvements. Analytical parameters were thoroughly assessed, and the innovative method demonstrated notable advantages, reducing extraction and purification times by approximately 74–80% and solvent consumption by around 94–97%. While the Soxhlet method has been the traditional method for years, the excessive use of solvent and the long extraction time have always been its limitations. The advantages of MAE over other extraction methods include lower solvent consumption and analyte loss, shorter processing time, and higher sample throughput. The QuEChERS method, which was originally developed for pesticide analysis in food, involves a combination of solvent extraction and dispersive solid-phase extraction (dSPE). Tavoloni et al. [25] employed QuEChERS techniques for the simultaneous determination of PBDEs and hexabromocyclododecanes (HBCDs) in fish, shellfish, and the muscle of terrestrial animals. The method involved the use of QuEChERS-like extraction and a two-step clean-up, followed by a dual instrumental detection, GC-MS/MS for PBDEs and LC-MS/MS for HBCDs [25]. The simultaneous application of ASE and SPE for the extraction and clean-up analysis of BFRs in the subcutaneous adipose tissue of Guiana Dolphins sampled across the Brazilian coast have also been reported by Vidal et al. [24].

Serum and Urine Samples

The analysis of BFRs in serum and urine samples have been reported by many researchers in a bid to understand the metabolism, transport, and elimination of BFRs in the human body. Several extraction techniques can be used to extract BFRs from serum and urine samples. Methods frequently used include LLE [27,28], SPE [29], QuEChERS [30], and ASE [31], while recent advancements in extraction methods have seen the use of novel microextraction techniques such as Solid-Phase Microextraction (SPME) and Liquid-Phase Microextraction (LPME). The extraction of Serum and urine samples using hollow fiber liquid-phase microextraction (HF-LPME) have been reported by Lin-lin et al. [32]. Lin-lin et al. [32] developed a method that employed the use of nitrogen-doped carbon nanotubes (N-CNTs) reinforced hollow fiber liquid-phase microextraction (HF-LPME) combined with high-performance liquid chromatography (HPLC) for the simultaneous determination of TBBPA and decabromodiphenyl oxide (BDE209) in serum and urine samples. The solvents used for the extraction were toluene-noctanol (1:1) and toluene-ethyl acetate (1:1). The hollow fiber membrane blocked the interference of macromolecules in the sample during the extraction process which played a role in purification. The study results showed quantitation limits (LOQs) ranges of 0.375–2.8 ng/mL and 1.25–9.4 ng/mL, respectively. The average recoveries for the two target analytes at three spiked levels ranged from 84.5–114%. The researchers concluded that the method could not only enrich TBBPA and BDE209 but also remove protein from biological samples at the same time.

Food and Feed

Solid food samples are usually blended into particulate size to increase the surface area, and liquid samples are homogenized to ensure the uniform distribution of BFRs throughout the sample prior to extraction. Soxhlet Extraction (SE) is widely used for extractions of BFRs from fat-containing food samples to extract lipophilic BFRs [33]. However, this method can be time-consuming and may require large amounts of solvent. Alternative methods include SPE [34], ASE [35], matrix solid-phase dispersion (MSPD) [36], pressurized liquid extraction (PLE) [37], and QuEChERS methods [38]. ASE is increasingly becoming the routine extraction method for the analysis of BFRs in food and feed [39,40]. However, multiple steps (combined extraction and clean-up) may be applied simultaneously when using ASE, consequently reducing analysis time and solvent consumption. This can be observed from the

analysis of brominated flame retardants (BFRs) in animal-derived food samples from Nigeria [40]. The recovery from the analysis ranged between 31 and 135%, and the method LOD ranged between 0.042 and 2.0 (ng/g). Xu et al. [36] designed a novel pretreatment method for the extraction of polybrominated diphenylethers (PBDEs) using matrix solid phase dispersion (MSPD) and depth purification using dispersive liquid–liquid micro-extraction (DLLME) from vegetables. The results showed satisfactory recoveries of spiked samples (82.9–113.8%, except for BDE-183 (58.5–82.5%)) and matrix effects (−3.3–18.2%). The limits of detection and the limits of quantification were in the range of 1.9–75.1 $\mu\text{g kg}^{-1}$ and 5.7–25.3 $\mu\text{g kg}^{-1}$, respectively. A novel and reliable analytical method was developed and validated for the simultaneous determination of 1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TDBP-TAZTO), and 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ) in environmental samples using high-performance liquid chromatography coupled to a tandem mass spectrometer [37]. The extraction efficiency of sediment and fish samples was tested with different techniques (pressurized liquid, solid-liquid, ultrasound-assisted, and Soxhlet extraction). Additionally, cleanup using modified multilayer silica gel (sediment) and gel permeation chromatography as well as Florisil columns (fish) with several solvent mixtures were performed. The best results were obtained with the PLE (optimal conditions: extraction solvent 100% toluene, extraction time 20 min, cycles two, extraction temperature 100 °C, and flushing volume 60%) compared to other solvent extraction methods. Mean recoveries ranged between 98 and 114%, and the limit of detection and limit of quantification were in the range of 0.4–1.3 $\mu\text{g kg}^{-1}$ for TDBP-TAZTO and 10–28 $\mu\text{g kg}^{-1}$ for TTBP-TAZ in surface sediment samples and 7–25 $\mu\text{g kg}^{-1}$ and 22–80 $\mu\text{g kg}^{-1}$ in fish samples (bream), respectively [37]. Most recent research articles employ QuEChERS methods for BFRs analysis. It involves extraction with acetonitrile, followed by dispersive solid-phase extraction (dSPE) cleanup, which can effectively remove matrix interferences. QuEChERS has gained widespread acceptance in food analysis due to its simplicity, efficiency, and ability to handle a wide range of food matrices. QuEChERS extraction, combined with a magnetic micro dispersive solid phase extraction (M μ dSPE), was optimized and evaluated for the trace analysis of nine brominated flame retardants in red fruit samples (strawberries, blueberries, and raspberries) using gas chromatography-mass spectrometry [38]. The study showed that recoveries of all target analytes were within the range of 65–141%, as well as demonstrating that the new sample preparation with magnetic nanoparticles could potentially be expanded to extract and pre-concentrate the BFRs in different red fruit samples [38]. The further application of QuEChERS using graphene-type materials as an alternative cleanup sorbent in GC–ECD/GC–MS/GC–MS/MS detection was used to analyze 12 brominated flame retardants in Capsicum cultivar samples. The results showed excellent recoveries ranging from 90 to 108%; limits of quantification were in the range of 0.35–0.82 $\mu\text{g/kg}$ [35].

2.1.2. Abiotics Samples

Various methods such as LLE, SPE, and ASE are commonly employed for extracting BFRs from abiotic media like water, soil, sediment, dust, air, and food contact article samples. LLE involves partitioning BFRs between two immiscible solvents, while SPE utilizes solid-phase sorbents to selectively retain BFRs for subsequent elution. ASE offers automated extraction with elevated temperature and pressure, expediting the extraction process from solid samples like soil and sediment.

Water Samples

BFRs are hydrophobic compounds, which indicates that they will have low solubility in water, and their levels in water, particularly in the dissolved phase, are expected to be very low as it is primarily governed by their water solubility. The hydrophobic nature of BFRs causes them to preferentially partition into organic phases, such as sediments, suspended particles, and organic matter, rather than remaining dissolved in water. This phenomenon is often described by the octanol–water partition coefficient (K_{ow}), which

quantifies the distribution of a compound between an organic solvent (octanol) and water. BFRs generally have high K_{ow} values, indicating their propensity to partition into organic phases. Despite their low water solubility, monitoring and assessing BFR levels in water and aquatic ecosystems are essential for understanding their fate, transport, and potential impacts on environmental and human health. Techniques such as solid-phase extraction (SPE) [41], LLE [28,42], and SPME [43] are commonly used to concentrate and extract BFRs from water samples for analysis. The simultaneous determination of ultra-trace TBBPA, tribromobiphenol A (tri-BBPA), dibromobiphenol A (di-BBPA), monobromobisphenol A (mono-BBPA), and bisphenol A (BPA) in Shuxi River water by solid phase extraction (SPE), and high-performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS), was developed by Xie et al. [42]. The results showed recovery rates in water samples were over 80.28%. SPE was selected as the extraction method in the study because the sample could be completely concentrated and purified simultaneously. Liang et al. [43] developed a method consisting of an online coupling of solid-phase microextraction and ultrahigh-resolution mass spectrometry for the rapid screening of eight PBDEs in water samples. The coupling of the SPME with ultrahigh-resolution mass spectrometry (UHRMS) was assisted by thermal desorption and solvent-assisted atmospheric pressure chemical ionization. The result showed limits of detection and quantification values ranging between 0.01–0.50 ng/mL and 0.05–4.00 ng/mL, respectively. The recoveries were 57.2–75.2% for quality control samples at spiking levels of 0.8–10 ng/mL (4–50 ng/mL for BDE209), with relative standard deviation less than 19.0%. This procedure was completed in 22 min, about 6 times faster than the routine workflow such as solid-phase extraction coupled with gas chromatography-mass spectrometry. The differences in recovery rates and detection limits among methods for extracting BFRs in water samples are influenced by several factors. Method-specific variables such as the choice of extraction technique, the optimization of extraction parameters, and sample preparation steps play a significant role. Sample matrix effects, including the composition of the water sample, the presence of organic matter, salinity, and interfering compounds, also affect these outcomes. Additionally, analytical considerations such as instrumental sensitivity, calibration methods, the use of internal standards, and thorough recovery studies are crucial. Understanding and optimizing these factors can improve the accuracy, precision, and sensitivity of studies of BFR in water.

Soil Samples, Sediment, Sewage Sludge and Biosolids

Depending on the soil's origin and the sampling technique used, soil samples may be pretreated by air drying, freeze drying, or mixing with anhydrous Na_2SO_4 before drying. Further pretreatment may involve sieving the samples through a stainless-steel wire mesh of different sizes. Pretreatment methods for sewage sludge and biosolids may include centrifugation to separate solids, filtration to remove particulate matter, and the addition of chemicals such as acids or bases for pH adjustment. Additionally, the samples may undergo freeze drying or lyophilization to remove excess water content before further processing. Extraction and clean-up techniques take into account the matrix effects which can arise from the presence of organic matter, mineral content, and soil particles that may co-extract with BFRs and interfere with their detection during analysis. Similarly, in sewage samples, matrix effects can stem from the complex mixture of organic and inorganic compounds, suspended solids, and microbial content, which can impact the efficiency of extraction and the accuracy of BFR quantification. SE [44,45] and PLE [46] were the major techniques reported for extraction of BFRs from sediment, sewage sludge, and biosolids. Both methods achieved high extraction efficiency and good recoveries of different BFRs. ASE has also been widely employed for the extraction of these samples. SE is a dependable, long-established technique known for its high recovery rates of non-polar compounds, though it requires a substantial amount of time and solvent. PLE enhances efficiency and recovery rates compared to SE, with lower solvent consumption and shorter extraction durations, making it effective for a wider variety of compounds. ASE delivers the highest efficiency and recovery rates, using minimal solvent and achieving the fastest extraction times, making it

ideal for contemporary, high-throughput laboratories. Ultimately, the choice of extraction method should be guided by the specific requirements of the analysis, including the type of target compounds, the matrix involved, and the available resources and equipment. Xie et al. [42] developed a simultaneous determination of ultra-trace TBBPA, tribromobiphenol A (tri-BBPA), dibromobiphenol A (di-BBPA), monobromobisphenol A (mono-BBPA), and bisphenol A (BPA) in soil and sediment samples found in Shuxi River by ASE and HPLC–MS/MS. The results showed recovery rates of over 79.40% and 75.65% in soil and sediment, the minimum detection limit was 0.0225–0.0525 ng g⁻¹, and RSD was less than 7.19%. Employing selective pressurized liquid extraction (S-PLE) and gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) quantification, McGrath et al. [46] examined the presence of eight PBDEs and six NBRs in biosolids samples from 15 wastewater treatment plants (WWTPs) in Western Australia. The extraction was followed by clean-up in a column containing Florisil and acidified silica eluted with 50:50 hexane/DCM, and reconstitution solvent was iso-octane and toluene (80:20). The result showed recovery values in the range of (80–120)% and LOQ values in the range of 0.03–120 µg/kg dw.

Food Contact Articles

There are limited reports on the analysis of BFRs in food contact articles. However, the analysis of BFRs in food contact articles (FCA) samples starts by first grinding or cutting the sample into small pieces to ensure uniformity. This step is particularly important for larger plastic objects or composite materials. Possible techniques for extraction may include SE, ASE, or PLE. Lestido-Cardama et al. employed ultrasonic assisted extraction (UAE) to extract BFRs from several food contact articles (FCAs) purchased in Spain [47]. The extraction was carried out in 1 mL of methanol-isopropanol (50:50 *v/v*) solution and in line cleanup using a PTFE membrane filter prior to DART-HRMS, XRF, and HPLC-MS/MS analysis. In evaluating extraction methods, ultrasonic extraction demonstrated effectiveness for extracting BFRs from polymeric materials, particularly when low levels are expected. This method not only saves solvent compared to the traditional Soxhlet extraction but also enhances efficiency. In their report, they selected the mixture of methanol and isopropanol due to their varying polarities, which makes them suitable for targeting a range of BFRs. The DART-HRMS and XRF were used as screening techniques for BFR identification. The HPLC-MS/MS method gave recoveries from 80 to 120% from LOD (≤ 0.02 µg/mL) and LOQ (≤ 0.05 µg/mL). The BFR concentrations in the polymeric food contact articles were found to range from below the limit of detection (LOD) to 260 µg/kg for TBP, below LOD to 2180 µg/kg for TBBPA, and below LOD to 9340 µg/kg for BDE-209.

Dust Samples

Dust samples are usually collected using commercial vacuum cleaners, and the nozzle of the vacuum cleaner is thoroughly cleaned with acetone before and after the collection of each sample to prevent cross-contamination [48]. Other methods of dust sampling may include: Surface Wipe Sampling using pre-cleaned wipes moistened with a suitable solvent (e.g., hexane) to wipe surfaces and collect dust particles; and Passive Dust Sampling, which involves the use of polyurethane foam (PUF) disks or polyethylene (PE) passive samplers in indoor environments to collect airborne dust over a specific period. Further methods involve Settled dust collection, Personal dust samplers, and Indoor dust traps in indoor ventilation systems or strategic locations to capture dust particles over time. The collected dust samples are sieved prior to extraction to remove extraneous matter and to obtain a homogenous sample of a particle size fraction that is more relevant to human exposure via dust ingestion or inhalation. Methods of dust extraction are similar to those of soil samples. The extraction of BFRs from dust samples can be achieved through several techniques, each offering distinct advantages and limitations in terms of extraction efficiency and recovery rates. The choice of extraction method should be guided by the specific requirements of the analysis, including the type of BFRs, the complexity of the dust matrix, and the available resources and equipment. SE, while reliable, is time-consuming

and solvent-intensive. UAE is faster and uses less solvent but may have variable efficiency. PLE/ASE and MAE offer high efficiency and recovery rates with reduced solvent use, but both require specialized equipment. MAE is also a good extraction choice for thermolabile BFRs. SPE is highly selective and uses less solvent but involves careful optimization and involves multiple steps, which can complicate the extraction procedure. The SFE employs supercritical CO₂, often with co-solvents, to extract BFRs. The extraction method offers very high extraction efficiency, particularly for non-polar and moderately polar BFRs, and it is environmentally friendly but necessitates high-pressure equipment and high initial costs. Hammel et al. [26] has reported the use of PLE for the extraction of HBCDDs and NBFRs in dust particles. In the study, the extraction was cleaned using two clean-up methods which included column clean-up (filled with activated aluminum oxide, deactivated silica, and some Na₂ SO₄ and eluted with hexane:dichloromethane (1:1)) and Gel Permeation Chromatography, followed by quantification using GC-ECNI-MS and LC-MS-MS. While the limit of quantification (LOQ) was not reported, the result obtained showed a recovery of 68–116%. The study on the presence of PBDE and NBFR in indoor dust reported by Guo et al. [49] employed PUF for sampling and a combination of UAE and Soxhlet extraction using acetone:hexane (1:1, *v:v*, 350 mL) for 24 h quantified by GCMS. The result also showed a recovery of (72.3–114)%. The BFRs in home dust and its contribution to brominated flame retardants' bioaccumulation in children's hair has been reported by Schachterle et al. [50]. The researchers employed a novel microextraction approach to determine quantitative levels of selected OPEs and BFRs sampled from residential air filters from HVAC systems using a small volume of solvent. The microextraction method involved a series of steps that incorporated solvent extraction in hexane/acetone with ultrasonic extraction; the cleanup method was online to the GC/MS and LC/MS quantification. The results from the study showed a recovery range between 70 and 130%, and the LOQ values ranged between 0.010 and 0.020 ng/μL.

Air Samples

Sampling methods for BFRs in outdoor air requires various techniques to collect air samples effectively for subsequent analysis. Major studies on BFRs in air that have been reported in the literature are performed using passive and active air techniques. Active air samplers offer precise control over sampling parameters and higher sampling rates, making them suitable for short-term or real-time monitoring; passive air samplers, on the other hand, are simpler, more cost-effective, and better suited for long-term monitoring or integrated sampling over extended periods. More often-used passive air samplers include polyurethane foam (PUF) Figure 1. and Glass Fiber Filters (GFFs). After air sampling for BFRs analysis, the collected samples need to undergo extraction to isolate and concentrate the BFRs from the sampling medium prior to analyses. The extraction method used depends on the nature of the BFRs and the sampling medium. Some common extraction methods include UAE or Soxhlet extraction [51], SPE [52], and PLE [53]. The choice of extraction method for BFRs in air samples should be based on the specific analytical requirements, including the need for precision, time constraints, and budget considerations. Each method offers distinct benefits and trade-offs which have been described in sections above, and selecting the most appropriate technique will depend on balancing these factors to achieve optimal results. Esplugas et al. [53] identified and quantified the indoor levels of 41 legacy and novel FRs, which include 20 OPFRs and 21 HFRs (8 PBDEs, 3 HBCDDs, 5 NBFRs, and 5 DEC)s. The passive air sampling method employed PUF and GFFs for the collection of the contaminated air samples. Extraction was achieved with n-hexane/acetone (1:1, *v/v*) in an ultrasonic bath and dried under a gentle stream of nitrogen before the reconstitution with 5 mL of n-hexane. The extraction Clean-up was achieved by solid phase extraction (SPE) and eluted with hexane:DCM (1:2 *v/v*). Finally, samples were dried with a stream of nitrogen and reconstituted with 40 μL of toluene, then subjected to GC-EI-MS-MS and LC-MS/MS quantification. The results from the study showed recoveries of (41 and 119%), and LOQ values ranged from (2–86) pg/m³. The occurrence and carcinogenic potential of

airborne PBDD/Fs and PCDD/Fs around a large-scale municipal solid waste incinerator were investigated by Li et al. [54]. The air samples were collected using PUF, and the samples ultrasonically extracted with 30 mL dichloromethane. Sample clean-up was carried out by sequential purification through an acid silica gel bed, a multi-layer silica column, and a Florisil column and a Trace GC Ultra gas chromatograph coupled to a DFS magnetic sector mass spectrometer were employed for the quantification [54]. The recovery recorded from the study was between 38 and 128%. Further details are presented in Table 1.

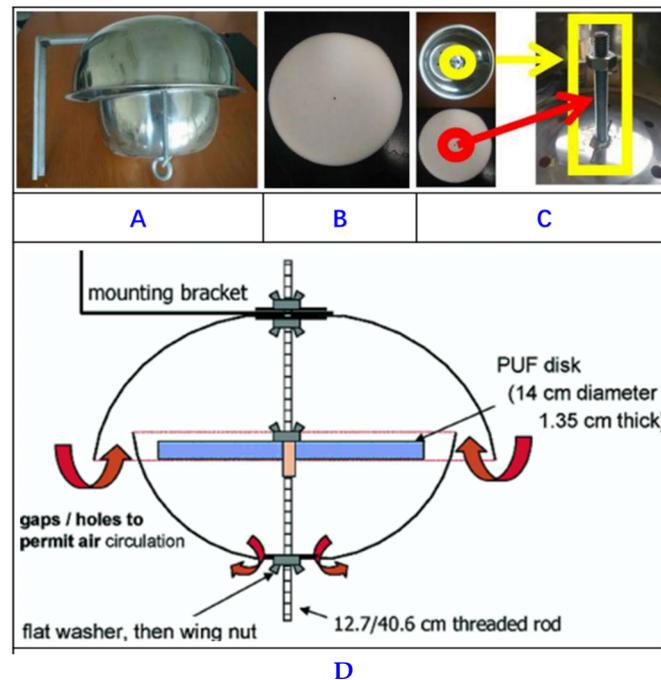


Figure 1. The passive air sampling device (A) and polyurethane foam disk (B) used in the study and the schemes of the device assembling (C) and passive air sampling principle (D); data are from [54].

Table 1. Summary analytical protocol for BFRs in different sample matrices.

BFRs	Sample Matrix	Pretreatment	Extraction	Clean-Up	Instrumental Analysis	Recovery (%)	Method LOQ (ng/g)	Refs.
Biotic Samples								
(PBDEs), and (HBCDD)	Food and feed	blended and sieved	hexane and acetone (3:1, <i>v/v</i>) accelerated solvent extractor 2 g of precleaned hydromatrix, 2 g of florisil, 3 g of alumina	in-cell clean-up (see pretreatment)	GCMS and LC-MS/MS	31–135%	0.042–2.0	[39,40]
PBDEs	vegetables		matrix solid phase dispersion (MSPD)	dispersive liquid–liquid micro-extraction (DLLME)	GC-MS	82.9–113.8%	5.7–25.3	[36]
triazine-BFRs	fish (bream) and surface sediment samples	freeze-dried and sieved	pressurized liquid, solid-liquid, ultrasound-assisted, and Soxhlet extraction	SPE (modified multilayer silica gel) (sediment), GPC, Florisil columns (fish)	LC-MS/MS.	98–114%	Varying values (0.4–80)	[37]
PBDE, and NBFRs	Capsicum		QuEChERS	graphene-type materials	GC-ECD/GC-MS/GC-MS/MS	90–108%	0.35–0.82	[35]
PBDEs	breast milk	manual breast milk pump, dried with diatomaceous earth	Soxhlet with hexane:acetone (4:1)	multilayer column including sulfuric acid-impregnated silica eluted with 250 mL hexane	GC-ECNI-MS	52–120%	Not reported	[26]
HBCDDs and NBFRs	breast milk	Collected manual breast milk pump, dried with	Soxhlet extraction hexane:dichloromethane (1:1)	multilayer column including sulfuric acid-impregnated silica eluted with 250 mL hexane	GC-ECNI-MS LC-MS-MS	52–120%	Not reported	[26]

Table 1. Cont.

BFRs	Sample Matrix	Pretreatment	Extraction	Clean-Up	Instrumental Analysis	Recovery (%)	Method LOQ (ng/g)	Refs.
PBDEs	breast milk	manual breast milk and freeze-dried	MAE	multilayer SPE column with 20 mL n-hexane:dichloromethane (4:1, <i>v/v</i>) elution solvent	GC- μ ECD or GC-MS/MS	54–67% (GC- μ ECD) 77–103% (GC-MS/MS)	0.01–0.13	[23]
NBFRs, PBDEs,	fish muscles	Dorsal fillets	Soxhlet extraction or UAE	- multilayer silica gel column, acid silica, activated silica and anhydrous Na ₂ SO ₄ ⁻ , hexane as elution solvent, in ultrapure nitrogen, - d-SPE	GC-MS	116.1–83.6%	Not reported	[22]
PBDEs, MeO-BDEs	Dolphins	subcutaneous adipose tissue	ASE system; solvent: dichloromethane:n-hexane (1:1, <i>v/v</i>)	sulfuric acid; solid-phase extraction eluted with dichloromethane:n-hexane (2:1, <i>v/v</i>) and toluene	GC-NCI-MS	90–120%	0.58–12	[24]
(PBDEs) and (HBCDs)	fish, shellfish and muscle		QuEChERS-like extraction	QuEChERS	GC-MS/MS, LC-MS/MS	72–97%	-	[25]
TBBPA and BDE209	Serum and urine		HF-LPME	HF-LPME	HPLC	84.5–114%	Serum (0.375–2.8 ng/mL), urine (1.25–9.4 ng/mL)	[32]
Abiotic samples								
PBDEs	Dust	heated to 37 °C then dried with diatomaceous earth	Soxhlet with hexane:acetone (4:1)	column 2 g activated aluminum oxide, 2 g sulfuric acid impregnated silica, Na ₂ SO ₄ eluted with 60 mL hexane	GC-ECNI-MS LC-MS-MS	68–116%	Not reported	[26]

Table 1. Cont.

BFRs	Sample Matrix	Pretreatment	Extraction	Clean-Up	Instrumental Analysis	Recovery (%)	Method LOQ (ng/g)	Refs.
HBCDDs and NBRFs	Dust	heated to 37 °C then dried with diatomaceous earth	Pressurized Liquid Extraction hexane:dichloromethane (1:1)	2 g activated aluminum oxide, 2 g deactivated silica and some Na ₂ SO ₄ and eluted with 60 mL hexane:dichloromethane (1:1). Gel Permeation Chromatography	GC-ECNI-MS LC-MS-MS	68–116%	-	[26]
PBDE and NBRF	Dust	PUF, pretreated vacuum cleaner, and sieved	- Soxhlet-extracted, acetone:hexane (1:1, v:v, 350 mL) for 24 h, - UAE	Isooctane, solvent-exchanged to isooctane with a gentle stream of nitrogen	GC-MS	72.3–114%	-	[49]
TCPP, TDCPP, TPHP, T24DtBPP, TBBPA, and TriBBPA	Dust	HVAC air filters, dust sieved	- Micro-extraction - Solvent extraction using hexane/acetone - UAE	on line auto-sampler	GC/MS, LC/MS	70–130%	0.010–0.020	[50]
TBBPA, tri-BBPA, di-BBPA, mono-BBPA, BPA	Water, soil and sediments	- Water was collected and filtered using GF/F filters - soil and sediment were dried, and sieved	SPE (water) ASE (soil and sediment)	nitrogen evaporator organic phase microporous filter membrane	HPLC–MS/MS	Water (80.28%) soil (79.40%) and sediments (75.65%)	0.27–0.64 (ng·mL ⁻¹)	[42]
PBDEs	water		SPME	SPME	GC-MS/MS, UHRMS	57.2–75.2%	0.05–4.00 (ng/mL)	[43]
(PBDEs; 28, 47, 99, 100, 153, 154, 183 and 209) NBRFs; (PBT), (PBEB), (HBB), (EH-TBB), (BTBPE) and (DBDPE))	biosolids	glass vials with PTFE lined lids, acetone rinsed and baked in a muffle furnace at 550 °C for 16 h	selective pressurized liquid extraction (SPLE) (ASE)	chromatographic column, columns containing Florisil and acidified silica eluted with (50:50) hexane/DCM, reconstituted with iso-octane and toluene (80:20)	GC-MS/MS	80–120%	0.03–120	[46]

Table 1. Cont.

BFRs	Sample Matrix	Pretreatment	Extraction	Clean-Up	Instrumental Analysis	Recovery (%)	Method LOQ (ng/g)	Refs.
8 PBDEs, 3 HBCDDs, 5 NBFRs	Air sample	(PUF) and (GFFs)	UAE	SPE	HBCDDs (LC-MS/MS) PBDEs and NBFRs (GC-EI- MS-MS)	41 and 119%	2–86 (pg/m ³)	[53]
PBDD/Fs and PCDD/Fs	Air sample	PUF	UAE extracted dichloromethane	acid silica gel bed, multi-layer silica column, and a Florisil column	GCMS	38 and 128%	-	[54]
TBP, TBBPA and BDE-209	FCA	cutting	Ultrasonic assisted extraction methanol- isopropanol	PTFE membrane filter	DART-HRMS, HPLC- MS/MS	82–120%	0.005–0.02	[47]

2.2. Clean-Up Methods

After BFR, extraction from environmental samples, various matrix components may remain in the extract, potentially interfering with subsequent analysis. The specific matrices present can vary depending on the sample type and the extraction method used. Some common matrices expected to be present in the extract after BFR extraction include lipids, proteins, inorganic salts and minerals, humic and fulvic acids and co-extracts such as pesticides, polychlorinated bi-phenyls (PCBs), or heavy metals. To overcome these challenges, various clean-up and purification methods, such as SPE (Esplugas et al., 2022), GPC [26], LLE [36], SPME [43], and matrix solid phase dispersion (MSPD), HF-LPME [32], are employed to remove interfering matrix components and concentrate the BFRs prior to analysis. Columns containing silica that may be neutral, activated, sulfuric acid impregnated, or potassium hydroxide impregnated may be employed for the removal of the matrixes eluted with suitable solvents. Anhydrous sodium sulphate is sometimes added to the columns for drying at the end of clean-up. The use of columns containing alumina and florosil have also been reported by researchers [55].

2.3. Analytical Instruments

A reliable, selective, sensitive, and rapid analytical method is vital for the accurate detection and quantification of trace environmental contaminants, including BFRs. To date, gas chromatography (GC) and liquid chromatography (LC)-based methods have been reported, and some representative analytical methods for BFR quantification are briefed in Table 1. Gas chromatography-mass spectrometry (GC-MS), gas chromatography-tandem mass spectrometry (GC-MS/MS), and liquid chromatography-tandem mass spectrometry (LC-MS/MS) are powerful instruments for structural identifications and play vital roles in BFR analysis in biological and other environmental samples. GC-MS is widely used for the analysis of BFRs due to its high sensitivity and selectivity. Sample preparation methods have been reported in previous sections following samples' collection and pretreatment, sample extraction, clean-up, and then GCMS analysis. Derivatization techniques may be employed to enhance the detection of certain BFRs. In addition, both GC and MS, combined with selective detectors, have been used for the determination of BFRs in environmental samples. Some examples include: a trace 1310 GC coupled to an ISQ™ single quadrupole mass spectrometer employed for the analysis of PBDEs and NBFRs [39]; GC-ECNI-MS [56]; GC-MS/MS; the GC-MS/MS (EI) method; and GC-ECD [35]. While various detectors have been attached to the GC during BFR analysis, most researches employing GC focused on GC-ECNI-MS combination. In the review, it was also observed that research on BFRs used GC to analyze PBDEs and NBFRs, while HBCDDs were analyzed using LC methods. This observation may be due to HBCDDs being relatively polar compounds which may degrade at high temperatures, a situation that may be observed during the GC-MS process.

LC-MS has also been used in analyzing BFRs in biota samples. It is often preferred over gas chromatography-mass spectrometry (GC-MS) for the analysis of certain compounds like hexabromocyclododecanes (HBCDDs). A major reason as described above is the polarity and volatility of HBCDDs. Some reports have shown the application of LC and various detectors in the analysis of BFRs; some reports include LC-MS, LC-MS/MS (ESI), High-Performance Liquid Chromatography (HPLC) [40], HPLC-MS/MS [47], and UHPLC-MS/MS. Lestido-Cardama et al. [47] analyze the effects of PE-MPs and TBBPA on *Rhinella arenarum* tadpoles at the laboratory scale. To verify the correct dosage, TBBPA concentration in the aquarium weekly were measured by direct UHPLC-MS/MS analysis. In general, these techniques offered low LOQs and good recoveries for most BFR congeners.

3. Distribution of BFRs in Different Matrices

Multiple studies have been conducted on the distribution of BFRs in different matrices including surface sediments, biota, water, food stuffs, air and dust, and soil and human samples. These studies are summarized in Table 2. Data from previous studies highlight the significant variability in concentrations of BFRs across different environmental matrices,

with the highest concentrations found in surface sediments from e-waste dismantling regions in China, particularly for PBDEs, which reach up to 401,000 ng/g dw. In contrast, the lowest concentrations are observed for Tetrabromobisphenol A (TBBPA) in office air and dust in Sweden, at less than 0.1 pg/m³. Other notable high concentrations include PBDEs in surface sediments and NBFs in water bodies impacted by industrial activities. These findings underscore the impact of improper waste management and industrial activities on environmental contamination and highlight the need for stringent monitoring and regulatory measures to mitigate potential health risks.

Table 2. Concentrations of BFRs and associated chemicals in different matrices.

Chemicals	Concentration	Occurrence	Country/Region	Reference
Surface Sediments				
Tetrabromobisphenol (TBBPA)	ND–12.591 µg/kg	surface sediment	Western Guangdong, China	[15]
	0.02–18.3 µg/kg	surface sediment	South China Coast	[13]
	19.8–1.52 × 10 ⁴ ng/g dw	A typical waste dismantling site	China	[14]
	0.003–0.31 ng/g dw, not detected (ND) to 1.11 ng/g dry weight	Mangrove wetlands	South China	[57]
	0.02–21.5 ng/g dw	Coast land	South China	[13]
Hexabromocyclododecane (HBCDs): α-, β-, and γ-HBCD	ND–6.307 µg/kg	surface sediment	South China Coast	[15]
Polybrominated diphenyl ethers (PBDEs)	0.345–401,000 ng/g dw	A typical e-waste dismantling region	China	[58]
7 Novel brominated flame retardants (NBFs)	0.581–73,100 ng/g dw	A typical e-waste dismantling region	China	[58]
Biota				
Tetrabromobisphenol (TBBPA)	0.56–22.1 ng/g ww	Biota species from two mangrove wetlands	South China	[57]
	ND–9.83 µg/kg ww	Zooplankton samples	Yellow Sea and Bohai Sea, Northern China	[59]
Tetrabromobisphenol-A-bis(2,3-dibromopropyl ether) (TBBPA-BDBPE)	<LOD–42.8 ng/g ww	Herring gull egg pools	Laurentian Great lakes, North American	[60]
Water				
Tetrabromobisphenol (TBBPA)	ND–0.46 µg/L	surface seawater	Northern China	[61]
	ND–12.279 ng/L	Weihe River Basin	China	[60]
	18.5–82.6 ng/L	Baiyang Lake	China	[62]
	ND–32.3 ng/L	Surface water	Taihu Lake, China	[63]
Polybrominated diphenyl ethers (PBDEs)	0.00226–0.00751 ng/L	Bohai Sea	China	[63]
	ND–71.77 ng/L	Surface water	Taizhou, China	[64]
	ND–4.28 ng/L	Sea	South China	[65]
	0.723–3.796 ng/L	Dongjiang River	China	[66]

Table 2. Cont.

Chemicals	Concentration	Occurrence	Country/Region	Reference
Novel brominated flame retardants (NBFRs)	0.0107–0.0104 ng/L	Bohai Sea	China	[64]
	ND–3.34 ng/L	Surface water	Taizhou, China	[66]
	ND–7.63 ng/L	Sea	South China	[65]
Decabromodiphenyl ethane (DBDPE)	2010 (ND–35,000) ng/L	Lian River and Beigang River	Guiyu, South China	[66]
	9.5 (ND–120) ng/L	Taizhou	East China	[67]
	7.28 (0.06–69.5) ng/L	Shihwa Lake	Republic of Korea	[68]
	3.29 (0.22–37.6) ng/L	Ulsan/Onsan Bays	Republic of Korea	[69]
1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE)	830 (ND–36,800) ng/L	Lian River and Beigang River	Guiyu, South China	[58]
	0.043 (ND–0.60) ng/L	Taizhou	East China	[69]
Food stuffs				
Novel brominated flame retardants (NBFRs): 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE or TBE), and bis(2-ethyl hexyl) tetrabromophthalate (BEH-TEBP or TBPH)	<0.42–170 ng/g lw	Food stuffs	UK	[70]
Polybrominated diphenyl ethers (PBDEs)	0.13–36 ng/g lw	Food stuffs	UK	[70]
Air and dust				
Tetrabromobisphenol (TBBPA)	<LOD–74.1 ng/g dw	Soil and road dust	western China	[71]
	ND–144 pg/m ³	Indoor dust	Sothern China	[72]
	ND–326 pg/m ³	Outdoor dust	Sothern China	[72]
	<0.1 pg/m ³	Office air and dust	Sweden	[73]
	69 ng/g dw	House dust	Republic of Korea	[74]
Polybrominated diphenyl ethers (PBDEs)	490–89,000 ng/g	Indoor dust, indoor air, and outdoor air	Birmingham, UK	[72]
	94–227 ng/g	Household dust	China	[75]
Hexabromocyclododecane (HBCD)	46–14,000 pg/m ³	Indoor and outdoor dust	Birmingham, UK	[64]
	1.06–14.1 µg/kg	Indoor dust, indoor and outdoor air	South China Coast	[13]
Novel brominated flame retardants (NBFRs)	22–11,000 pg/m ³	Indoor dust, indoor and outdoor air	Birmingham, UK	[64]
Soil				
Tetrabromobisphenol (TBBPA)	<LOD–33.8 ng/g dw	Soil	Chongqing, western China	[71]
	0.025–78.6 ng/g dw	Soil	Republic of Korea	[76]

Table 2. Cont.

Chemicals	Concentration	Occurrence	Country/Region	Reference
Human sample				
Tetrabromobisphenol (TBBPA)	<LOD-42 ng/g lw	Breast milk	Beijing, China	[56]
	<LOD-15.1 ng/g lw	Breast milk	French	[77]
	4.73 ng/g lw	Breast milk	China	[78]
	ND-1.08 ng/g	Hair	China	[79]
	0.0793-1.15 µg/L	Urine	China	[80]
Novel halogenated flame retardants (NHFRs)	Maximum 6930 pg g ⁻¹ lipid	Breast milk	Canada	[81]
methoxy-polybrominated diphenyl ethers (MeO-PBDEs)	Maximum 1600 pg g ⁻¹ lipid	Breast milk	Canada	[81]

ND: no detected; LOD-limit of detection.

3.1. Surface Sediment

Chen X. et al. [15] detected TBBPA in surface sediment samples from eight rivers and three reservoirs in Western Guangdong, China, with a detection frequency of 85.27%, and the sediment ranged from not detected (ND) to 12.59 µg/kg. Pan et al. [13] revealed that the average concentrations of TBBPA in sediments from 24 fishing ports in South China Coast ranged from 0.02 to 18.3 ng/g dw and that the detection rates for both TBBPA and HBCDDs were 100%. Tetrabromobisphenol (TBBPA) has been detected from a typical electronic waste (e-waste) dismantling site in Southern China, with concentrations in the range of 19.8–1.52 × 10⁴ ng/g dw [14]. Li et al. [57] measured the levels of TBBPA ranging from 0.003–0.31 and not detected (nd) to 1.11 ng/g dry weight in the sediments at Mangrove wetlands in South China. The concentrations of TBBPA in the fishing-port sediments of a cost land in South China were found to be in the range of 0.02–21.5 ng/g dw by Pan et al. [13]. Chen et al. [15] revealed the concentration of HBCDs in the surface sediment of a South China Coast ranged from ND to 6.31 µg/kg. PBDEs levels in sediment from Guiyu, a typical e-waste dismantling region in China, were in the range of 0.345–401,000 ng/g dw, as reported by Siyuan et al. [58]. The levels of seven novel brominated flame retardants (NBFRs) in sediment from Guiyu, a typical e-waste dismantling region in China, reported by Siyuan et al. [58] ranged from 0.581 to 73,100 ng/g dw. The highest concentrations of BFRs are found in e-waste dismantling regions, indicating significant contamination likely due to improper disposal and recycling practices.

3.2. Biota

Li et al. [57] investigated the distribution, bioaccumulation, and bio magnification of TBBPA in various biota species from two mangrove wetlands in the Pearl River Estuary (PRE) and the Jiulong River Estuary (JRE) in South China. The TBBPA levels ranged from 0.56 to 22.1 ng/g lipid weight in the biota species from the PRE and from not detectable (nd) to 56.3 ng/g lipid weight in the biota species from the JRE. The bioaccumulation of TBBPA in these species were evaluated using the Bioaccumulation Factor (BAF), which is defined as the ratio of the concentration of a substance in an organism to the concentration in the surrounding environment (sediment or water).

Gauthier et al. [60] measured TBBPA-BDBPE concentrations in herring gull egg pools from the Laurentian Great Lakes of North America, with levels ranging from below the limit of detection (LOD) to 42.8 ng/g wet weight. These findings indicate significant bioaccumulation in herring gulls, which are top predators in their ecosystem, highlighting the potential for bio magnification through the food chain.

Gong et al. [59] reported TBBPA levels in zooplankton samples from the Yellow Sea and Bohai Sea, ranging from not detectable (ND) to 9.83 µg/kg (wet weight). The

bioaccumulation in zooplankton, which are primary consumers, suggests an entry point for TBBPA into the marine food web.

The presence of TBBPA-BDBPE in biota, especially in mangrove wetlands and zooplankton, indicates significant bioaccumulation potential. This poses ecological risks through trophic transfer and bio magnification, ultimately affecting wildlife and human health due to the consumption of contaminated species. Detailed BAF calculations specific to each species and environmental media are essential for a comprehensive understanding of bioaccumulation dynamics.

3.2.1. Water

Gong et al. [59] found varying levels of TBBPA in surface seawater samples in the Yellow Sea and Bohai Sea, ranging from ND to 0.46 µg/L. Wang et al. [61] reported that the TBBPA concentrations in water samples in Weihe River Basin, China were in the range of not detected N.D to 12.279 ng/L (mean value of 0.937 ng/L), Aixue et al. [62] recorded 18.5–82.6 ng/L in Baiyang Lake, China and reported ND–32.3 ng/L in surface water at Taihu Lake, China. PBDEs detected by Liu et al. [64] in Bohai Sea, China ranged from 0.00226 to 0.00751 ng/L, by Ling et al. in [82] in surface water in Taizhou, China ranged from nd to 71.77 ng/L., by Feng et al. [83] in the South China Sea ranged from nd to 4.28 ng/L, and in Dongjiang River, China ranged from 0.723–3.796 ng/L [83]. According to Liu. et al. [64] NBFRs ranged from 0.0107 to 0.0104 ng/L in Bohai Sea, China, while in Taizhou, China they ranged from nd to 3.34 ng/L according to Ling et al. [82], and in the South China Sea they ranged from nd to 7.63 ng/L [65]. In the case of Decabromodiphenyl ethane (DBDPE) in Lian River and Beigang River, Guiyu, South China, the concentration ranged from nd to 35,000 ng/L. As detected by Liu et al. [63] in Taizhou, East China the range was 9.5 (nd) to 120 ng/L. As detected by Ling et al. [58] in Shihwa Lake, Republic of Korea, the range was 7.28 (0.06–69.5) ng/L [69], and the range in Ulsan/Onsan Bays, Guiyu, South China was 3.29 (0.22–37.6) ng/L [69]. Ling et al. [58] measured BTBPE concentrations in Lian River and Beigang River, Guiyu, South China as 830 (nd–36,800) ng/L, and 0.043 (nd–0.60) ng/L was found by Ling et al. [58] in Taizhou, East China. Variability in concentrations of TBBPA, PBDEs, NBFRs, DBDPE, and BTBPE across different water bodies indicates localized sources of contamination. High levels in certain areas, like the Lian and Beigang Rivers, indicate severe pollution requiring targeted interventions.

3.2.2. Food

The concentrations of NBFRs in foodstuffs expressed by Yulong et al. [70] was <0.42–170 ng/g lw, a research conducted in the UK. They also found the PBDE concentration ranged from 0.13 to 36 ng/g lw. The detection of NBFRs and PBDEs in food samples from the UK indicates the potential risk for human exposure through diet.

3.2.3. Air and Dust

The concentrations of TBBPA found in soil and road dust in Western China ranged from <LOD to 74.1 ng/g dw [71], in indoor dust in Southern China from ND to 144 pg/m³, and outdoors from ND to 326 pg/m³ according to Ma et al. [72], and in office air and dust in Sweden < 0.1 pg/m³ and in house dust in Republic of Korea 69 ng/g dw. PBDE concentrations in indoor and outdoor dust in Birmingham, UK [64] were detected in the range of 490–89,000 ng/g, and a concentration of 94–227 ng/g was detected in household dust in China by Jing et al. [75]. HBCD concentrations measured in indoor and outdoor dust in Birmingham, UK ranged from 46 to 14,000 pg/m³ [64], and indoor dust and indoor and outdoor air on the South China Coast was found to contain a concentration of 1.06–14.1 µg/kg [13]. Ma et al. [72] found concentrations of NBFRs ranging from 22 to 11,000 pg/m³ in indoor dust and indoor and outdoor air in Birmingham, UK. High concentrations in indoor environments, particularly of TBBPA and HBCD in urban and industrial areas, highlight the importance of controlling emissions and improving indoor air quality to reduce human exposure.

3.2.4. Soil

Tetrabromobisphenol (TBBPA) concentrations of $< \text{LOD} - 33.8 \text{ ng/g dw}$ were measured in soil by Lu et al. [71] in Chongqing, western China and of $0.025\text{--}78.6 \text{ ng/g dw}$ in the Republic of Korea by Jeon et al. [76].

3.2.5. Human Sample

TBBPA concentrations of $< \text{LOD} - 42 \text{ ng/g lw}$ were found in breast milk by Huang et al. [56] in Beijing, China, of $< \text{LOD} - 15.1 \text{ ng/g lw}$ in France by Inthavong et al. [77] and of 4.73 ng/g lw by Hu et al. [78] in China. In China, Barghi et al. [79] measured $\text{ND} - 1.08 \text{ ng/g}$ of TBBPA in hair, and Xu et al. [80] found $0.0793\text{--}1.15 \text{ }\mu\text{g/L}$. In Canada, NHFRs and MeO-PBDEs in breast milk measured by Dorothea et al. [81] ranged from Maximum 6930 pg g^{-1} lipid and Maximum 1600 pg g^{-1} lipid, respectively. The detection of BFRs in breast milk, hair, and urine underscores the alarmingly widespread exposure to these chemicals.

4. Transport Mechanisms of BFRs

Understanding the transport mechanisms of BFRs and associated chemicals is crucial for assessing their environmental fate and potential risks. BFRs are released into the environment in three main ways: (1) as volatile substances are released directly into the environment, (2) as products containing these chemicals break down and release the chemicals into the environment, and (3) as products come into direct contact with environmental media (Figure 2). Moreover, BFRs can interact with other emerging contaminants such as heavy metals and micro(nano)plastics (M/NPs), complicating their environmental behavior and impact [84]. The co-occurrence of BFRs and heavy metals can lead to complex chemical interactions that influence their mobility, bioavailability, and toxicity. Heavy metals can bind to BFRs, potentially altering their transport dynamics and enhancing their persistence in the environment. Studies have shown that the presence of heavy metals can affect the sorption and desorption processes of BFRs in soil and aquatic systems, modifying their environmental fate [85]. The hydrophobic nature of both BFRs and M/NPs enables BFRs to adsorb onto plastic particles, which can then be transported over long distances by water currents and wind [86]. This interaction can increase the potential for the bioaccumulation and biomagnification of BFRs in aquatic organisms, as M/NPs are readily ingested by marine life. Additionally, the degradation of M/NPs can release adsorbed BFRs back into the environment, further complicating their ecological impact [86].

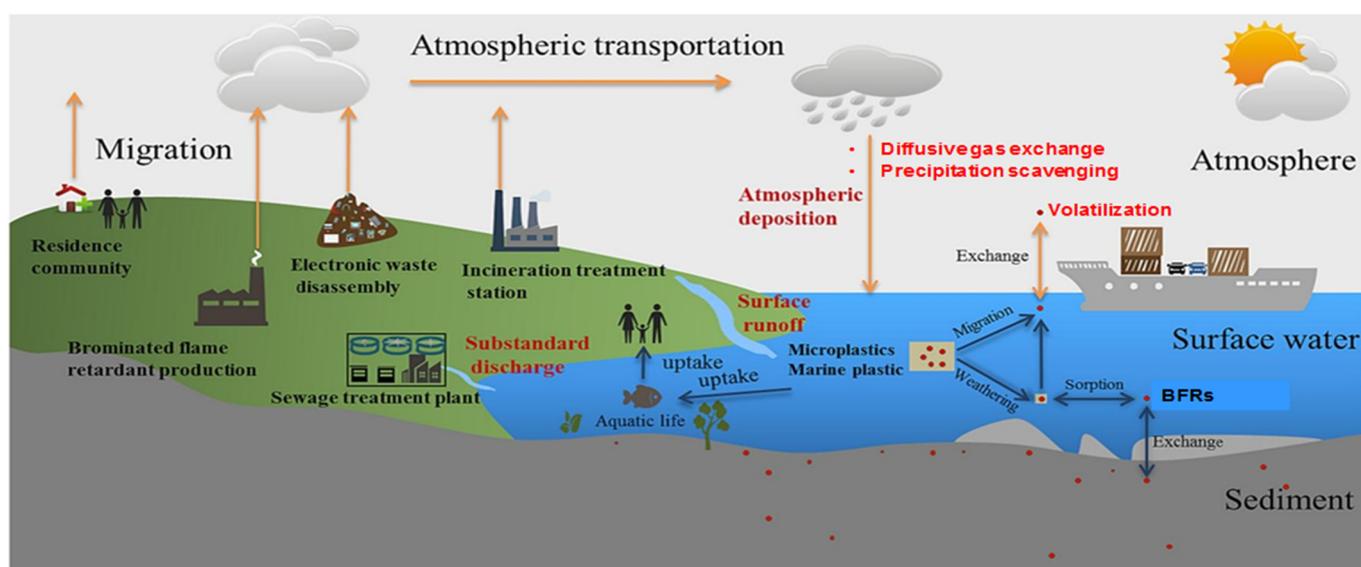


Figure 2. Migration pathways of BFRs in the environment (modified from Wang et al. [87]).

BFRs may evaporatively or by fugitive migration reach the atmosphere during manufacturing and usage. In a similar vein, these substances may evaporate from garbage during disposal. BFRs discharged into the atmosphere can readily interact with particles and sink into the aquatic environment because of their octanol–water partition coefficient ($\log K_{ow}$). The amount of BFRs in water can be greatly impacted by runoff from polluted soils. For instance, Wang et al. [87] discovered that in the coastal East China Sea, surface runoff was responsible for 15.1% of the PBDE contamination. Cui and Wang [88] found that summertime concentrations of PBDEs were considerably greater in Wuhan than wintertime concentrations. They hypothesized that this difference may be attributed to summertime rainfall runoff.

This section discusses the transport mechanisms of BFRs in the atmosphere, surface water, and soil, focusing on their dispersion, deposition, sorption, mobility, and contaminant transfer pathways [89]. These factors are also responsible for the movement of BFRs. Transport is a movement caused by ambient wind flow and direction. Dispersion results from local turbulence/disturbance, while deposition is the downward movement of pollutants to the ground surface, which relies on precipitation, scavenging, and sedimentation [90]. However, studies covering the transport mechanisms of BFRs are still scarce.

4.1. Atmospheric Dispersion and Deposition Dynamics

BFRs can be emitted into the atmosphere during their production, use, and disposal phases. Once in the atmosphere, BFRs can undergo long-range transport through processes such as advection (horizontal movement of air masses, which can transport BFRs over long distances) and diffusion (random movement of BFR molecules in the air, leading to their dispersion).

These mechanisms significantly influence the deposition of BFRs from the atmosphere. Studies have shown that the deposition of BFRs can occur through diffusive gas exchange or by precipitation scavenging from the gas phase, which include wet deposition processes, and is influenced by seasonal atmospheric variability [91]. Diffusive gas exchange refers to the transfer of BFRs in their gaseous form from the atmosphere directly onto surfaces through molecular diffusion and air-surface exchange processes [92]. This process covers the dry deposition of airborne pollutants. The deposition of BFRs in soils, surface waters, and vegetation can result in their accumulation over time, leading to persistence and bioaccumulation [93].

Precipitation scavenging plays a crucial role in the wet deposition of hydrophobic organic chemicals, including BFRs, and is typically more significant than dry deposition [94]. It is considered the most important process for removing many semivolatile and non-volatile organic contaminants from the atmosphere [94]. Wet deposition involves the removal of BFRs from the atmosphere through precipitation, such as rain or snow [91]. The wet process can be characterized by a wet scavenging coefficient (defined as the ratio of the pollutant mass removed by precipitation to the total pollutant mass in the atmosphere) [95]. The wet scavenging of atmospheric pollutants includes in-cloud scavenging processes and below-cloud scavenging processes [95,96]. Below-cloud atmospheric particles are removed by raindrops via Brownian diffusion, interception, and impaction [97]. The below-cloud scavenging coefficient can be estimated using Equation (1) [66]:

$$\lambda(d_p) = \int_0^{\infty} \frac{\pi}{4} D^2 V(D) E(D, d_p) N(D) dD \quad (1)$$

The variables in this case are the aerosol diameter (d_p), raindrop size distribution function (N), raindrop fall velocity (V), and capture efficiency (E). There are two components to λ : (1) the surface-to-volume ratio's impact is incorporated into the complex function of the raindrop size distribution to determine the fractional area swept by the falling raindrops; (2) E represents the proportion of aerosol particles in the raindrop sweep volume that are genuinely caught [66].

Therefore, factors such as collection efficiency, the terminal velocity of raindrops, raindrop size distribution, and particle size distribution play important roles in below-cloud scavenging [9,98]. During the later stages of rainstorms, high concentrations of aerosols can significantly enhance precipitation efficiency, leading to more intense and localized precipitation clusters [98]. These processes were demonstrated in a study by Oh et al. [91], who quantified 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH) and brominated diphenyl ethers 47 (BDE-47) in almost all precipitation samples from Saturna Island and Tadoussac in Canada.

The movement of BFRs in the atmosphere is mainly influenced by their physical and chemical properties, along with weather conditions such as temperature etc. as it directly affects vapor pressure and octanol–air partition coefficients (K_{OA}) [55]. Oh et al. [91] showed how seasonal changes affect the distribution of BFRs in the air in Canada. They discovered that the levels of TBECH and BDE-47 measured by active air samplers closely followed the average air temperature. These levels were higher in the warmer months (April to August) and lower in the colder months (September to March). This relationship between temperature and the concentration of these chemicals in the air is often explained by temperature-driven exchanges between the air and surfaces or by temperature-dependent emission rates [98]. In indoor air and dust over 15 months in a test home, Guo et al. [49] showed that the distribution of NBFRs' dependence on temperature and relative humidity was not obvious. However, for Σ 9NBFRs, except for hexabromobenzene (HBBZ) and 2-bromoallyl-2,4,6-tribromophenyl ether (BATE), the temporal variations in the concentration coincided with those in the temperature. Most BFR concentrations were mainly affected by the temperature and relative humidity. Therefore, it can be deduced that the effect of temperature on BFRs can be compound-dependent. Li et al. [54] found that lower-molecular-weight BFRs, such as BDE17, BDE28, BDE47, ATE, PBT, and PBEB, were more sensitive to temperature changes compared to higher-molecular-weight BFRs. This sensitivity is attributed to the increase in emissions of these BFRs with higher temperatures, with emission rates from consumer materials rising sharply [99].

4.2. Water Transport and Fate Processes

The surface or groundwater transport of BFRs is primarily influenced by their hydrophobic nature and tendency to partition to organic matter [52]. BFRs can enter surface waters through direct discharge from industrial facilities, runoff from treated surfaces, and atmospheric deposition (Figure 1). Once in surface waters, BFRs can undergo various fate processes, including sorption, transformation, transport, and volatilization [55].

Sorption is a key process that controls the fate of BFRs in surface waters. BFRs tend to sorb to suspended particles including microplastics and sediment in water bodies, leading to their accumulation in these matrices and then their consumption by aquatic biota [41,55]. Wang et al. [52] reported a high bioaccumulation factor (BAF) of (>5000) in aquatic biota (invertebrates, fish, and reptiles), which was due to the lipophilic nature of BFRs as they are easily sequestered in lipids [54,100]. These can also influence the transport of BFRs in surface waters, as sorbed or ingested BFRs can be transported with the aquatic biota serving as a vector in the aquatic environment [90].

Transformation processes, such as photodegradation and biodegradation, can alter the fate of BFRs in surface waters. Photodegradation breaks down BFRs using sunlight, while biodegradation breaks them down using microorganisms [101]. These processes can create transformation products with different environmental properties and toxicity than the original compounds. Dirtu et al. [101] reviewed the transformation of BFRs, and they found that in biota, BFRs undergo degradation pathways such as reductive debromination and Phase I oxidative metabolism. For PBDEs, reductive debromination converts hepta- to deca-BDE congeners into tetra- to hexa-PBDEs, while Phase I metabolism produces hydroxylated compounds (e.g., HO-PBDEs). Phase II conjugation (glucuronidation or sulfation) may also occur. HBCD undergoes *in vivo* metabolism producing Phase I metabolism products (HO-compounds) through oxidative metabolism, dehydrobromination or debromination, and

stereospecific metabolism with isomer interconversion. Studies on rats, aquatic organisms, and/or microorganisms have shown that debromination and Phase II conjugation are major pathways for TBBPA metabolism [101].

Abiotic factors in aquatic environments can significantly impact the phototransformation of BFRs. Recently, Feng et al. [65] conducted a study on the phototransformation of TBBPA in alkaline saline water under simulated sunlight irradiation. They investigated the effects of various abiotic factors, including the initial concentration of TBBPA, chloride ion concentration, solution pH, inorganic anions and cations, and dissolved organic matter (DOM). The results revealed that the rate of TBBPA phototransformation increased with a decrease in the initial TBBPA concentration, increasing chloride ion concentration, and higher solution pH. Scavenging experiments indicated that hydroxyl radicals ($\bullet\text{OH}$), singlet oxygen ($^1\text{O}_2$), superoxide radicals ($\text{O}_2\bullet^-$), and triplet excited state TBBPA (3TBBPA^*) all played roles in the phototransformation of TBBPA. Additionally, the presence of nitrate (NO_3^-), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), magnesium ions (Mg^{2+}), calcium ions (Ca^{2+}), ferric ions (Fe^{3+}), and fulvic acid (FA) inhibited the phototransformation of TBBPA in their study.

Huang et al. [56] conducted a study evaluating the anaerobic biotransformation of two non-brominated flame retardants (NBFRs), specifically 1,2,5,6-tetrabromocyclooctane (β -TBCO) and 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), using the *Dehalococcoides mccartyi* strain CG1. Their findings indicated that both β -TBCO and DPTE were readily transformed by *D. mccartyi* CG1, with observed rate constants (k_{obs} values) of $0.0218 \pm 0.0015 \text{ h}^{-1}$ and $0.0089 \pm 0.0003 \text{ h}^{-1}$, respectively. In the case of β -TBCO, the compound appeared to undergo dibromo-elimination followed by epoxidation, resulting in the formation of 4,5-dibromo-9-oxabicyclo[6.1.0]nonane (Figure 3A). On the other hand, DPTE experienced debromination at the benzene ring, with the ortho-bromine being removed prior to para-bromine rather than at the carbon chain (Figure 3B). The study also observed significant carbon and bromine isotope fractionations during the biotransformation of β -TBCO and DPTE, indicating that the breaking of the carbon–bromine (C–Br) bond is the rate-limiting step in their biotransformation process.

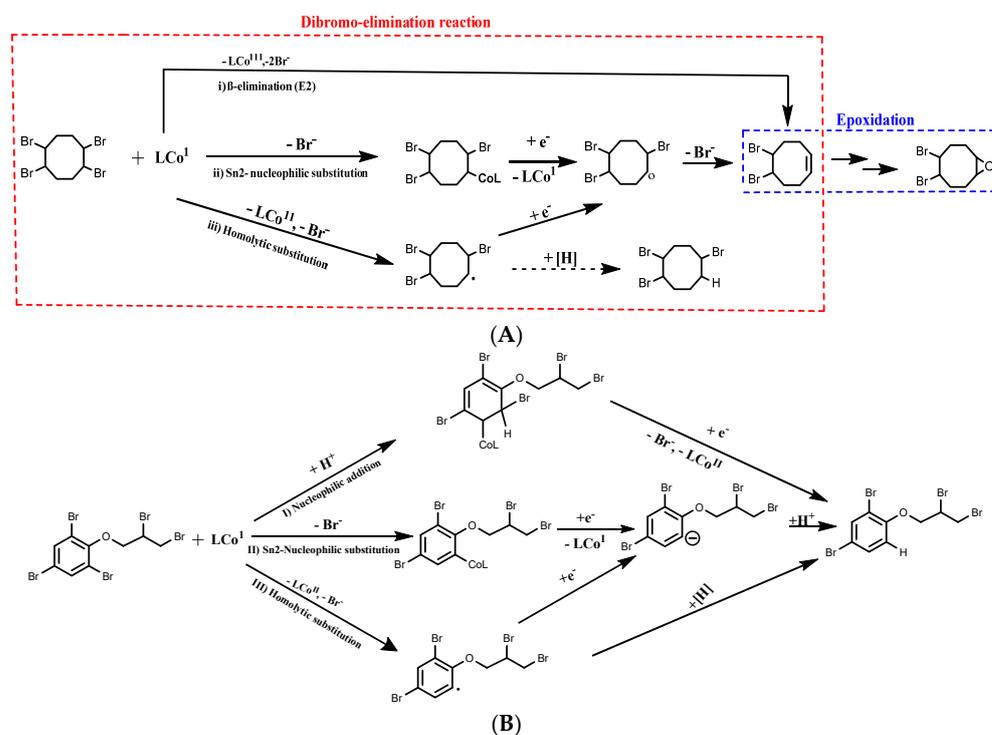


Figure 3. Postulated reaction mechanisms for anaerobic microbial transformation of β -TBCO (A) and DPTE (B) (Adapted from [56]).

Based on the identified products and isotope fractionation patterns, the study suggested that β -elimination (E2) and S_N2 -nucleophilic substitution are the most likely microbial transformation mechanisms for β -TBCO and DPTE, respectively (Figure 4). These findings provide valuable insights for assessing the potential of natural attenuation and the environmental risks associated with β -TBCO and DPTE.

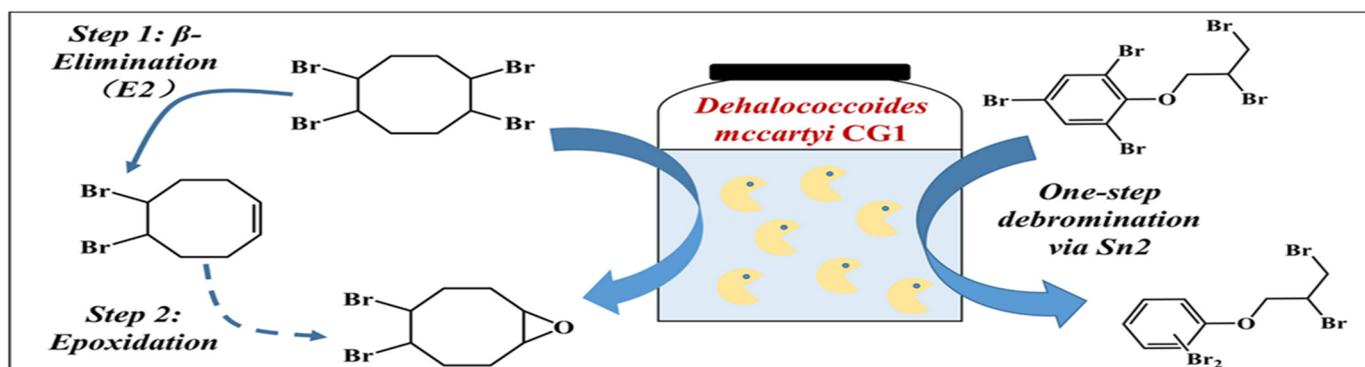


Figure 4. Main microbial transformation mechanisms for β -TBCO and DPTE involve β -elimination (E2) and S_N2 -nucleophilic substitution (Adapted from Huang et al. [56]).

4.3. Soil Sorption and Fate Processes

In soil, BFRs can sorb to soil particles and organic matter, which can affect their mobility and transport. The sorption of BFRs to soil can lead to their accumulation in soil matrices, where they can persist for long periods [55]. The sorption and mobility of BFRs in soil is influenced by factors such as soil properties including soil organic matter content (SOM), pH, ionic composition, and clay content as well as specific BFR properties [49,99,102].

Sun et al. [99] investigated the sorption behavior of TBBPA in two soils with different characteristics through batch equilibrium experiments. They also studied the impacts of ionic strength and pH on the sorption process. The study revealed that fast sorption was more significant than slow sorption in the process and higher for silt loam soil compared to loamy clay soils. Nonlinear sorption isotherms were observed, and the Freundlich model effectively described the sorption behavior of TBBPA. SOM played a predominant role in the sorption process, contributing approximately 90% to the total sorption. The desorption hysteresis of TBBPA was observed in single-cycle sorption and desorption experiments, and results showed that the sorbed amount of TBBPA decreased with increasing solution pH and increased with increasing ionic strength, with the effects of ionic strength primarily attributed to changes in solution pH. In another study, Venkatesan and Halden [103] conducted a 3-year outdoor mesocosm study to assess the environmental persistence of BFRs in biosolids-amended soil. They reported a total polybrominated diphenyl ether (PBDE) concentration in biosolids composites of $9400 \pm 960 \mu\text{g}/\text{kg}$ dry weight, with deca-BDE constituting 57%, followed by nona- and penta-BDE at 18% and 13%, respectively. In outdoor soil mesocosms, over 99% of the initial mass of BFRs in the biosolids/soil mixtures (1:2) persisted throughout the three-year monitoring period.

4.3.1. BFRs Transformation in Soil

BFRs in soil are transformed physically, chemically, and metabolically by biological activities, resulting in the production of hydrobrominated, hydroxylation, and methoxylation BFRs. The environment and public health may also be negatively impacted by these degradation products. Thus, the process of transformation in soil is crucial. The two primary transformation mechanisms for BFRs in soil are photolysis and microbial degradation [49]. In contrast to water systems that are homogeneous or heterogeneous, organic contaminants in surface soil photodegrade slowly. This primarily has to do with how earth blocks light but in contrast to typical ways that organic contaminants in soil change.

BFRs have the ability to absorb ultraviolet rays in the UV-A range (315–400 nm). When exposed to irradiation, they undergo degradation or photolysis, leading to the loss of bromine atoms (debromination) and possible rearrangement by cyclization [64]. The debromination process, necessary for creating hydrobrominated products, involves the gradual removal of bromine atoms. As BFRs vary in the number of bromine atoms they contain, their effects on photolysis processes also vary. Generally, debromination processes tend to occur more readily in the benzene rings that are more heavily brominated, especially when there is a significant difference in the number of bromine substitutions between two rings [104]. For BFRs with fewer bromine atoms, ortho bromine is more photoreactive than para bromine. However, this difference is not statistically significant for BFRs with greater degrees of bromination [103,104]. During the cyclization process, intramolecular cyclization occurs, leading to the detachment of HBr and the production of further hazardous brominated dioxins and furans. The discharge of these photolysis products increases the hazards to human health [105].

BFRs can also undergo transformation in soil through the action of microorganisms. While there are numerous reports on the biodegradation of BFRs, current research on the impact of indigenous soil microorganisms on BFRs through debromination is limited, and specific studies on the microbial degradation of NBFRs by bacteria or fungi are scarce [55]. Most existing research has focused on traditional BFRs, particularly PBDEs.

In soil, the biodegradation of BFRs primarily occurs through two pathways: anaerobic debromination and aerobic biodegradation [106]. Anaerobic debromination involves the removal of bromine atoms from BFRs in an oxygen-limited environment, while aerobic biodegradation occurs in the presence of oxygen. The microbial degradation of BFRs can also be influenced by the presence of plant in the soil. Sun et al. [99] conducted a study to investigate the fate and metabolites of ¹⁴C-labeled tetrabromobisphenol A (14C-TBBPA) in a submerged soil system with an anoxic–oxic interface, both with and without the presence of rice (*Oryza sativa*) and reed (*Phragmites australis*) seedlings. In the unplanted soil, TBBPA dissipated with a half-life of 20.8 days, accompanied by mineralization (11.5% of initial TBBPA) and the significant formation of bound residues (60.8%). The study identified twelve metabolites, with ten found in unplanted soil and seven in planted soil. These metabolites were formed through four interconnected pathways: oxidative skeletal cleavage, O-methylation, type II ipso-substitution, and reductive debromination. Interestingly, the presence of seedlings significantly reduced the mineralization of 14C-TBBPA and the formation of bound residues while simultaneously stimulating debromination and O-methylation processes. These findings suggest a complex interplay between plant presence and microbial activity in the fate and transformation of TBBPA in soil environments.

4.3.2. Plant Uptake of BFRs in Soil

Plants play a crucial role in terrestrial ecosystems, especially in soil environments. They have the ability to absorb and metabolize BFRs, which can then transfer from the soil to the aboveground parts of plants. This process can lead to the accumulation of BFRs in the food chain.

The scientific community has extensively discussed the effects of BFRs on plant absorption and phytotoxicity [107]. Studies have specifically investigated BFR absorption by various plant species such as vegetables, tobacco leaves, and maize plant in both soil-based trials [99] and hydroponic solutions [36]. However, hydroponic research is known to have limitations, particularly in replicating the complex interactions present in soil ecosystems. These interactions can significantly influence the availability of contaminants, highlighting the need for caution when extrapolating findings from hydroponic studies to real-world soil environments.

Recently, Beggio et al. [108] conducted a study using the RHIZOtest, a soil-based biotest optimized for organic substances, to investigate the absorption and translocation of four PBDEs and four NBFRs in tomato plants (*Solanum lycopersicum* L.). Their findings revealed higher concentrations of NBFRs in both the roots (ranging from 0.23 to 8.01 ng g⁻¹

dw for PBDEs and from 1.25 to 18.51 ng g⁻¹ dw for NBFRs) and the shoots (ranging from 0.09 to 5.58 ng g⁻¹ dw and from 0.47 to 7.78 ng g⁻¹ dw for PBDEs). The average values of the soil-root concentration factor (RCF) for PBDEs were lower than those for NBFRs at both initial spiking levels. However, no significant differences were found between PBDEs and NBFRs in the root-shoot transfer factor (TF) calculations. These findings suggest that the characteristics of PBDEs and NBFRs can explain the differences and similarities within and between the two groups of compounds reported in the RCF and TF. Their study also observed a decreasing trend in computed RCF and TF values as the number of bromine atoms in the PBDEs increased. Additionally, a strong negative linear association was found between the RCF values and the corresponding log K_{ow} values for PBDEs, indicating that the hydrophobicity of PBDEs influences their root uptake. The hydrophobicity of NBFRs was found to negatively correlate with root absorption; however, this relationship was not observed during root-to-shoot transfer. The presence of a second aromatic ring in NBFRs, such as biphenyl NBFRs (BTBPE and DBDPE), was identified as a key factor affecting their uptake and translocation potential, as these compounds exhibited lower uptake and decreased translocation potential compared to monophenyl PBEB and HBB.

The studies generally suggest that inside the plant, BFRs can undergo various metabolic transformations. Plants have enzymes that can metabolize BFRs to less toxic or more easily excretable forms. The metabolism of BFRs in plants can lead to the formation of metabolites that may have different chemical properties and toxicity profiles compared to the parent compounds. Furthermore, several factors influence the uptake and metabolism of BFRs in plants, including the concentration and duration of BFR exposure, soil properties (e.g., organic matter content, pH), plant species, and environmental conditions (e.g., temperature, humidity).

Understanding the transport mechanisms of BFRs and associated chemicals is crucial for assessing their environmental fate and potential risks. Further research is needed to improve our understanding of the fate and transport of BFRs in the terrestrial environment and to develop strategies to mitigate their impact on human health and the environment.

5. Risks Associated with BFRs and Associated Chemicals

BFRs, including PBDEs, Hexabromocyclododecanes (HBCDs), and Tetrabromobisphenol-A (TBBP-A), have been demonstrated to induce adverse effects on endocrine, reproductive, and behavioral functions in laboratory animals [105]. Accumulating evidence underscores the potential of BFRs to disrupt endocrine signaling pathways and impact the central nervous and reproductive systems. Notably, various BFR congeners have shown affinity for estrogen, progesterone, and androgen receptors, indicative of their endocrine-disrupting potency. Furthermore, BFRs have been implicated in the inhibition of enzymes crucial for steroid hormone metabolism. Hydroxylated PBDEs, structurally analogous to thyroid hormones, possess the capability to displace endogenous hormones from the plasma transporter protein transthyretin, thereby interfering with thyroid function [106]. These findings highlight the intricate mechanisms through which BFRs exert their toxic effects on hormonal regulation and underscore the importance of further research to elucidate their health impacts and inform regulatory measures.

5.1. Categorization of BFRs

- Polybrominated Diphenyl Ethers (PBDEs)

These are a class of chemicals known for their exceptional stability. They have a standard structure characterized by a brominated diphenyl ether with the chemical formula C₁₂H_(0–9)Br_(1–10)O. This class includes 209 related compounds that differ based on the number and position of bromine atoms [109]. PBDEs are hydrophobic contaminants, meaning they are insoluble in water, and they possess a high log K_{ow} value, indicating their tendency to bioaccumulate. Examples of PBDE formulations include Decabromodiphenyl ether (DecaBDE), Octabromodiphenyl ether (OctaBDE), and Pentabromodiphenyl ether (PentaBDE). The most common commercial mixture of PentaBDE consists of approximately

28% BDE-47 and BDE-99. The commercial formulations of OctaBDE typically contain between 11% and 22% BDE-197 and between 13% and 42% BDE-183. In contrast, DecaBDE mixtures are composed of more than 97% 3,3',4,4',5,5',6,6'-decabromodiphenyl ether (BDE-209) [110].

- Hexabromocyclododecane (HBCD)

HBCD is a non-aromatic flame retardant extensively used in thermoplastic and styrene-based polymers. These polymers are integral in manufacturing packaging materials, pillows, construction items, automobiles, textiles, insulating boards, and electrical products [111]. Research indicates that HBCD is bioaccumulative, persistent, and hazardous, with the capability to persist in the environment for extended periods. It can disperse through various pathways, including air, plants, water, soil, animals, human skin, and even breast milk [112–114]. HBCD's toxicity is notable for its impact on developmental processes and neuroendocrine functions in organisms, making it a significant concern [110]. Numerous studies have established that HBCD acts as a hepatotoxicant, developmental neurotoxin, and endocrine disruptor in humans.

- Tetrabromobisphenol (TBBPA)

TBBPA decomposes into various byproducts such as bisphenol A, di- and tri-bromophenol, and 2,4,6-tribromophenol when exposed to UV irradiation. In contrast, PBDEs, including 3,3',4,4',5,5',6,6'-decabromodiphenyl ether (BDE-209), degrade in both organic and aqueous environments [115]. The chemical structure of TBBPA is primarily covalently bonded to polymers (approximately 90%), which reduces its potential for environmental leaching compared to other brominated flame retardants (BFRs) that act as additives [109,111]. The International Agency for Research on Cancer (IARC) has classified TBBPA as a probable carcinogen [116]. TBBPA derivatives, especially ethers, are considered biologically active and may adversely affect human health [109]. Due to its high lipophilicity and low aqueous solubility, TBBPA tends to adsorb onto soil surfaces, increasing the risk of environmental contamination [117–121].

- Polybrominated Biphenyls (PBBs)

PBBs are halogenated compounds in which one to ten hydrogen atoms in biphenyl are replaced with bromine atoms in various combinations. At room temperature, they typically appear as beige powders, white, or off-white substances. These compounds are used in numerous applications, including electronics, synthetic fibers, lacquers, and vehicle upholstery. PBBs are characterized by their high volatility and water insolubility, making them extremely stable and persistent in the environment [122]. In 1976, the United States banned PBBs after they were found in animal feed, leading to the exposure of millions of people through the consumption of contaminated food such as milk, meat, and eggs. The International Agency for Research on Cancer (IARC) has classified PBBs as "possibly carcinogenic" to humans. They were also banned in the European Union in 1984 [110].

- Novel Brominated Fire Retardants

In response to legislative restrictions on traditional brominated flame retardants (BFRs) like PBDEs, novel brominated flame retardants (NBFRs) have been developed as alternatives. These compounds are also referred to as "new", "emerging", "non-PBDEs", "current-use", or "alternate" BFRs [111]. NBFRs are defined as those BFRs that are either newly introduced to the market or have been recently detected in the environment [111]. Examples are mentioned in Table 3.

Table 3. Risks of various types of novel brominated flame retardants on living beings.

	Novel Bromine Fire Retardants		References
1	2 ethylhexyl-2,3,4,5 tetrabromobenzoate (EH-TBB)	Potentially an endocrine disruptor	[93]
2	Bis (2-ethylhexyl) tetrabromophthalate (BEH-TEBP)	Potentially an endocrine disruptor and very toxic to aquatic life with long lasting effects	[123]
3	Decabromodiphenyl ethane (DBDPE)	Potentially an endocrine disruptor and very toxic to aquatic life with long lasting effects	[93]
4	1,2-bis (2,4,6 tribromophenoxy) ethane (BTBPE)	Potentially an endocrine disruptor Suspected to be a carcinogen and mutagen	[93]
5	1,2 bromo-4-(1,2 dibromoethyl)cyclohexane (DBE-DBCH)	Suspected to be a carcinogen and mutagen	[124]
6	Tetrabromobisphenol A Bis (2,3 dibromopropyl)ether (TBBPA-BDBPE)	Potentially bioaccumulate and toxic endocrine disruptor	[123]
7	Hexabromo benzene (HBB)	Suspected to be bio-accumulative	[93]

5.2. Health Effects of BFR and Chemical Exposure: Developmental, Neurological, and Endocrine Disruption Risks

The health risks stemming from exposure to Brominated Flame Retardants (BFRs) can be categorized into five main areas: thyroid disorders, diabetes, reproductive health, and neurobehavioral and developmental disorders. Specifically, PBDEs, a subset of BFRs, have been associated with various adverse health outcomes including neurotoxicity, thyroid hormone dysregulation, endocrine disruption, and compromised semen quality [125]. Given that PBDEs can traverse the placental barrier, maternal exposure can approximate fetal exposure.

Thyroid Disorders: PBDE exposure during critical developmental stages can disrupt thyroid hormone (TH) levels, impairing brain growth and differentiation, potentially leading to mental retardation. Even small deviations in TH levels during pregnancy or at birth have been linked to cognitive deficits. Studies on rodents have consistently demonstrated reductions in thyroid stimulating hormone (TSH) following developmental exposure to PBDEs, underscoring their thyroid disrupting potential [125].

Diabetes: While some studies, such as Turyk et al. [126] have not found clear associations between PBDE exposure and diabetes, they suggest that PBDE body burden may impact diabetes outcomes in individuals with hypothyroid disease.

Reproductive Health: BFR exposure has been linked to both direct and indirect effects on reproductive health, with implications for pediatric outcomes. High prenatal exposure to PBDEs has been associated with early pubertal development in girls and irregular menstrual periods. Additionally, sons of women exposed to elevated levels of BFRs exhibited an increased likelihood of male genitourinary conditions. Maternal PBDE concentrations have also been correlated with reduced infant birth weights and decreased fecundability [126,127].

Neurodevelopment: Studies on mice have demonstrated the developmental neurotoxicity of various PBDE congeners, resulting in long-term alterations in spontaneous locomotor activity. Furthermore, children exposed to higher levels of PBDEs exhibited lower scores on mental and physical developmental tests during early childhood, suggesting potential neurodevelopmental impacts [128,129].

5.3. Environmental Hazards of BFRs and Associated Chemicals

BFRs have recently sparked much debate because of their long-term environmental toxicity, persistence, and bioaccumulation [130]. The most significant constraints are the maximum toxicity in living beings, and alternative uses of BFRs are the most significant

limitations to BFR commercial applications. BFRs, including PBDEs, TBBPA, and HBCD, have higher concentrations in humans and wildlife due to their large manufacturing volume. Other types of HBCD and PBBs are created in small amounts and have little or no impact on humans or the environment. Bioaccumulation provides information about chemicals prevalent in living organisms. BFRs enter the aquatic ecosystem through point and non-point sources, through various partitioning, degrading, and transit processes. BFRs with high lipophilicity and K_{ow} -related increasing molecular weight may have the tendency to accumulate at higher levels through the food chain. However, high lipophilicity often contributes to low solubility, high adsorption on sediment, or poor oral absorption. They also persist within the human body for a long period of time after ingestion as they are stored in lipid deposits. Several food items (dairy products, fish, meat, eggs, poultry) have been recognized as the principal source of BFR exposure in the general population. In the years 2001–2009, the European monitoring programme reported for eight PBDEs (BDE-28, -47, -99, -100, -153, -154, -183, and -209) in 4000 samples of food. BDE-209 was maximum in plant- and animal-based foods items, while an elevated concentration of BDE-47 was found in fish and child diet products [125,131].

5.4. Regulatory Frameworks and Risk Mitigation Strategies for BFR and Chemical Management

Regulatory frameworks and risk mitigation strategies for managing Brominated Flame Retardants (BFRs) and other chemicals aim to safeguard both human health and the environment. Notably, BFRs like PBDEs, Polychlorinated Biphenyls (PCBs), Hexabromocyclododecane (HBCD), Tetrabromobisphenol A, and DBDPE have been classified as Persistent Organic Pollutants (POPs) by the Stockholm Convention, leading to restrictions or outright bans on their use.

Directive 2003/11/EC prohibits the marketing and use of pentaBDEs and octaBDEs in concentrations exceeding 0.1% by mass. Furthermore, Directive 2002/95/EC restricts the presence of PBBs and PBDEs in new electrical and electronic equipment introduced to the market since July 2006, although decaBDE use in polymeric applications was initially exempted. However, a subsequent ruling by the European Court of Justice in July 2008 prohibited decaBDE utilization in electronics and electrical applications. Nonetheless, decaBDE remains permissible in plastics as per EU directives.

Furthermore, the European Chemicals Agency (ECHA), under the REACH framework, imposed restrictions on HBCD usage within the EU, permitting its application only for authorized specific purposes. These regulatory measures underscore the commitment to minimizing BFR exposure and mitigating associated risks, aligning with international efforts to address the environmental and health implications posed by these persistent pollutants [125].

6. Conclusions and Future Perspectives

BFRs play a crucial role in enhancing the fire safety of numerous consumer products. However, their widespread use has resulted in significant environmental and health concerns due to their persistence, bioaccumulation, and potential toxicity. This review has underscored the importance of understanding the analytical methods for detecting and quantifying BFRs, their distribution in various environmental matrices, their transport mechanisms, and the associated risks. Current research demonstrates that BFRs can significantly impact endocrine, reproductive, and neurological systems, highlighting the need for comprehensive monitoring and management strategies. While advanced analytical techniques have improved our ability to detect and quantify BFRs, gaps remain in fully understanding their long-term effects and the mechanisms underlying their toxicity.

Future Perspectives

- **Enhanced Analytical Techniques:** The continued development of more sensitive and selective analytical methods is crucial. This includes improving detection limits,

increasing the accuracy of quantification, and expanding the range of detectable BFRs in complex matrices.

- **Comprehensive Monitoring Programs:** Establishing robust, large-scale monitoring programs to track the occurrence and distribution of BFRs across different environmental and biological media. This will provide a clearer picture of their global impact and aid in risk assessment.
- **Mechanistic Studies:** Further research into the mechanisms of BFR toxicity is needed. Understanding how BFRs interact with biological systems at the molecular level will help elucidate their health effects and support the development of mitigation strategies.
- **Regulatory Frameworks:** Strengthening regulatory frameworks to manage the production, use, and disposal of BFRs. This includes phasing out the most hazardous BFRs, promoting safer alternatives, and enforcing stricter environmental and health standards.

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