



Review article

Management of waste containing polybrominated diphenyl ethers: A review

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are substances used as flame retardants that can be released into the environment through volatilization, leaching, and abrasion throughout the useful life of the articles that contain them, especially at the end of their life cycle because PBDEs do not chemically bind to the initial materials (electrical and electronic equipment, textiles, materials used in transport vehicles, toys, among others). Research has shown that the toxic effects and risks of PBDEs to ecosystems and human health are greater than their benefits owing to their neurotoxicity, toxicity to the endocrine and reproductive systems, and possible carcinogenicity. This review shows the current situation of management of waste containing PBDEs (plastics, sludge, soil, and ash) and the characterization, valorization, treatment, and final disposal of these wastes, to minimize their impacts on ecosystems and human health are analyzed. Wastes with concentrations greater than 1000 mg/kg of PBDE should be considered as hazardous waste. This research identifies the methods available to reduce the risk in their management; at the same time, it provides innovative ideas for the integrated management of PBDE-containing wastes, prioritizing their valorization and disposal.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of synthetic compounds widely used as flame retardants and may be found in various plastics commonly used in furniture, textiles, electrical and electronic equipment (WEEE), transportation sector, toys, among others, to retard combustion and provide escape time in case of fire [1–3]. However, the benefits of PBDEs are offset by their toxic effects and risks to ecosystems and human health. Scientific studies conducted in the last two decades have demonstrated their presence worldwide and their persistence in soil, sediment, and air [4,5].

Therefore, PBDEs have gradually been included in the list of persistent organic pollutants (POPs). The Conference of the Parties to the Stockholm Convention prohibits the production of penta-BDE formulations that include tetrabromodiphenyl ether (tetra-BDE) and pentabromodiphenyl ether (penta-BDE) (decision SC-4/18); it also prohibits octa-PBD formulations that include, hexabromodiphenyl ether (hexa-BDE) and heptabromodiphenyl ether (hepta-BDE) (decision SC-4/14), these PBDEs were included in Annex A in May 2009 [6,7]; finally, prohibits the production of decabromodiphenyl ether (deca-BDE or BDE-209) formulations, was included in Annex A

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(elimination) of the Convention (decision SC-8/10) in May 2017. The only permitted uses are in the production of aircraft and spare parts for motor and agricultural vehicles or machinery manufactured before its restriction [8], in accordance with Part IX of Annex A.

Currently, although the commercial production of PBDEs is prohibited, many products and materials contain them; and the emissions generated from these products and materials during their useful life are relevant [3,7]. Thus, PBDEs have been found in children's toys and kitchen utensils [9].

Therefore, the generation of waste containing PBDEs is of great concern, the greatest of which is their presence in recycled plastics. As plastic recycling processes are not designed to remove chemical additives, PBDEs in obsolete plastic items may remain in the materials after reprocessing. This means that PBDEs in one type of plastic product (e.g., WEEE) can later be introduced into recycled plastics used for other applications [10–12]. There are also secondary wastes formed by the release of PBDEs from plastics, such as sludge from wastewater treatment plants (WWTPs), sediments, dust and soil from e-waste recovery sites, bottom ash, among others [13–16].

The integrated management of waste containing PBDEs is of great importance because it minimizes the risks to human health and the environment. This integrated management according to D.S. 014-2017-MINAM includes the stages of characterization, valorization, treatment, and final disposal.

Management of waste containing PBDEs involves a selection process based on their concentration in the waste: if their concentration is less than 1,000 mg/kg (1.0×10^6 ng/g), the waste can be recycled and if their concentration is higher, the waste is classified as hazardous waste [17] and must be pretreated or treated before valorization to make new plastics, or else disposed of by the pyrolysis process for cogeneration, or disposed of in a safety landfill.

Secondary wastes formed by the release of PBDEs to the environment such as ashes, sludge, sediments, and soil with high PBDE content should be recirculated in the incineration furnace with gasification-moderate or intense low oxygen dilution (GASMILD)-type

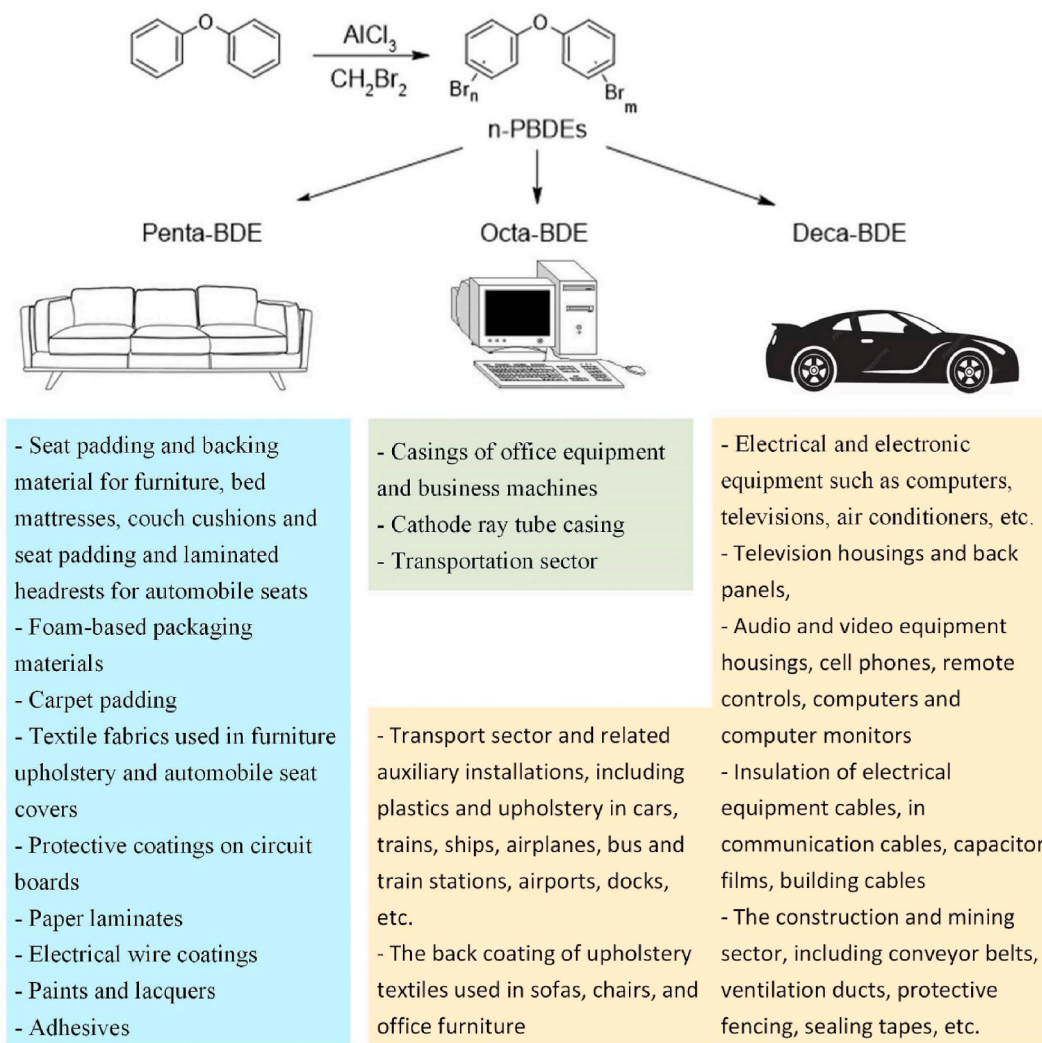


Fig. 1. Generation mechanism and presence of PBDE in different materials.

technologies or sent to a safe landfill; gaseous emissions with PBDE should be incinerated at 1,100 °C so that during pyrolysis, emissions are below the detectable limit [17].

In this review, the characterization and management technologies of PBDE-containing waste such as plastics, sludge, soils, and ashes have been thoroughly discussed to minimize the release of hazardous substances into the environment as part of the circular economy. This research prioritizes the valorization of PBDE-containing waste and proposes integrated waste management.

2. PBDE generation

PBDEs are produced through bromination of diphenyl ether in the presence of aluminum chloride (AlCl_3) as the catalyst (Friedel–Crafts catalyst) in dibromomethane solvent [4]. PBDEs include 209 congeners characterized by the amount of bromine (Br) in each ring. PBDEs have a formula of $\text{C}_{12}\text{H}_{(10-x)}\text{Br}_x\text{O}$, where $x = n + m$, x is the sum of Br of each ring, and can vary from 1 to 10 (Fig. 1). Commercial formulations include three PBDEs: penta-BDE, octa-BDE, and deca-BDE. However, each formulation is a mixture of diphenyl ethers with different degrees of bromination. PBDEs are chemically stable compounds with low vapor pressures, which favors their permanence in the environment. Boiling temperatures vary between 310 °C and 425 °C [18,19]. Their solubility is high in organic solvents and low in water, which is accentuated by increasing number of Br atoms in the molecule, which favors their bioaccumulation in living organisms [18] (Table 1).

Penta-BDE products were dominated by the BDE congeners BDE-47, BDE-74, BDE-99, and BDE-100 [1,20], and were generally applied to soft polymers such as flexible polyurethane foam which was 95 % used in seat padding and backing material for household furniture, bed mattresses, couch cushions, and in seat padding and laminated headrests for automobile seats, and 5 % in the treatment of foam-based packaging materials and carpet padding, as well as other materials such as textiles, fabrics, polyesters used in furniture upholstery and automobile seat covers, in epoxy resins used as protective coatings for electrical wires and circuit boards, in unsaturated polyesters, in paper laminates, in flexible polyvinyl chloride used as a coating for electrical cables, in rubber, in paints and lacquers, in rigid polyurethane foam and in adhesives [21–23].

The octa-BDE formulation contained congeners BDE-153, BDE-154, BDE-175, BDE-196, DBE-197, BDE-207, and mainly BDE-183 [1,20] which was used 95 % in hard plastics such as acrylonitrile butadiene styrene, and 5 % in high impact polystyrene, poly(butylene terephthalate), polyamide polymers, polycarbonate, nylon, polyolefin, phenol-formaldehyde resins, low-density polyethylene, polycarbonate, and unsaturated polyesters. These materials were used to manufacture the outer casings of electronic and electrical equipment, such as PC casings, office equipment such as copying machines and business printers, particularly for cathode ray tube casings; their use was also applied in the transportation sector [21–23].

The deca-BDE formulation contained a fully brominated compound (BDE-209), with small proportions of nona- (BDE-206, BDE-207, and BDE-208) and octa-BDE (BDE-196) [1,20]. Deca-BDE was applied in common plastic such as high impact polystyrene, polybutylene terephthalate, nylon, polypropylene, polyethylene, and unsaturated polyesters. These were used 70 % in electrical and electronic equipment such as computers, televisions, air conditioners, washing machines, refrigerator components, stove hoods, in the manufacture of television housings and back panels, in audio and video equipment housings, cell phones, remote controls, computers and computer monitors; 10 % in the insulation of electrical equipment cables, in communication cables, capacitor films, building cables, 10 % in the transport sector and related auxiliary installations, including plastics and upholstery in cars, trains, ships, airplanes, bus and train stations, airports, docks, etc.; 10 % in the construction and mining sector, including conveyor belts, ventilation ducts, protective fencing, sealing tapes, etc. Deca-BDE is also used to treat the back coating of upholstery textiles used in sofas, chairs, and office furniture [4,20,22–24] (Fig. 1).

According to the Third Report of the Stockholm Convention [25], the residues that may contain PBDEs are the following:

Table 1
Properties of some of the PBDE congeners [18].

Property	Pentabromodiphenyl ether (Penta-BDE)	Octabromodiphenyl ether (Octa-BDE)	Decabromodiphenyl ether (Deca-BDE)
Molecular mass (g/mol)	485.8 (tetra-BDE) 564.7 (penta-BDE)	643.6 (hexa-BDE) 722.3 (hepta-BDE) 801.4 (octa-BDE)	880.4 (nona-BDE) 959.2 (deca-BDE)
Physical state (20 °C; 101.325 kPa)	Viscous liquid or semisolid, white crystalline solid (pure penta-BDE isomers)	Dust	Crystalline powder
Vapor pressure (21 °C; Pa)	4.69×10^{-5}	6.59×10^{-6} 1.58×10^{-6} – 4.68×10^{-7} (hexa- and hepta-BDE; 25 °C)	4.63×10^{-6} 2.95×10^{-9} (estimated for deca-BDE)
Solubility in water (25 °C; $\mu\text{g/L}$)	10.9 (tetra-BDE) 2.4 (penta-BDE)	0.5	<0.1
Registration K_{ow}	10.53–11.31 (tetra- and penta-BDE)	12.78–13.61 (hepta- and octa-BDE)	14.44–15.27 (estimated for nona- and deca- BDE)
Henry's law constant (25 °C; $\text{Pa}\cdot\text{m}^3/\text{mol}$)	11	10.6 (estimated)	>44 (estimated)

- WEEE: computers, home electronic equipment, office equipment, household and other appliances containing laminated printed circuit boards, plastic outer casings, and plastic inner parts such as various components produced in small quantities with instrument cases made of rigid polyurethane elastomers.
- Means of transportation: automobiles, railways, airplanes, and ships with interiors made of textile and plastic materials and electrical components.
- Construction materials: foam fillings, insulating boards, foam insulation, pipes, wall and floor panels, plastic coatings, resins, etc.
- Furniture: upholstered furniture, furniture covers, mattresses, and flexible foam components, packaging made from polyurethane foam.
- Textile products: curtains, carpets, foam sheets, tents, waterproof tarpaulins, work clothes and protective clothing.
- Packaging: packaging made from polyurethane foam.

PBDEs have been mainly manufactured in the United States, Israel, Germany, the Netherlands, Japan, and China. In 1999, approximately 67,000 tonnes of the three commercial mixtures (penta-, octa-, deca-BDE) were sold for industrial use [26].

Before 2004, the use of penta-BDE was very common: 85,000 tonnes was used in the United States (97 % of world production) and 15,000 tonnes in Europe [27]. Commercial penta-BDE (which includes the congeners tetra-BDE and penta-BDE) and octa-BDE (which includes the congeners hexa-BDE and hepta-BDE) mixtures have been banned in the European Union since 2004, and in China since March 2007 [23] by Stockholm Convention decisions SC-4/18 and SC-4/14, respectively (Table 2). World production of deca-BDE between 1970 and 2005 reached approximately 1.25 million tonnes. Owing to Stockholm Convention decision SC-8/10, the United States banned the use of deca-BDE in residential televisions (TVs), computers, and upholstered furniture in 2011 and suspended the manufacture and import of PBDEs in 2013. The use of deca-BDE, called BDE-209, is restricted to the production of parts for vehicles and aircraft and textile products excluding clothing and toys, building insulation, and enclosures with a content of less than 10 %. With these decisions, it was estimated that by 2020, the amount of PBDE produced would be 1.60 million tonnes [7,28] (Table 3), consisting mainly of deca-BDE, with a final disposal requirement of 0.01 million tonnes [29].

However, articles manufactured before their ban are still in use and may be accumulated as common waste. Therefore, substantial volumes of these substances remain in circulation through recycling processes [7,28].

PBDEs have been detected in different places on the planet, including Antarctica and northern polar regions [31]. In many places around the world, PBDE contamination occurs due to waste landfills. In Nigeria, analysis of soil and plant samples collected from landfills and nearby sites demonstrated that PBDE contamination in soil is sufficient to cause significant exposure of humans through accumulation because the levels in the surface layer of the soil were 112–366 ng/g dm while those in the bottom soil layer were 26.8–39.7 ng/g dm [32]. For plants, levels in the roots were 25.0–60.5 ng/g dm and those in the shoots were 8.45–32.2 ng/g dm. Hence, there is a significant risk to residents and ecosystems in places near landfills. PBDEs can be released into the environment during their manufacture, throughout the useful life of the articles that contain them, and during waste management. When introduced into the environment, PBDEs adhere to dust particles, which accumulate on the surfaces of items, e.g., electrical equipment, and are diffused into various environmental compartments [25].

3. Characterization of waste that containing PBDEs

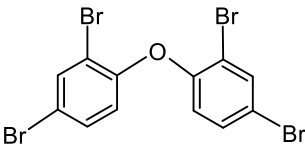
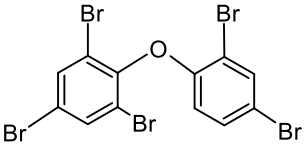
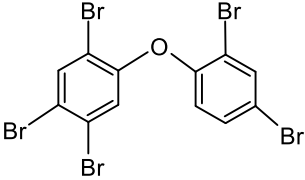
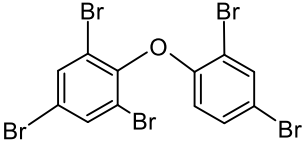
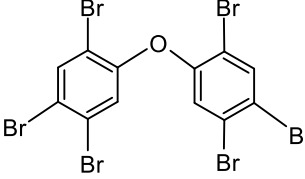
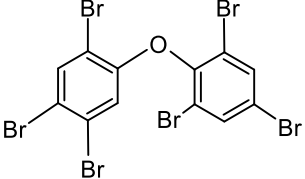
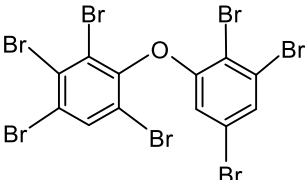
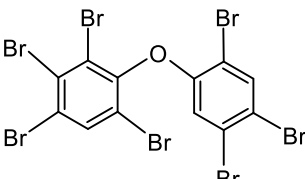
Penta- and octa-BDEs were applied to materials through coating or immersion processes [23,33]. Solid deca-BDE is combined with other ingredients and molded to form the final product. Owing to their structure and chemical properties, PBDEs do not chemically bind to the materials to which they are added [34], and therefore are released from products and materials into the environment during their use. Wastes that may release PBDEs consist of primary plastic wastes from WEEE, textiles, materials used in transport vehicles, and toys, as well as secondary wastes such as dust from waste recycling sites, sludge from WWTPs, ash from municipal waste incineration plants, and dust from disposal sites resuspended by transit. These secondary wastes have a high affinity for PBDEs and form chemical bonds increasing their stability [2].

3.1. Potential PBDE emissions from waste

WEEEs generated in amounts of 4–8 kg per person per year [35,36] have PBDE concentrations of 6.6 to 1.8×10^8 ng/g [10,11,23,37], with CRT-TV monitors and printers having the highest PBDE content and LCD monitors having the lowest content; the most common congener was BDE-209 and the least common were BDE-47 and BDE-99, all of which were detected. Textile wastes used for furniture and foams have wide PBDE concentrations from 1,194.4 to 2.0×10^7 ng/g [23,33,38], with upholstered furniture made from polyurethane foam having the highest values [39] and curtains having the lowest concentration. The congener detected in the highest proportion was BDE-209, and in lower proportion were BDE-206, and BDE-207. Transportation wastes used in parts of automobiles, railways, airplanes, and ships have PBDE concentrations ranging from 9,000 to 6.58×10^7 ng/g, with seat fabric with the highest proportion and foams with the lowest concentration. The congener in the highest proportion was BDE-209, and in lower proportions were BDE-206, BDE-47, and BDE-99 [23,40,41]. Toy waste presented concentrations between 100 and 3.23×10^7 ng/g; toys manufactured before 2016 presented the highest PBDE concentrations [9,23]. The congener with the highest proportion was BDE-209, and in lower proportion were BDE-183, BDE-147, and BDE-196 (Table 4).

Secondary residues such as dust in dwellings near recycling centers contains 44.7 to 0.3×10^6 ng/g [13,14,42–44] and occur during the recycling of these materials, for the processing of new materials with PBDEs, by Stockholm Convention decisions SC-4/14, SC-4/18 and SC-8/10, the highest values are obtained in places where the recycling activity has a larger scale. The shredding process promotes

Table 2
Stockholm convention prohibited BDE products.

Commercial product	Congener	Structure	Name	Decision
Pentabromodiphenyl ether	BDE-47		Tetrabromodiphenyl ether	SC-4/18
	BDE-74		Pentabromodiphenyl ether	
	BDE-99			
	BDE-100			
Octabromodiphenyl ether	BDE-153		Hexabromodiphenyl ether	SC-4/14
	BDE-154			
	BDE-175		Heptabromodiphenyl ether	
	BDE-183			

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Table 2 (continued)

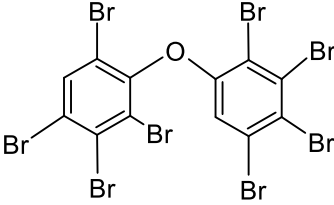
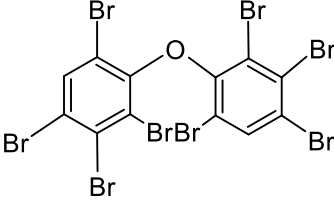
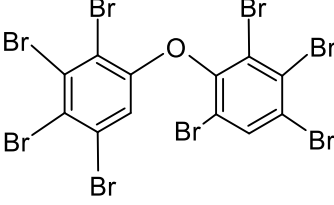
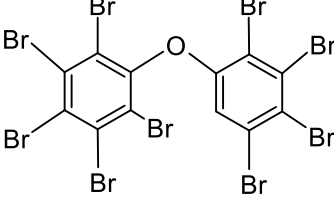
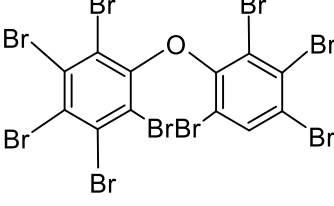
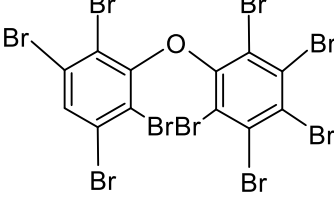
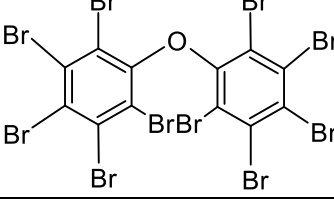
Commercial product	Congener	Structure	Name	Decision
	BDE-196		Octabromodiphenyl ether	
	BDE-197			
Decabromodiphenyl ether	BDE-196		Octabromodiphenyl ether	SC-8/10
	BDE-206		Nonabromodiphenyl ether	
	BDE-207			
	BDE-208			
	BDE-209		Decabromodiphenyl ether	

Table 3
Estimated total production of PBDE from 556 commercial mixtures.

Commercial mix	Quantity (million tonnes) 1970–2005	Estimated in 2020	Reference
Penta-BDE	0.091–0.105	0.175	
Octa-BDE	0.103–0.119	0.130	[7,30]
Deca-BDE	1.100–1.250	1.600	

Table 4
PBDE content in waste.

Waste	Range (ng/g)	Country	Reference
Primary waste			
Electrical and electronic equipment	1,200–180,000,000	Brazil	[12]
	6.6–21,000	Belarus	[11]
	630–15,200	China	[10]
	1,943,000–39,000,000	Miscellaneous	[23]
Textiles	25,922–560,000	Belgium	[33]
	11,843,000–20,003,000	Miscellaneous	[23]
	1,194.4–654,959	Korea	[38]
Transportation	9,000–137,000	Miscellaneous	[23]
	34,500–3,121,000	China	[41]
	1,000–65,842,000	Korea	[40]
Toys	69,000–32,300,000	Miscellaneous	[23]
	100–2,500,000	UK	[9]
Secondary waste			
Dust in dwellings near recycling centers	130–12,000	Vietnam	[13]
	1,375–334,413	China	[42]
	173–237,000	China	[43]
	44.7–247,000	China	[14]
	44.8–63,300	China	[44]
Sludge from WWTPs	131–7,122 BDE-209	Italy	[15]
	230–82,000 BDE-209	Canada	[45]
	9.9–5,010 BDE-209	China	[46]
	200–2,153 BDE-209	China	[47]
	620 BDE-209	Canada	[26]
Municipal waste incinerator ash (bottom ash)	20.4–186	Taiwan	[48]
	29–243	Taiwan	[49]
	1.7–4.1	Japan	[50]
Landfill soil resuspension dust	12.3–824	China	[51]
	1,440	China	[52]
	13,330–71,840	Nigeria – China	[53]
	2.4–95	Asia	[16]
	141–302	Nigeria	[54]

the generation and emission of contaminated dust. In Belgium [55], the presence of PBDEs was found in 16 waste-crushing plants. The results showed 253.8 ng/m²·day of BDE-209 in areas near the waste processing plants. These concentrations are high compared to those observed in most remote (0.45 ng/m²·day) and rural areas studied around the world (4.3 ng/m²·day) and were like those measured in other shredding sites (203 ng/m²·day) in China; therefore, the effects of this exposure on the health of workers and residents in the vicinity of these facilities are a great concern. In the period of 2017–2020 in China, PBDE content in household dust increased from 1,844 to 8,648 ng/g [56], and households near recycling sites presented concentrations between 44 and 63,300 ng/g, much higher than those in other locations. The congener in the highest proportion was BDE-209 and in lower proportion were BDE-206, BDE-207, BDE-208, and BDE-183 [44]. Sludge residues from WWTPs contain 9.9 to 0.082 × 10⁶ ng/g [15,26,45–47], whereas that from primary treatment plants has a higher concentration than biological treatment sludge due to higher biological degradation of PBDEs. The congener in the highest proportion was BDE-209 and in lower proportion were BDE-47, BDE-99, BDE-153, BDE-206, BDE-207, and BDE-208. Wastes from incineration plants, such as bottom ash, have concentrations of 1.7–243 ng/g [48–50]; these concentrations are lower than those reported for other wastes. Dust residues in landfills resulting from soil resuspension by passing vehicles contain 2.4 to 0.072 × 10⁶ ng/g. The congener in the highest proportion was BDE-209 and in lower proportion were BDE-47, BDE-99, BDE-153, BDE-207, and BDE-208 [16,32,51–53] (Table 4).

The concentration of BDE-209 found in the different studies carried out between 2007 and 2024, presented a higher value in plastics used in the transportation sector; while the concentration in secondary waste, ashes, and landfill soils, presented the lowest values (Fig. 2) [9–11,13–16,26,37,38,40–44,46–49,52,53]. PBDEs released from waste are lipophilic compounds and tend to accumulate along the food chain. Their presence has been recorded in food products for direct consumption such as fish and seafood and indirect consumption such as fishmeal [57]. In fishmeal samples from different continents and countries (the United States, China, Chile, Peru, Ecuador, Russia, Denmark, Vietnam, Thailand, and Malaysia), an average PBDE value of 75.8 ng/g lipid was determined.

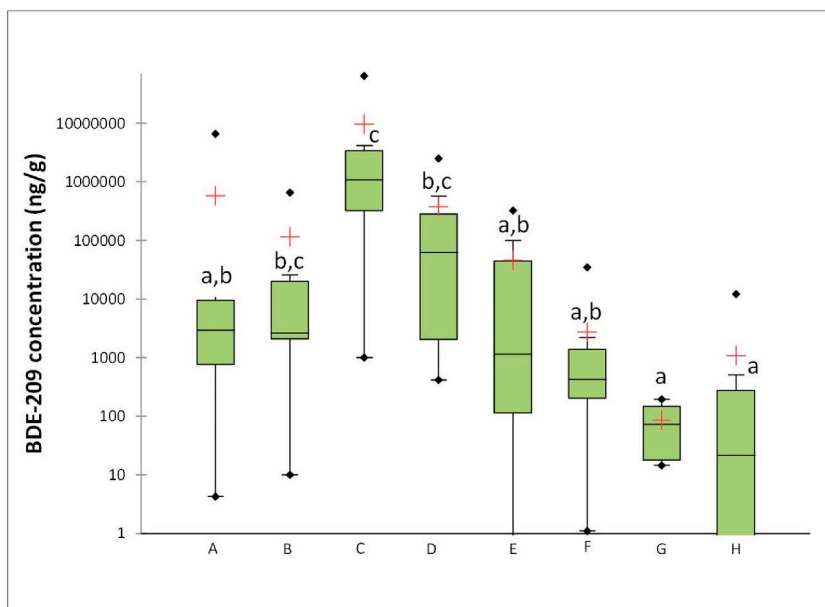


Fig. 2. Plot of BDE-209 concentrations, mean (+), minimum and maximum values (◆) of primary (A = electrical and electronic equipment, B = textiles, C = transportation, D = toys) and secondary (E = dust in dwellings near recycling centers, F = sludge from WWTPs, G = Municipal waste incinerator ash - bottom ash, H = landfill soil resuspension dust) residues. ^{a,b,c} Different letters imply statistically significant differences ($p < 0.05$) determined by Dunn's multiple pairwise comparisons.

The congener in the highest proportion in fish feed was BDE-209 and in lower proportion were BDE-47 and BDE-28. The highest average PBDE values were detected in samples from China (78.2 ng/g lipid) and the United States (22.0 ng/g lipid). Fishmeal from South America contained 3.98 ng/g lipid of PBDEs. The highest level of PBDEs (1,498 ng/g lipid) was found in a fishmeal sample from northern China [58].

Several studies have indicated that brominated flame retardants (BFRs) are neurotoxic, toxic to the endocrine system and particularly the reproductive system, and even carcinogenic. PBDE levels are associated with DNA methylation (DNAm) changes in blood, DNAm is a biomarker of serum PBDE levels and is associated with the risk of developing breast cancer at the time of menopause [59–61]. Exposure to PBDEs poses a significant risk for breast cancer; generally, exposure to all compounds with low bromination numbers in their structure could considerably increase the risk of endocrine-related cancers [62]. The risk is higher in women; however, comprehensive understanding of the toxic effects of PBDEs on the human body is still lacking [63]. Exposure routes include ingestion of foods containing PBDEs and ingestion of dust with PBDEs, the latter being the most common route of exposure for school and preschool children [64], mainly because their activities are performed at the ground level and they have a greater willingness to put their hands into their mouth.

3.2. Soil and solid waste analysis method

PBDEs are detected in the laboratory according to the EPA standardized method 1614A. A portion of the waste is crushed and pulverized, and PBDEs are extracted with toluene for 30 min. Other extraction techniques that have been developed and show good efficiency for PBDE extraction are ultrasound-assisted extraction using QuEChERS and microwave-assisted extraction [2]. The crude extracts are combined with an internal standard isotopically labeled with $^{13}\text{C}_{12}$ -labeled PBDEs and are analyzed via high-resolution gas chromatography with high-resolution mass spectrometry upon isotopic dilution [37,50].

The detection of PBDEs is expensive and requires specialized laboratories and highly trained personnel. Attempts have been made to apply X-ray fluorescence (XRF) to perform measurements more quickly; however, currently, the results of these studies have concluded that XRF only measures elemental Br and cannot detect the exact concentrations of the different isomers [65]. Additionally, the limit of quantification for Br is 5,000 ng/g, a high value compared to the required limits. Therefore, there is a need to develop more accessible analysis methods [9,65].

4. The integrated management of waste containing PBDEs

Waste plastics, sludge, sediments, ashes, and soils containing PBDEs must be managed in an integrated manner to minimize their entry into the environment. This management involves proper characterization, segregation, storage and recovery processes, treatment, and final disposal. Valorization produces new plastic products, energy, and soil material. Pretreatment conditions the PBDE-containing waste for a recovery or final disposal process, such as shredding, manual separation, and washing. Treatment aims to

reduce the PBDE concentration or immobilize the PBDE in the waste to be treated. At final disposal, the treated PBDE wastes are either permanently stored or destroyed before release (Fig. 3).

4.1. Valorization of waste containing PBDEs

4.1.1. Recycling of plastics containing PBDEs

Recycling of plastics containing PBDEs is a process allowed by Stockholm Convention decisions SC-4/18 and SC-4/14 for the production of articles that may contain flame retardant components. In the plastics recycling process, thermal treatment is required for the formation of the new plastic; but the formation of dioxins and furans makes the thermal treatment of waste on an industrial scale difficult, and in some cases, it may be necessary to separate PBDEs from polymeric materials before treatment, which considerably reduces the economic benefits of thermal treatment of waste.

Several studies have shown that when plastics are recycled via thermal treatment without pretreatment, the polymer matrix considerably affects the yield and formation temperature of polybrominated dioxins and furans during pyrolysis and combustion of PBDE-containing materials. Pure PBDEs decompose to form dioxins at $>600\text{ }^{\circ}\text{C}$ [34]; however, co-pyrolysis of the polystyrene polymer matrix with PBDEs leads to the formation of dioxins at lower temperatures ($350\text{ }^{\circ}\text{C}$ - $400\text{ }^{\circ}\text{C}$) [66]. Polyester-based plastics such as polyethylene terephthalate and poly(butylene terephthalate) generate dioxins and furans compared to polyethylene, polystyrene, and polypropylene when subjected to high temperatures [67,68]. Generally, dioxins are formed at $600\text{ }^{\circ}\text{C}$ - $1,000\text{ }^{\circ}\text{C}$ when plastic mixtures undergo thermal treatment [34]. Another study has determined that 10 % of recycled plastic products have unintentional concentrations of PBDEs insufficient to confer fire resistance [50], suggesting the incorporation of plastics containing PBDE from WEEE.

Pretreatment is also required to avoid the generation of dioxins with thermal treatment. The application of mechanical pretreatments, such as manual dismantling, is necessary in the recycling of plastics containing PBDEs, such as those used in TVs and monitors; for vehicle plastics with high foam contents, dismantling, decontamination, and shredding are necessary. Another form of recycling is by chemical treatment involving foam depolymerization processes for the production of monomers and new polymers [69]. These pretreatments can involve photodegradation by ultraviolet light in a low-pressure reactor, where 90 % PBDE degradation is achieved in 15 min, maintaining the thermal and structural properties of the virgin polymers [70]. Another pretreatment is the mechanochemical treatment in a ball mill, where friction generates enough energy for the debromination and mineralization within 8 h of PBDEs in the presence of zero-valent metals such as Fe-SiO₂ [1,71].

4.1.2. Energy recovery from plastics containing PBDEs

Valorization by energy recovery from plastics through combustion by pyrolysis or incineration in 2018 was 5,500 tonnes miles [72]. In many cases, this recovery includes the uses of plastic waste containing PBDEs that unintentionally generate dibenzo-p-dioxins and brominated dibenzofurans (PBDFs), substances extremely dangerous for human health and the environment [18]. Knowledge of the mechanism of this transformation is limited due to the low number of studies and the analytic difficulty of detecting these substances. Recently, a transformation mechanism has been proposed, where it is observed that furans formation occurs by five pathways: the first and most accepted one is by direct removal of HB, the second pathway is by removal of Br₂, the third pathway is by the connection of the ortho C-(H) atoms, the fourth pathway is by ortho C-Br bond fission and cyclization, and the fifth pathway is by keto-ether isomerism and binding of the pivot carbon with bromination [67] (Fig. 4). This study confirms that the arrangement of Br

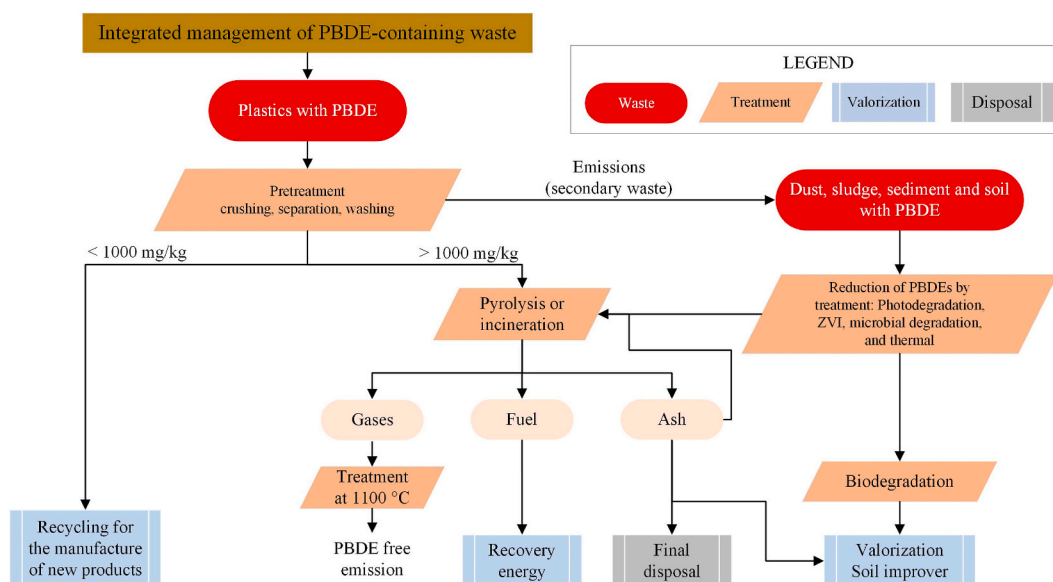


Fig. 3. Flowchart for the integrated management of PBDE-containing waste.

atoms and the level of bromination influence the formation of polybrominated dioxins and furans from PBDEs: less brominated compounds generate more dioxanes and furans during pyrolysis and combustion than highly brominated PBDEs. To avoid the formation of PBDFS in the valorization of plastics containing PBDEs by energy recovery, plastics with concentrations less than 1000 mg/kg that have undergone PBDE degradation pretreatment [1,69–71] and flue gas post-treatment at 1100 °C [69] should be used.

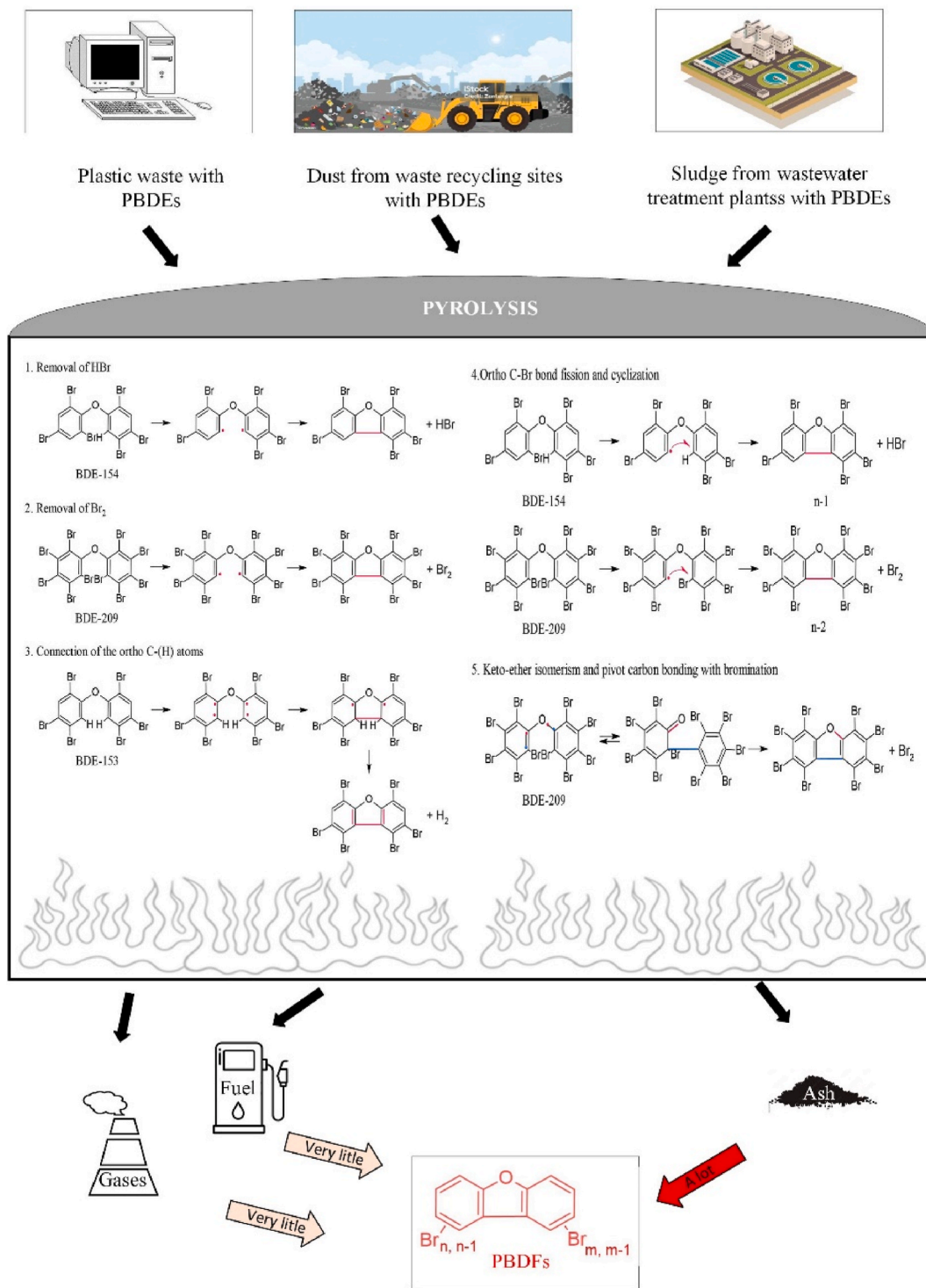


Fig. 4. Five-step mechanism for transforming PBDEs to furans, adapted from Wang et al. [67].

4.1.3. Valorization of PBDE-containing soils, sludge, and ash

One way to valorize PBDE-containing soils is through their industrial co-processing in the production of cement clinker. Soils with PBDE concentrations of 4,160–25,000 mg/kg can be treated, with PBDE removal efficiencies greater than 99.9 %, and included in cement production [73].

Agricultural reuse of biosolids (sludge or sediments) may represent an important and unregulated potential pathway for the transfer of PBDEs from WWTPs to soil. PBDEs have been shown to persist in soils receiving contaminated biosolids with residence times of up to 1,440 days [21]. Moreover, numerous studies have shown concerning data: PBDEs can move from soil to the edible parts of food crops, indicating that agricultural reuse of contaminated biosolids poses a risk of dietary exposure to the human population. Currently, no limits have been established for PBDE levels in sewage sludge. Pretreatment of soils and sludge by ball mill or incineration allows PBDE removal, reducing the risk of mobilization to groundwater or crops [1,71,74] when disposed of on the ground.

4.2. PBDE-containing waste treatment

Treatment methodologies for wastes such as sludge, sediments, soils, or ashes containing PBDEs aim to degrade, stabilize, or immobilize PBDEs from the solid matrix reducing the risk of release into the environment. The methodologies reviewed include physicochemical treatment, chemical treatment, biological treatment, among others.

4.2.1. Chemical treatment

In plastic, soil, sludge, and sediment systems, the degradation of PBDEs occurs through photodegradation and reduction by zero-valent iron (ZVI) [1,70].

Photodegradation treatment, applied to PBDE-containing plastics, can remove more than 90 % of the PBDE without damaging the plastic matrix when using a low-pressure reactor and irradiation for 15 min with ultraviolet/visible light between 240 and 400 nm. The degradation mechanism is by debromination of the PBDE and photooxidation of the by-products until their mineralization to carbon dioxide and water [1,70].

The ZVI treatment comprises three pathways. In the first pathway, the oxidation of water transfers electrons from the ZVI surface to the PBDE. In the second pathway, organic compounds are reduced by a corrosion intermediate (Fe^{2+}). In the third pathway, reductive debromination occurs by the hydrogen produced via corrosion [1–3,71]. This treatment can be enhanced by the use of a ball mill that provides sufficient activation energy to promote complete mineralization of PBDEs [71].

An alternative treatment for the processing of PBDE-containing ash and sludge from WWTPs is thermal treatment with recirculation of sludge and ash using the GASMILD technology, which achieves a PBDE removal of up to 98.4 % [74]. In this system, uniform temperature distribution is achieved and ignition of the fuel material is not affected, because the ash suspended in the gas stream enhances heat absorption, self-ignition and promotes turbulent mixing, which improves combustion.

4.2.2. Physicochemical treatment

As PBDEs accumulate in sludge, it is necessary to develop more advanced sludge treatment methods, because conventional treatments allow low removal of PBDEs. In WWTPs of Canada, Italy, and China, BDE-209 was the predominant congener found in biosolids in the range of 9.9–82000 ng/g dm, followed by BDE-47 and BDE-99. These congeners constituted a substantial proportion of PBDE loading in raw sludge and biosolids [15,26,45,47].

Physicochemical treatments of PBDE-containing sludge, such as pelletization performed by heating the sludge for 20 min at a temperature between 85 and 90 °C, and alkaline stabilization performed by the addition of cement kiln dust and lime and drying at 50 °C, did not considerably alter the overall and individual congener loading in the raw sludge and treated biosolids. Unlike physical and chemical treatment processes, important transformations were observed in a wide range of congeners in biological sludge treatment processes. However, the average mass accumulation of the most toxic lower congeners was close to 5 % of the total mass flux of Σ PBDE–Br in the treated biosolids [26]. The treatment of PBDE-containing sludge with a ball mill when using zero iron as a reducing agent for PBDE-containing plastics can be an important alternative to mineralize PBDEs like that reported by other studies [71], where additionally heating and production of PBDFs is avoided since the energy released by friction is sufficient to carry out mineralization.

4.2.3. Biological treatment

The biological treatment of PBDE-containing wastes involves the evaluation of the natural attenuation, biostimulation, and bioaugmentation processes of a species with the ability to degrade PBDEs under aerobic or anaerobic conditions [3,75–77], as well as the risk involved in the formation of less brominated congeners and their mineralization.

A half-life value of 277.2 days was determined under anaerobic conditions for BDE-209, in sediment by natural attenuation [75]. This value is higher than expected for less brominated PBDEs [1]. Using biostimulation, it was possible to reduce this value to 141.2 days. To simulate biostimulation, sodium formate as a carbon source and ethanol as an electron donor were added to the sediments. Bioaugmentation was performed by enriching the sediments with the culture of *Dehalobium chloro-coercia* strain DF-1. No modifications were made to the third set to account for natural attenuation. The biostimulation, bioaugmentation, and natural attenuation strategies resulted in BDE-209 reductions of 55.3 %, 40.2 %, and 30.9 %, respectively, after 180 days. The pseudo-first-order rate constants for the reduction were calculated to be 0.0049, 0.0028, and 0.0025 day⁻¹ for biostimulation, bioaugmentation, and natural attenuation, respectively. The degradation rates of BDE-209 reported by other authors determined under different conditions present a variation of two orders of magnitude between the minimum and maximum values (0.00013–0.041 day⁻¹) [75]. The biotransformation mechanism of BDE-209 identified by HRGC/HRMS was presented [76] (Fig. 5).

The low biodegradation of PBDEs in the environment is attributed to their chemical structures. Some authors [77–79] highlight that the resistance of PBDEs to biodegradation is due to energy delocalization and the high density of the electronic cloud, which greatly reduces their susceptibility to nucleophilic attack. This resistance increases with an increasing number of Br atoms, which are larger and further limit the potential of microbial intracellular transformation processes [77].

Biodegradation depends on the number of substituted Br atoms: each congener of PBDEs has different physicochemical properties, persistence, and toxicity; for example, the greater the number of Br substitutions, the lower the water solubility [80]. However, biodegradation changes the behavioral patterns of congeners through the conversion of one congener into another; thus, bio-accumulative congeners can be reduced by biostimulation and source control. The aerobic and anaerobic degradation pathways involve *ortho*-, *meta*-, and *para*-debromination processes, ether-bond cleavage, aromatic ring opening, and oxidation of the formed chains [3,81].

It has been reported that several mixed microorganisms or pure cultures of bacterial strains, including *Sulfurospirillum multivorans*, *Dehalobacter restrictus*, *Dehalococcoides* sp., and *Desulfitobacterium hafniense*, can debrominate PBDEs [1,76]. The debromination of PBDE fits well with the first-order kinetic equations: $S = S_0 \exp(-k_1 t)$, $t_{1/2} = \ln 2/k_1$, where t is the time, S_0 is the initial concentration of the PBDE, S is the PBDE concentration at time t and k_1 is the debromination rate constant [76].

4.3. Disposal methodologies

Disposal methods for waste containing PBDEs are disposal in landfills, safety landfills, and incineration [8], this depends on the classification of the waste as common, hazardous, or high calorific value [35,82].

4.3.1. Classification of PBDE-containing wastes

In the European Union, landfill disposal of plastics is prohibited due to their high calorific value [35]. Owing to the toxicity of PBDEs, waste containing PBDEs is considered hazardous and must be treated as such.

The limit concentration of 1,000 mg/kg is considered for the sum of penta- and/or octa-BDE to classify waste as hazardous and manage it as such. The European Directive 2012/19/EU states that plastic containing BFRs must be removed from any WEEE collected separately. The concentration of Br in plastics is very heterogeneous; it is found in high concentrations in plastics from large household appliances, but high values have also been found in some commonly used items [17].

Attempts have been made to build inventories of PBDEs associated with waste polymers to estimate the amount of waste that needs special treatment and prevent them from entering recycling [83]. Also, a proposal has been made to classify plastics and identify plastics with Br content greater than 2000 mg/kg. This classification process can be performed using high-resolution near-infrared devices [84]. As an alternative to the classification process, solvent washing treatments can be used for the extraction of brominated additives and debromination.

In Latin America, there is no regulation on waste containing PBDEs and most waste is not treated. In Brazil, it has been estimated that the amount of WEEE containing PBDEs exceeds 25,000 tonnes/year, containing 470 tonnes/year of PBDEs. These approximate values demonstrate that the amount of waste that must be managed as hazardous waste is significant [37]. The situation is similar in other countries in the region, including Peru. The current absence of both Brazilian and Peruvian legislation on maximum permissible concentrations of PBDEs in waste means that there is no regulatory incentive to measure PBDEs in waste. If it is assumed that the concentration of all PBDE congeners in polyvinyl chloride is equal to 1,000 mg/kg and according to the Solid Waste Management

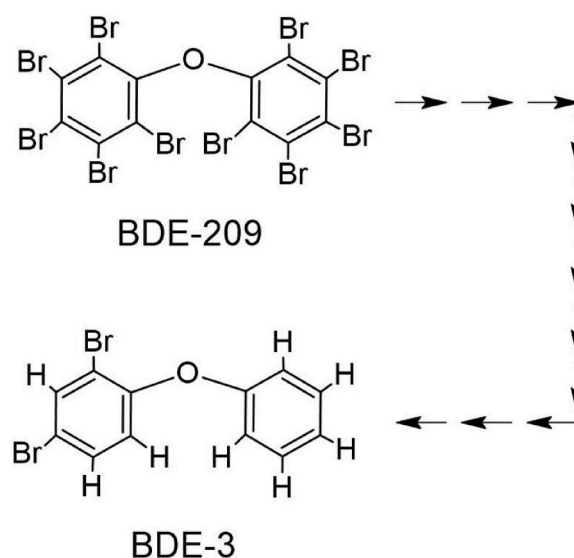


Fig. 5. Proposed debromination for biotransformation of BDE-209 to BDE-3 [76].

Information System (SIGERSOL), 21,418 tonnes of polyvinyl chloride waste was generated in Peru in 2022, then the amount of PBDE associated with this waste can be predicted to be 21,418 kg/year.

4.3.2. Incineration and pyrolysis

Direct incineration of PBDE-containing plastic waste in two stages should be considered so that it first allows the removal of PBDEs and then the removal of dioxins formed in the second chamber at 1,100 °C [69].

Conventional pyrolysis is proposed by several authors as a treatment alternative where a pretreatment step is applied for the debromination of the products to avoid the formation of dioxins, but the capture of residual brominated byproducts during pyrolysis (thermochemical recycling) remains one of the main challenges of this route [85,86].

During the thermal treatment process, the gases containing PBDD/Fs are degraded at temperatures above 1,100 °C, and the mechanism is similar to those described for PCDD/Fs dioxins. The degradation mechanism follows two main routes: the first route involves debromination reactions by cleavage of the C–Br bond by the presence of high-energy electrons. The second route involves the breaking of the C–O bond by the vibration of the molecules by the action of electrons, which generates instability of the dioxin molecules. Finally, the presence of oxidative species such as OH, O₃, and O radicals leads to the complete oxidation of dioxin molecules [87].

In Japan, controlled co-incineration at 1,100 °C was applied to crushed TV casing waste containing 5.9 % (59,000 mg/kg) of deca-BDE with common industrial waste, managing to eliminate deca-BDE by 99.999 %. It was shown that Br derived from deca-BDE was concentrated in the bottom ash and sealing water. Bottom ash from municipal incinerators containing in the leaching test between 1.03 and 7.99 ng/L [49] should be disposed in safety landfills. Bottom ash can also be recirculated using a GASMILD-type methodology to reduce the PBDE and PBDFs content in the ash for safe disposal [74].

There is increasing interest in thermal conversion technologies, such as hydrothermal liquefaction and supercritical water oxidation, which process the feed material under high-pressure/high-temperature conditions to valorize the sludge stream and recover valuable resources [26]. In this technology, the generation of highly active free radicals, such as *OH, can easily dehydrogenate and hydroxylate dioxins, allowing the removal of PBDD/Fs dioxins [87].

4.3.3. Landfill or safety landfill disposal

In many countries, PBDE-containing waste are deposited in landfills without any treatment; for example, in some places in China, high PBDE concentrations in electronic waste (e-waste) such as CRT-TV plastic (11.31 mg/kg), refrigerators (6.63 mg/kg), desktop mainframes (2.81 mg/kg), and dust from dismantling sites [10] have been detected. Other cases are miscellaneous e-waste in Brazil containing BDE-209 concentrations of 2.7–55 mg/kg [12].

PBDE content in the landfill leachate has values of <1.0 to 1,020 ng/L due to e-waste disposal [88], and to prevent these substances from reaching groundwater, safety landfills have a geomembrane liner that isolates the leachate from groundwater. When fires occur in landfills, PBDEs can double their concentration in the air [89]. In addition, dust stirring from the landfill soil and flares when burning methane gases released in the landfill can be additional sources of PBDE emissions, so the entry of plastics with PBDEs should be restricted.

5. Conclusions and prospects

Synthetic chemical compounds that belong to the group of PBDEs were widely used as flame retardants in various commonly used products, namely, furniture, plastics, textiles, electrical, and electronic equipment, until their inclusion in the list of POPs of the Stockholm Convention, restricting their use for some specific activities, especially BDE-209 widely distributed in the environment.

PBDEs can be released into the environment through volatilization, leaching, and abrasion throughout the useful life of the articles that contain them. The crushing process promotes the generation and emission of contaminated dust, forming secondary wastes such as sludge, sediments, ashes, and soils contaminated with PBDEs.

Given that the amount of plastic from WEEE has increased disproportionately in recent years due to the massive consumption of electronic devices and their short useful life, it is necessary to implement integrated management of waste containing PBDEs in all countries.

Within an integrated management, the recovery of PBDE-containing plastics for the production of new plastics requires only mechanical pretreatment (manual separation, shredding, washing) if the PBDE content is less than 1000 mg/kg. If the PBDE content in the plastic waste, sludge, sediment, dust, ash is higher than 1000 mg/kg, treatments such as photodegradation, zero valence iron, thermal treatment, or biodegradation are required to reduce their concentration and valorize the waste as energy recovery or soil improver; or proceed to their final disposal in a safe way, minimizing the risk of release into the environment. This review proposes a methodology for the integrated management of PBDE-containing wastes based on the available information, to provide researchers with a guide to consider for the development of alternatives for recovery, treatment, and final disposal.

CRediT authorship contribution statement

Olga Kostenko: Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Lisveth Flores del Pino:** Supervision, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Paola Jorge-Montalvo:** Visualization, Validation, Funding acquisition, Data curation. **Lizardo Visitación-Figueroa:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Methodology,

Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Data availability statement

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