

Analysis of the sources, toxicity, and control methods of polybrominated diphenyl ethers

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Abstract. As fire safety standards continue to rise in all sectors of society, flame retardants are increasingly being used as a key material, such as polybrominated diphenyl ethers (PBDEs). PBDEs have become a focus of public and environmental protection attention due to their difficult degradation, easy accumulation in the environment, and transfer through the food chain. This research will investigate the main sources of PBDEs and analyze in detail the migration, transformation and distribution patterns in water, atmosphere, soil and biosphere, with a view to providing a scientific basis for the subsequent environmental monitoring and management. In addition, the physicochemical properties of PBDEs which are directly related to their persistence and potential for bioaccumulation in the environment, will be systematically described. This research will delve into the specific human health hazards of PBDEs. Given the hazardous nature of PBDEs, this research will propose a series of targeted strategies and measures aimed at mitigating or preventing their toxic effects.

Keywords: PBDEs; Sources; Distribution; Poisonous.

1. Introduction

Brominated flame retardants were first widely used in the 1970s, with rapid industrialization leading to increasingly stringent fire safety standards and rapid growth in the production of plastics, which led to the widespread use of brominated flame retardants globally. Brominated flame retardants are a group of aliphatic, alicyclic, aromatic and aromatic-aliphatic brominated compounds used to improve the flame retardancy of materials. Polybrominated diphenyl ethers (PBDEs) are one type of brominated flame retardants, which are inexpensive, have excellent performance and have little effect on the properties of materials, making them popular in the fields of transportation, aerospace, and furniture to prevent fires and reduce the occurrence of fires.

The chemical structure of PBDEs consists of a biphenyl skeleton and multiple bromine atoms, with different degrees and sites of bromination that can give rise to a wide range of isomers. These isomers have different flame retardant effects in applications, but also raise their own unique environmental and health concerns. PBDEs and their derivatives, such as hydroxylated polybrominated biphenyls (OH-PBDEs) and methoxylated polybrominated diphenyl ethers (MeO-PBDEs), are persistent organic pollutants (POPs) that are widely present in the environment, and these compounds have a wide range of toxic effects, including neurotoxicity, endocrine, endocrine disruption, reproductive developmental toxicity, immune system toxicity, and carcinogenicity [1, 2]. PBDEs may bind to hormone receptors in the body and interfere with hormone signaling, thereby affecting normal physiological and developmental processes. In addition, PBDEs affect hormone synthesis, metabolism and elimination, such as interfering with the synthesis and metabolism of thyroid hormones, which further affects the function of the thyroid gland and disrupts the balance of other hormones. PBDEs have a negative effect on the endocrine glands, causing hormonal abnormalities and thus reproductive harm. PBDEs may interfere with hormonal feedback mechanisms in the body, altering hormonal regulation and causing overall endocrine dysregulation. Endocrine disruption can also increase the chances of developing cancer. Since these substances are difficult to degrade in the environment, they can accumulate in living organisms through the air, water and soil, thus posing a potential threat to human and animal health.

The aim of this paper is to define the sources, distribution, the toxicity of PBDEs to document the specific hazards of PBDEs and to summarize what measures or technologies are currently available to reduce the environmental contamination and bioaccumulation of PBDEs.

2. Sources and distribution of PBDEs

2.1. Sources

The content of PBDEs in indoor decorative materials, furniture and electrical appliances, can reach 5-30%. During use, PBDEs escape into the air to varying degrees as temperatures change, resulting in generally higher levels of PBDEs in indoor air than outdoor. During the dismantling of e-waste, a large amount of incineration and baking results in the continuous release of PBDEs into the environment from plastics and other wastes. Primitive processes such as simple acid dissolution or direct incineration can be used to increase local environmental exposure levels to PBDEs above normal. By collecting blood and calculating the levels of PBDEs, the PBDE mass fraction in the exposed group was as high as 240.00 ng/g, a level that not only surpassed the 93.00 ng/g in the control group, but also exceeded the values reported in a number of international studies [1]. PBDE levels in the exposed group were similar to those of populations in certain e-waste dismantling regions, such as dismantling workers in Guiyu (130 ng/g) and adults in Laizhou Bay (240 ng/g), indicating that local e-waste dismantling activities over a long period of time are the main reason for the high levels of PBDEs [1].

2.2. Distribution

The aquatic environment is an important part of the global cycle of PBDEs, which can enter the aquatic environment through surface runoff, atmospheric dry and wet leaching, and other means. Because of the low water solubility of PBDEs, the levels of PBDEs in natural environmental waters are generally not high, mostly for detection to a few hundred pg/L, with higher levels in estuarine areas or effluent from wastewater treatment plants. For example, the Guiyu section of the Lianjiang River was significantly polluted by PBDEs in sediments under the influence of electronic dismantling and industrial activities, with concentrations as high as 7470 to 193000 ng/g, which were far more than those in the sediments of water sources upstream of the Lianjiang River (10.2 to 2120 ng/g). Among them, BDE-209 was the most prominent, accounting for 50.3%. High concentrations of PBDEs were also detected at the e-waste disposal site in the Maozhou River Basin in Shenzhen, ranging from 230 to 36392 ng/g, with BDE-209 accounting for more than 96% [2]. Near Singil Stream, a man-made lake in Stone Frog, South Korea, PBDEs levels in the water spiked to 18700 ng/g, significantly higher than in surrounding waters due to the concentration of chemical and electrical plants [3]. The distribution of PBDEs in the oceans also varies, with residues of lower brominated diphenyl ethers in the oceans increasing with increasing latitude, while the opposite is true for higher brominated diphenyl ethers, which shows an increase with decreasing latitude. Overall, PBDEs residues are generally higher in the Northern Hemisphere than in the Southern Hemisphere. In European waters, PBDEs pollution gradually decreased from south to north, with the most significant pollution along the southern coast, followed by the Baltic Sea, and the least in the Arctic periphery. In North America, the levels of PBDEs in organisms were higher in the near-shore than in the open ocean away from the continent. In Asia, the East China Sea was significantly more polluted by PBDEs than other Asian seas. In addition, the atmospheric transport distance of PBDEs is negatively correlated with their bromination level, with the higher the number of bromine atoms, the shorter the transport distance. PBDEs levels in organisms were significantly higher in the nearshore than in the open ocean due to the influence of land-based discharges [4].

PBDEs are found in the atmosphere in both the gas phase and the particulate phase, with highly brominated diphenyl ethers being more enriched in the particulate phase, and less in the gas phase. This phenomenon is attributed to the fact that the vapor pressure of PBDEs decreases with increasing bromine content. PBDEs production plants, waste incineration facilities, and waste electronics

recycling sites are key emission sources. The concentrations of PBDEs in outdoor dust in these typically polluted areas were significantly high. Under the current technological conditions, for every 1000 kilograms of PBDEs produced, approximately 22 kilograms of PBDEs are released into the atmosphere [5]. Globally, atmospheric concentrations of PBDEs are particularly high in Asia, and China is the leader, with concentrations of PBDEs ranging from 2.0 to 787 pg/m^3 , which significantly exceeds the records of the United States and Europe from a decade ago. Within the same geographical area, the concentration of PBDEs is distributed in a distinct pattern, with urban areas significantly higher than rural areas, and industrial areas far exceeding non-industrial areas. For example, in Chicago the concentration of PBDEs is 33-77 pg/m^3 , which is much higher than that in rural areas (4.4-21 pg/m^3) [6]. In China, atmospheric concentrations of PBDEs in the production sites of selected brominated flame retardants are alarmingly high, ranging from 16000 to 240000 pg/m^3 . In addition, e-waste dismantling activities also have a significant impact on the atmospheric concentrations of PBDEs. Guiyu, as an important base for e-waste dismantling, has an atmospheric sigma PBDEs concentration soaring to 5379-47187 pg/m^3 , which is 58-691 times higher than that of Guangzhou and Hong Kong, emphasizing the significant environmental effect [7].

Soils from the waste plastics resource disposal site and industrial concentration area in Laizhou Bay, contained PBDEs as high as 1.25 to 3673.4 ng/g and 73 to 2629 ng/g , respectively, which are significantly higher than that of farmland soils in Taizhou around the dismantling plant of waste electrical and electronic equipment (2.96 to 200 ng/g). In contrast, urban soils far from industrial areas, such as those in the urban area of Shanghai, had lower levels of PBDEs, ranging from 0.024 to 3.797 ng/g [8]. It is noteworthy that PBDEs have been able to spread across long distances to remote areas such as the Tibetan Plateau, confirming their ability to migrate over long distances despite the low total levels. Industrial pollution, especially the emission of industrial wastewater and exhaust gases, is still the main source of PBDEs in soils. There are differences in the congener composition of PBDEs in soil under the influence of different pollution sources. PBDEs in soil from waste plastics disposal sites mainly originated from plastic additives containing decabromodiphenyl ether (DBDE), while PBDEs in soil from the Yellow River agricultural irrigation area in the Hetao Plain originated more from the use of low-brominated diphenyl ethers (LBDEs) in agricultural land films. In the Tibetan Plateau, where human activities are rare and far from major industrial sources, PBDEs in the soil are mostly low BDE species that are transported long distances. Soil characteristics such as organic matter content, clay mineral content, altitude, and depth of the soil also affect the distribution and composition of PBDEs in soil. In general, the concentration of PBDEs decreases with increasing soil depth. Lower brominated PBDEs have a higher transport capacity compared to higher brominated PBDEs [9].

PBDEs in environmental media can enter living organisms through diffusion, respiration, and active and passive absorption. These substances are transported and bioconcentrated in organisms along the food chain, and may eventually enter the human body, thus posing a potential risk to the ecosystem and human health. The distribution characteristics of PBDEs in organisms are influenced by a variety of factors, including differences in biological species, the level of pollution in the environment, and the specificity of individual tissue.

Taking vegetables as an example, vegetables, as foodstuffs consumed in large quantities in daily life, grow in environments that are closely related to the atmosphere, soil and water bodies, and have a high possibility of being contaminated by PBDEs. The average content of PBDEs in vegetables in various provinces of China was 18.4 pg/g , with BDE-99 as the main pollutant. In particular, the contribution of PBDEs contamination was significantly higher in vegetables from Shaanxi (35%), Ningxia (29%), Shanghai (49%), Hubei (29%), and Beijing (54%). It is noteworthy that both megacities, Beijing and Shanghai, exhibited high levels of PBDEs contamination, revealing a strong association between PBDEs content in vegetables and the level of contamination [10]. Further analysis revealed that the types of vegetables and their edible parts had a significant effect on the PBDEs content. On vegetables sold in the Beijing market, it was noted that leafy vegetables generally contained higher levels of PBDEs than fruiting vegetables. In commonly consumed leafy vegetables,

the content of PBDEs varied significantly among different parts. These findings suggest that for leafy vegetables, the edible part (leaves) tends to contain higher levels of PBDEs, while the stem or peduncle contains relatively low levels [11].

Due to their remarkable fat-soluble properties, PBDEs tend to accumulate and become enriched in adipose tissue. This property leads to significant differences in the distribution of PBDEs in different tissues of the same animal. Adipose tissues tended to contain higher concentrations of PBDEs, whereas tissues with lower adipose content had lower concentrations. Through a series of feeding experiments targeting widely used BDE-209, during the initial period of exposure in mice, the highest concentrations of BDE-209 were found in the liver, followed by the plasma and intestine. However, BDE-209 concentrations in adipose tissue eventually peaked with longer exposure times [12]. Wang et al. consistently fed BDE-209-containing diets to hens in a 50-day study and found a gradual increase in BDE-209 levels in various tissues of hens. The total PBDEs in the tissues were ranked as follows: highest in liver, followed by blood, skin, intestines, stomach, and to a lesser extent in thighs, and the lowest in breasts. This finding suggests that consumption of liver poses the greatest risk of exposure to PBDEs, whereas chicken breast has a relatively low exposure risk [13].

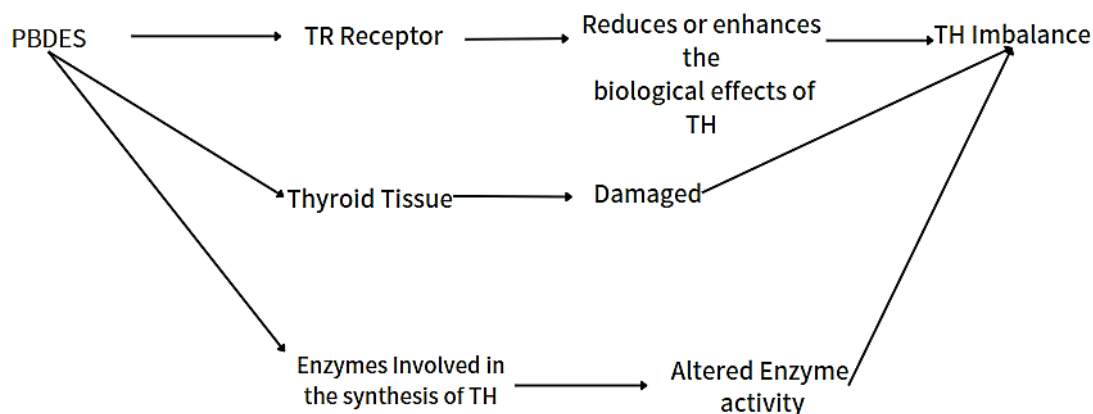


Figure 1. Thyrotoxic mechanisms of PBDEs [14].

3. Toxicity of PBDEs

PBDEs are very stable in the environment, and it is difficult for them to persist in soil, sediment, atmosphere and other environmental media through physical, chemical or biological degradation. The solubility of PBDEs in water is very low, but they have strong lipophilicity, and are easily soluble in organic solvents, which makes them easy to be absorbed by living organisms and enriched in higher organisms through the transmission of food chains. PBDEs are easily absorbed by organisms and enriched to higher concentrations in higher organisms through the food chain.

3.1. Thyroid toxicity

The main role of thyroid hormones is to promote metabolism and maintain normal growth and development of the body, and they have a strong influence on the development of the bones and nervous system. The main types of thyroid hormones are T3 (3, 30, 5-triiodothyronine) and T4 (3, 30, 5, 50-tetraiodothyronine), which regulate metabolism, growth rate, and mediate other body systems. PBDEs are one of the common endocrine disruptors because of their structural resemblance to thyroid hormones, especially hydroxylated PBDEs and T3 and T4. PBDEs compete for binding to the thyroid hormone receptor (TR), and they impede the transport and metabolism of thyroid hormone (TH), allowing the body's thyroid hormone secretion to become imbalanced, which in turn affect the function of the organism. Both BDE-47 and BDE-71 affect the levels of TH in the body by interfering with gene transcription and signaling processes within the hypothalamic-pituitary-thyroid axis [14, 15]. In addition, PBDEs act directly on thyroid tissue, causing damage to thyroid cells and preventing

the normal synthesis of thyroid hormones. They also affect the enzymes involved in thyroid hormone synthesis, altering their activity and interfering with the process of thyroid hormone synthesis. Therefore, the toxicity of PBDEs has these aspects: preventing the synthesis, transport and distribution of TH, and competing with TH for transport proteins (Figure 1).

3.2. Thyroid toxicity

As the detoxification factory in the human body, the liver is responsible for transforming toxic substances into harmless or low-toxicity forms and eliminating them from the body. This complex detoxification process involves a number of mechanisms: chemical transformation, excretion, accumulation and release, and phagocytosis. Metabolically produced wastes are normally eliminated from the body by two main routes. Water-soluble substances are excreted in bile or urine, while fat-soluble substances need to be converted to water-soluble substances or inactivated by an enzyme system before they can be eliminated. PBDEs are highly lipophilic and bioconcentrating, so that PBDEs entering the organism may concentrate in the liver. The mechanism of hepatic detoxification depends on the presence of a large number of cytochrome P450 mixed-function oxidases, CYPs, which inactivate lipid-soluble exogenous compounds through monooxygenation and convert them to water-soluble substances. Subsequently, these water-soluble substances are excreted from the body, mainly in the form of urine [16].

3.3. Reproductive developmental toxicity

The reproductive developmental toxicity of PBDEs is characterized by reduced sperm quality and reproductive system abnormalities in males, prolonged fertilization cycle and apoptosis in females. In human spermatozoa, long-term exposure to PBDEs resulted in a decrease in sperm concentration, viability, and testicular size in males. Hong et al. found that BDE-47 triggered an oxidative stress effect in rotifers, which resulted in a significant increase in reactive oxygen species (ROS) *in vivo*. This increase caused severe damage to the ovarian microstructure, which may be an important reason why BDE-47 significantly inhibited the egg production and reproduction frequency of rotifers [17].

4. Degradation and control methods for PBDEs

The common degradation methods include photodegradation, plant degradation, microbial degradation, zero-valent iron degradation and Fenton degradation. Photodegradation, as a key degradation mechanism of PBDEs in the natural environment, significantly affects their environmental fate. This process utilizes the energy of ultraviolet light to induce photochemical reactions of PBDEs, mainly through the gradual debromination of PBDEs to form lower brominated diphenyl ethers (LBDEs), or through the intramolecular cyclization of PBDEs to remove HBr, which is converted to brominated dioxin-like compounds. Phytodegradation shows another purification power of nature, which relies on the metabolic activity of plants to convert PBDEs into harmless or low-toxicity substances. In particular, aquatic plants can efficiently absorb and immobilize PBDEs in sediments and promote degradation through their reduction mechanism. Plants such as alfalfa, corn, radish, zucchini, ryegrass, and pumpkin have shown effective degradation of PBDEs in the environment, which indicates their potential for remediation of contaminated waters and soils. Microbial degradation is more complex and diverse, covering aerobic, anaerobic and synergistic modes of degradation. Aerobic microorganisms have become a research hotspot with their faster degradation rate, while anaerobic microorganisms play an important role under specific conditions, and both of them can complement each other to realize more efficient combined degradation under certain circumstances. In addition, zero-valent iron degradation and Fenton degradation, as chemical degradation pathways, provide new ideas for the degradation of PBDEs through hydrodebromination and hydroxylation under reduction, respectively. Therefore, there is an urgent need to strengthen in-depth research on safe and efficient degradation methods in the future, through the integration of various degradation technologies, aiming to develop both economic and efficient degradation

programs, to ensure that the degradation process is not only effective, but also to avoid secondary pollution, so as to comprehensively deal with the environmental pollution problems such as PBDEs.

The government should strengthen the legal framework for the management of PBDEs, explicitly restrict or prohibit their production, circulation and use through legislation, and impose severe legal sanctions for violations in order to strengthen the supervision of production enterprises. At the same time, the government should actively promote scientific research and innovation, encourage the development of environmentally friendly flame retardants, and accelerate the application of environmentally friendly flame retardants through tax incentives, financial subsidies and other policy measures to guide the market to transition to an environmentally friendly direction. In the production process, the government should advocate enterprises to adopt advanced production processes to reduce the leakage and emission of PBDEs, and strengthen the environmental education and training of employees to ensure that they recognize the hazards of PBDEs and comply with environmental regulations. For waste management, the government needs to establish an effective system of separate collection and disposal to ensure that waste containing PBDEs is effectively separated. When disposing of waste, priority should be given to resource utilization, while waste that cannot be reused should be disposed of in a safe manner, such as efficient incineration and special landfills, to minimize the impact on the environment.

In order to enhance the analytical method for the detection of PBDEs, it is firstly necessary to optimize the pretreatment steps, including the use of efficient techniques such as Soxhlet extraction, degreasing by automated GPC system and purification by multilayer silica gel chromatography columns, in order to improve the extraction rate and purification of PBDEs in the samples, and to ensure the accuracy and reproducibility of the pretreatment so as to reduce the operational errors. It is crucial to improve the instrumental analysis techniques. It is recommended to use high sensitivity instruments such as GC-MS and GC-MS/MS, combined with full scan and selective ion scan modes, and to optimize the inlet temperature, carrier gas flow rate, column type and warming procedure, in order to ensure the accuracy and reliability of the analysis results. In addition, detailed standard operating procedures (SOPs) for testing and analysis are established, covering sample collection, pre-treatment, instrumental analysis and data processing, to standardize and normalize the process. Quality control and quality assurance are strengthened, including blank experiments, spiked recovery experiments and parallel sample analysis to ensure the accuracy of analytical results, and instruments are regularly maintained and calibrated. Technological innovation and method optimization should be encouraged, researchers and technicians should be promoted to explore new detection technologies and methods, and international exchanges and cooperation should be strengthened to learn from international advanced experience in order to enhance the overall level of PBDEs detection and analysis. In addition, in view of the emergence of emerging pollutants, attention should also be paid to the research of detection and analysis methods of emerging pollutants while strengthening the detection and analysis of traditional PBDEs.

5. Conclusion

PBDEs mainly come from flame retardants in upholstery, furniture and electrical appliances, and their content can reach 5% to 30%, and will escape into the air with temperature changes. The dismantling of electronic waste and improper handling during the production of flame retardants may also result in the release or leakage of PBDEs. PBDEs are widely distributed in various environments due to their characteristics of low vapor pressure, high lipophilicity, difficult degradability, and bioconcentration. PBDEs in food mainly originate from these four environments and finally accumulate in the human body, generating toxicity in the thyroid, liver and reproductive development. Therefore, it is necessary to seek control measures for PBDEs from various aspects, such as controlling the sources, developing alternative flame retardants, and researching degradation and detection methods.

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