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**Chapter**

# Polybrominated Diphenyl Ethers (PBDEs) as Emerging Environmental Pollutants: Advances in Sample Preparation and Detection Techniques

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## Abstract

Environmental pollution has been a challenging phenomenon in most developing countries, due to the weak enforcement of environmental regulations. As a result, humans and animals are exposed to different environmental pollutants, which threaten their very existence. Some of the emerging pollutants of great concern are polybrominated diphenyl ethers (PBDEs) since they are categorized as probable human carcinogens and are also known to bioaccumulate in fatty tissues of animals and humans, reaching toxic levels upon continued exposure. Monitoring of these pollutants is therefore paramount as it contributes to addressing the problem of human exposure and environmental pollution. Their monitoring involves sample preparation methods followed by quantification with various detection techniques. Sample preparation methods that aim at reducing matrix interferences, enriching analytes and transfer of analytes to a desirable solvent, have evolved from conventional methods to advanced methods that facilitate the detection of these chemicals at very low concentrations. Likewise, detection techniques have advanced from chromatographic detection techniques to miniaturized systems that involve sensors. This chapter discusses PBDEs as emerging pollutants, their sources, and toxicological implications on humans, as well as advances in sample preparation methods and detection techniques in the determination of PBDEs.

**Keywords:** polybrominated diphenyl ethers, persistent organic pollutants, pollution, emerging pollutants, detection techniques

## 1. Introduction

The preservation and conservation of the environment are of great significance for healthy living. However, efforts to conserve the environment have been futile due to escalated pollution from biogenic and anthropogenic sources, which constantly release pollutants to the environment [1]. In the recent past, increased industrial and agricultural activities have immensely contributed to the pollution

of aquatic environments such as rivers and streams, which pose major detrimental environmental problems to humans [2]. It is evident that industrial development has generated a myriad of new chemicals produced and applied in daily activity, which is becoming a major concern for citizens, the research community, and authorities [3]. Among the pollutant chemicals that have been introduced into the environment are polybrominated diphenyl ethers (PBDEs). PBDEs are toxic, lipophilic, hydrophobic, and persistent artificial chemicals characterized by high physical and chemical stability [4]. They are commonly applied as flame retardants in polymer products such as electronics, plastics, textiles, and building materials [5, 6]. PBDEs have become a growing concern over the last two decades due to their ubiquity, persistence and accumulation capacity in the environment, as well as their potential risks to human health and wildlife [7, 8]. PBDEs are normally additive compounds, meaning they are not covalently bound to the polymeric products [9]. Therefore, they may leach out into the surrounding environment during their production, usage, disposal, or recycling process [10]. PBDEs can be transported away from their sources for long-ranges through aqueous and/or terrestrial environmental compartments [11, 12]. In this context, monitoring and assessment of environmental pollution by these compounds are very important.

Their determination involves a series of steps from sample pre-treatment to quantification of analytes using various detection systems. Different sample preparation strategies that range from conventional to advanced strategies have been applied for the determination of PBDEs in environmental samples. Some of the conventional sample enrichment methods include Soxhlet extraction [13, 14] and liquid-liquid extraction (LLE) [15]. More recently, ultrasound-assisted extraction (UAE) [16, 17], pressurized liquid extraction (PLE) [18, 19], microwave-assisted extraction (MAE), solid-phase extraction (SPE), and solid-phase microextraction (SPME) have exhibited successful extraction of PBDEs from environmental samples [20, 21]. The application of SPE and SPME has advanced from conventional adsorbent formats to the most improved formats which allow easy transfer of analytes from their complex matrices. This has been achieved by using novel adsorbent materials to replace conventional silica-based adsorbents which exhibit low selectivity towards targeted analytes [22]. Similarly, analytical techniques for the qualitative and quantitative determination of PBDEs have advanced from well-known gas chromatography-electron capture detection (GC-ECD) to sensor-based techniques that are more advantageous in terms of excellent selectivity, with opportunities for *in-situ* application. The following sections provide detailed information on PBDEs, advances in sample pre-treatment methods and detection techniques with a view of providing the current state-of-the-art as far as their monitoring is concerned.

## 2. Polybrominated diphenyl ethers

### 2.1 The chemistry of PBDEs

PBDEs comprise of two halogenated aromatic rings bonded by an ester bond and are classified in relation to the number and position of bromine atoms in a particular molecule [23]. They have a general molecular formula of $C_{12}H_{(10-x)}Br_xO$, where x is the number of bromine atoms in a molecule with numerical values [x = 1, 2, 3, ..., 10 = m + n] (**Figure 1**). Substitution of bromine atoms can take place at 10 possible positions on the two benzene rings resulting in 209 possible congeners [24].
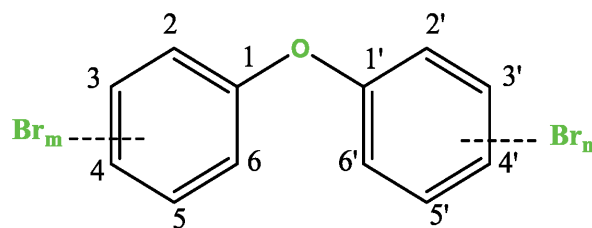
**Figure 1.**
*General structural formula of PBDEs.*

Different congeners are easily identified by their corresponding IUPAC numbers ranging from 1 to 209. In this case, 2,2′,4,4′-tetrabromodiphenyl ether is BDE-47, with bromine atoms in ortho and para positions on the first and second benzene rings, respectively (**Figure 2**).
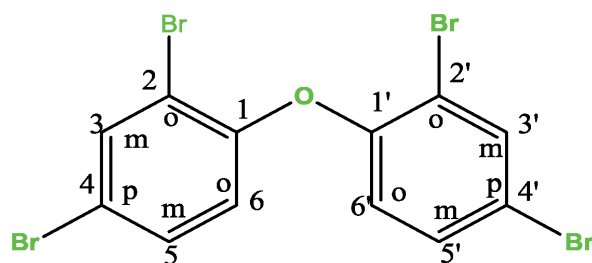
**Figure 2.**
*Chemical structure of 2,2′,4,4′-tetrabromodiphenyl ether (BDE 47).*

Molecules with one to four bromine atoms are classified as low molecular mass PBDEs, whereas the ones with five to ten bromine atoms are categorized as high molecular mass PBDEs. Less brominated PBDEs are more persistent and toxic than highly brominated diphenyl ethers [25]. The substitution pattern also affects the physicochemical properties of PBDEs, whereby the solubility of PBDEs decreases significantly with an increase in bromine substitution. The aqueous solubility ($S_W$) of low molecular mass PBDEs at room temperature ranges from $6.57 \times 10^{-7}$ to $7.82 \times 10^{-11}$ mol $L^{-1}$ while those of high molecular mass have aqueous solubility values lower than $7.82 \times 10^{-11}$ mol $L^{-1}$ [26]. A wide range of PBDE congeners exhibit high lipophilic capacity and high resistance to degradation; a property that makes them bioaccumulate and magnify in biota [7]. PBDEs are also associated with high octanol-air partition coefficients ($K_{OA}$) with values ranging between 9.3 and 12.0 from BDE-17 to -126, which is approximately 1 to 2 orders of magnitude greater than PCBs [27]. Therefore, PBDEs are easily transported through air from one point to another, increasing their chances of exposure to humans. Dissolved organic matter has shown a high tendency to interact with hydrophobic compounds such as PBDEs, which hinders their mobility and degradation in the environment [28]. Reported binding coefficients of PBDEs (log $K_{DOC}$) towards organic matter range from 5.1 to 7.14, which implicates the high capability of PBDEs to adsorb and partition on organic matter [29].

## 2.2 Global production and regulation of PBDEs

PBDEs were commercially produced in three technical mixtures, typically known as pentaBDE, octaBDE, and decaBDE, basing on the number of bromine atoms [10]. By early 2000, the global production of commercial PBDE formulations was approximately 67,000 tons in the ratio 1:1.98:14.8 for octa-BDE, penta-BDE, and deca-BDE respectively, of which the United States production was

approximately 50% of the global production [30]. Several governmental regulations and international environmental agencies have restricted and completely banned the use and production of some PBDE congeners [31]. In 2004, the European Union phased out the use and production of penta-BDE and octa-BDE. Consequently, in December 2004, Great Lakes Chemical Corporation, a sole manufacturer of penta-BDE and octa-BDE in North America, voluntarily phased out the production of these BDE formulations [32]. These efforts were boosted by the Stockholm Convention in 2012 when it listed commercial octa-BDE and penta-BDE among persistent organic pollutants that need to be eliminated. Despite the ban in the production of most PBDEs, they are still reported in air, soil and aquatic environments, which is attributed to their stability and subsequent release from techno-ecosystems, and production of deca-BDE, which still continues to be produced in some countries [33, 34].

## 2.3 PBDEs in the environment and their toxicological implications

There are diverse pathways by which PBDEs enter the environment. Major environmental sources of PBDE pollution comprise of leakage from consumer products and industrial facilities that synthesize PBDEs or PBDE-containing products [5]. Besides, PBDEs may enter the aquatic environment from illegal disposal of obsolete electrical appliances and electronic devices flame-retarded with PBDEs or other PBDEs-containing products [7]. They can also enter the aquatic environment through raw sewage and into the surrounding air through volatilization from products containing PBDEs and toxic fumes from e-waste recycling plants [35]. Since the first discovery of PBDEs in the aquatic environment on the West coast of Sweden in 1981, several studies have reported the presence of PBDEs in the environment [36]. This is despite the strict regulatory measures imposed by some governments and international environmental agencies to phase out some PBDE congeners and subsequent reduction in the production of particular PBDEs. BDE-47, 99, 100, and 153 are the ones that are frequently investigated because they are primary components of commercial mixtures, therefore, their ratios in the environment are expected to be significantly high. Moreover, less substituted BDE congeners such as BDE-28 and 47 are more toxic and non-biodegradable, hence their investigation in the environment and biota is of great significance in the monitoring of these pollutants [37]. Soil and sediment harbour higher concentrations of PBDEs, which is attributed to the organic carbon content, which makes them a sink for most organic pollutants [38]. Elevated levels of PBDEs have since been reported in agricultural soils after the application of sewage sludge at a concentration of 21 to 690 ng g$^{-1}$ dry weight (dw) [39]. From statistics, human beings spend more than 70% of their lifetime indoors, in occupational offices, homes, learning institutions, and transport vehicles, and are therefore exposed to an array of contaminants from indoor dust [40]. The highest levels of PBDEs in dust samples have been reported in major industrialized cities in China and Europe at a concentration of 397–40,236 ng g$^{-1}$ and 950–54,000 ng g$^{-1}$, respectively [41, 42], with comparably lower levels of 1710 ng g$^{-1}$ in African regions [43]. **Table 1** presents a summary of reported PBDE levels in selected environmental matrices.

The principal route for PBDE exposure to humans was thought to be through food consumption [58]. However, inhalation of contaminated indoor and outdoor dust is also a significant pathway via which human beings may be exposed to PBDEs [46, 59]. Dermal absorption is another potential route for PBDE exposure [60]. Numerous studies have reported levels up to 160.3 ng g$^{-1}$ of PBDEs in human samples, such as serum and milk. Increased application of PBDEs in electronics has significantly aroused more research work on the concentration of these pollutants

| Country | Sample matrix | Concentration | Reference |
|---|---|---|---|
| South Africa | River water | 2.60–4.83 ng L$^{-1}$ | [44] |
| North America | River water | 0.00013–0.01 ng L$^{-1}$ | [45] |
| Great Britain | Indoor dust | 950–54,000 ng g$^{-1}$ | [46] |
| South Africa | Home dust | 1710 ng g$^{-1}$ | [43] |
| | Office dust | 1520 ng g$^{-1}$ | |
| Nigeria | Indoor dust | 3700–19,000 ng g$^{-1}$ | [47] |
| China | Indoor dust | 397–40,236 ng g$^{-1}$ | [41] |
| Uganda | Air | 0.00340–0.00984 ng m$^{-3}$ | [48] |
| Kenya | Soil | 0.19–35.64 ng g$^{-1}$ | [49] |
| China | Soil | 4.8–533 ng g$^{-1}$ | [50] |
| China | Sediment | 0.03- 5.22 ng g$^{-1}$ | [51] |
| China | Sediment | 0.13–1.98 ng g$^{-1}$ | [52] |
| Sweden | Sewage sludge | nd-450 ng g$^{-1}$ | [53] |
| Spain | Sewage sludge | 197–1185 ng g$^{-1}$ | [39] |
| Kuwait | Sewage sludge | 52.5–377$^{*}$ ng g$^{-1}$ | [54] |
| USA | Serum | 5.0–27.9 | [55] |
| South Africa | Tigerfish | 5.8 | [56] |
| Uganda | Breast milk | 0.59–8.11 | [57] |

nd, not detected.
$^{*}$Mean concentration.

**Table 1.**
*Levels of PBDEs reported in the environment and biota from different locales worldwide.*

in the blood of workers in e-waste processing plants and other exposed populations [61]. BDE 47, 153, and 209 are the most predominant congeners reported in human serum and milk [55, 62]. The toxicity of PBDEs is backed up by numerous epidemiological studies. Scientific research has linked PBDE exposure to an array of adverse health effects [63]. To mention a few, penta- and octa-BDEs at a concentration of 10,000 ng g$^{-1}$ have been associated with disruption of thyroid hormone homeostasis [7]. Moreover, penta- and tetra-BDEs, within the range of 8000–18,000 ng g$^{-1}$, have been reported to affect the neurodevelopment of mice [64]. Exposure to high levels of deca-BDEs is likely to cause breast cancer [7]. PBDEs have been linked to developmental neurotoxicity and hence leading to severe effects on cognitive ability, behaviour, and health of both animals and humans [65, 66]. Several studies have also linked PBDEs with adverse effects on the human reproductive system. In particular, BDE-47, BDE-153, and BDE-154 in the range of 0.2–1.6 ng g$^{-1}$ have been confirmed to have negative impacts on testosterone, luteinizing hormone, and estradiol [67]. Therefore, there is a need to have robust, accurate and reproducible methods to quantify PBDEs in different environmental matrices. The sections that follow will discuss these aspects with a particular focus on aquatic media.

## 3. Sample pre-treatment methods

Sample pre-treatment steps such as pre-concentration and clean-up are paramount before instrumental analysis [2, 68]. These steps ensure that analytes are enriched and converted into the right form/state to achieve their detection and any matrix that may interfere with the determination of the analytes is removed [69].

The choice of sample pre-treatment step is dependent on the physicochemical properties of the targeted analytes, their concentration in the environment, and the complexity of matrix interference [70, 71]. Soxhlet extraction, a traditional liquid-solid extraction method, has been used for decades in the extraction of analytes from their complex solid matrices. With the combination of polar and non-polar solvents, the Soxhlet extraction strategy has been proved to be efficacious, achieving extraction efficiencies greater than 70% [72, 73]. However, this method is hindered by several factors such as long extraction duration, excessive solvent consumption, and the need for subsequent clean-up steps [74]. With increasing demand for economical and fast sample extraction strategies with high enrichment factors, coupled with SPE clean-up procedures, techniques such as UAE, PLE, MAE, and supercritical fluid extraction (SFE) have been adopted in enrichment of analytes from solid matrices.

UAE encompasses the introduction of a finely divided sample contained in a sample holder in an ultrasonic bath with solvent and subjected to ultrasonic radiation. UAE is a vital technique in achieving sustainable green chemistry and is primarily employed in the extraction of analytes from solid sample matrices [75, 76]. This technique can achieve complete extraction with high reproducibility within a short duration. Moreover, small quantities of extraction solvents are used as compared to conventional Soxhlet extraction [77]. Methanol, acetonitrile, ethanol, and acetone are typical extractants used in this method in minimal volume. UAE based on ultrasound assisted-dispersive solid phase extraction (UAE-DSPE) coupled to GC-MS has been reported to achieve exemplary limits of detection and extraction efficiencies for 7 BDE congeners from dust samples collected from air conditioning filters in the range of 1.4–8.4 ng g$^{-1}$ and 90–102%, respectively [78]. Some of the benefits of UAE include faster kinetics and an increase in extraction yield. Ultrasound can also reduce the operating temperature allowing the extraction of thermally labile compounds [79].

Unlike traditional Soxhlet extraction that consumes a large volume of solvent, PLE, also referred to as pressurized solvent extraction, has been of great interest due to its extraction effectiveness. Extraction of analytes from their environmental matrices is achieved via a synergistic mechanism that proceeds through liquid solvents at elevated temperature and pressure, which altogether enhance extraction throughput as compared with other techniques performed at ordinary atmospheric conditions [80]. PLE is viewed as another 'green' option for traditional sample extraction methods. High temperature accomplishes a higher dispersion rate, while high pressure keeps the extraction solvent below its boiling point. During the determination of brominated flame retardants in e-waste samples, PLE and UAE were evaluated in regard to extraction efficiencies. PLE demonstrated high extraction efficiencies of 95–100% as compared to 10–50% for UAE [81]. When contrasted with the conventional methods, PLE shows a decrease in extraction time and a significant decrease in the overall consumption of organic solvents [82].

Another type of extraction technique that enables a three-fold reduction in extraction time and solvent is MAE. This is a sample extraction method that employs microwave energy to extract analytes from solid sample matrices in contact with extraction solvents. Microwave energy directly generates heat which initiates molecular motion of the analytes in the solid-solvent complex mixture, hence facilitating the mass transfer of the target analyte from the solid matrix to the extracting solvent [83, 84]. MAE has been reported to achieve good recoveries of 80–106%, 72.4–108.4%, and 80–110% in the extraction/pre-concentration of PBDEs from airborne particulate matter [85], e-waste materials [86], and sewage sludge samples [87], respectively. Compared with Soxhlet extraction, MAE achieves better recoveries and uses small amounts of solvents (30 mL versus 200 mL for

Soxhlet extraction), at the same time allowing control of extraction parameters, such as extraction time and temperature [88]. However, MAE has some shortcomings, whereby the extracted sample usually contains some matrix interferences, such as lipids and lipophilic compounds, therefore, filtration and clean-up steps are required, which subsequently consume extra organic solvents.

Supercritical fluid extraction (SFE) is another method employed to extract PBDEs from solid matrices. Supercritical $CO_2$ is often used as an extracting solvent, which has the capability of attaining recoveries above 97%. Moreover, the extraction efficiency of SFE can be further improved by the use of modifiers such as acetonitrile, toluene, and tetrahydrofuran [89]. A successful application of SFE in the extraction of PBDEs from polymeric materials was reported by Peng et al. [90]. The authors used supercritical $CO_2$ as a solvent and SFE operating parameters such as temperature and pressure were optimized at 65°C and 20 MPa, respectively, achieving 97.6% extraction efficiency. This technique is a greener alternative to other techniques that use a large volume of solvents.

Numerous methodologies have been adopted in the determination of PBDE pollutants in liquid matrices. SPE and conventional LLE have been embraced as routine extraction techniques for PBDEs in liquid samples. The extractive capability of LLE is based on the transfer of analytes from an aqueous polar phase to a non-polar organic phase [91]. LLE coupled with GC-MS has been applied in the determination of 13 PBDEs and their metabolites in water, with recoveries of 77%-102% [92]. LLE has also been a desirable extraction method in the preparation of biota samples for the determination of PBDEs. Recently, a study aimed at assessing *in utero* exposure of 24 tri- to deca- BDE congeners on primiparous mothers in Kampala, Uganda reported a successful application of LLE, with appreciable recoveries of 81–91% [93]. However, LLE has some shortcomings; it suffers from low recovery, poor selectivity, high matrix interference in chromatographic analysis and increased sample loads [94]. In addition, the extraction of PBDEs from water samples requires extremely large volumes of solvents due to their hydrophobic character and low concentration in water, thus limiting its applications [95]. To overcome these challenges, different configurations of SPE have been adopted in sample enrichment strategies. SPE is a modern sample pre-treatment technique employed to concentrate analytes from liquid samples and to remove matrix interferents during the clean-up step, achieving exemplary recoveries and reproducible results over LLE [96, 97]. SPE protocols are usually performed by the use of a small column or separation cartridge packed with an appropriate sorbent material [98, 99]. Target analytes are adsorbed by the sorbent materials and later eluted with a solvent that has a greater affinity for the analytes. The chemistry behind this separation is based on intermolecular forces between the analytes, active sites of the adsorbent, and the liquid phase of the matrix [100]. SPE can be performed through an on-line or off-line approach. The on-line SPE configuration, which may enable automation, is directly coupled with specific analytical systems such as gas chromatography (GC) or high-performance liquid chromatography (HPLC). Whereas in the off-line protocol, a pre-concentration step is done separately using cartridges and further eluting the adsorbed analyte with an appropriate solvent for eventual chromatographic analysis [101]. Because of its robustness and flexibility, SPE has been widely employed in different analytical procedures in pre-concentration and clean-up steps in the determination of PBDEs [96, 102].

While SPE continues to be used because of its affordability and ease of use, other formats that offer high enrichment factors and shorter extraction times, such as SPME, stir-bar sorptive extraction (SBSE) and dispersive solid-phase extraction (DSPE), have been introduced [103]. SPME is an innovation and improvement of conventional SPE. Its stationary phase comprises of fused-silica fibers coated with a

polydimethylsiloxane (PDMS) layer which are reusable. With this new formulation, the application of SPE has become versatile such that it can accommodate small volumes of samples. Furthermore, SPME has been considered an almost solvent-free extraction technique and can be easily automated as compared to conventional SPE [104, 105]. A miniaturized SPME has been applied in the extraction of PBDEs in environmental water samples followed by GC-MS quantitation, with low limits of detection and appreciable recoveries of 76.5–125.4% [106]. SBSE is a similar technique to SPME that has been adopted in the enrichment of PBDEs in liquid samples due to its improved extraction efficiency. The stir bars are coated with a thinner PDMS layer, as opposed to a thicker layer in SPME, a factor that allows improved enrichment efficiency [107, 108]. DSPE is another format of SPE based on the dispersion of solid sorbent materials in liquid samples to facilitate the isolation and extraction of target analytes from the complex sample matrix. In this process, matrix interferences remain embedded in the supernatant, which is later discarded while the target analyte is bound to the sorbent material and which is eventually eluted with a viable solvent [109]. DSPE has been employed in the enrichment and determination of PBDEs with recoveries within the range of 60–140% [110].

### 3.1 Advances in SPE sorbents

Complexity and matrix interferences encountered during sample preparation steps have attracted the invention of more selective sorbents to replace conventional silica sorbents that are associated with a number of drawbacks, such as instability at extreme pHs and low extraction efficiencies [111]. The new sorbents that include, nanocomposite materials, metal-organic frameworks, and molecularly imprinted polymers, among others, are characterized with high sensitivity and selectivity towards various environmental organic pollutants. They achieve fast dispersion and efficient recycling when applied in complex sample matrices [112, 113]. Reported nanocomposite sorbents in SPE for PBDE-containing samples include carbon nanotubes, graphene oxide (GO) [114, 115], and magnetic nanocomposite materials [113]. However, nanocomposite sorbents in classical SPE schemes have been associated with various drawbacks. A few of these challenges have been described in flow as well as batch systems, which originate from a slow flow rate of the sample through the packed SPE column and difficulty in separating the sorbent from the large volume of aqueous sample [113].

Other sorbent materials with fascinating properties are metal-organic frameworks (MOFs). These are hybrids of organic and inorganic materials characterized by a porous structure, large surface area, uniform nanoscale cavities, high adsorption capacity, and high thermal and chemical stability. Due to these advantageous properties, this class of materials has recently attracted enormous attention in the field of sample preparation [116]. The development of MOF adsorbents is still at its infancy stages, therefore, a limited number of studies have reported their application particularly in enrichment and determination of environmental PBDEs. A zirconium-based metal-organic framework material (UiO-66-OH) is a good example of a MOF. It has been synthesized and successfully applied as an adsorbent in SPME for enrichment and detection of 5 BDE congeners in milk samples using GC-MS, with low limits of detection in the range of 0.15–0.35 ng $L^{-1}$ and excellent recoveries of 74.7%–118.0% [117]. A contrast study using silica-based sorbents in SPE for determination of 12 PBDEs in human serum, achieved mean recoveries of 64–95% and limits of detection in the range of 0.1–4.0 ng $g^{-1}$ by using GC-MS [102], an evidence that MOF sorbents offer promising analytical results as compared with conventional sorbents.

With growing interest in sorbents that offer extraordinary extractive capability in SPE, molecularly imprinted polymers (MIPs) have been extensively explored

as attractive options due to their robustness and selectivity towards particular target analytes providing exemplary substitute sorbents in sample clean-up and pre-concentration steps, especially in SPE and SPME [118]. MIPs are synthesized through molecular imprinting technology that involves polymerizing functional and cross-linking monomers in the presence of a target analyte, followed by the removal of the analyte to leave behind analyte-specific cavities. Their selectivity enables substantive removal of matrix interferents during the sample pre-treatment step [119]. MIP-based sorbents are readily available substitutes to silica-based adsorbents, which are reported to suffer from matrix interference, low selectivity, and sensitivity towards organic pollutants and may involve multiple steps that are labour-intensive for complete removal of interferences [120]. For example, commercial molecularly imprinted solid-phase extraction (MISPE) cartridges alongside alkaline extraction have been applied in aqueous enrichment and quantitation of PBDEs using GC-MS [121]. The extraction of PBDEs using MISPE gave recoveries above 60% compared to alkaline extraction which was below 60%. This confirms the selectivity capability of MIPs towards PBDEs from a complex environmental matrix. A more recent study has also reported recoveries of 60–87% in clean-up of soil and sediment samples using dummy molecularly imprinted polymers as SPE sorbent materials during determination of BDE-47 and BDE-99 [122].

| Sample preparation technique | PBDE congeners | Sample analyzed | Analytical technique | % Recoveries | Reference |
|---|---|---|---|---|---|
| SPE | BDE-28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183 & 209 | Human serum | GC-ECD | 64–95 | [102] |
| | BDE-47 and 99 | Soil and bottom sediment | GC-MS | 60–87 | [125] |
| PLE | BDE-28, 47, 99, 100, 153, 154 & 183 | Soil | GC-MS | 95 ± 9 | [68] |
| | BDE-28, 47, 99, 100, 154, 155 & 183 | Soil and sediment | GC-MS | 84–103 | [92] |
| LLE | BDE-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183 & 190 | Soil and sediment | GC-MS | 85–103 | [92] |
| Soxhlet extraction | 42 mono- to deca-BDEs | Indoor dust sample | GC-MS | ≥ 70 | [72] |
| UAE | BDE-1, 3, 7, 8, 28 & 47 | Industrial effluent | HPLC | 98.7 | [126] |
| SPME | BDE-49, 99, 100, 153 & 154 | Milk and water | GC-ECD | 90–119 | [127] |
| MAE | BDE-47, 99, 100, 138, 153, 154, 184 & 209 | Sewage sludge | GC-MS | 80–110 | [87] |

**Table 2.**
*Examples of sample preparation strategies.*

However, a wide range of limitations still exist in MIPs, especially their poor water compatibility. Consequently, since MIPs and target analytes mainly interact through hydrogen-bonding, their recognition capability would be easily disturbed by polar solvents such as water. Therefore, the adsorption process is normally performed in non-polar or low-polar solvents such as dichloromethane and *n*-hexane rather than polar solvents. Additionally, polar solvents have a tendency to occupy binding sites, which affects the recognition capacity for the target analytes. In this context, it is necessary to continually invent new synthesis strategies for water-compatible MIPs [123, 124]. A summary of some of the sample pre-concentation strategies and their extraction efficiencies is presented in **Table 2**.

## 4. Analytical techniques for the detection of PBDEs

Sample pre-treatment steps are followed by quantification of the analytes using various detection systems. The choice of detection system depends on the physicochemical properties of the target analyte and the required detection levels. Detection techniques for quantification of PBDEs have evolved from liquid chromatography to gas chromatography and recently, miniaturized systems that involve the use of sensors. For chromatographic techniques, it's important to optimize the operational parameters to actualize reliable instrumental results. It is highly recommended to use a sample injector with programmed temperature vaporization (PTV) to avoid degradation of thermally labile BDE congeners. Additionally, the temperature of injection should be accurately defined, especially when using a split/splitless injector, which minimizes chances of thermal degradation of higher BDEs congers as well as discrimination of lower brominated congeners [95, 128]. The choice of a column is another important aspect in the analysis of PBDEs where lower brominated congeners are well separated on longer columns, whereas higher brominated congeners are well separated on shorter columns. In the case of a mixture comprising of a wide range of BDE congeners, a short column is highly recommended, which well separates nona- and deca-BDEs [129]. HPLC coupled with mass spectrometry (MS), is one of the chromatographic techniques which has rarely been applied in the quantification of some PBDE congeners. The HPLC separation is hindered by several factors such as poor solubility of highly brominated diphenyl ethers in the polar solvents of the mobile phase, especially in reversed-phase, and, thus, requiring the sample to be enriched with an organic modifier. Normal phase HPLC has offered better separation of some PBDEs though it still results in incomplete separation, especially when an electrospray ionization detector is incorporated [130]. One group used an automated on-line sample pre-concentration device coupled with HPLC-MS to determine decabrodiphenyl ether in human serum samples. This method achieved detection limits of 26.0 ng L$^{-1}$ [130]. Otherwise, better detection limits of 0.2-25 ng L$^{-1}$ were tenable when similar samples were analyzed for 12 PBDEs including decabromodiphenyl ether using gas chromatography-electron capture detection (GC-ECD) [102]. However, GC-ECD exhibits low selectivity and suffers from matrix interferences originating especially from halogenated species, as compared to GC-MS, which overcomes these challenges [131]. Fontana et al. [16] employed a coupled system, ultrasound-assisted emulsification microextraction-GC-MS (UAEMA-GC-MS) to determine PBDEs in water samples, with appreciably low detection limits of 1–2 ng L$^{-1}$. Moreover, lower limits of detection are achievable when tandem-mass spectrometry (MS$^2$) is utilized. For example, GC-MS$^2$ has been reported to achieve detection limits within the range of 0.002–0.0136 ng g$^{-1}$ lipid weight (lw) in the determination of PBDEs in breast milk and serum samples [132].

With the recent technological revolution, a more sensitive mass spectrometer, a high-resolution mass spectrometer (HRMS), has been found to be a promising alternative to a conventional mass spectrometer as it identifies the analyte without mass fragmentation and at the lowest mass unit [133]. With this new format of detection, very low detection limits of 0.000262–0.046 ng g$^{-1}$ for 23 PBDEs in dust samples were achieved [134]. However, GC-HRMS is more expensive than conventional GC-MS, compelling researchers to often rely on GC-MS since it is less expensive and readily available. Besides, the demand for techniques that provide rapid results at minimal cost has resulted in the introduction of sensor technology in the determination of PBDEs. In this context, various detection systems have been fabricated and shown a discerning capability in the detection of PBDEs. For instance, an immunoassay detection system based on graphene oxide-polydimethylsiloxane has demonstrated desirable limits of detection of 0.018 ng g$^{-1}$ for PBDEs in a standard solution and environmental water samples [135]. Similarly, a novel electrochemical immunoassay sensor used for the detection of BDE-28, 47, 99, 100, 153, and 154 in food samples, achieved a detection limit of 0.00018 ng L$^{-1}$ [136]. These limits are comparable with those obtained by HPLC, GC-MS, or GC-HRMS. A surface-enhanced Raman scattering-based sensor is another detection system that has been successfully applied for rapid detection of BDE 47 in aqueous media, with detection limits of 0.0364 ng L$^{-1}$ [137]. The use of sensory techniques is cheaper and a low concentration of contaminants can be detected. Moreover, the analysis duration is reduced from 10 minutes to 3 minutes. Thus, these sensor methods offer scope for further evaluation.

## 5. Conclusion

This chapter has discussed PBDEs as emerging environmental pollutants, their sources, and toxicological implications on humans and their determination in the environment. Sample pre-concentration methods for PBDE-containing samples that include UAE, PLE, UAME, PLE, SFE, SPE, SPME, SBSE, and DSPE have been critically reviewed as preferred alternatives to LLE and Soxhlet extraction due to their enhanced extraction efficiency. Novel SPE and SPME sorbents that provide the desired selectivity in the determination of PBDEs have also been discussed. Though these sorbents are promising, their application in MISPE in the determination of PBDEs has been scantly employed and its dynamics are still at its infancy stages. Therefore, there is room for continuous introduction of highly selective materials for the quantification of PBDEs in the environment. Alongside the evolution of sample pre-treatment techniques for the detection of PBDEs, rapid sensor-based techniques that achieve the desired figures of merit similar to traditional instrumentation techniques have demonstrated great potential.

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## Conflict of interest

The authors declare no conflict of interest.

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## References

[1] Priti and K. Mandal, "Review on evolution of municipal solid waste management in India: practices, challenges and policy implications," *J. Mater. Cycles Waste Manag.*, vol. 21, pp. 1263-1279, 2019.

[2] Martín-Pozo L, de Alarcón-Gómez B, Rodríguez-Gómez R, García-Córcoles MT, Çipa M, Zafra-Gómez A. Analytical methods for the determination of emerging contaminants in sewage sludge samples. A review. *Talanta*. 2019;**192**:508-533

[3] Adeyemo OK. Consequences of pollution and degradation of Nigerian aquatic environment on fisheries resources. *Environmentalist*. 2004;**23**:297-306

[4] C. Bogdal, A. C. Gerecke, P. Schmid, N. V Heeb, and M. Sturm, "Temporal trends, congener patterns, and sources of octa-, nona-, and decabromodiphenyl ethers (PBDE) and hexabromocyclododecanes (HBCD) in Swiss lake sediments," *Environ. Sci. Technol.*, vol. 42, pp. 6378-6384, 2008.

[5] Vonderheide AP, Mueller KE, Meija J, Welsh GL. Polybrominated diphenyl ethers: Causes for concern and knowledge gaps regarding environmental distribution, fate and toxicity. *Sci. Total Environ.* 2008;**400**:425-436

[6] A. Besis and C. Samara, "Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor environments - A review on occurrence and human exposure," *Environ. Pollut.*, vol. 169, pp. 217-229, 2012.

[7] Darnerud PO, Eriksen GS, Jóhannesson T, Larsen PB, Viluksela M. Polybrominated diphenyl ethers: Occurrence, dietary exposure, and toxicology chemical and physical properties of PBDEs. *Environ. Health Perspect.* 2001;**109**:49-68

[8] Mariussen E et al. Elevated levels of polybrominated diphenyl ethers (PBDEs) in fish from Lake Mjøsa, Norway. *Sci. Total Environ.* 2007;**390**:132-141

[9] B. Li, M. N. Danon-schaffer, and J. R. Grace, "Occurrence of PFCs and PBDEs in landfill leachates from across Canada," *Water, Air Soil Pollut.*, vol. 223, pp. 3365-3372, 2012.

[10] Petreas M, Oros D. Polybrominated diphenyl ethers in California wastestreams. *Chemosphere*. 2009;**74**:996-1001

[11] Gouin T, Thomas GO, Chaemfa C, Harner T. Concentrations of decabromodiphenyl ether in air from Southern Ontario: Implications for particle-bound transport. *Chemosphere*. 2006;**64**:256-261

[12] Mandalakis M, Atsarou V, Stephanou EG. Airborne PBDEs in specialized occupational settings, houses and outdoor urban areas in Greece. *Environ. Pollut.* 2008;**155**:375-382

[13] Ocio AB, Lobet JML, Omingo JLD, Orbella JC, Eixido AT. Polybrominated diphenyl ethers (PBDEs) in foodstuffs: Human exposure through the diet. *J. Agric. Food Chem.* 2003;**51**:3191-3195

[14] Wang P et al. Evaluation of Soxhlet extraction, accelerated solvent extraction and microwave-assisted extraction for the determination of polychlorinated biphenyls and polybrominated diphenyl ethers in soil and fish samples. *Anal. Chim. Acta*. 2010;**663**:43-48

[15] Quiroz R, Arellano L, Grimalt JO, Fern P. Analysis of polybrominated diphenyl ethers in atmospheric deposition and snow samples by solid-phase disk extraction. *J. Chromatogr. A*. 2008;**1192**:147-151

[16] Fontana AR, Wuilloud RG, Martínez LD, Altamirano JC. Simple approach based on ultrasound-assisted emulsification-microextraction for determination of polibrominated flame retardants in water samples by gas chromatography-mass spectrometry. *J. Chromatogr. A*. 2009;**1216**:147-153

[17] E. Bizkarguenaga et al., "Focused ultrasound assisted extraction for the determination of PBDEs in vegetables and amended soil," *Talanta*, vol. 119, pp. 53-59, 2014.

[18] Ghosh R, Hageman KJ, Björklund E. Selective pressurized liquid extraction of three classes of halogenated contaminants in fish. *J. Chromatogr. A*. 2011;**1218**:7242-7247

[19] Vazquez-roig P, Picó Y. Pressurized liquid extraction of organic contaminants in environmental and food samples. *Trends Anal. Chem.* 2015;**71**:55-64

[20] M. Karlsson, A. Julander, B. Van Bavel, and G. Lindstro, "Solid-phase extraction of polybrominated diphenyl ethers in human plasma-comparison with an open column extraction method," *Chromatographia*, vol. 61, pp. 67-73, 2005.

[21] Liu X et al. Solid-phase extraction combined with dispersive liquid – liquid microextraction for the determination for polybrominated diphenyl ethers in different environmental matrices. *J. Chromatogr. A*. 2009;**1216**:2220-2226

[22] Zhang M, Zeng J, Wang Y, Chen X. Developments and trends of molecularly imprinted solid-phase microextraction. *J. Chromatogr. Sci.* 2013;**51**:577-586

[23] Stapleton HM. Instrumental methods and challenges in quantifying polybrominated diphenyl ethers in environmental extracts. *Anal Bioanal Chem*. 2006;**386**:807-817

[24] Rigét F, Vorkamp K, Dietz R, Rastogi SC. Temporal trend studies on polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in ringed seals from East Greenland. *J. Environ. Monit.* 2006;**8**:1000-1005

[25] A. Schecter, M. Pavuk, O. Päpke, J. J. Ryan, L. Birnbaum, and R. Rosen, "Polybrominated diphenyl ethers (PBDEs) in U.S. mothers' milk," *Environ. Health Perspect.*, vol. 111, pp. 1723-1729, 2003.

[26] Kuramochi H, Maeda K, Kawamoto K. Physicochemical properties of selected polybrominated diphenyl ethers and extension of the UNIFAC model to brominated aromatic compounds. *Chemosphere*. 2007;**67**:1858-1865

[27] Harner T, Shoeib M. Measurements of octanol-air partition coefficients (KOA) for polybrominated diphenyl ethers (PBDEs): Predicting partitioning in the environment. *J. Chem. Eng.* 2002;**47**:228-232

[28] Wei-haas ML, Hageman KJ, Chin Y. Partitioning of polybrominated diphenyl ethers to dissolved organic matter isolated from Arctic surface waters. *Environ. Sci. Technol.* 2014;**48**:4852-4859

[29] Li Y et al. Influences of binding to dissolved organic matter on hydrophobic organic compounds in a multi-contaminant system: Coefficients, mechanisms and ecological risks. *Environ. Pollut.* 2015;**206**:461-468

[30] Winid B. Environmental threats of natural water contamination with polybrominated diphenyl ethers (PBDEs). *Polish J. Environ. Stud.* 2015;**24**:47-55

[31] Siddiqi MA, Kurt RD. Polybrominate diphenyl ethers

(PBDEs): New pollutants-old diseases. *Clin. Med. Reaserach*. 2003;**1**:281-290

[32] Rodigari F, Crane D, Sericano J. Levels and Distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and Bivalves from the San Francisco Estuary. *Environ. Sci. Technol*. 2005;**39**:33-41

[33] Kodavanti PRS, Valdez MC, Yamashita N. *Brominated flame retardants and perfluorinated chemicals*. Third Edit: Elsevier Inc.; 2018

[34] Taylor P, Akutsu K. Food additives & contaminants: Part B: Surveillance dietary intake estimations of polybrominated diphenyl ethers (PBDES) based on a total diet study in Osaka, Japan View Dataset. *Food Addit. Contam.* 2008;**1**:58-68

[35] Darnerud PO, Hallgren S. Polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and chlorinated paraffins (CPs) in rats - Testing interactions and mechanisms for thyroid hormone effects. *Toxicology*. 2002;**177**:227-243

[36] Sjödin A, Hagmar L, Klasson-wehler E, Kronholm-diab K, Jakobsson E, Bergman A. Flame retardant exposure: Polybrominated diphenyl ethers in blood from Swedish workers. *Environ. Health Perspect.* 1999;**107**:643-648

[37] P. R. S. Kodavanti, J. E. Royland, C. Osorio, W. M. Winnik, and P. Ortiz, "Developmental exposure to a commercial PBDE mixture: Effects on protein networks in the cerebellum and hippocampus of rats," *Environ. Health Perspect.*, vol. 123, pp. 428-436, 2015.

[38] Gevao B, Ghadban AN, Uddin S, Jaward FM, Bahloul M, Zafar J. Polybrominated diphenyl ethers (PBDEs) in soils along a rural-urban-rural transect: Sources, concentration gradients, and profiles. *Environ. Pollut.* 2011;**159**:3666-3672

[39] Eljarrat E, Labandeira A, Marsh G. Effect of sewage sludges contaminated with polybrominated diphenylethers on agricultural soils. *Chemosphere*. 2008;**71**:1079-1086

[40] Huang Y, Chen L, Peng X, Xu Z, Ye Z. PBDEs in indoor dust in South-Central China : Characteristics and implications. *Chemosphere*. 2010;**78**:169-174

[41] Kang Y, Wang HS, Cheung KC, Wong MH. Polybrominated diphenyl ethers (PBDEs) in indoor dust and human hair. *Atmos. Environ.* 2011;**45**:2386-2393

[42] Harrad S, Ibarra C, Diamond M, Melymuk L, Robson M, Douwes J. Polybrominated diphenyl ethers in domestic indoor dust from Canada, New Zealand, United Kingdom and United States. *Environ. Int.* 2008;**34**:232-238

[43] Abafe OA, Martincigh BS. Polybrominated diphenyl ethers and polychlorinated biphenyls in indoor dust in Durban, South Africa. *Environ. Sci. Pollut. Res.* 2015;**25**:547-556

[44] Daso AP, Fatoki OS, Odendaal JP. Occurrence of polybrominated diphenyl ethers (PBDEs) samples from the Diep River, Cape Town, South Africa. *Environ. Sci. Pollut.* 2013;**20**:5168-5176

[45] Streets SS, Henderson SA, Stoner AD, Carlson DL, Simcik MF, Swackhamer DL. Partitioning and bioaccumulation of PBDEs and PCBs in Lake Michigan. *Environ. Sci. Technol.* 2006;**40**:7263-7269

[46] Banasik M, Hardy M, Stedeford T. An assessment of the human risks from exposure to polybrominated diphenyl ethers (PBDEs) in house dust. *Chemosphere*. 2009;**77**:704-705

[47] Harrad S, Abdallah MA, Oluseyi T. Polybrominated diphenyl ethers and polychlorinated biphenyls in dust from cars, homes, and offices in Lagos, Nigeria. *Chemosphere*. 2016;**146**:346-353

[48] Arinaitwe K, Muir DCG, Kiremire BT, Fellin P, Li H, Teixeira C. Polybrominated diphenyl ethers and alternative flame retardants in air and precipitation samples from the Northern Lake Victoria region, East Africa. *Environ. Sci. Technol.* 2014;**66**:1453-1461

[49] H. Sun, Y. Qi, D. Zhang, Q. X. Li, and J. Wang, "Concentrations, distribution, sources and risk assessment of organohalogenated contaminants in soils from Kenya, Eastern Africa," *Environ. Pollut.*, vol. 209, pp. 177-185, 2016.

[50] Wang Y, Luo C, Li J, Yin H, Li X, Zhang G. Characterization of PBDEs in soils and vegetations near an e-waste recycling site in South China. *Environ. Pollut.* 2011;**159**:2443-2448

[51] Chen L et al. PBDEs in sediments of the Beijiang River, China: Levels, distribution, and influence of total organic carbon. *Chemosphere*. 2009;**76**:226-231

[52] Zhao X, Zhang H, Ni Y, Lu X, Zhang X, Su F. Polybrominated diphenyl ethers in sediments of the Daliao River Estuary, China: Levels, distribution and their influencing factors. *Chemosphere*. 2011;**82**:1262-1267

[53] Karin O, Warman K, Tomas O. Distribution and levels of brominated flame retardants in sewage sludge. *Chemosphere*. 2002;**48**:805-809

[54] Gevao B, Muzaini S, Helaleh M. Occurrence and concentrations of polybrominated diphenyl ethers in sewage sludge from three wastewater treatment plants in Kuwait. *Chemosphere*. 2008;**71**:242-247

[55] Sjödin A, Wong L, Jones RS, Park A, Zhang Y, Hodge C. Serum concentrations of polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyl (PBB) in the United States population: 2003-2004. *Environ. Sci. Technol.* 2008;**42**:1377-1384

[56] Wepener V, Smit N, Covaci A, Dyke S, Bervoets L. Seasonal bioaccumulation of organohalogens in Tigerfish, Hydrocynus vittatus castelnau, from Lake Pongolapoort, South Africa. *Bull Env. Contam Toxicol*. 2012;**88**:277-282

[57] Matovu H, Sillanpää M, Ssebugere P. Polybrominated diphenyl ethers in mothers' breast milk and associated health risk to nursing infants in Uganda. *Sci. Total Environ.* 2019;**692**:1106-1115

[58] Ni H, Ding C, Lu S, Yin X, Olatunbosun S. Food as a main route of adult exposure to PBDEs in Shenzhen, China. *Sci. Total Environ.* 2012;**437**:10-14

[59] N. Wu, T. Herrmann, O. Paepke, J. Tickner, R. Hale, and E. Harvey, "Human exposure to PBDEs: Associations of PBDE body burdens with food consumption and house dust concentrations," vol. 41, pp. 1584-1589, 2007.

[60] Abdallah MA, Pawar G, Harrad S. Effect of bromine substitution on human dermal absorption of polybrominated diphenyl ethers effect of bromine substitution on human dermal absorption of polybrominated diphenyl ethers. *Environ. Sci. Technol.* 2015;**49**:10976-10983

[61] Kuo L, Cade SE, Cullinan V, Schultz IR. Polybrominated diphenyl ethers (PBDEs) in plasma from e-waste recyclers, outdoor and indoor workers in the Puget Sound, WA region. *Chemosphere*. 2019;**219**:209-216

[62] Wang C, Lin Z, Dong Q, Lin Z, Lin K, Wang J. Ecotoxicology and environmental safety polybrominated diphenyl ethers (PBDEs) in human serum from Southeast China. *Ecotoxicol. Environ. Saf.* 2012;**78**:206-211

[63] He Y, Murphy MB, Yu RM, Lam MH, Hecker M, Giesy JP. Effects of 20 PBDE metabolites on steroidogenesis in the H295R cell line. *Toxicol. Appl. Pharmacol.* 2008;**176**:230-238

[64] Ji K, Choi K, Giesy JP, Musarrat J, Takeda S. Genotoxicity of several polybrominated diphenyl ethers (PBDEs) and hydroxylated PBDEs, and their mechanisms of toxicity. *Environ. Sci. Technol.* 2011;**45**:5003-5008

[65] Eriksson P, Jakobsson E, Fredriksson A. Brominated flame retardants: A novel class of developmental neurotoxicants in our environment? *Environ. Health Perspect.* 2001;**109**:903-908

[66] Chen L, Huang C, Yu L, Zhu B, Lam J, Zhou B. Prenatal transfer of polybrominated diphenyl ethers (PBDEs) results in developmental neurotoxicity in zebra fish larvae. *Environ. Sci. Technol.* 2012;**46**:9727-9734

[67] Roze E, Meijer L, Bakker A, Van Braeckel KNJA, Sauer PJJ, Bos AF. Prenatal exposure to organohalogens, including brominated flame retardants, influences motor, cognitive, and behavioral performance at school age. *Environ. Health Perspect.* 2009;**117**:1953-1958

[68] Zhang Z, Shanmugam M, Rhind SM. PLE and GC-MS determination of polybrominated diphenyl ethers in soils. *Chromatographia*. 2010;**72**:535-543

[69] Kole PL, Venkatesh G, Kotecha J, Sheshala R. Recent advances in sample preparation techniques for effective bioanalytical methods. *Biomed. Chromatogr.* 2011;**25**:199-217

[70] Covaci A, Voorspoels S, Ramos L, Neels H, Blust R. Recent developments in the analysis of brominated flame retardants and brominated natural compounds. *J. Chromatogr. A*. 2007;**1153**:145-171

[71] Berton P, Lana NB, Ríos JM, García-reyes JF, Altamirano JC. State of the art of environmentally friendly sample preparation approaches for determination of PBDEs and metabolites in environmental and biological samples : A critical review. *Anal. Chim. Acta*. 2016;**905**:24-41

[72] Gevao B et al. House dust as a source of human exposure to polybrominated diphenyl ethers in Kuwait. *Chemosphere*. 2006;**64**:603-608

[73] Castro L, Capote P. Soxhlet extraction : Past and present panacea. *J. Chromatogr. A*. 2010;**1217**:2383-2389

[74] Da C, Wang R, Ye J, Yang S. Sediment records of polybrominated diphenyl ethers (PBDEs) in Huaihe River, China: Implications for historical production and household usage of PBDE-containing products. *Environ. Pollut.* 2019;**254**:112955-112963

[75] Hemwimol S, Pavasant P, Shotipruk A. Ultrasound-assisted extraction of anthraquinones from roots of Morinda citrifolia. *Ultrason. Sonochem.* 2006;**13**:543-548

[76] Tadeo L, Rosa AP, Albero B. Ultrasound-assisted extraction of organic contaminants. *Trends Anal. Chem.* 2019;**118**:739-750

[77] Chemat F, Rombaut N, Sicaire A, Meullemiestre A, Abert-vian M. Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. *Ultrason. Sonochem.* 2017;**34**:540-560

[78] Śmiełowska M, Zabiegała B. Determination of polybrominated diphenyl ethers (PBDEs) in dust samples collected in air conditioning filters of different usage – method development. *J. Chromatogr. A*. 2018;**1565**:57-67

[79] A. Jorge Moreda-Pineiro and Moreda-pineiro, "Combined assisted extraction techniques as green sample pre-treatments in food analysis," *Trends Anal. Chem.*, vol. 118, pp. 1-18, 2019.

[80] Mustafa A, Turner C. Pressurized liquid extraction as a green approach in food and herbal plants extraction : A review. *Anal. Chim. Acta*. 2011;**703**:8-18

[81] Vilaplana F, Karlsson P, Ribes-Greus A, Ivarsson P, Karlsson S. Analysis of brominated flame retardants in styrenic polymers. Comparison of the extraction efficiency of ultrasonication, microwave-assisted extraction and pressurised liquid extraction. *J. Chromatogr. A*. 2008;**1196-1197**:139-146

[82] Andreu V, Pic Y. Pressurized liquid extraction of organic contaminants in environmental and food samples. *Trends Anal. Chem.* 2019;**118**:709-721

[83] Flórez N, Conde E, Domínguez H. Microwave assisted water extraction of plant compounds. *J. Chem. Technol. Biotechnol.* 2015;**90**:590-607

[84] Llompart M, Celeiro M, Dagnac T. Microwave-assisted extraction of pharmaceuticals, personal care products and industrial contaminants in the environment. *Trends Anal. Chem.* 2019;**116**:136-150

[85] Beser MI, Beltrán J, Yusà V. Design of experiment approach for the optimization of polybrominated diphenyl ethers determination in fine airborne particulate matter by microwave-assisted extraction and gas chromatography coupled to tandem mass spectrometry. *J. Chromatogr. A*. 2014;**1323**:1-10

[86] Li Y, Wang T, Hashi Y, Li H, Lin J. Determination of brominated flame retardants in electrical and electronic equipments with microwave-assisted extraction and gas chromatography-mass spectrometry. *Talanta*. 2009;**78**:1429-1435

[87] Shin M, Svoboda ML, Falletta P. Microwave-assisted extraction (MAE) for the determination of polybrominated diphenylethers (PBDEs) in sewage sludge. *Anal Bioanal Chem*. 2007;**387**:2923-2929

[88] Pérez-Lemus N, López-Serna R, Pérez-Elvira SI, Barrado E. Analytical methodologies for the determination of pharmaceuticals and personal care products (PPCPs) in sewage sludge: A critical review. *Anal. Chim. Acta*. 2019;**1083**:19-40

[89] Shao M, Jiang J, Li M, Wu L, Hu M. Recent developments in the analysis of polybrominated diphenyl ethers and polybrominated biphenyls in plastic. *Rev. Anal. Chem.* 2016;**35**:133-143

[90] Peng S, Liang S, Yu M, Li X. Extraction of polybrominated diphenyl ethers contained in waste high impact polystyrene by supercritical carbon dioxide. *J. Mater. Cycles Waste Manag.* 2014;**16**:178-185

[91] Pedersen-Bjergaard S, Rasmussen KE, Grønhaug Halvorsen T. Liquid-liquid extraction procedures for sample enrichment in capillary zone electrophoresis. *J. Chromatogr. A*. 2000;**902**(1):91-105

[92] Hu X, Hu D, Chen W, Wu B, Lin C. Simultaneous determination of methoxylated polybrominated diphenyl ethers and polybrominated diphenyl ethers in water, soil and sediment from China by GC-MS. *J. Chromatogr. Sci.* 2015;**53**:1239-1249

[93] Matovu H, Ssebugere P, Ssebugere P. Prenatal exposure levels of polybrominated diphenyl ethers in mother-infant pairs and their transplacental transfer characteristics in Uganda (East Africa). *Environ. Pollut.* 2020;**258**:113723-113767

[94] Zhou S, Song Q, Tang Y, Naidong W. Critical review of development, validation, and transfer for high throughput bioanalytical LC-MS/MS methods. *Curr. Pharm. Anal.* 2006;**1**:3-14

[95] Fulara I, Czaplicka M. Methods for determination of polybrominated diphenyl ethers in environmental samples – review. *J. Sep. Sci.* 2012;**35**:2075-2087

[96] Chen Y, Xia L, Liang R, Lu Z, Li L, Huo B. Advanced materials for sample preparation in recent decade. *Trends Anal. Chem.* 2019;**120**:115652-115666

[97] Han F et al. Solid-phase extraction of seventeen alternative flame retardants in water as determined by ultra-high-performance liquid chromatography-tandem mass spectrometry. *J. Chromatogr. A*. 2019;**1602**:64-73

[98] Wille SMR, Lambert WEE. Recent developments in extraction procedures relevant to analytical toxicology. *Anal Bioanal Chem*. 2007;**388**:1381-1391

[99] Huck CW, Bonn GK. Recent developments in polymer-based sorbents for solid-phase extraction Recent developments in polymer-based sorbents for solid-phase extraction. *J. Chromatogr. A*. 2000;**9673**:51-72

[100] García-Córcoles MT et al. Chromatographic methods for the determination of emerging contaminants in natural water and wastewater samples: A Review. *Crit. Rev. Anal. Chem.* 2019;**49**:160-186

[101] Vasapollo G et al. Molecularly imprinted polymers: Present and future prospective. *Int. J. Mol. Sci.* 2011;**12**:5908-5945

[102] Covaci A, Voorspoels S. Optimization of the determination of polybrominated diphenyl ethers in human serum using solid-phase extraction and gas chromatography-electron capture negative ionization mass spectrometry. *J. Chromatogr. B*. 2005;**827**:216-223

[103] Vallecillos L, Pocurull E, Borrull F. A simple and automated method to determine macrocyclic musk fragrances in sewage sludge samples by headspace solid-phase microextraction and gas chromatography – mass spectrometry. *J. Chromatogr. A*. 2013;**1314**:38-43

[104] Seidi S, Yamini Y, Rezazadeh M. Electrochemically assisted solid based extraction techniques: A review. *Talanta*. 2015;**132**:339-353

[105] Madikizela LM, Ncube S, Chimuka L. Recent Developments in Selective Materials for Solid Phase Extraction. *Chromatographia*. 2019;**82**:1171-1189

[106] Liu L, Meng WK, Zhou YS, Wang X, Xu GJ, Wang ML. B-Ketoenamine-linked covalent organic framework coating for ultra-high-performance solid-phase microextraction of polybrominated diphenyl ethers from environmental samples. *Chem. Eng. J.* 2019;**356**:926-933

[107] Kelemen H, Hancu G, Papp LA. Analytical methodologies for the determination of endocrine disrupting compounds in biological and environmental samples. *Biomed. Chromatogr.* 2019;**2013**:1-23

[108] Rocha-Gutiérrez BA, Lee WY, Shane Walker W. Mass balance and mass loading of polybrominated diphenyl ethers (PBDEs) in a tertiary wastewater

treatment plant using SBSE-TD-GC/MS. *Water Sci. Technol.* 2016;**73**:302-308

[109] Rejczak T, Tuzimski T. A review of recent developments and trends in the QuEChERS sample preparation approach. *Open Chem.* 2015;**13**:980-1010

[110] Lu D et al. Determination of polybrominated diphenyl ethers and polychlorinated biphenyls in fishery and aquaculture products using sequential solid phase extraction and large volume injection gas chromatography/tandem mass spectrometry. *J. Chromatogr. B.* 2014;**945-946**:75-83

[111] Fontanals N, Marc RM. Materials for solid-phase extraction of organic compounds. *Separations*. 2019;**6**:56-82

[112] Ayazi Z. Application of nanocomposite-based sorbents in microextraction techniques. *Analyst*. 2017;**142**:721-739

[113] Yu M, Wang L, Hu L, Li Y, Luo D, Mei S. Recent applications of magnetic composites as extraction adsorbents for determination of environmental pollutants. *Trends Anal. Chem.* 2019;**119**:115611

[114] Zhang W, Sun Y, Wu C, Xing J, Li J. Polymer-functionalized single-walled carbon nanotubes as a novel sol-gel solid-phase micro-extraction coated fiber for determination of poly-brominated diphenyl ethers in water samples with gas chromatography-electron capture detection. *Anal. Chem.* 2009;**81**:2912-2920

[115] Xiang L, Sheng H, Bian Y, Kang J, Yang X, Herzberger A. Optimization of sample pretreatment based on graphene oxide dispersed acid silica gel for determination of polybrominated diphenyl ethers in vegetables near an e-waste recycling plant. *Bull. Environ. Contam. Toxicol.* 2019;**103**:23-27

[116] Li X, Ma W, Li H, Bai Y, Liu H. Metal-organic frameworks as advanced sorbents in sample preparation for small organic analytes. *Coord. Chem. Rev.* 2019;**397**:1-13

[117] H. L. Jiang, N. Li, X. Wang, X. Y. Wei, R. S. Zhao, and J. M. Lin, "A zirconium-based metal-organic framework material for solid-phase microextraction of trace polybrominated diphenyl ethers from milk," *Food Chem.*, vol. 317, no. 126436, 2020.

[118] Chidambara A, Duong D, Version D, Chidambara A. Molecularly imprinted polymers for sample preparation and biosensing in food analysis: progress and perspectives. *Biosens. Bioelectron.* 2017;**91**:606-615

[119] Li G, Row KH, Li G, Row KH. Recent applications of molecularly imprinted polymers (MIPs) on micro-extraction techniques. *Sep. Purif. Rev.* 2018;**47**:1-18

[120] He Y, Concheiro-Guisan M. Microextraction sample preparation techniques in forensic analytical toxicology. *Biomed. Chromatogr.* 2019;**33**:634-645

[121] Roszko M, Szymczyk K, Renata J. Simultaneous separation of chlorinated/brominated dioxins, poly- chlorinated biphenyls, polybrominated diphenyl ethers and their methoxylated derivatives from hydroxylated analogs on molecularly imprinted polymers prior to gas/liquid chromatography. *Talanta*. 2015;**144**:171-183

[122] Marć M, Wieczorek PP. Application potential of dummy molecularly imprinted polymers as solid-phase extraction sorbents for determination of low-mass polybrominated diphenyl ethers in soil and sediment samples. *Microchem. J.* 2019;**144**:461-468

[123] Hu Y, Pan J, Zhang K, Lian H, Li G. Novel applications of molecularly-imprinted polymers in sample preparation. *Trends Anal. Chem.* 2013;**43**:37-52

[124] Ansari S, Karimi M. Novel developments and trends of analytical methods for drug analysis in biological and environmental samples by molecularly imprinted polymers. *Trends Anal. Chem.* 2017;**89**:146-162

[125] Marć M, Panuszko A, Namieśnik J, Wieczorek PP. Preparation and characterization of dummy-template molecularly imprinted polymers as potential sorbents for the recognition of selected polybrominated diphenyl ethers. *Anal. Chim. Acta*. 2018;**1030**:77-95

[126] He K, Lv Y, Chen Y. Optimized determination of polybrominated diphenyl ethers by ultrasound-assisted liquid-liquid extraction and high-performance liquid chromatography. *J. Sep. Sci*. 2014;**37**:2874-2881

[127] Wang JX, Jiang DQ, Gu ZY, Yan XP. Multiwalled carbon nanotubes coated fibers for solid-phase microextraction of polybrominated diphenyl ethers in water and milk samples before gas chromatography with electron-capture detection. *J. Chromatogr. A*. 2006;**1137**:8-14

[128] Blanco SL, Vieites JM. Single-run determination of polybrominated diphenyl ethers (PBDEs) di- to deca-brominated in fish meal, fish and fish feed by isotope dilution: Application of automated sample purification and gas chromatography/ion trap tandem mass spectrometry (GC/ITMS). *Anal. Chim. Acta*. 2010;**672**:137-146

[129] Vonderheide AP. A review of the challenges in the chemical analysis of the polybrominated diphenyl ethers. *Microchem. J.* 2009;**92**:49-57

[130] Lin X, Li H, He X, Hashi Y, Lin J, Wang Z. Automated online pretreatment and cleanup recycle coupled with high-performance liquid chromatography-mass spectrometry for determination of deca-bromodiphenyl ether in human serum. *J. Sep. Sci*. 2012;**35**:2553-2558

[131] Stapleton HM et al. Determination of polybrominated diphenyl ethers in indoor dust standard reference materials. *Anal Bioanal Chem*; 2005

[132] Butryn DM, Gross MS, Chi LH, Schecter A, Olson JR, Aga DS. 'One-shot' analysis of polybrominated diphenyl ethers and their hydroxylated and methoxylated analogs in human breast milk and serum using gas chromatography-tandem mass spectrometry. *Anal. Chim. Acta*. 2015;**892**:140-147

[133] Schecter A, Päpke O, Kuang CT, Joseph J, Harris TR, Dahlgren J. Polybrominated diphenyl ether flame retardants in the U.S. population: Current levels, temporal trends, and comparison with dioxins, dibenzofurans, and polychlorinated biphenyls. *J. Occup. Environ. Med.* 2005;**47**:199-211

[134] Gou YY, Hsu YC, Chao HR, Que DE, Tayo LL, Lin CH. Pollution characteristics and diurnal variations in polybrominated diphenyl ethers in indoor and outdoor air from vehicle dismantler factories in Southern Taiwan. *Aerosol Air Qual. Res.* 2016;**16**:1931-1941

[135] Chałupniak A, Merkoçi A. Toward integrated detection and graphene-based removal of contaminants in a lab-on-a-chip platform. *Nano Res.* 2017;**10**:2296-2310

[136] Bettazzi F, Martellini T, Shelver WL, Cincinelli A, Lanciotti E, Palchetti I. Development of an

electrochemical immunoassay for the detection of polybrominated diphenyl ethers (PBDEs). *Electroanalysis*. 2016;**28**:1817-1823

[137] Sun Z, Du J, Yan L, Jing C. Rapid detection of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) using a portable Au-colloid SERS sensor. *J. Raman Spectrosc*. 2014;**45**:745-749