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Review

State of the art of environmentally friendly sample preparation approaches for determination of PBDEs and metabolites in environmental and biological samples: A critical review

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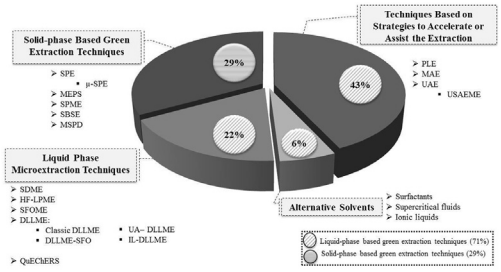
HIGHLIGHTS

- Green sample preparation approach for determination of PBDEs and metabolites.
- Liquid phase microextraction are used mostly for liquid samples treatment.
- Alternative solvents are scarcely used in PBDEs determination.
- Solvent assisted extraction are preferred for PBDEs' leaching from solid samples.
- Scarce reports of green analytical methodology for metabolites determination.

GRAPHICAL ABSTRACT



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ABSTRACT

Green chemistry principles for developing methodologies have gained attention in analytical chemistry in recent decades. A growing number of analytical techniques have been proposed for determination of organic persistent pollutants in environmental and biological samples. In this light, the current review aims to present state-of-the-art sample preparation approaches based on green analytical principles proposed for the determination of polybrominated diphenyl ethers (PBDEs) and metabolites (OH-PBDEs and MeO-PBDEs) in environmental and biological samples. Approaches to lower the solvent consumption and accelerate the extraction, such as pressurized liquid extraction, microwave-assisted extraction, and ultrasound-assisted extraction, are discussed in this review. Special attention is paid to miniaturized sample preparation methodologies and strategies proposed to reduce organic solvent consumption. Additionally, extraction techniques based on alternative solvents (surfactants, supercritical fluids, or ionic liquids) are also commented in this work, even though these are scarcely used for determination of PBDEs. In addition to liquid-based extraction techniques, solid-based analytical techniques are also addressed. The development of greener, faster and simpler sample preparation approaches has increased in recent years (2003–2013). Among green extraction techniques, those based on the liquid phase predominate over those based on the solid phase (71% *vs.* 29%, respectively). For solid samples, solvent

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assisted extraction techniques are preferred for leaching of PBDEs, and liquid phase microextraction techniques are mostly used for liquid samples. Likewise, green characteristics of the instrumental analysis used after the extraction and clean-up steps are briefly discussed.

Contents

1. Introduction

According to global demographic predictions, the human population will reach nine billion around the year 2050 [1]. Together with the worldwide economic and technological advances, the expected significant rise in chemical production has aroused special concern [1,2]. Thus, a holistic projection of the fate of the environment highlights the need for environment-friendly chemistry. The term 'Green Chemistry' was first suggested by Anastas in 1991, referring to the use of chemicals and processes that reduce risks to the environment and humans [2]. Green analytical chemistry arises as a new trend in this concept, promoting analytical techniques that require minimum consumption of solvents and reagents and thus reducing risks to the environment and humans [3].

Analytical methodologies commonly used for pollutant determination in biological and environmental samples include the following steps: sampling, sample conditioning (handling, storage, pre-cleaning), sample preparation (extraction, clean-up, and preconcentration), and instrumental analysis [4]. The sample preparation step is considered to be the bottleneck of the analysis because it is the most laborious, polluting, and time-consuming. Currently, waste volumes can be reduced using miniaturized and/or assisted extraction techniques, or simply by using alternative solvents, among other promising solutions [1]. Green extraction techniques have advantages over traditional techniques (liquid–liquid extraction (LLE) or solid-phase extraction (SPE)), including preserving or enhancing the analytical performance of the methodology, and operator risk and wastes generation are significantly reduced, leading to simple and low-cost analytical alternatives [5].

In the last years, environment-friendly techniques have been extensively used for extraction and preconcentration of inorganic and organic pollutants [6]. For the latter, polybrominated diphenyl ethers (PBDEs) received special attention due to their ubiquity, persistence and accumulation capability in the environment, as well as their adverse effects on human health and wildlife. Effects on nervous, reproductive, and endocrine systems in humans and wildlife were attributed to these pollutants [7]. PBDEs can be transported long-ranges away from the source through aqueous and/or terrestrial environmental compartments [8,9]. Due to their nonpolar character, these pollutants can easily accumulate not only in sediments and soils but also in fatty tissues, and they can be biomagnified through the food web [10]. Usually assumed as metabolites of PBDEs, hydroxylated- (OH-PBDEs) and methoxylated-PBDEs (MeO-PBDEs) have been identified as natural compounds in marine environments [10,11]. Because OH-PBDEs and MeO-PBDEs were considered and reported as metabolites in most of the publications included in this review, these compounds will be referred to here as "PBDE metabolites". The toxicity of OH-PBDEs and MeO-PBDEs is still under study, although adverse effects on biota cannot be ruled out due to their similarity to PBDEs in terms of their chemical structure [12]. Consequently, studies of the distribution, transport, bioaccumulation, and biomagnification of PBDEs and their metabolites have become a significant issue for environmental and toxicological sciences.

From the perspective of green analytical chemistry, direct chromatographic analysis after the sample extraction step is highly recommended whenever possible [13]. However, this is rarely possible due to incompatibility issues with the analytical instrument, which might cause its plugging or deterioration. Additionally, it is important to consider that because of the complexity of environmental or biological matrices, sample clean-up is necessary for enhancing the signal/noise ratio of the analytical signals and thus achieving lower limits of detection (LODs). Consequently, after sample extraction, clean-up and preconcentration approaches are required to achieve LODs compatible with the requirement of determining low concentrations of PBDEs and/or metabolites in environmental or biological samples.

During the last decade (2003–2013), a dramatic increase in the number of articles published on the PBDE issue has occurred. Among them, there are approximately 100 papers focused on analytical methodologies based on green analytical techniques for determination of PBDEs and/or their metabolites (Fig. 1a). Almost 70% of them were published within the last five years. Furthermore, more than 70% of the revised analytical methodologies were proposed for determination of congeners BDE-47, -99, -100, -153, and -154, whereas only 26% and 12% were proposed for BDE-209 and metabolites, respectively (Fig. 1b).

In the present review, the state-of-the-art of green analytical approaches in the sample preparation step used for the

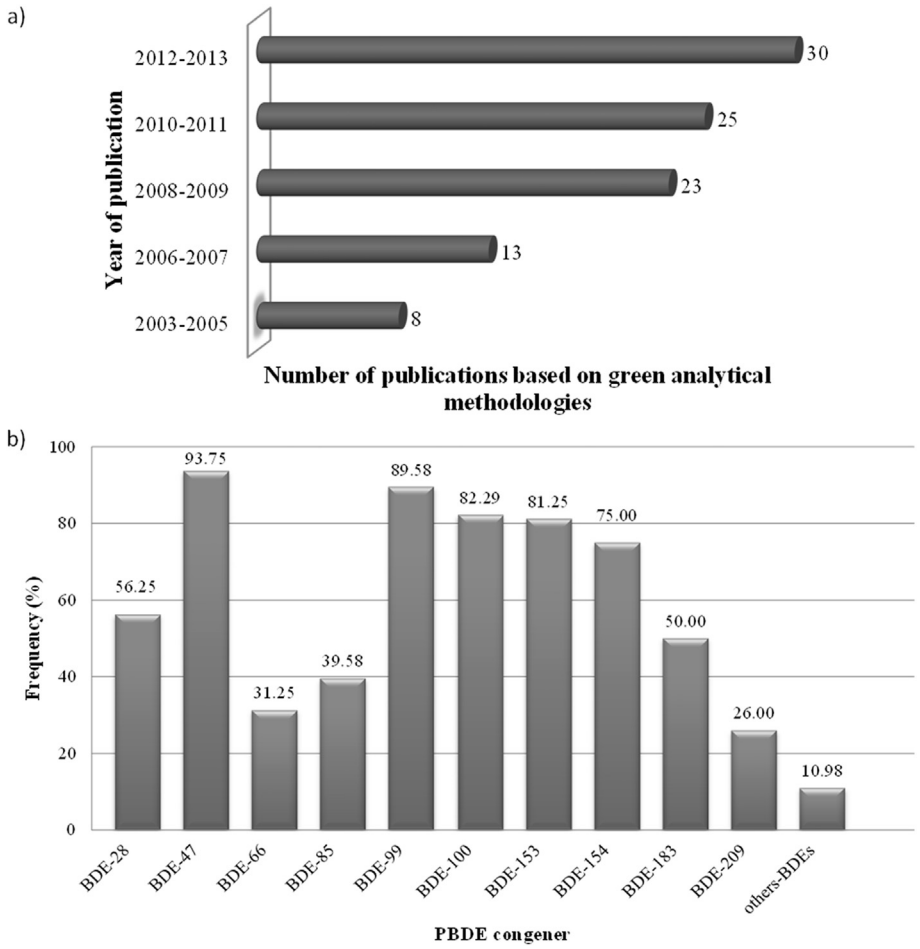

Fig. 1. a) Number of publications based on green analytical methodologies for analysis of PBDEs in the last decade; b) frequency of PBDEs congeners analysed (%) in selected publications (2003–2013).

determination of PBDEs and metabolites in biological and environmental samples are discussed. To facilitate a better understanding, green techniques that are mostly used in sample preparation (presented and classified in Fig. 2) are grouped as liquid- (assisted solvent extraction techniques, liquid-phase microextraction techniques, and alternative solvents) and solid-based extraction techniques. Evaluation of their advantages and disadvantages, as well as highlights of research gaps, is included. As

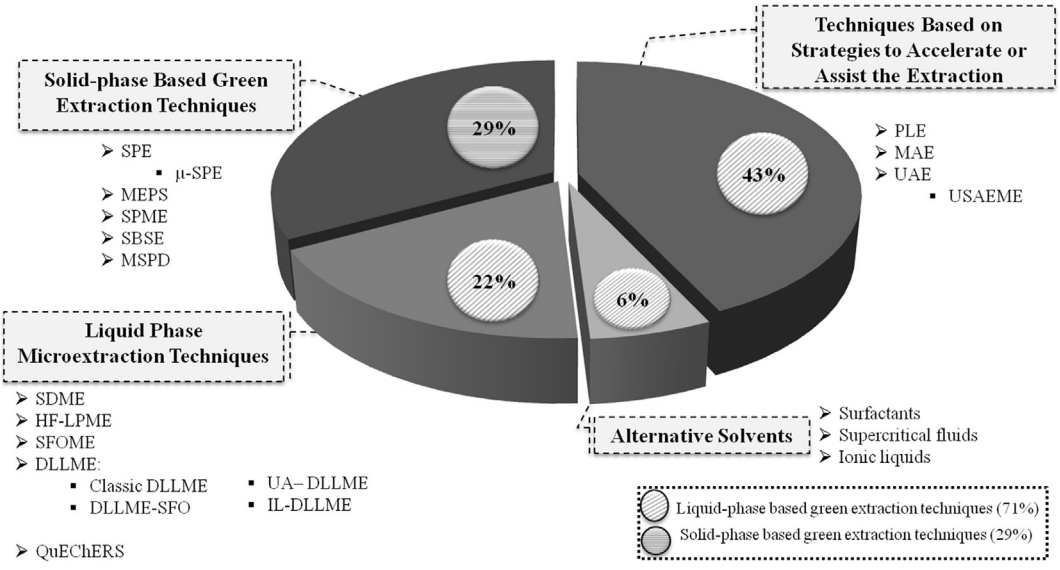

Fig. 2. Green analytical techniques used during the extraction step for determination of PBDEs and metabolites.

mentioned above, the number of publications about analytical methodologies based on green approaches for determination of PBDE metabolites is scarce; therefore, these approaches are discussed in a separate section for proper analysis. Because the sample preparation step is conditioned not only by the size and the complexity of the sample but also by the next step, a short discussion of these steps in the determination of these pollutants (*i.e.,* instrumental analysis) is included.

2. Sample preparation step

Selection of sample preparation techniques is conditioned mainly by the physicochemical properties of the target analytes, their concentrations in environmental or biological samples, and the complexity of the sample matrices. Furthermore, after sample preparation, analytes should render in a form and concentration compatible with the analytical instrument used for analysis [14]. In the case of PBDEs and metabolites, the usage of organic solvents is required for extraction due to their low polarity. Soxhlet extraction (SE) and solid phase extraction (SPE) stand out as the default techniques for exhaustive extraction of PBDEs and metabolites from environmental and biological matrices due to their simple operation and availability in most laboratories [12]. However, consumption of large volumes of organic solvents (*e.g.,* hexane (Hex) and/or dichloromethane (DCM)) is still an important disadvantage. Furthermore, using large volumes of organic solvents efficiently extracts not only PBDEs but also concomitants that can interfere during their determination. Consequently, the use of environmentally friendly, selective, and efficient techniques is of interest.

Even when not in the scope of this review, it is important to consider the preconditioning of samples. From the perspective of green chemistry, those samples that avoid the usage of organic solvents during their preconditioning (*e.g.,* using high temperatures) should be preferred. Because extensive reviews on sampling techniques used for determination of PBDEs were recently published by Król et al. [15] and by Fulara and Czaplicka [16], this topic will not be reviewed here.

2.1. Sample preparation for determination of PBDEs

2.1.1. Liquid phase-based green extraction techniques

2.1.1.1. Techniques based on strategies to accelerate or assist the extraction. One of the strategies for decreasing the volumes of organic solvents during the extraction is changing the physical conditions of the system to enhance the extraction efficiency. Among these strategies, the use of high pressure, microwave, and ultrasound were proposed for the following techniques: pressurized liquid extraction (PLE or accelerated solvent extraction, ASE), microwave-assisted extraction (MAE), and ultrasound-assisted extraction (UAE), respectively. Modifying pressure and temperature (for PLE) or temperature with the addition of energetic waves (for MAE and UAE) allows the viscosity of the solvent to be decreased while accelerating the mass transfer from the sample to the solvent. Their efficiency, together with their outstanding rapidity and low solvent consumption, lead these to be the most frequently reported green extraction techniques for leaching of PBDEs from solid environmental sample matrices prior to analysis (Table 1).

PLE is one of the green extraction techniques most commonly used (*ca.* 70% of the analysed solvent assisted extraction techniques used for extraction of PBDEs) to extract PBDEs from solid and semi-solid matrices, including environmental [17–27] and biological samples (Table 1) [20,21,28–36].

In comparison with SE, the solvent condition inside the PLE cell approaches a supercritical state, achieving high temperatures that increase sample solubility and provide a higher analyte diffusion rate along with greater penetration of the solvent. However, at the same time, increased undesired coextraction of matrix lipids is observed, so that final extracts may require additional clean-up steps, especially for biological samples. PLE has been applied not only for solid samples but also for extracting PBDEs from liquid biological samples, including milk cream and breast milk [20,37–40]. Although this technique allows control of temperature and pressure variables in the extraction process, only the temperature was reported to affect the extraction efficiency of PBDEs (due to its impact on solvent viscosity and extraction kinetics). On the other hand, particular attention is recommended for extraction temperature selection to avoid debromination, especially for highly brominated congeners (hexa-to deca-BDE) that decomposed at temperatures near 300 °C [15,41]. Furthermore, an additional advantage of PLE is the possibility of carrying out an in-cell clean-up (usually Florisil or silica columns as fat removers), which simplifies the sample preparation step and reduces the time consumption. Because acidified silica may damage the stainless steel parts of the equipment [42] in cases where samples have higher concentrations of fat, an additional step using a transfer pipette filled with acidified silica (44% w/w sulphuric acid) is recommended [28,43].

Within this classification, MAE is another efficient, simple and fast technique proposed for extraction of PBDEs in sewage sludge [44], in fish and mussel tissues, and in human adipose tissue [45,46]. MAE significantly reduces solvent use to as low as 20 mL of solvent per sample. Solvents under pressure and temperature control achieve conditions above their boiling point; however, they remain liquid, which promotes analyte diffusion. Due to microwave requirements, polar solvents such as methanol are used for heating of the extraction solvent, which is generally non-polar. Thus, mixtures such as acetone:n-Hex, isopropanol:cyclohexane, xylene:dichloromethane or methanol:toluene are generally used. The extraction of BDE-209 from e-waste resulted in low extraction yields due to its high molecular weight and its non-polar nature [47,48]. Although SE and MAE yielded similar results in fish and mussel samples, slightly lower recoveries of BDE-47, -99, and -100 and shorter extraction times were reported using MAE (15% variation) [45]. However, Shin et al., reported an improvement in recovery values against SE when MAE was used for extracting PBDEs from sewage samples, especially for BDE-209 (>90% recovery using MAE *vs. ca.* 35% or lower with SE) [44]. Recoveries were comparable (>90%) for the rest of the PBDE congeners (BDE-47, -99, -100, -138, -153, -154, and -183) [44].

A third option within the reported techniques based on solvent assisted extraction is UAE. It was suggested for extraction of PBDEs from environmental (wastewater, sediment, soil, sludge and dust) [11,49–53] and biological samples of complex matrices (plants, egg, chicken, sheep liver, mollusc, and fish), with recovery values comparable to those obtained with PLE, SE, and heat extraction [30,50,53–55]. UAE uses high-energy ultrasound to disperse and disaggregate the solid sample into the extracting solvent, increasing its surface-to-volume ratio and thus facilitating the analyte extraction [56]. A miniaturized version of UAE was proposed by Fontana et al. for extraction of PBDEs from water samples using only 100 μL chloroform as an extracting solvent [57]. To increase the power of the ultrasonic technique, a focused ultrasonic probe (Focused-UAE) directly immersed in the extraction solutions was recently proposed, increasing the power 100 times in comparison with traditional ultrasonic baths [58]. It was used for the extraction of PBDEs from dust, vegetables and soil, with similar recoveries compared with using MAE. Even when the extraction technique allowed analytical methodologies to achieve low LODs (in the range

Table 1
Methodologies based on solvent assisted extraction techniques reported for analysis of PBDEs in environmental and biological samples.

Technique	Characteristics	Sample	Analysed PBDEs	Methodology[a]	Ref.
PLE	◦ Time: up to 40 min ◦ Solvent consumption[b]: generally up to 100 mL ◦ Extraction temp.: 100–150 °C	Airborne	BDE-15, -17, -20, -25, -28, -32, -35, -36, -39, -47, -62, -66, -71, -99, -100, -153, -154, -183	**PLE**-GC-qMS	[17]
		Sediment	BDE-1, -2, -3, -7, -8, -10, -11, -12, -13, -15, -17, -25, -28, -30, -32, -33, -35, -47, -49, -66, -71, -75, -77, -85, -99, -100, -116, -118, -119, -126, -138, -153, -154, -155, -166, -181, -183, -190	**PLE**-GC-MS	[18]
		Sediment	BDE-47, -99, -119, -153	f.d.-**PLE**-SPE-GC-ECD	[22]
		Sediment	BDE-28, -47, -99, -100, -153, -154, -183, -196, -197, -206, -207, -209	**PLE**-MC-LC-MS/MS	[23]
		Sediment, soil	BDE-17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154, -183, -190,-209	f.d.-**PLE**-SPE-HRGC-MS	[24]
		Soil	BDE-28, -47, -99, -100, -153, -154, -183	**PLE**-MC-GC-MS	[19]
		Sediment, milk, fish	BDE-1, -2, -3, -7, -8, -10, -11, -12, -13, -15, -17, -25, -28, -30, -32, -33, -35, -37, -47, -49, -66, -71, -75, -77, -85, -99, -100, -116, -118, -119, -126, -138, -153, -154, -155, -166, -181, -183, -190	**PLE**-GPC-GC-HRMS	[20]
		Dust	BDE-28, -47, -99, -100, -153, -154, -183	**PLE**-LC-MS/MS	[25]
		Dust	BDE-28, -37, -47, -49, -66, -77, -85, -99, -100, -153, -154, -183, -196, -197, -203, -206, -207, -209	**PLE**-GC-qMS	[26]
		Sewage sludge	BDE-47, -99,-100, -153, -154, -183, -196, -197, -203, -205, -209	**PLE**-UPLC-MS	[27]
		Sediments, molluscs, fish, crustaceans, seabirds	BDE-28, -47, -66, -77, -85, -99, -100, -138, -153, -154, -183	f.d.-**PLE**-SPE-HRGC-HRMS	[21]
		Filtering species, crustaceans, Molluscs, fish	BDE-28, -47, -99, -100, -153, -154, -183, -209	f.d.-**PLE**-Sulphuric Acid-SPE-GC-MS	[34]
		Fish and shellfish	BDE-28, -47, -66, -85, -99, -100, -153, -154, -183	f.d.-**PLE**-SPE-GC-MS/MS	[28,43]
		Fish	BDE-28, -47, -66, -85, -99, -100, -138, -153, -154	**PLE**-GC-MS/MS	[29]
		Fish	BDE-1, -2, -3, -4, -6, -7, -8, -9, -10, -13, -15, -17, -18, -19, -25, -26, -28, -29, -31, -32, -37, 47, -49, -50, -51, -52, -66, -74, -75, -77, -85, -99, -100, -101, -102, -118, -119, -138, -139, -140, -153, -154, -155, -183, -184, -187, -188, -196, -197, -201, -202, -203, -206, -207, -208, -209	**PLE**-GPC-GC-HRMS	[36]
		Sea lion bubbler tissue	BDE-17, -25, -28, -30, -33, -47, -49, -66, -71, -75, -85, -99, -100, -116, -119, -138, -153, -154, -155, -156, -181, -183, -190, -191, -203, -205, -206, -209	**PLE**-SEC-SPE-GC-MS	[31]
		Sheep liver tissue	BDE-28, -47, -99, -100, -153, -154, -183	**PLE**-GC-MS	[30]
		Albatross, tuna, and polar bear liver tissue	BDE-7, -15, -17, -28, -30, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -139, -140, -153, -154, -183	f.d.-**PLE**-SPE-HRGC-HRMS	[32]
		Liver squid tissue	BDE-28, -30, -33, -47, -75, -85, -99, -153, -154, -155	f.d.-**PLE**-GPC-SPE-GC-MS	[33]
		Whale tissue	BDE-28, -47, -99, -100, -153, -154, -183	**PLE**-GC-MS	[35]
		Milk cream	BDE-28, -47, -99, -100, -153, -154	**PLE**-SPE-GC-(QqQ)MS	[38]
		Breast milk	BDE-28, -47, -99, -100, -153, -154, -183, -209	f.d.-**PLE**-GPC-sulphuric acid-SPE-GC-MS	[40]
		Breast milk	BDE-1, -2, -3, -7, -8, -10, -11, -12, -13, -15, -17, -25, -28, -30, -32, -33, -35, -37, -47, -49, -66, -71, -75, -77, -85, -99, -100, -105, -116, -119, -126, -138, -140, -153, -154, -155, -166, -181, -183, -190	f.d.-**PLE**-SPE-GC-MS	[37]
		Breast milk	BDE-1, -2, -3, -7, -8, -10, -11, -12, -13, -15, -17, -25, -28, -30, -32, -33, -35, -37, -47, -49, -66, -71, -75, -77, -85, -99, -100, -105, -116, -119, -126, -138, -140, -153, -154, -155, -166, -181, -183, -190	f.d.-**PLE**-Sulphuric Acid-GC-HRMS	[39]
		Plants	BDE-17, -47, -66, -100, -153, -183 and PCBs	**PLE**-GC-(QqQ)MS	[42]
MAE	◦ Extraction temp.: 100–130 °C ◦ Time: up to 60 min ◦ Solvent consumption[b]: up to 30 mL	Fish and mussel	BDE-47, -99, -100 and PCBs	**MAE**-GPC-GC-MS	[45]
		Sewage sludge	BDE-47, -99, -100, -138, -153, -154, -183, -209	**MAE**-MC-GC-qMS	[44]
		Human adipose tissue	BDE-47, -99, -100, -153, -154	**MAE**-SPE-GC-qMS	[46]

Table 1 (*continued*)

Technique	Characteristics	Sample	Analysed PBDEs	Methodology[a]	Ref.
UAE	◦ Extraction temp.: up to 65 °C	Sediment, sewage sludge, dust	BDE-28, -47, -99, -100, -153, -154, -183, -209, and other flame retardants	**UAE**-SPE-GC-MS/MS	[49]
	◦ Time: up to 60 min	Sewage sludge	BDE-28, - 47, -66, -68, -85, -99, -138, -153, -154, -183	**UAE**-SPE-GC-MS	[11]
	◦ Solvent consumption[b]: up to 100 mL	Dust	BDE-1, -2, -3, -7, -8, -10, -11, -12, -13, -15, -17, -25, -28, -30, -32, -33, -35, -37, -47, -49, -66, -71, -75, -77, -85, -99, -100, -116, -118, -119, -126, -138, -153, -154, -155, -166, -181, -183, -190	**Focused UAE**-GC-MS/MS	[58]
		Dust	BDE-28, -47, -99, -100, -153, -154, -183, -209	**UAE**-LC-MS/MS	[52]
		Soil	BDE-3, -15, -28, -47, -99, -100, -153, -154, -183, -196, -197, -206, -207, -209	**UAE**-Sulphuric Acid-GPC-SPE-GC-MS	[51]
		Tap and river waters	BDE-47, -99, -100, -153	**USAEME**-GC-MS/MS	[57]
		Fish	BDE-3, -7, -15, -17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -138, -153, -154, -156, -183, -184, -191, -196,-197, -206, -207, -209	**UAE**-F-l.f.-MC-GC-HRMS	[55]
		Water, soil, sediment, plant, mollusc, fish	BDE-28, -47, -66, -68, -85, -99, -138, -153, -154, -183	**UAE**-SPE-MC-GC-MS	[53]
		Plants, fish, mollusc, wastewater	BDE-28, -47, -66, -68, -99	f.d.-**UAE**-SPE-GC-MS	[50]
Optimization of different assisted extraction techniques		Mysids and fish	BDE-47, -99, -119, -153, -190	**PLE (or MAE)**-MC-GC-ECD	[60]
		Soil	BDE-17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154, -183, -190	**PLE (or MAE)**-MC-HRGC-HRMS	[61]
		Fish			
		Dust	BDE-17, -28, -47, -66, -71, -99, -100, -138, -153, -154, -181, -209	**PLE (or UAE)**-SPE-GC-μECD	[62]

Abbreviations are found in the *Abbreviations* Appendix. Other abbreviations: f.d.: freeze-drying; qMS: single quadrupole MS; MS/MS: tandem MS; HRGC: high resolution GC; HRMS: high resolution MS; SEC: size exclusion chromatography; QqQ: triple quadrupole MS.

[a] Green extraction techniques are bold highlighted.

[b] Mostly DCM, Hex or a mixture of them.

of 0.05–0.8 ng g^{-1}) in a short time (20 s), one of its major disadvantages is that only one sample can be extracted at a time [58]. Ultrasonic radiation was also proposed as a strategy to accelerate liquid- and solid-based microextraction techniques (described in the next section).

There are several reports comparing the performance of different assisted solvent extraction techniques for extracting PBDEs from biological samples. PLE and MAE can be fully automated, and thus unattended extractions can be performed overnight to improve sample preparation throughput. However, PLE and MAE require sophisticated and expensive instrumentation, and no special laboratory equipment is needed for UAE. Furthermore, numerous samples can be processed at the same time because solvent loss is negligible after 48 h [59]. The intraday extracts can be filtered on the next day, if time is limited, without a loss of quality. The number of samples to be simultaneously processed would thus be limited by the size of the ultrasonic bath. Tapie et al., who evaluated MAE and PLE for extraction of PBDEs from shrimp and fish, concluded that MAE, coupled with a clean-up step using an acidified silica gel column, can be used in low-fat matrices [60]. On the other hand, although the acidic PLE procedure (*i.e.*, PLE with on-line acid purification and clean-up on an acidified silica gel column) is slower (24 *vs.* 32 samples per day using MAE), it exhibited better performance in terms of recovery and reproducibility in fatty samples such as eel muscle (over 40% lipid d.w.) [60]. Because MAE and UAE techniques require clean-up of the extract before instrumental analysis, this might increase the possibilities of loss of analytes or extract contamination, together with increases in preparation time and solvent consumption. Many authors found lower PBDE recoveries from soil, plant, and fish samples when UAE or MAE were used for extraction, compared with those found when using PLE or SE [19,42,61]. However, only one of the extraction techniques (usually PLE) was optimized in these reports. The same extraction conditions (solvent type, extraction time) were then applied to the other techniques for comparison. On the other hand, Król et al., who optimized PLE, UAE, and SE, reported comparable PBDEs recoveries (>70%) in house dust samples [62], showing the importance of optimizing each extraction technique for proper comparison.

2.1.1.2. Liquid phase microextraction techniques. In recent years, liquid phase microextractions (LPME) have been proposed as a sample pretreatment procedure to overcome some drawbacks of the conventional LLE. As seen in Table 2, in aqueous samples with relatively simple matrices, such as tap, lake, or river water, a single microextraction technique is enough for extraction of PBDEs and preconcentration, thus accelerating the sample preparation step and reducing consumption of organic solvents.

Dispersive liquid–liquid microextraction (DLLME), the LPME technique mostly used for extraction of PBDEs (Table 2), is based on a three-solvent system where a mixture of extracting and dispersing solvents is added to the donor phase (sample bulk) and induced to a microemulsion. The large extent of the surface contact between the tiny droplets of the microemulsion and the analytes accelerates the mass-transfer processes of the analytes from the aqueous phase to the organic phase, thus enhancing extraction efficiencies in a short time (usually less than 10 min) [63]. DLLME has been successfully used for extraction of PBDEs from landfill

Table 2
Methodologies based on liquid phase microextraction techniques and/or using alternative solvents for analysis of PBDEs in environmental and biological samples.

LPME technique	Sample	Analysed PBDEs	Methodology[b]	Organic solvents consumed (mL)	Recov. (%)	LOD (ng L^{-1})	RSD (%)	Ref.
DLLME	River water Wastewater	BDE-209	**DLLME**-HPLC-UV	**DLLME**: acetone (1), tetrachloroethylene (0.01)	102 96	n.r.	<5.5 <6.3	[64]
	Tap and lake waters Landfill leachate	BDE-28, -47, -99, -209	**DLLME**-HPLC-VWD	**DLLME**: ACN (1), tetrachloroethane (0.02)	>90 >87	12 - 55	<6.3	[65]
	Lake, river and tap waters	BDE-209	**DLLME**-HPLC-VWD	**DLLME**: tetrahydrofuran (1), tetrachloroethane (0.02)	>90	200	<3.5	[66]
	River and lake waters	BDE-28, -47, -99, -100, -153, -154, -183, -209	**UA-DLLME**-GC-MS	**UA-DLLME**: acetone (1), tetrachloroethylene (0.01)	>76	0.4–2.15	<8.4	[67]
	Well, river, and sea waters Landfill leachate Plants tissue	BDE-28, -47, -85, -99, -100, -153, -154	F.d.-LLE-SPE-**DLLME**-GC-ECD	**LLE**: Hex:acetone (1:1) (10), ACN (2) **SPE**: DCM (2), methanol (5), Hex (2) **DLLME**: ACN (1), tetrachloroethane (0.022), Hex (0.020)	>67 >62 >62	0.03–0.15 0.04–0.16[c]	<7.9 <11	[68]
	Milk	BDE-47, -100, -154, -153	Sap.-LLE-SPE-**DLLME**-GC-MS	**Sap.** + **LLE**: acetone (1), Hex (5) **SPE**: DCM (2), Hex (7), acetone (2) **DLLME**: chlorobenzene (0.019)	>74	200–400	<8.5	[69]
	Milk	BDE-47, -100, -99, -85, -154, -153	Sap.-LLE-**DLLME**-GC-qMS	**Sap.** + **LLE**: ethanol (1), petroleum ether (20) **DLLME**: ACN (2), tetrachloethane (0.022), Hex (0.015)	>78	12–290	<11	[70]
	Snail, frog, and fish tissues	BDE-47, -85, -99, -100, -154, -153	F.d.-LLE-**DLLME**-GC-MS	**LLE**: acetone (10) **DLLME**: chlorobenzene (0.033)	>75	2400–4900[c]	<11	[71]
	River water Urine	BDE-4 7,-99, -154, -183	**TA-IL-DLLME**-HPLC-VWD	**TA-IL-DLLME**: methanol (1.015), IL [C_8MIM][PF_6] (0.04)	>81	100–400	<3.8 <8.0	[94]
	Sediment	BDE-209	UAE-**DLLME-SFO**-HPLC-UV	**UAE**: acetone (25) **DLLME-SFO**: 1-dodecanol (0.035)	>82	n.r.	n.r.	[73]
	Sediment	BDE-209	**DLLME-SFO**-HPLC-UV	**DLLME-SFO**: methanol (1), dodecanol (0.035)	>98	5.6[c]	<8.3	[79]
	Sediment	BDE-47, -99, -100, -153	**UAE-DLLME-SFO**-GC-MS/MS	**UAE**: methanol (1.2) **DLLME-SFO**: 1-dodecanol (0.022)	>71	0.5–1.8[c]	<9.2	[74]
	Sediment	BDE-47, -99, -100, -153	**UAE**-dSPE-**DLLME**-GC-MS/MS	**UAE**: acetone (1.5) **DLLME**: carbon tetrachloride (0.06)	>80	20–60[c]	<9.8	[72]
SDME	Tap and lake waters	BDE-209	**SDME**-HPLC-VWD	**SDME**: toluene (0.003)	>92	700	<4.4	[75]
HF-LPME	Human serum Soil Dust Lake water	BDE-28, -47, -99, -100	**UAE-HF-LPME**-GC-ICP-MS Or **HF-LPME**-GC-ICP-MS	**Soil (UAE)**: methanol (3) **HF-LPME**: decane (0.004), methanol (3)	>85 >87 >87 >99	15.2–40.5	<7.5 <10 <10 <3.9	[76]
SFOME	River water Urine	BDE-28, -47, -99, -154, -183, -209	**SFOME**-HPLC-VWD	**SFOME**: 2-dodecanol (0.025)	>81 >92	10–40	<7.3 <7.8	[78]

QuEChERS	Fish	BDE-28, -37, -47, -49, -66, -77, -85, -99, -100, -153, -154, -183, -196, -197, -203, -206, -207, -209	**QuEChERS**-mini SPE-GC-(QqQ)MS	**QuEChERS**: ethyl acetate (10); Mini SPE: not reported	>70	n.r.	<16	[83]
	Fish	BDE-28, -47, -99, -100, -153, -154, -183	**QuEChERS**-dSPE-GC-(QqQ)MS	**QuEChERS**: ACN (10)	>83	500–10,000[c]	<23	[85]
	Fish and shrimp	BDE-28, -47, -99, -100, -153, -154, -183	**QuEChERS-mini SPE**-GC-TOF-MS	**QuEChERS**: ethyl acetate (10); **Mini SPE**: Hex:DCM (1:1) (20–60)	>79	n.r.	<12	[84]
SFE	Ringed seals	BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, -183	**SFE**-SPE-MC-GC-MS	SPE: Hex (n.r.), DCM (n.r.)	n.r.	n.r.	n.r.	[89]
	Cetaceans	BDE-47, -99, -100, -138, -153, -154	**SFE**-SPE-GC-MS	SPE: Hex (2), DCM (2)	>33	n.r.	n.r.	[88]
	Fish and shellfish	BDE-47, -99, -100	**SFE-HS-SPME**-GC-MS/MS	**SFE**: Hex (2) **HS-SPME**: None[a]	>82	1.8–8.9[c]	<17	[86]
	Dust	BDE-28, -47, -99,-100, -153, -154, -183,-209	**SFE**-LC-MS/MS	**SFE**: DCM (0.75)	>87	n.r.	<24	[90]
CPE	Tap, river, and lake waters Soil	BDE-47, -99, -100, -153	**CPE-UABE**-GC-MS/MS Soil: **UAE-CPE-UABE**- GC-MS/MS	**CPE**: Triton X-114 (0.040) **UABE**: isooctane (0.050)	>96 ~20	1–2 1000–3700[c]	<8.3 <9.5	[92]

Abbreviations are found in the *Abbreviations* Appendix. Other abbreviations: n.r.: not reported; VWD: variable wavelength detector; f.d.: freeze-drying; qMS: single quadrupole MS; MS/MS: tandem MS; Sap.: saponification.

[a] Thermal desorption.

[b] Green extraction techniques are bold highlighted.

[c] (ng kg^{-1}).

leachate and environmental water samples [64–66], with recoveries higher than 87% (Table 2). To favour the microemulsion formation and increase extraction efficiencies, an ultrasound-assisted DLLME (UA-DLLME) technique was proposed for the determination of PBDEs in water samples [67]. For analysis of solid and semi-solid samples, including sediment, plant and animal tissues, or milk, a combination of SPE, UAE, LLE, or a freezing step, followed by DLLME, is frequently proposed (Table 2) [68–74]. Note that, even when these technique arrangements improve the analytical performance of the methodologies (satisfactory recoveries, PBDEs isolation, and reduction of matrix effects on instrumental analysis), their design and optimization are more difficult because the compatibility of the extractant obtained from one technique with that of the next technique needs to be considered.

Other LPME techniques, including single drop microextraction (SDME), hollow-fibre LPME (HF-LPME), and solidification of floating organic drop microextraction (SFOME), were used for extraction of PBDEs, mostly from liquid samples (environmental water, Table 2). SDME is based on the partition of analytes between the aqueous (donor) phase and a droplet of extracting solvent, which hangs from the tip of a microsyringe needle. By comparing it with the DLLME, it is evident that the contact area between the phases is lower in SDME. This limits the extraction efficiency and thus the required time for obtaining comparable performance. Furthermore, practical drawbacks include the difficulty of handling large droplets and the easy dislodgement of the organic solvent suspended in the needle during extraction, especially when samples are vigorously stirred. Li et al. proposed an SDME-High Performance Liquid Chromatography (HPLC, or LC) methodology for BDE-209 determination in water samples, obtaining a 0.7 ng mL^{-1} LOD and a recovery higher than 92% [75]. Hollow fibres (HF) were proposed to overcome the practical drawbacks of SDME, avoiding direct contact between the samples and the extracting solvent and preventing solvent loss during sample agitation. In the HF, the solvent is distributed all along the fibre. This provides an extended contact area between the solvent and the sample, thus enhancing the extraction efficiency of the technique. The HF has additional advantages: it is low-cost, it does not require specialized devices, and sample carryover is avoided because it is disposable. Using decane as an extracting solvent, HF-LPME was proposed for extraction of PBDEs from complex samples including soil, dust, environmental waters, and human serum [76]. Like most of the liquid-based techniques, its application requires an aqueous phase as the donor phase, and thus PBDEs were initially extracted from solid samples using the UAE technique [76]. Finally, the SFOME technique introduces the use of organic solvents with particular characteristics, including melting points near room temperature (*ca.* 10–30 °C), densities below 1 g mL^{-1}, viscosities higher than 0.85 mPa s, and low toxicity [77]. Another feature of the SFOME technique is that the centrifugation step is avoided from the sample preparation: after analyte extraction, the sample vial is placed into a cold water bath to solidify the organic solvent, which floats and gets separated from the aqueous solvent. This technique was proposed for extraction of PBDEs from water and urine samples, using 2-dodecanol as the extracting solvent [78]. Even when these solvents allow an easy phase separation, their high viscosities (*e.g.*, viscosities of n-dodecane, decane, and hexane are 1.36, 0.85, and 0.29 mPa s, respectively) slow down the rate of mass transfer between phases and hence limit the performance of the SFO extraction technique. Thus, the combination of a dispersive microextraction technique (DLLME) using organic solvents with low melting points (SFO) was proposed to improve SFO performance for the extraction of BDE-209 from sediment samples [79]. As can be observed in Table 2, this combination improved the analytical performance of the technique, achieving higher recoveries and lower LODs in comparison with DLLME techniques proposed for the determination of PBDEs in sediment samples.

Although QuEChERS (Quick, Easy, Cheap, Efficient, Robust and Secure) is not considered a microextraction technique, the green approach that frames this work leads us to consider this technique in the present analysis. This technique was initially introduced to extract relatively polar pesticides from fruits and vegetables [80]. However, its application has been extended to other compounds of environmental concern [81], including PBDEs. Briefly, in this technique, analytes are extracted from solid samples using a 1/1 v/w ratio of organic solvents (ethyl acetate or acetonitrile, ACN) to sample. After vigorous manual shaking, anhydrous $MgSO_4$ and NaCl are added to promote phase separation by salting-out effect and dehydration of the organic phase [82]. Prior to instrumental analysis, silica mini-columns or d-SPE are used for extract clean-up (discussed in Section 3), diminishing solvent consumption during this step (Table 3) [83–85]. Although this approach was reported for extraction of PBDEs from fish and shrimp tissues (Table 2), with recoveries higher than 70% [83–85], a closer look at the solvents used reveals that this technique is mostly used for extraction of polar compounds, thus limiting its application for the extraction of the most polar PBDEs congeners. Surprisingly, there are no publications applying this technique to the extraction of OH-PBDEs, which are considered to be more polar.

2.1.1.3. Alternative solvents. Supercritical fluid extraction (SFE) is a technique based on the use of solvents at temperatures and pressures above their critical points. Carbon dioxide (sc-CO_2) is generally used as a supercritical solvent due to its low critical temperature (Tc = 32 °C), although it has a relatively high critical pressure (Pc = 72 atm). Its main advantages over other liquid-based extractions are rapid extraction kinetics due to the high-diffusivity of the dense solvent, avoiding large volumes of organic solvents. Furthermore, extract clean-up can be performed inside the SFE extraction chamber, for instance, layering together acidic silica and basic alumina [86]. The clean extract obtained when using sc-CO_2 as an extraction solvent allows the on-line coupling of SFE with analytical instrumentation, especially gas chromatography (GC), using different devices interfacing extraction and analysis [87]. Despite these advantages, SFE does not have widespread use, mainly due to safety issues associated with high-temperature and high-pressure gases. Another drawback is the lack of commercial instrumentation to automatize SFE. As seen in Table 2, SFE (using sc-CO_2) was combined with solid phase microextraction (SPME)-GC- mass spectrometry (MS) for determination of PBDEs and polychlorinated biphenyls (PCBs) in seals, cetaceans, fish and shellfish species, obtaining recoveries higher than 82% for low-brominated PBDEs [86,88,89]. To increase the polarity range of the analytes that could potentially be extracted, a solvent with permanent dipole moments (the supercritical fluid 1,1,1,2-tetrafluoroethane) was explored. It was used to extract PBDEs from house dust samples. The best recovery for BDE-209 (86.5 ± 6.1%) was achieved with high temperatures (200 °C) and pre-wetted dust with DCM [90].

Cloud point extraction (CPE) is an extraction technique based on the affinity of the analytes for surfactants (usually nonionic surfactants), which are amphiphilic molecules. When the surfactant concentration is higher than the critical micelle concentration (CMC), which varies depending on the selected surfactant, its solubility decreases and micelles are formed upon alteration of solution conditions (temperature, pressure, or addition of salt or additives) [91]. The structural arrangement of surfactant micelles allows sparingly soluble or water-insoluble substances to enhance their affinity for micelles. Interactions between surfactant and analyte may be electrostatic and/or hydrophobic [91]. Although this is

Table 3
Methodologies based on solid-phase extraction techniques reported for analysis of PBDEs in environmental and biological samples.

Technique	Sample	Analysed PBDEs	Methodology[b]	Solvent consumption (mL)	Recov. (%)	LOD (ng L^{-1})	RDS (%)	Ref.
μ-SPE	Soil	BDE-28, -47, -99, -100, -153, -154, -183	**μ-SPE-UABE**-GC-μECD	**UABE**: Hex (1)	>70	26–66[c]	<10	[96]
MEPS	Wastewater	BDE-28, -37, -47, -49, -66, -85, -99, -100, -153, -154, -183	**MEPS**-GC-TOF-MS	**MEPS**: isooctane (0.015)	>70	0.5–9.5	<12	[97]
SPME	Tap and river waters Wastewater	BDE-28, -47, -99, -100, -153, -154, -183	**SPME**-GC-(QqQ)MS	None[a]	>79 >78	0.25–0.62	<9.4	[100]
	River, wastewater and milk	BDE-47, -99, -100, -154, -153	**SPME**-GC-ECD	None[a]	>90	3.6–8.6	<8.8	[101]
	Environmental waters	BDE-28, -47, -99, -100, -153, -154, -183	**SPME**-GC-(QqQ)MS	None[a]	>77	0.2–0.6	<9.5	[103]
	Canal waters	BDE-47, -49, -99, -153, -154	**SPME**-GC-qMS	None[a]	>74	0.2–5.3	<7.8	[102]
	Sea water	BDE-47, -99, and other contaminants	**SPME**-GC-MS	**SPME**: Hex (0.1)	>83	0.04–0.21	<8.6	[104]
	Wastewater	BDE-15, -28, -47, -100, -153, -154, -183,-209	**SPME**-GC-μECD (and GC-MS)	None[a]	n.r.	0.18–8.77	18	[105]
HS-SPME	River water	BDE-47, -99, -100, -153	**HS-SPME**-GC-MS/MS	**HS-SPME**: methanol (0.05)	>95	0.03–0.12	<13	[107]
	Tap water Wastewater	BDE-3, 47, -85, -99, -100, 153, 154	**HS-SPME**-GC-MS/MS	None[a]	>87 >74	0.02–0.19	<21 <25	[108]
	Wastewater	BDE-28, -47, -99, -100, -153, -154	**HS-SPME**-GC-ECD	None[a]	>74	1.1–16	<9.1	[109]
	Reservoir water Wastewater	BDE-35, -47, -77, -99, -100, -153, -154	**HS-SPME**-GC-ECD	None[a]	>81 >74	0.08–0.8	<7.5	[110]
	River water	BDE-28, -47, -99, -100, -153, -154	**HS-SPME**-GC-μECD	None[a]	>83	0.1–0.2	<8.3	[112]
	Soil	BDE-17, -47, -66, -85, -99, -100, -138, -153,-154	**HS-SPME**-GC-qMS	**HS-SPME**: methanol (0.005)	>78	13–78.3[c]	<10	[111]
	Sediment Soil	BDE-47, -85, -99, -100, -153, -154	**HS-SPME**-GC-MS/MS	None[a]	>81 >95	5.2–625[c]	<12	[113]
	Sediment	BDE-47, -85, -99, -100, -153, -154	oxid.-**HS-SPME**-GC-MS/MS	None[a]	>76	n.r.	<14	[115]
	Sewage sludge	BDE-47, -85, -99, -100, -153, -154	**UAE-HS-SPME**-GC-MS/MS	**UAE**: Hex (8) **HS-SPME**: None[a]	>96	10–1200[c]	<13	[114]
	Fish and shellfish	BDE-47, -99, -100	**SFE-HS-SPME**-GC-MS/MS	**SFE**: Hex (2) **HS-SPME**: None[a]	>82	1.8–8.9[c]	<17	[86]
SBSE	Surface water	BDE-28, -47, -66, -85, -99, -100, -138, -153, -154	**SBSE**-GC-MS	**SBSE**: methanol (20)	>99	0.4–9.5	<5	[116]
	Wastewater Sewage sludge	BDE-47, -99, -100	(Waste water) **SBSE**-GC-MS (Sewage sludge) UAE-**SBSE**-GC-MS	**SBSE**: methanol (5.8) **UAE**: acetone:Hex (2:3) (40)	>91	0.29–24.5[c]	n.r.	[117]
	Sediment	BDE-28, -47, -99, -100, -153,-154	**PLE-SBSE**-GC–(QqQ)MS	**PLE**: methanol (50) **SBSE**: None[a]	>63	1–4[c]	<35	[119]
	Sediment	BDE-28, -47, -77, -99, -100, -153, -154	**UAE-SBSE**-GC-MS	**UAE**: methanol (2.2) **SBSE**: None[a]	>63	0.0005–0.05	<15	[118]
					>66	0.3–203.4	<12	[120]

(*continued on next page*)

Table 3 (*continued*)

Technique	Sample	Analysed PBDEs	Methodology[b]	Solvent consumption (mL)	Recov. (%)	LOD (ng L^{-1})	RDS (%)	Ref.
	Wastewater Sediment	BDE-47, -85, -99, -100, -153, -154, -183, -196, -197, -206, -207	**SBSE-UABE**-GC-MS (Sediment) **UAE-SBSE-UABE**-GC-MS	**SBSE**: methanol (12) **UABE**: ACN (1.5) **UAE**: methanol (15)				
MSPD	Mussels and cockles	BDE 47, -99, -100	**Mini MSPD-SPME**-GC-ECD	**Mini MSPD**: ACN (1.2) **SPME**: Hex (1.3)	>100	3000–7100[c]	<23	[128]
	Chicken fat Beef fat Fish muscle	BDE-47, -85, -99, -100, -153, -154	**MSPD**-SPE-GC-ECD	**MSPD**: Hex (20) SPE: Hex:DCM (80:20) (12)	>90 >74 >80	n.r.	<10 <5 <9	[122]
	Mammals adipose tissue; Chicken and trout muscle	BDE-17, -28, -47, -66, -85, -99, -100, -153, -154, -183	**MSPD**-SPE-GC-MS/MS	**MSPD**: Hex:acetone (1:1) (400) SPE: not reported	>80	70–1300[c]	<13	[124]
	Sewage sludge	BDE-17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154, -183, -190, -209	**MSPD-UABE**-SPE-GC-MS	**UABE**-SPE: DCM (12)	>78	50–500[c]	<10	[121]
	Molluscs	BDE-47, -49, -71, -85, -99, -100, -153, -154, -183, -197, -209	**MSPD**-GC-qMS	**MSPD**: DCM (10), isooctane (0.2)	>86	10–171[c]	<8.4	[126]
	Human placenta	BDE-1, -2, -3, -7, -8, -10, -11, -12, -13, -15, -17, -25, -28, -30, -32, -33, -35, -37, -47, -49, -66, -71, -75, -77, -85, -99, -100, -116, -118, -119, -126, -138, -153, -154, -155, -166, -181, -183, -190, -196, -206, -207, -209	**MSPD**-GPC-SPE-GC-MS	**MSPD**: Hex:DCM (8:2) (100) GPC: Hex:DCM (1:1) (140) SPE: Hex (40)	>91	1.6–53.8[c]	<12	[125]
	Eel muscle	BDE-3, -7, -15, -17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154, -156, -183, -184, -191, -194, -195, -196, -197, -198, -198, -199, -200, -201, -202, -203, -204, -205, -206, -207, -208 -209	**MSPD-UABE**-Sulphuric Acid-SPE-GC-(QqQ)MS	**MSPD-UABE**: Hex:DCM (1:1) (40) SPE: Hex:DCM (1:1) (41), Hex (35)	>56	50–5000[c]	<20	[123]
	Soil Tree bark Fish	BDE-17, -28, -47, -66, -85	**MSPD**-GC-ECD	**MSPD**: Hex:DCM (1:1) (1), acetone (1)	>70 >51 >24	5.3–91.2[c]	<20 n.r. n.r.	[127]

Abbreviations are found in the *Abbreviations* Appendix. Other abbreviations: n.r.: not reported; TOF-MS: Time of flight MS; f.d.: freeze-drying; qMS: single quadrupole MS; MS/MS: tandem MS; QqQ: triple quadrupole MS. oxid.: oxidation; mini: miniaturized.

[a] Thermal desorption.

[b] Green extraction techniques are bold highlighted.

[c] (ng/kg).

a simple and low-cost extraction technique, one of its major drawbacks is that the surfactant phase cannot be directly injected into GC instruments because of its high viscosity and low volatility. This was overcome by Fontana et al., who proposed an ultrasound-assisted back extraction (UABE) with isooctane (40 μL) after extraction of PBDEs by CPE [92]. The isooctane phase was then analysed by GC-MS without further clean-up. The procedure was applied for determination of PBDEs in drinking, lake, and river water samples, with satisfactory recoveries (>96%). However, lower recoveries (*ca.* 20%) were obtained when this method was directly applied to samples with more complex matrices (*e.g.,* soil), without prior leaching [92].

Ionic liquids (ILs) are proposed as alternative solvents for LPME due to their immiscibility with water, high thermal stability, and negligible vapour pressure. However, their low volatility hinders their use for direct injection into GC instruments [93]. The use of ILs for extraction and preconcentration of PBDEs is a field scarcely explored for extraction of PBDEs. The only IL-based technique was reported by Zhao et al., who proposed a microextraction technique termed temperature-assisted IL-DLLME, which uses the IL 1-octyl-3-methylimidazolium hexafluorophosphate as the accepting phase to extract PBDEs from the liquid samples (river water and human urine) [94]. Extraction recoveries higher than 83% were achieved under the optimized conditions [94]. It is worth mentioning that this green chemistry field could lead to surprising results, considering that the physical and chemical properties of the ILs can be tuned by properly selecting their cations and anions. Consequently, selective and efficient extracting solvents for PBDEs can be obtained with the proper combination of cation and anion in an IL.

2.1.2. Solid phase-based green extraction techniques

Solid phase extraction (SPE) is widely used in sample preparation for determination of PBDEs in environmental and biological samples [15,16,95]. Depending on the sample complexity, it allows one-step extraction, preconcentration and clean-up by direct solvent elution through a multilayer column filled with a selected sorbent bed (*e.g.,* silica gel, or alumina). However, for most of the solid phase-based techniques, including SPE, the analytes need to be dissolved in a liquid matrix, thus limiting the application of these approaches.

To minimize organic solvent consumption, different miniaturized-SPE techniques were proposed for determination of PBDEs, including micro-solid-phase extraction (μ-SPE), microextraction in packed syringe (MEPS), and SPME. These novel techniques are based on the adsorption of analytes onto sorbent materials, followed by a desorption process, usually with high temperature or low volumes of organic solvents (Table 3).

Operated at a smaller scale than SPE (10 mg of the polymer), μ-SPE was used for extraction of PBDEs from soil samples by packing a polymer of copper (II) isonicotinate inside a porous envelope of polypropylene (0.8 × 0.5 cm) [96]. A gram of soil sample was placed into a vial preloaded with water, and the μ-SPE device was added to the system. After 1 h of stirring, analytes were back-extracted (UABE) from the μ-SPE device with only 1 mL Hex. No further clean-up was required before GC- micro electron capture detector (μECD) analysis. Because water was used as the agent for leaching the analytes from the soil sample, the technique was limited to low-brominated PBDEs, achieving recoveries higher than 70% [96]. Lower amounts of the solid extractant (1 mg) are used in MEPS, which can be coupled directly to GC or LC. The sorbent is placed into a microsyringe (100–250 μL) as a plug, and the sample (10–250 μL) is then withdrawn through the syringe by an autosampler. To increase the sensitivity of the method, the sample is pumped up and down through the syringe 50 times by the autosampler. After the analytes are adsorbed to the packed solid sorbent, they are directly eluted into the instrument using 15 μL of isooctane. MEPS coupled with GC-TOFMS was recently used for determination of PBDEs in wastewater, with an extraction time of *ca.* 4 min, PBDEs recoveries >71%, and LODs in the range of 0.5–4.5 ng L^{-1} [97]. It is expected that when the MEPS is used in samples with more complex matrices, a clean-up step will be needed after this approach.

Another alternative extensively used is SPME, in which the sorbent coating (10–150 μm) is applied over a thin silica fibre mounted on a syringe needle. Sorbent coatings are polymeric materials that have a gum-like or even liquid-like state, with similar properties to those of organic solvents [98]. A thermal desorption (solvent-less technique) of PBDEs directly into the GC injection port is possible because the extraction system can be used in a similar manner to the GC injector syringe. Even when sensitivity is improved due to the large specific surface and strong adsorption capability of the fibres, the extraction is rarely quantitative, it is usually non exhaustive, and it has low absolute recoveries [98]. Other drawbacks include the cost, fragility, and relatively short lifetime of the fibres (*ca.* 100 samples), as well as carryover effects [99]. As seen in Table 3, direct SPME has been applied for extraction of PBDEs from aqueous samples using different SPME sorbent materials, including Fe_3O_4-coated bamboo charcoal fibres [100], carbon nanotubes [101], graphene-based coating [102] or etched stainless steel wire [103]. A polymer-coated hollow fibre was proposed by Basheer et al. for on-site sampling and preconcentration [104]. The fibre was placed in a vial containing the 10 mL water sampled. After extraction (10 min), the fibre was preserved in a sealed container and taken to the laboratory where analytes were back-extracted with 100 μL Hex [104]. The analytes adsorbed on the fibres were transported to the laboratory, and hauling of large sample volumes was avoided [104]. Furthermore, to increase SPME selectivity, a molecularly imprinted polymer-SPME device based on a fibre-type organically modified silicate has been developed for SPME-GC for analysis of PBDEs in waste water [105]. When applied in headspace mode (HS-SPME), SPME selectivity is improved while avoiding contamination with non-volatile substances and thus prolonging fibre lifetime. Due to the low volatility of these analytes, relatively high temperatures (circa 100 °C) are required to achieve equilibration conditions with shorter extraction times [106]. Using commercially available polyacrylate (PA) and polydimethylsiloxane (PDMS) as sorbent materials, HS-SPME has been used to extract PBDEs from environmental water samples [107,108]. Other stationary phases including carbon nanotubes (multiwalled or polymer-functionalized single-walled), permethylated-β-cyclodextrin/hydroxyl-termination silicone oil coated fibres, or perfluorinated ion doped polyaniline fibres were also used in HS-SPME for extraction of PBDEs from environmental waters and soil samples [109–112]. Even when SPME applications in aqueous samples can be easily achieved, its use is challenging for the determination of PBDEs in solid samples. Salgado-Petinal et al. and Zhou et al. proposed HS-SPME techniques coupled with GC-MS for determination of PBDEs in soil and sediment samples, without an additional clean-up step or a previous solvent-based extraction, achieving PBDEs recoveries higher than 78% [111,113]. SPME was also used for preconcentration and clean-up steps after green extraction procedures (MAE, UAE, or SFE) for extraction of PBDEs from soils, sediments, sewage sludge, and biological solid samples [86,114]. An alternative to liquid-extraction procedures before HS-SPME was proposed by Montes et al., who combined HS-SPME with a simultaneous oxidative sample treatment for extraction of PBDEs from sediment samples [115]. Using this strategy, PBDEs recoveries higher than 75% were achieved [115].

The stir bar sorptive extraction (SBSE) technique is based on stir bars coated with PDMS as an extracting phase. After the extraction

time, PBDEs are usually introduced quantitatively into the GC by thermal desorption, thus ensuring high sensitivity because the entire extract is analysed [98]. In comparison with SPME, this technique also requires an aqueous donor phase, but a special interface is required for thermal desorption. Even when this is a simple technique with minimum to negligible solvent consumption, extraction times must usually be longer than 20 h to achieve satisfactory recoveries. Furthermore, because the PDMS phase is non-polar, higher recoveries are obtained for analytes with log $K_{o/w}$ values above 3 [98], which is the case of PBDEs with log $K_{o/w}$ values in the range of 5.88–10 [41]. As shown in Table 3, up to 50 μL methanol can be added to the sample bulk as a matrix modifier to increase the efficiency of extraction of PBDEs; therefore, this technique should be considered to consume a low quantity of solvent, rather than being a solvent-free approach. The versatility of SBSE coupled in-line with GC through thermal desorption has been shown to be effective for determination of PBDEs in various matrices, including environmental water, wastewater and sewage sludge, and sediments [116–118]. Hence, prior to SBSE, PBDEs are usually extracted from solid samples with another green extraction technique, such as UAE or PLE [117–120]. To avoid possible degradation of high-brominated PBDEs by thermal desorption, UABE was used by Serôdio et al. after extraction with SBSE for determination of PBDEs in wastewater and sediments [120].

Matrix solid-phase dispersion (MSPD) may be used as an alternative technique for the simultaneous extraction and clean-up (fat removal) of PBDEs from environmental (sewage sludge [11,121]) and biological samples (human, fish, molluscs, mammals, and chicken tissues [122–126]). MSPD is based on a blending process between solid samples with an appropriate sorbent, generally silica gel, acidified silica, Florisil, or deactivated alumina. After extraction, the mixture is packed into a column and PBDEs are eluted, usually with Hex, DCM, or a mixture of them. To favour elution of the compounds with minimum organic solvent consumption, elution is assisted by ultrasonic radiation [121,123]. Liu et al. developed a novel graphene-assisted MSPD (GA-MSPD) technique for extraction of PBDEs and metabolites from soil, tree bark, and fish [127]. In comparison with other sorbents that are also used for MSPD, such as C_{18} silica, Florisil or carbon nanotubes, GA-MSPD allows similar recoveries of PBDEs, but higher recoveries of PBDE metabolites (more than 10% higher than recoveries obtained from the rest of the solvents). Further advantages include short extraction times (*ca.* 15 min) and low solvent consumption (2:1 mL Hex:DCM, 1 mL acetone) [127]. A further improvement of MSPD was proposed by Moliner-Martinez et al., who developed a miniaturized MSPD by reducing the amounts of sample (on the order of 0.1 g) and sorbent (0.5 g) to be considered [128]. Determination of PBDEs in mussel and cockle samples was achieved using miniaturized MSPD coupled with SPME-GC-ECD, with minimal solvent consumption (1.3 mL) and with recoveries of 100% [128].

2.2. Sample preparation for determination of PBDE metabolites

In the last decades, determination of PBDE metabolites has attracted much interest within different fields of science, including, chemistry, toxicology, biology, and ecology. This concern is based mainly on the potential health risks associated with human and animal exposure to these compounds. Supporting these endeavours, chemists search for sensitive methods for measuring environmental and biological concentrations.

Methodologies based on the green approaches previously described were also used for the determination of PBDE metabolites. Solid-based techniques and solvent-assisted extraction techniques were used for analysis of OH-PBDEs and MeO-PBDEs from environmental and biological samples, including macroalgae, plants, animal tissues (from fish, shellfish, crustaceans, cetaceans, molluscs, seabirds, polar bears, and sea lions), milk, wastewater, sewage sludge, and sediment [11,21,31–34,39,43,50,88,89,129,130]. However, analytical figures of merit were not reported in most of these publications, making their discussion and comparison more difficult, if not impossible. Furthermore, the extraction techniques and clean-up procedures have generally mimicked those optimized for PBDEs.

The difference in physical-chemical properties between PBDEs and the considered metabolites has been exploited to selectively separate these compounds. A single extract using Hex/DCM containing MeO-PBDEs and PBDEs was obtained after MSPD, followed by a second elution of the solid phase with acetone to recover OH-PBDEs [127]. Furthermore, Sun et al. demonstrated that, using a single multilayer column after UAE, it is possible to separate PBDEs, MeO-PBDEs and OH-PBDEs by simply using different ratios of DCM and Hex for elution [53]. This technique was applied on environmental matrices including water, soil, sediment, plants, molluscs, and fish, with recoveries higher than 70% for all of the analytes [53]. A third option to distinctively determine PBDEs and metabolites was using PLE-gel permeation chromatography (GPC) -SPE to obtain a single fraction (Hex:DCM (1:1) as solvents) containing all of the analytes [20]. The extract was first analysed by GC-HRMS for determination of PBDEs, followed by its acetylation, for OH- and MeO-BDEs determination using GC-HRMS [20]. Recoveries higher than 60% were achieved for most of the analytes when the methodology was applied to sediment, fish, and milk samples [20].

As can be inferred from this section, the development of methods based on green strategies should be focused on the determination of PBDE metabolites because these need to be properly monitored in the environment. The substantial versatility and number of green analytical approaches will assist in making these improvements because different solvents and strategies can be used to achieve the analytical separation.

3. Clean-up step and instrumental analysis

As previously mentioned, and as reflected in Tables 2 and 3, samples with complex matrices require clean-up steps prior to instrumental analysis of PBDEs. Even when clean-up is considered in the sample preparation step, this is discussed separately because it is common to both liquid- or solid-based approaches. One of the most important disadvantages faced for most of the techniques discussed in the previous sections is their lack of selectivity. This drawback is exclusive not only for green approaches but also for traditional techniques. One of the most relevant interferences present in the extract from biological samples is from lipids, due to the similar chemical behaviour during the extraction steps. The clean-up techniques mostly reported for removing these from extracts of fatty samples are simple- or multi-layer columns of Florisil, neutral alumina, or silica gel, and/or GPC, which act as fat retainers [14]. However, their retention capacity is limited, and large amounts of solid extractant are required, while increasing the loss of analytes. Other alternatives used for extract clean-up include dispersive solid phase extraction (d-SPE) and freezing-lipid filtration (F-l.f.) after sample extraction [54,55,71,72]. In the former technique, the sorbent material is added into an aliquot of the extract to remove matrix interferences, thus avoiding the passage of the extract through a SPE column and requiring smaller quantities of sorbent and solvent, as well as saving time and labour. The large amount of lipids coextracted can also be removed by freezing the lipids through submitting the extract to cold temperatures, followed by filtration, thus simplifying the clean-up step. In the case of samples with high concentrations of fat (>5% fat), destructive clean-up procedures based on sulphuric acid (liquid

sulphuric acid or silica modified with sulphuric acid (44%, w/w)) are frequently used [14,28,43]. Because PBDEs and metabolites can resist these extreme conditions, they are used to remove lipids and other oxidizable components through hydrolysis and/or oxidation of the organic matter of the sample extract.

After the green extraction techniques and the clean-up step (when needed), PBDEs and metabolites are usually determined by GC-based instrumental analysis. Specifically, approximately 85% of the reported methodologies that include green analytical extraction techniques used GC-based instruments, and most of them (~83%) were coupled with mass spectrometry (MS) detection. Even when the ECD is also used (~17%) due to its selectivity for halogens, unambiguous identification is not possible and misinterpretation easily occurs [131]. Comprehensive reviews were published on these instrumental techniques for analysis of PBDEs [15,16,132]. Additionally, Protka et al. discussed greener approaches in GC, including selection of carrier gas, the use of shorter columns, temperature, GC-high resolution mass spectrometry (GC-HRMS), fast GC, and two-dimensional GC (GC x GC) as strategies to make GC greener [13]. In addition to its environmentally friendly design, GC x GC was proposed by Covaci et al. as a promising solution for analysis of PBDEs that avoids degradation and/or co-elution [132].

A special consideration during instrumental analysis should be taken with thermolabile BDE-209 and OH-PBDEs, which may be determined by liquid chromatography (LC) to avoid high-temperature degradation and derivatization of these metabolites prior to GC, respectively. However, LC is used only in 14% of the analysed methodologies coupled with UV (~57%) or MS (~43%). From the perspective of green chemistry, this instrumental technique still requires a considerable amount of solvent for the run. Reduction of the particle size would lead to an improvement in the chromatographic resolution. Therefore, the column dimension could be reduced in length and diameter, thus reducing the analysis time, solvent consumption and waste generation [13]. Despite the improvement in the chromatographic resolution, it will not reach average gas chromatography peak capacity; therefore, the number of congeners that could be analysed by LC would be smaller than for GC. However, the sample preparation step could be simpler for LC than for GC, and it could avoid thermodegradation of the congeners. Therefore, it is worth focussing some effort in this sense because the sample preparation is usually the bottleneck of the analysis.

4. Conclusions

The growing concern from various scientific fields, including environmental and toxicological fields, regarding the analysis of PBDEs and metabolites, together with the interest of analytical chemists in following the green chemistry principles, converges in the development of greener analytical methodologies for their determination. Among green extraction techniques for determination of PBDEs, those based on liquid phase extraction predominate over those based on solid phase extraction (71% *vs.* 29%, respectively). For solid samples, solvent assisted extraction techniques are preferred for leaching of PBDEs, and liquid phase microextraction techniques are mostly used for liquid samples. The number of publications about analytical methodologies based on green approaches for determination of PBDE metabolites is notoriously scarce.

The growing interest is encouraged by the achieved analytical performance, even when complex environmental and biological matrixes are analysed. The analytical figures of merit for the green approaches described in the present review were comparable, or even better, than those achieved by traditional techniques. Additionally, the cost, time of analysis, and the volumes of organic solvents are minimized when using these approaches, thus simplifying analytical procedures, improving operational safety, and reducing pollution. Encouraging the use of environment-friendly analytical methodologies not only directly promotes the reduction of waste generated in the lab assays, but it will also lead to the development of environmental consciousness, which is essential to future generations. Significant advances in the development of greener, faster and simpler methodologies are expected, especially for PBDE metabolites, as well as an increase in regulatory norms for analytical laboratories.

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Appendix

Abbreviations

Analytical techniques	
μ-SPE	Micro-solid phase extraction
CPE	Cloud point extraction
DLLME	Dispersive liquid–liquid microextraction
dSPE	Dispersive-solid phase extraction
ECD	Electron capture detector
F-l.f.	Freezing-lipid filtration
GC	Gas chromatography
GPC	Gel permeation chromatography
HF-LPME	Hollow fibre-liquid phase microextraction
HPLC	High performance liquid chromatography
HS-SPME	Headspace solid phase microextraction
ICP-MS	Inductively coupled plasma-MS
LLE	Liquid–liquid extraction
LPME	Liquid phase microextraction
MAE	Microwave assisted extraction
MC	Multilayer column
MEPS	Microextraction in packed syringe

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(*continued*)

Analytical techniques	
MS	Mass spectrometry
MSPD	Matrix solid-phase dispersion
PLE (or ASE)	Pressurized liquid extraction (or accelerated solvent extraction)
QuEChERS	Quick, easy, cheap, effective, rugged and safe
SBSE	Stir bar sorptive extraction
SDME	Single drop microextraction
SFE	Supercritical fluid extraction
SFOME	Solidified floating organic drop microextraction
SPE	Solid phase extraction
SPME	Solid phase microextraction
TA-IL-DLLME	Temperature assisted IL-DLLME
UABE	Ultrasound assisted back extraction
UA-DLLME	Ultrasound-ASSISTED DLLME
UAE	Ultrasound assisted extraction
UPLC	Ultra-HPLC
Other abbreviations	
ACN	Acetonitrile
DCM	Dichloromethane
Hex	Hexane
IL	Ionic liquid

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