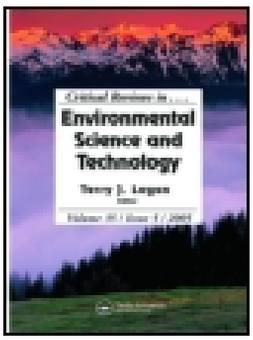

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Environmental Issues of Polybrominated Diphenyl Ethers

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Abstract:

Polybrominated diphenyl ethers (PBDEs) are among the emerging contaminants that have been traced in almost all environmental compartments for the past 30 years. Their continued application as flame retardant additives, persistence in nature due to fluorine groups, global atmospheric transport and analytical challenges due to interferences and different properties of congeners indicate the urgent need of finding solutions to their use. The increasing level of PBDEs in the environment and especially human tissues is alarming due to their potential neurological effects, cancer proliferation and thyroid hormone imbalance. Therefore, strict regulations need to be applied in all countries to control the PBDEs production consumption and disposal into the environment. Studies have shown that conventional wastewater treatment plants are unable to degrade PBDEs resulting in the transport of 60-90% of PBDEs to soil through biosolids application. On the other hand, advanced treatment processes, such as ultraviolet light, advanced oxidation and photocatalytic degradation showed promising potential for removing PBDEs from wastewater (70-100% degradation efficiency). Polybrominated Diphenyl Ethers can

be replaced by natural flame retardants, such as nanoclay or new polymers, such as Bishydroxydeoxybenzoin which have no environmental or health problems compared to PBDEs.

Keywords Analytical challenges; environment; polybrominated diphenyl ethers;

PBDEs; transport; treatment

Introduction:

Polybrominated Diphenyl Ethers (PBDEs) are flame-retardant additives used in different industries including paints, textiles, plastics, building materials, carpets, and vehicles Since they are not covalently bonded to the matrices, during their life time they migrate into environment (de la Cal *et al.*, 2003, Guerra *et al.*, 2011).. Similarities in the structures of PBDEs to polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs), proven to have toxic effects, implied that PBDEs can also be harmful to biota and environment (Wang *et al.*, 2016). There are reports stating that PBDEs can interfere with thyroid hormone metabolism and act as endocrine disruptors (Allen *et al.*, 2016, Khalil *et al.*, 2016).

Theoretically, there are 209 congeners of PBDEs, but only three mixtures of PBDEs namely penta-, octa- and deca-BDE (Table 1) are commercially available (Vonderheide *et al.*, 2008). In addition to their high lipophilicity and Henry's constant (Table 1), these compounds are resistant to different agents, such as acids, bases, oxidizing and reducing compounds. Therefore, they are extremely persistent when they are released to the different environmental compartments (Kim *et al.*, 2017). The annual global use of PBDEs has increased from 40,000 tons in 1990 to 67,390 tons in 2000 (Table 2), showing more than 67% growth in 10 years. Similarly, the levels for PBDE in human tissues, blood and milk seem to be increased during the few past decades (Ben Hassine *et al.*, 2015, Eljarrat *et al.*, 2003, Fromme *et al.*, 2016, Kim *et al.*, 2005, Qiu *et al.*, 2009). Therefore, it is necessary to summarize and analyze the state of knowledge about the PBDEs related issues in environment in order to decide if the benefit is worth the prejudices and the need of replace them for less toxic compounds.

Clearly PBDEs pollution is mainly focused at urban and industrial areas were the products are applied and used as well as in the final waste deposits. In this sense, it is pertinent to first ask if they represent a difference in fire safety. Wang *et al.* reported features of China's Urban Fires concluding that education is the main factor reducing the incidence of urban fires since 2003 and second is the investment in fire safe installations in the buildings (Wang *et al.*, 2015). This observation would indicate that using toxic flame retardants could be outdoby upgrading the fire security in buildings. The second question to be addressed is how to move to a generation of nontoxic flame retardants while addressing the treatment and degradation of those already produced.

In recent years, several articles have provided advances of knowledge on different environmental aspects of PBDEs (Covaci *et al.*, 2007, Domingo, 2012). Here are presented the last decade main advances on PBDEs as its environmental presence, toxicity, transport, fate, analytical challenges and possible treatment methods in order to facilitate a proper evaluation of the current situation.

Toxicological concerns

Many studies established the omnipresence of PBDE in environmental compartments and trophic magnification at alarming levels. Therefore, they are almost always present in terrestrial and aquatic animals, since the conventional solid waste and wastewater treatment does not remove the pollutant efficiently to a non-toxic concentration level and results in high bioconcentration and biomagnification potential (Burreau *et al.*, 2004, Burreau *et al.*, 2006, Wu *et al.*, 2009). Releasing effluents containing PBDEs into the environment introduces these compounds into the aquatic/terrestrial food chain, which results in their bioaccumulation and biomagnification in the

animal tissues. Wu *et al*. reported significant increased concentrations of BDE 47 in contaminated freshwater food web from South China (Wu *et al.*, 2009).

The toxicology of PBDEs is poorly understood except for decaBDE, yet in general PBDEs are linked to tumor proliferation, teratogenicity for the nervous system and thyroidal disruption (Muhammad *et al.*, 2003). PBDEs have low acute toxicity, with an oral LD50 greater than 5 g/kg. Upon chronic exposure, the main affected organs are the liver, kidney, thyroid gland and reproductive system (Allen *et al.*, 2016, Gross, 2016, Khalil *et al.*, 2016, Wang *et al.*, 2016). Generally, different PBDEs show similar toxicological effects/properties in which decaBDE shows lesser effects than other lower brominated congeners(Costa *et al.*, 2008).

In humans, tetra-BDE (2,2',4,4' tetra-brominated diphenyl ether) was suggested to be carcinogenic, since its association with adipose tissue levels with increased non-Hodgkin lymphoma in a group of cancer patients (Hardell *et al.*, 1998a, Hardell *et al.*, 1998b). Another study associated acute lymphoblastic leukemia (ALL) and octa and nonaBDEs (Ward *et al.*, 2014). Yet another study suggested the increase in population exposure to PolyHalogenated Aromatic Hydrocarbons (PHAH) and particularly PBDE as a possible reason for increased incidence of thyroid cancer (Zhang *et al.*, 2008). Also long-term PBDE exposure of rats has been shown to modify cell functions that contribute to metabolic disease and/or cancer susceptibilities (Dunnick *et al.*, 2012). Still it is considered that there is not strong proof on their carcinogenicity. Hence, neither the International Agency for Research on Cancer (IARC) nor the U.S. Department of Health and Human Services (DHHS) have classified the carcinogenicity of any PBDE, till date.

There is a maximized exposure and related potential chronic intoxication in people working in transportation. In this sense there are controversial opinions. For example, Harrad & Abdallah (2011) indicated that BDE-209 was higher in cabin dust and at the same time, that concentrations in the front seats were higher than in the back seats (Harrad *et al.*, 2011). Mandalakis *et al* reported that the daily inhalation intake of PBDEs during commuting reached up to 2909 $pg.day^{-1}$ (median 221 $pg.day^{-1}$) and contributed 29% of the overall daily exposure to PBDEs via inhalation and that new cars present higher levels than used units (Mandalakis *et al.*, 2008). Olukunle et al (2015) indicated that BDE-209 was the most prevalent congener in all the samples. This observation is similar to other studies reported for BDE-209 in dust samples from cars in the UK and USA (Olukunle *et al.*, 2015).

One of the current greatest concerns for potential toxic effects of PBDEs relates to their neurotoxicity in early childhood (Costa *et al.*, 2008, Hoffman *et al.*, 2016, Zhang *et al.*, 2016a). This concern is due to infant and toddlers presenting the highest PBDEs per kilo linked to uptake via indoor dust and breast milk (Costa *et al.*, 2007, Guo *et al.*, 2016). Moreover, previous studies reported cytotoxicity (He *et al.*, 2009, He *et al.*, 2008, Tagliaferri *et al.*, 2010), apoptosis (He *et al.*, 2008), ROS production(He *et al.*, 2008), DNA damage(Gao *et al.*, 2009, He *et al.*, 2008) and chromosomal abnormalities (He *et al.*, 2008) in human cell cultures with PBDE.

Hydroxyl-PBDEs are not industrially produced and are usually manufactured via metabolic transformation of anthropogenic polybrominated diphenyl ethers (PBDEs). In addition, OH-PBDEs can also be produced naturally in the marine environment, (by algae or cyanobacteria) (Malmberg *et al.*, 2005). Because of the structural similarities of hydroxyl-PBDE congeners with the hormones T2, T3 and T4, specific congeners may alter the biological action of these

hormones (Muhammad *et al.*, 2003). Even with a short period of exposure, less brominated PBDE congeners disrupt the thyroid resulting in malfunction and hormonal imbalance. For instance, rats develop hyperplasia due to the reduced thyroid levels by penta-BDE. Also, this reduced the number of T4 in mice (Fowles *et al.*, 1994). Similarly, highly brominated PBDE congeners as decaBDE with an exposure period of 90 days caused thyroid hyperplasia and tumours in mice (Muhammad *et al.*, 2003). In the case of occupational health hazard, workers who were exposed to decaBDE in a manufacturing plant developed clinical hypothyroidism (Bahn *et al.*, 1980).

Two more studies proved PBDEs to be estrogen disruptors as shown by eleven PBDEs with considerable estrogen disrupting properties. Of all, PBDE-100, 75 and 51 exhibited very high potential for estrogen disruption (Korach *et al.*, 1988, Meerts *et al.*, 2001). At higher concentrations, some hydroxy-PBDEs showed more potent inducing effects than estradiol leading to 50% induction that varied from 2.5 to 7.3 μM (Meerts *et al.*, 2001). Hence, in addition to thyroid disruption, hydroxyl_PBDEs also showed estrogen disruption properties. According to the reports named above, there are enough evidences that PBDEs have negative impacts on human health and the ecosystem and their utilization must be carefully evaluated to avoid such impacts.

Legislation

Poly brominated biphenyls (PBB) manufacturing stopped in US in late 1970s and since then PBDEs were widely used as an alternative to PBB. Three types of PBDEs were commercially used until 2005 (PentaBDE, OctaBDE, and DecaBDE). Following the environmental and health

concerns over PBDE, the production of octaBDE and pentaBDE were stopped in US following a voluntary agreement with the major manufacturer of pentaBDE and octaBDE to cease production. As of August 2006, under the Significant New Use Rule (SNUR), the USEPA started regulating the manufacturing, import and commercialization of pentaBDE and octaBDE. Many states in US have already enacted bans on octaBDE and pentaBDE and few states, such as Maine and Washington also banned DecaBDE (Environmental Protection Agency, 2006, Environmental Protection Agency, 2008, Environmental Protection Agency, 2012). When compared to US, Canada implemented strict regulations for the control of PBDE. Currently PBDEs production, sale, use, import or import of products containing them is banned in Canada (tetraBDE, pentaBDE, hexaBDE, heptaBDE, octaBDE, nonaBDE and decaBDE congeners); due to the toxic features listed in CEPA (Canadian Environmental Protection Act) 1999 (i.e. tetra, penta and hexaBDEs), (Environment Canada, 2008). As a result of regulations, the highest level of PBDEs in sludge had been associated to North America until 2007 and since then highest PBDE concentrations in sludge have been reported in Asia (Kim *et al.*, 2017).

Countries in Europe were well aware about the adverse toxicological effects of PBDEs since late 1980s and took measures to control their use. From 1980 to 1990, countries, such as Germany, Switzerland and the Netherlands banned PentaBDEs. According to EU's Restriction of Hazardous Substances (RoHS), DecaBDE was prohibited in 2002 (European Union, 2002). Again in 2004, European Union banned all products containing 0.1% or more penta- or octaBDE. In 2005, European Commission lifted the ban on decaBDE for the use in plastics despite the fact that it also contains penta- or octaBDE (commercial mixtures) which exceed the maximum allowed concentration of 0.1%. However, following the concerns raised by the

European Parliament, EU approved a complete ban on decaBDEs. Further, in 2005, pentaBDE was added to the European Union list of persistent organic pollutants (POPs) which obliges the governments to regulate the "use, export, import and disposal of pentaBDE aiming to reduce the transport of pentaBDE in environmental matrices (Ward *et al.*, 2008). Stockholm convention has provided some strict regulations on the use of PBDEs that are listed under POPs (persistent organic pollutants) since 2009. This guidance has been revised in 2017 (UNEP, 2017). As a result of EU regulations, a declining trend in the flux of PBDEs at some locations in lakes was observed since 2004 (Akortia *et al.*, 2016).Risk assessment studies showed that BDE-47 and BDE-99 are highly toxic. The predicted no-effect concentrations (PNEC) of these compounds were estimated to be 0.6 ng L^{-1} and 0.5 ng L^{-1} respectively for BDE-47 and BDE-99 (von der Ohe *et al.*, 2011). Federal Environmental Quality Guidelines for Polybrominated Diphenyl Ethers (PBDEs) provided the ecotoxicological sediment quality criteria for PDBEs in sediments which reported a concentration of 0.4, 63 and 9 ng/g dw, respectively for penta-, octa- and deca-BDEs (Environmen Canada, 2013). Governing bodies in the developed world have established and implemented environmentally sound strategies to eliminate the potential threat caused by PBDEs to human health and environment. In the developing world, such regulations do not exist. In China, no strict management policies or regulations were promulgated until date to manage PBDEs(Ni *et al.*, 2013). Even though RoHS legislation has been revised recently, and restricts the use of decaBDE for phones (mobile and fixed) and printers, but other appliances allow the use of decaBDE. In India, restriction of hazardous substances under the e-waste (management and handling) and Rules-2012 limit the use of PBDEs in electricals and electronics. The list prescribes the threshold limit of 0.01 wt% of PBDEs in homogenous materials. The rest of the

countries in the Asian and African world do not possess any strict regulations for the management of PBDEs, moreover, these countries are the larger producers of PBDEs. Due to economic aspects, such as lower labor costs and absence of strict environmental regulations, these countries receive large quantities of e-wastes every year (Breivik *et al.*, 2014) to be further disassembled and burned causing health impacts in the local population and entering to the atmosphere (Feldt *et al.*, 2014).

Environmental presence

Due to versatile physico-chemical properties of PBDEs congeners such as log Kow and vapor pressure, they exist in different parts of the environment. In Table 3 and Table 4, the related data to the concentrations of BDE-209 and total PBDEs in different environmental compartment including air, water and sediments around the world are listed.

Outdoor and indoor air

Several studies around the world have lately published on the presence of PBDEs in indoor and outdoor air. In fact, low brominated PBDEs are volatile congeners (e.g., BDE-47 and -99) and dominate in the vapor state, but in low concentrations of several $pg.m^{-3}$ (Butt *et al.*, 2004, Farrar *et al.*, 2004, Shoeib *et al.*, 2004, Strandberg *et al.*, 2001, ter Schure *et al.*, 2004). Bergman *et al.* in 1997 examined the air in offices (working places) that use electronic technologies (e.g. computers) and found PBDE in all samples due to the fact that electronic devices are the source of PBDE particles in indoor air (Bergman *et al.*, 1997). Later, they compared the concentrations of PBDE in air from an electronics recycling plant, an office and outdoors. The highest concentrations were contained in the recycling plant air (Bergman *et al.*, 1999). Also, PBDEs

were found in every atmospheric sample collected by Strandberg *et al*. from the Great Lakes region (Strandberg *et al.*, 2001). According to Wilford *et al,* PBDEs median concentrations in Canadian homes indoor air was approximately 50 times higher than the concentrations in outdoor air (Wilford *et al.*, 2004).

Surface water

PBDE concentrations in Lake Michigan water increased more than five folds in the time period of 1997-1999 (Stapleton *et al.*, 2001). Same authors confirmed the existence of the PentaBDE in an entire Lake Michigan food web (Stapleton *et al.*, 2003). In the Netherlands, Western Scheldt river, high levels of DecaBDE (4600 $\mu g.kg^{-1}$) were adsorbed onto suspended particulate matter (de Boer *et al.*, 2003). In Cairo, the highest observed PBDE concentrations belonged to BDE 209, ranging from 40.2, to 1,540 ng.g−1 as the lowest the domiciliary exposure and the highest exposure was reported in cars. These values represent 8 to 46 times the Penta BDE concentrations. Non-PBDE flame retardants on the contrary are 7 to 55 times less concentrated than ∑PBDEs. Therefore, both types of flame retardants are in the lowest reported range. The adults and toddlers estimated dust intake therefore seems to be below reference dose values (Hassan et al 2015). However, it has to be taken onto account that people working in transportation are much more exposed than others, since the values in cars (and trucks) are much higher than domicile (Hassan et al., 2015). At Lago Maggiore (Italy), PBEB, HBB, and BTBPE in sediments were in low concentrations. However, as in Egypt, BDE-209 dominated all samples (Poma *et al.*, 2014). This indicates the prevalence accumulation of deca-BDE formulations in both cases. Also, other congeners, such as BDE-47, BDE-99, and BDE-100 were detected in this Italian lake, confirming that penta-BDE formulations are still in use. Decabromodiphenyl ethane

(DBDPE) is also present in Lago Maggiore in comparable amounts to BDE-209. Since the author indicates a positive correlation between DBDPE and BDE-209, DBDPE is becoming main NBFRs in Northern Italy, which can be probably extrapolated to whole Europe due to shared regulations.

Aquatic biota

Kuehl *et al*. reported the existence of PBDEs in North American waters for the first time by collecting samples from bottlenose dolphins during the mass mortality event alongside the Atlantic coasts in 1987 and 1988 (Kuehl *et al.*, 1991). In the same time period, Watanabe *et al*. confirmed the presence of PBDEs in marine fish and shellfish in Osaka Bay, Japan (Watanabe *et al.*, 1987). Also, whales blubber in the Faroe Islands, in the Atlantic, contained 19 tetra- to hexabrominated diphenyl ethers with a predominance of TeBDE and PeBDE accounting for 70% of total PBDEs (Lindström *et al.*, 1999).

Most of the studies were carried out on sites near factories or potential sources of PBDEs, which explains their presence in water or in aquatic life. But even in the Canadian Arctic, where there is almost no industrial activity, Ikonomou *et al*. found over 37 PBDE congeners in ringed seal blubber during 1981, 1991, 1996, and 2000 (Ikonomou *et al.*, 2002). The levels of these congeners increased through the years. This trend may be explained as a result of PBDEs travelling via atmospheric transport from the industries in Asia, Europe and North America to Arctic water (Barrie *et al.*, 1992). Spatial trends of ΣPBDEs in European Arctic implied that it is more contaminated than the North American Arctic, which is due to the transport pathways from highly populated western and central Europe and eastern North America (Iqbal *et al.*, 2017).

Sediments and soil

Sediments and soils are adequate deposition sites for PBDEs. In fact, multiple research studies have been carried out to prove their existence in these two compartments of the environment. In 29 of 30 Australian soils samples PBDE was detected with concentration of up to 13200 ng g^{-1} (McGrath *et al.*, 2016). In US, Hadley Lake in Indiana, presence of PBDEs in sediments (19-36 ng g^{-1}dw) was confirmed by Dodder *et al*. (Dodder *et al.*, 2002). In comparison to North America, analysis of sediments from different European sites revealed higher levels of PBDEs i.e, 200-1700 ng g^{-1}dw (de Wit, 2002, Sellström *et al.*, 1998). In the West Midlands, UK, soil in 10 sites was examined over one year in search for PBDEs. They reported that increasing distance from the city center decreases PBDEs levels (Harrad *et al.*, 2006b).Table 3 and Table 4 resume the investigations of other researchers on detection of these compounds in European countries. In other studies that were carried out in Asia, researchers found up to 4250 ng.g^{-1} of PBDEs in soils at an e-waste dismantling site in Guangdong Province of South China (Leung *et al.*, 2007, Wang *et al.*, 2005).

Most reports of PBDEs originate from North America, Europe and recently few of them in Asia. It seems logical because these three regions dominate in production of PBDEs, but it has been proven that these compounds are a global problem because of their export, wastes and atmospheric transport. More research has to be done in the other regions, such as South America, Africa, the Middle East and others to substantiate their worldwide presence and problem.

Fate and partial compartmentalization

Heavy PBDEs or higher brominated compounds are known for their low volatility, low water solubility and bioaccumulation. But they have a strong adsorption to soils and sediments. Lighter PBDEs can be volatile, soluble in water, bioavailable, degradable and they can be adsorbed. The fate of PBDEs in the environment can be air--water exchange, deposition on water and soils, riverine runoff, sorption, degradation and bioaccumulation in biota. There are recent reports on bioaccumulation of PBDEs in killer whales and dolphins even near the artic (Alava *et al.*, 2016, Lavandier *et al.*, 2016, Salvadó *et al.*, 2016). Air and water are primary transporters of PBDEs, while soils and sediments are final sinks (Fig. 1). Table 5 shows the half-lives of two important categories of PBDE congeners in different environmental compartments.

In sewage treatment plant

Sewage treatment plants (STP) are likely major source of PBDEs in the receiving environment, such as freshwater, coastal marine and soils. The fate of PBDEs in STP has recently gained attention of multiple researchers. PentaBDE congeners were detected in all stages of the STP process, with an 950.4 mg/day (9%) ending up into the Detroit River with the treated effluent (Song *et al.*, 2006). Concentrations in sludge were up to 2,217 $ng.g^{-1}$ in Germany where more than half is used as fertilizer with about 500 kg/acre BDE (Knoth *et al.*, 2007).

Analytical Challenges:

In the past twenty years, methods for determination of PBDEs concentration in different environmental matrices have experienced massive development. Generally, analytical methods

for determination of PBDEs are difficult due to complexity of matrices, existence of vast number of congeners, low concentration and interferences of similar compounds, such as PCBs and PBBs (Eljarrat *et al.*, 2003). Typically, for analysis of PBDEs, the sample is first extracted with an organic solvent or through other methods, such as solid phase microextraction (SPME). Lipids and other high molecular weight compounds, such as paint and polymers should be removed using either concentrated H_2SO_4 or gel permeation chromatography (GPC). In some cases, the sample needs further clean-up to remove interfering compounds (Dufour *et al.*, 2016). The purified extract is then subjected to one of the methods including gas chromatography (GC), liquid chromatography (LC) or their coupled setup with mass spectrometry (MS), namely GC-MS and LC-MS (Stapleton, 2006).

Extraction and clean up

There are several challenges with each matrix that may influence the recovery of each method. For example, the constituents of soils including mineral and organic phases tend to adsorb PBDEs as Mueller *et al.* observed a rapid decline in PBDE recovery over time in a solvent extraction procedure (Mueller *et al.*, 2006). For sediments, the partitioning of different congeners is dependent on sediment grain size so that higher brominated congeners tend to adsorb onto smaller grains (Sánchez-Brunete *et al.*, 2006). In aqueous matrices, such as water, wastewater, serum and milk, biodegradation can play a significant role and therefore preservation of sample before analysis is of importance (Rayne *et al.*, 2003b, Vonderheide *et al.*, 2006). In the case of wastewater samples, there is a possibility of adsorption of PBDEs to biosolids that should be taken into account in extraction and cleanup stage (North, 2004). There are also several problems with air and dust samples since temperature can affect the partitioning coefficient and photo-

degradation can take place under sunlight exposure (Stapleton *et al.*, 2008). Therefore, the extraction and cleanup methods should be wisely selected to ensure proper determination of PBDEs. The conventional techniques that are employed in different stages of PBDEs determination for variety of samples are listed in Table 6 along with their drawbacks. The conventional methods for extraction of target compounds from liquid and solid samples are liquid-liquid extraction (LLE) and Soxhlet extraction. These methods are time consuming and need considerable amount of solvents. Researchers tried new methods in order to achieve the highest performance in terms of required time, recovery rate and cost. De la Cal *et al.* employed the pressurized liquid extraction (PLE) method for extraction of PBDEs from sediments prior to injection to GC column and claimed that this method can obtain comparable results to the typical time-consuming Soxhlet extraction or solid phase extraction methods and decrease the preparation time from several days to 30 minutes (de la Cal *et al.*, 2003). Also, a successful use of this method for extraction of PBDEs from dusts and human milk was developed (Lacorte *et al.*, 2008, Stapleton *et al.*, 2005) but Harrad *et al.* found that in some cases, the recovery of this method ranged from 45 to 67% (Harrad *et al.*, 2006a). Bayen *et al.* employed microwave-assisted extraction (MAE) for extraction of three PBDE congeners (47, 99 and 100) and reported that the results were comparable to Soxhlet extraction method (less than 15% variation) with less time consumption (Bayen *et al.*, 2004). Also, Tan *et al.* used MAE method for extraction of PBDEs from dust and their relative standard deviations (RSD) were in the range of 0.4-32% (Tan *et al.*, 2007). Recently, Berton *et al.* coupled ultrasound assisted extraction (UAE), cloud point extraction (CPE) and ultrasound back-extraction (UABE) techniques for simultaneous extraction, pre-concentration and clean-up of PBDEs in milk samples and reported 68-70% recovery and

0.05 -- 0.5 ng g^{-1} dw limits of detection (LODs) (Berton *et al.*, 2017). To sum up, one of the main challenges of extraction and clean-up is that the researchers should already have an idea about the other constituents in the sample to select the right combination of methods. Also, more work is required for increasing the efficiency and reducing the cost and time of extraction and clean-up processes. Since using organic solvents and working at high temperatures compromise the metrics of green chemistry, researchers should try to use more environmentally friendly methods (Cruz *et al.*, 2017). Berton *et al.* summarized the environmental aspects of different methods of extraction and clean-up in determination of PBDEs (Berton *et al.*, 2016).

Liquid and gas chromatography

Liquid chromatography (LC) has not been optimized for PBDEs analysis due to its low resolving power compared to GC (Covaci *et al.*, 2007). Generally, this technique is considered when physical characteristics of compounds disallow using of GC technique (Vonderheide, 2009). Petropoulou *et al.* employed LC-MS-MS for determination of 12 hydroxylated PBDE congeners that are formed from the metabolism of PBDEs in humans, rats and mice (Petropoulou *et al.*, 2014). However, their results showed lower accuracy and precision. In contrast, gas chromatography technique has been extensively used for determination of PBDEs in different environmental matrices.

Thomsen *et al.* compared GC coupled with electron capture negative ionization low-resolution mass spectrometry LRMS (ECNI) and electron ionization high-resolution mass spectrometry HRMS (EI) for determination of PBDEs concentrations in plasma, serum and milk. The obtained RSD for LRMS (ECNI) and HRMS (EI) were in the range of 4.7--8.4% and 0.6--10%, respectively. They concluded that LRMS (ECNI) was suitable for routine analysis while HRMS

(EI) showed better performance for new sample matrices due to availability of different isotope labeled (^{13}C) PBDEs in the market (Thomsen *et al.*, 2002). Thermal degradation of certain congeners especially BDE-209 was a challenge for determination of these compounds. To overcome this problem, using short columns and also using f [13C]-labelled BDE 209 for isotopic dilution in ECNI-MS was successfully employed (Covaci *et al.*, 2007). Eljarrat *et al.* found that EI approach gives better structural understanding by providing information about molecular ions and sequential losses of bromine atoms (Eljarrat *et al.*, 2002). They also observed that EI is affected by PCBs interferences, while ENCI is affected by brominated compounds, such as PBBs (Eljarrat *et al.*, 2003). Due to massive improvement in clean-up and detection techniques, the interference of PCBs and PBBs can be overcome by measurement of PBDE concentration. For example, adsorption chromatography was able to remove co-extracted biogenic materials in the sample and prevent the interferences. Zhang and Rhind used glass column chromatographic sorbent for fractionation of PBDEs and PCBs and reported higher efficiency compared to SPE cartridge though its solvent consumption was 10 folds more than SPE (Zhang *et al.*, 2011b). Barco-Bonilla *et al.* combined SPE and UAE methods and succeeded in simultaneous determination of PBDEs and PCBs in sediment samples using GC-HRMS. They reported LOD lower than 0.03 ng L^{-1} (Barco-Bonilla *et al.*, 2015). In addition, using tandem mass spectroscopy techniques e.g. GC-MS-MS provides higher selectivity in the discrimination of other halogenated organics from PBDEs (Lagalante *et al.*, 2008). For example, Medina et al. used GC-MS-MS for simultaneous measurement of 30 PBDEs and PCBs in human breast tissues and obtained results with LOD down to 0.1 μg/kg (Medina *et al.*, 2009). Camino-Sánchez used GC-MS-MS for simultaneous determination of 80 compounds from PBDEs, PCBs and other

organic compounds and obtained results with LOD lower than 1 ng/kg (Camino-Sánchez *et al.*, 2011). Multidimensional chromatography is another technique which can provide comprehensive data and highest separation level compared to other techniques. Ubukata *et al.* and Ballesteros-me *et al.* used GC × GC two dimensional columns coupled with mass spectrometer to measure the concentration of PBDEs and PCBs in different matrices, such ass plastic baby toys and dust and obtained significant LOD (down to 0.15 µg/kg) (Ballesteros-Gómez *et al.*, 2013, Ubukata *et al.*, 2015). However, this technique provides an enormous data set that required software tools and respective knowledge and experience to facilitate the interpretation. Choosing the appropriate detection method depends on level of selectivity or sensitivity demands (Cruz *et al.*, 2017).

Environmental Remediation

The most common PBDEs presently used are tetra, penta, octa and deca BDEs. Their log K_{ow} values are around 6.15, 7.32, 8.65 and 12.61 respectively for tetra, penta, octa and decaBDEs. Hence, they possess very low water solubility and high binding affinity to particles resulting in accumulation on solid substances during the treatment process. These properties increased their persistence in the environment. Conventionally, the removal process of this pollutant from environment can occur via three routes: wastewater treatment plants, incinerators, and landfills as illustrated in Fig. 1.

Studies from Canada reported that PBDEs do not appear to be degraded remarkably or removed by conventional processes in wastewater treatment plants, such as aerobic biological treatment, anaerobic, anoxic, dissolved air flotation, or multimedia media filtration. In this particular study,

an overall removal efficiency observed was 93% and major removal was obtained through sorption onto wastewater sludge (Rayne *et al.*, 2005). These high levels of accumulation on biosolids can accumulate in soil with the soil application of biosolids. Similar results were reported from China for later studies. About 19 PBDE congeners were present with BDE209 accounting for the largest proportion and removal was constituted majorly by accumulation on the sludge (60%) (Xiang *et al.*, 2013). Another study from a conventional wastewater treatment plant reported 91% removal and from the sewage sludge contributing 0.7kg/year of PBDEs directly discharged to the river(Song *et al.*, 2006). In all these studies, least brominated PBDEs responded to the treatment and were effectively removed while the highly brominated PBDEs, such as decaBDE showed resistance towards the treatment process and tend to accumulate in the solid fraction. Other reported studies (de Wit, 2002, Hagenmaier *et al.*, 1992, Hale *et al.*, 2003, Hale *et al.*, 2001a, Nylund *et al.*, 1992, Öberg *et al.*, 2002) also pointed towards the accumulation of PBDEs on the wastewater sludge and confirmed ineffective removal by conventional methods.

Dewatered sludge from various countries showed different concentrations of PBDEs on solid fractions. In US, the total concentration of tri- to hepta-BDEs is reported to be in the range of 1100 to 2290 ng/g of the dewatered sludge(Hale *et al.*, 2001a). In China, these figures were 6.2--57 ng/g (sum of tri- to hepta-BDEs) (Wang *et al.*, 2007b) and in European countries, the values ranged from 100-300 ng/g (sum of tri- to pepta-BDEs) in the dewatered sludge(de Wit, 2002, Hagenmaier *et al.*, 1992, Nylund *et al.*, 1992, Öberg *et al.*, 2002).

Municipal solid wastes contain a large amount of PBDE congeners from e- wastes, household waste and paints. Usually, these wastes will be moved to the landfill sites or for the incineration

process and these processes are considered as the common treatment methods. Recently, studies from Canada reported the presence of PBDE in landfill leachate with a concentration varying from 1,020 to 21,300 ng/L with decaBDE as the dominant PBDE in the matrix (Li *et al.*, 2012). Estimated average ∑PBDE loadings from an urban landfill to the environment were estimated to be 3.5 tonnes/year in Canada(Li *et al.*, 2012). Incineration also does not remove the contaminants permanently from the environment. Studies reported that during incineration at up to 1652 °F (900 °C), PBDEs are transformed into polybrominated dibenzodioxins (BrDDs) and polybrominated dibenzofurans (BrDFs) (Buser, 1986) and the toxicity of these by-products are unknown which is a matter of further concern.

Advanced treatment methods, such as UV treatment, advanced oxidation and photocatalytic processes have shown good potential for removing PBDEs from wastewater. Table 7 presents some of these advanced treatment methods. All these studies reported removal efficiency of 70-100%, though they did not investigate the degradation by-products and its potential toxic effects.

Relatively recent studies have investigated the potential of various aerobic and anaerobic microbes for the degradation and removal of PBDEs from environment. Since accumulation in sludge or soil is a certain possibility of PBDEs transport process the advantages of microbial degradation process must be explored in the future studies being microbial degradation as a feasible process in most of the solid substances such as soils, wastewater sludge and sediments. Several recent studies have investigated the removal efficiencies / potential degradation capacities of various microbial communities for the degradation of PBDEs (Chen *et al.*, 2015, Stiborova *et al.*, 2015a, Stiborova *et al.*, 2015b, Yang *et al.*, 2014). In general, these studies

reported removal efficiency ranging from 45-80% for various PBDEs. However, a recent study from Hong kong in sewage treatment plants reported a removal efficiency close to 90% for BDE-47, BDE-99 BDE-209(Man *et al.*, 2015). Recently biotransformation of deca-BDE was reported using indigenous bacterium isolated from PBDEs contaminated environment. *Lysinibacillus fusiformis strain DB-1*isolated from sediments of LianjiangRiver, Guiyu in Guangdong of China has demonstrated more than 80% of removal efficiency for the removal of deca-BDE in a realistic environmental condition such as river sediments (Deng *et al.*, 2011). Studies are also demonstrated the rapid degradation of PBDEs though various microbes. In this study reported from USA which was carried out in soil; soil microbes were able to degrade DE-71 within few minutes(Vonderheide *et al.*, 2006)

Future perspectives

The detection of PBDE congeners in environmental compartments has raised major concerns throughout the world. Since the invention of this compound, it has been widely used, irrespective of the region for the production of various goods. It is well-proven that PBDE causes certain health problem for humans and other living organisms. Present regulations regarding the management of the PBDE are poorly developed in the developed countries. The developing world does not even possess any governmental regulations for the control of PBDE. Hence, strict regulations must be implemented throughout the world for the management of this persistent organic pollutant (POP), especially in countries, such as China where a rapidly developing electronic market is present. Rule of 3R (Reduce, Reuse, Recycle) can be applied as an effective approach for management of PBDE but it cannot be considered as a permanent solution.

There must be a collective approach to regulate PBDEs since it used in various industries with a line of application from electronics, clothing to large scale firefighting. The partnerships between multiple industries and multiple producers of the raw chemical must be made for the unified regulations. Few of such partnerships were made during the past decade, such as Voluntary Children's Chemical Evaluation Program (VCCEP), providing data on health effects, exposure scenarios and risk of 23 chemicals that affect children. The Environmental Protection Agency (EPA) works collectively with the VCCEP to initiate risk assessments. Another recently formed partnership was the Furniture Flame Retardency Partnership, which focused on the application of flame-retardants in furniture. It includes members of the furniture industry, environmental groups, chemical manufacturers, fire safety advocates, the National Institute of Standards and Technology and the Consumer Product Safety Commission. This partnership is on a starting stage and has not yet produced any major revolution regarding the management of PBDEs. Still, this initiative was able to provide wide awareness about the chemical.

The assessment of PBDE must be continued and intensified to monitor its environmental fate, exposure pathways, degradation by-products and entry mechanism in human as well as animal tissues. In this regard, the least studied area is the PBDE by-products, such as polybrominated dibenzodioxins (BrDDs) and polybrominated dibenzofurans (BrDFs) and their toxicity. The modern and advanced treatments may effectively remove/degrade PDBE from the environment but simultaneously the by-products can be the contaminants of emerging concern in future, which needs to be extensively studied.

Apart from controlling the consumption of PBDEs, finding less harmful alternatives or developing materials with inherently flame-resistance for building and electronics can be helpful

to environment and human health. Efforts to produce eco-friendly retardants are ongoing throughout the world (El-Shafei *et al.*, 2015, Merk *et al.*, 2015) and which is promising towards a sustainable future. These efforts include eco-friendly flame retardants for cotton fabrics and polyester fabric (El-Shafei *et al.*, 2015, Pan *et al.*, 2015).In addition recent studies were also focused on the production of eco-friendly flame retardant paper (Köklükaya *et al.*, 2015). Currently, aerospace industry uses several inherently non-flammable plastics, but they are too expensive to be used for electronics. Therefore, further research is needed to develop economically viable non-flammable materials, such as polymers based on Bishydroxydeoxybenzoin (BHDB) which produce water after burning. Recently, using phosphorus-based flame retardants for electronics and nanoclays for cabling attracted the attention of industries. However, all environmental aspects of alternatives should be assessed before their commercialization since there are possible neurotoxicological effects derived from the metabolites of phosphorus-based flame retardants (Betts, 2008). It is noteworthy that more than half of novel retardants are of similar concern, persistent and of long range transport (Zhang *et al.*, 2016b). Given these similar trends, it is important to reinforce research on the new generations of flame retardants that are already visibly replacing penta-BDE in the environment.

Discussion

Polybrominated Diphenyl Ethers (PBDEs) are flame retardants derived from bromination of diphenyl ether. Three PBDE mixtures, namely penta, octa and deca-BDE are commercially available and used in industries to produce printed circuit boards, electrical connectors, electrical appliance housings, coatings, padding foams and insulation. Several developed countries have

already banned penta and octa-BDE, due to its toxicological concerns. DecaBDE has been reported more in research and therefore degradation pathways and degradation products are known.

In the environment, the sources of PBDEs are textiles, plastics, building materials, carpets, vehicles and e-waste recycling operations. The concentrations of PBDEs are higher in indoor air than outdoor air leading to potential adverse impacts on humans through inhalation. Likewise, the presence of congeners of PBDEs in outdoor air in the Arctic indicates that PBDEs are capable of long range atmospheric transport. Moreover, the PBDEs are difficult to be removed by conventional treatment processes in wastewater treatment plants, such as aerobic biological treatment or anaerobic digestion, and these compounds are resistant to different chemicals, such as acids, bases, oxidizing and reducing compounds. Thus, PBDEs are accumulated in sewage sludge, biosolids and sediments. Hence, the possibility of bioavailability for these compounds for the terrestrial and aquatic ecosystems is high. Bioaccumulation and hence potential for trophic magnification of PBDEs causes serious risks to humans. PBDEs are even detected in human milk, blood serum and cord blood. Even though PBDEs have low acute toxicity, the major concern is their endocrine disruption capability. As a result, PBDEs have been associated with cancer proliferation, neurodevelopmental toxicity and thyroid hormone imbalance.

Due to the low half-lives of PBDEs and congeners in the environment, and potential health effects, the government of certain countries in Europe and North America have established and implemented environmentally sound strategies for the management of PBDEs. However, these strict regulations must be applied in all countries throughout the world due to the air transport of these compounds has been proven even in the isolated regions of North and South pole.

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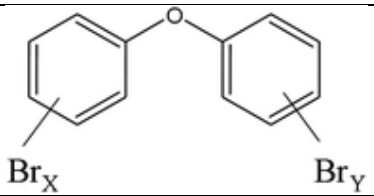
Table 1: Physico-chemical proprieties of PBDEs

Physical-chemical properties	PBDEs			References
Chemical structures of PBDEs				(Swarthout *et al.*, 2008)
Technical product most use and highly brominated (X+Y)	Penta -- BDE[a]	Octa -- BDE[a]	Deca -- BDE[a]	(de Wit, 2002)
	5	8	10	
Physical form	semi-solid	Powder / flake	Crystalline powder	(Genty *et al.*, 2009)
Number of congeners	46	12	1	(Genty *et al.*, 2009)
CAS No	32534-81-9	32536-52-0	1163-19-5	(Genty *et al.*, 2009)
Molecular Formula	$C_{12}H_5Br_5O$	$C_{12}H_2OBr_8$	$C_{12}Br_{10}O$	(Sjödin *et al.*, 2003)
Molecular weight	564.69	801.38	959.17	(Sjödin *et al.*, 2003)
Relative density at 25°C	2.25 -- 2.28	2.76	3.0	(Hardy, 2002, NLM, 2012a, Sweeney *et al.*, 2000)
Water Solubility ($mg.L^{-1}$) at 25°C	2.4×10^{-3}	0.5×10^{-3}	0.1×10^{-3}	(Hardy, 2002, Rahman *et al.*, 2001, Stenzel *et al.*, 1997)
Log Kow	7.32	8.4-8.9	12.61	(Braekevelt *et al.*, 2003,

				Sjödin *et al.*, 2003)
Henry's constant ($Pa.m^3.mol^{-1}$)	0.60	0.03	0.04	(Cetin *et al.*, 2005, NLM, 2012a)
Vapor pressure[b] (Pa) at 25°C	1.76×10^{-5}	1.73×10^{-7}	1.26×10^{-12}	(Hoh *et al.*, 2005, NLM, 2012a, Strandberg *et al.*, 2001)
Melting point (°C)	93	200	300	(Darnerud *et al.*, 2001, Palm *et al.*, 2002)
Log Koc	4.34	4.99	6.25	(Hardy, 2002, NLM, 2012a, NLM, 2012b)

a: Commercial samples

b: calculated data (interpolated)

Table 2: Estimated world market demand for PBDEs

Years	PBDEs	Global demand	Europe	North American	Asia	Rest of the World
1990[a]	Penta	4000	-	-	-	-
	Octa	6000	-	-	-	-
	Deca	30 000	-	-	-	-
	Total	40 000	-	-	-	-
1999	Penta	8500 [a]	210 [b]	8290	-	-
	Octa	3825 [a]	450 [b]	1375	2000 [b]	-
	Deca	54 800 [a]	7500 [b]	24 300	23 000 [b]	-
	Total	67 125 [a]	8160	33 965	25000	-
2001	Penta	7500 [a]	150[c]	7100	150 [c]	100 [c]
	Octa	3790 [a]	610 [c]	1500 [c]	1500 [c]	180 [c]
	Deca	56 100 [a]	7600 [c]	24 500 [c]	23 000 [c]	1050 [c]
	Total	67 390 [a]	8360	33 100	24650	1330
2002	Penta	-	-	-	-	-
	Octa	-	-	-	-	-
	Deca	65677[d]	-	-	-	-
	Total	-	-	-	-	-
2003	Penta	-	-	-	-	-
	Octa	-	-	-	-	-

	Deca	56418[d]	-	-	-	-
	Total	-	-	-	-	-

[a]: data from (Hites, 2006)

[b:] data from (de Wit, 2002)

[c]: data from (Tan *et al.*, 2007)

[d] = data from (Guerra *et al.*, 2011)

Table 3: BDE-209 in environment

Matrix	Location / region	Countries	Concentrations			Analysis Method	No. Samples	Ref.
			Minimum	Mean	Maximum			
Indoor Air (pg.m^{-3})	Munich	Germany	0.87	33.3	438	GCMS (SXH)	34	(Fromme *et al.*, 2009)
Indoor Dust (ng.g^{-1})	Ottawa	Canada	74	1100	10000	GCMS (SXH)	68	(Wilford *et al.*, 2005)
	Albany	USA	327	2810	9210	GCMS (SXH)	12	(Johnson-Restrepo *et al.*, 2009)
	Washington, D.C		162	2090	8750	GCMS (ASE)	16	(Stapleton *et al.*, 2005)
	Massachusetts		814.4	4702.0	185600	GCMS (ASE)	108	(Allen *et al.*, 2008)
	Munich	Germany	29.7	354	1460	GCMS (SXH)	34	(Fromme *et al.*, 2009)
	-	Kuwait	0.8	128.8	338.1	GCMS (SXH)	17	(Gevao *et al.*, 2006)
	Brisbane	Australia	95	377	1585	GCMS (ASE)	120	(Toms *et al.*, 2009)
	Guangzhou	China	11.6	550.2	2412.6	GCMS (UE)	9	(Peng *et al.*, 2009)
Sewage sludge/ Biosolids (ng g^{-1} dry weight)	different locations	Netherlands	310	350	920	GCMS (SXH)	9	(de Boer *et al.*, 2003)
	Ontario	Canada	637	-	6930	n.d	n.d	(Hale *et al.*, 2003)
	4 states	USA	84.8	-	4890	n.d	n.d	(Hale *et al.*, 2001a)
	Wisconsin		-	510	-	n.d	3	(Hale *et al.*, 2003)
	Michigan		-	466	-	n.d	8	(Hale *et al.*, 2003)
	North Carolina		37400	-	58800	GCMS (ASE)	n.d	(La Guardia *et al.*, 2007)
	California		1010	1183	1440	GCMS (LLE)	6	(North, 2004)
	26 cities	China	n.d.	68.5	1108.7	GCMS (SXH)	31	(Wang *et al.*, 2007b)
	Guangzhou		150	6586	22894	GCMS (UE)	9	(Peng *et al.*, 2009)
	Shanghai		30.9	2370	34900	GCMS (SXH)	28	(Yang *et al.*, 2011)
	Umm Haylaman	Kuwait	16.4	360.4	1595.6	GCMS (SXH)	18	(Gevao *et al.*, 2008)
	different locations	Czech Republic	27	-	1709.4	GCMS (SXH)	15	(Nápravníková *et al.*, 2008)
	Rhine-Main	Germany	97.1	256	2217	GCMS (SXH)	39	(Knoth *et al.*, 2007)
	different locations	Spain	80.6	-	1082	GCMS (SXH)	n.d.	(Eljarrat *et al.*, 2008)
	different locations	Sweden [c]	n.d.	11	390	GCMS (LLE)	116	(Öberg *et al.*, 2002)
	different locations	Switzerland	138	310	617	GC/ECD (SXH)	16	(Kupper *et al.*, 2008)
	different urban locations	Australia	81	880	3780	GCMS (ASE)	16	(Clarke *et al.*, 2008)
	McMurdo and Scott (Antarctica)	USA and New Zealand	219	-	1320	GCMS (ASE)	4	(Hale *et al.*, 2008)
Surface water (ng L^{-1})	different locations	China	0.33	-	65.24	GCMS (UE)	96	(Guan *et al.*, 2007)
	San Francisco	USA	0.012	-	0.191	GCMS (ASE)	33	(Oros *et al.*, 2005)
	Dongjiang	China	21.3	1440	7340	GCMS (SXH)	33	(Mai *et al.*, 2005)
	Guiyu		16.9	35.9	62.2	GCMS (SXH)	5	(Luo *et al.*, 2007)
	Beijing		n.d.	237.01	742.53	GCMS (SXH)	8	(Wang *et al.*, 2007a)
	Hangzhou		0.16	13.4	94.6	GCMS (SXH)	32	(Chen *et al.*, 2006)
	different locations	South Korea	0.22	27.4	493	GCMS (SXH)	25	(Moon *et al.*, 2007)
	Lombardy	Italy	1.6	-	15.3	GCMS (SXH)	70	(Guzzella *et al.*, 2008)
	Antwerp	Belgium	n.d.	-	8413	GCMS (SXH)	3	(Covaci *et al.*, 2005)
	different locations	Czech Republic	0.1	-	276.4	GCMS (SXH)	15	(Nápravníková *et al.*, 2008)
	McMurdo and Scott (Antarctica)	USA and New Zealand	-	-	1820	GCMS (ASE)	n.d.	(Hale *et al.*, 2008)
Sediment (ng.g^{-1} wet weight)	Monzón	Spain	2.1	-	40	GCMS (SPLE)	23	(Eljarrat *et al.*, 2004b)
	different locations	Denmark	n.d.	-	21.5	GCMS (SXH)	6	(Christensen *et al.*, 2001)
	different locations	Netherlands	4	22	510	GCMS (SXH)	22	(de Boer *et al.*, 2003)
	Indiana	USA	19	-	36	GCMS (SXH)	4	(Dodder *et al.*, 2002)

n.d.: No data

SXH: Soxhlet ASE: Accelerated solvent extraction

UE: Ultrasonic extraction

LLE: Liquid-liquid extraction

SPLE: Selective pressurized liquid extraction

Table 4: Total PBDE concentrations in environment

Matrix	Location / sample type	Countries	concentrations of Σ PBDE			Analysis Method	No. Samples	Reference
			Minimum	Mean	Maximum			
Indoor / outdoor Air (pg.m^{-3})	Toronto	Canada	31.2	42.1	59.2	GCMS (SXH)	14	(Butt *et al.*, 2004)
	Toronto		88	-	1250	GCMS (SXH)	36	(Gouin *et al.*, 2002)
	Ottawa		2	120	3600	GCMS (SXH)	31	(Wilford *et al.*, 2004)
	Alert (Arctic)		-	240	-	n.d.	n.d.	(de Wit *et al.*, 2004)
	Tagish (Arctic)		-	424	-	n.d.	n.d.	
	different locations		-	100	-	GCMS (SXH)	31	(Wilford *et al.*, 2004)
	Munich	Germany	8.24	73.1	477	GCMS (SXH)	34	(Fromme *et al.*, 2009)
	Milan	Italy	n.d.	-	106.71	GCMS (SXH)	7	(Mariani *et al.*, 2008)
	different locations	China	0.13	-	340	GCMS (SXH)	32	(Jaward *et al.*, 2005)
	different locations	Japan	5.0	-	71		20	
	different locations	Singapore	10.0	-	-29		10	
	different locations	South Korea	2.0	-	27		15	
	Near recycling plant	Taiwan	23	-	53	n.d.	n.d.	(Watanabe *et al.*, 1992)
	Near recycling plant	Japan	7	-	21			
	Ammarnâs	Sweden	-	1	-	GCMS (SE)	n.d.	(de Wit, 2000)
	Hoburgen		-	8	-			
Indoor Dust (ng.g^{-1})	Ottawa	Canada	170	5500	170000	GCMS (SXH)	68	(Wilford *et al.*, 2005)
	Washington, D.C	USA	780	5900	30 100	GCMS (ASE)	16	(Stapleton *et al.*, 2005)
	Albany		380	3190	9340	GCMS (SXH)	12	(Johnson-Restrepo *et al.*, 2009)
	Massachusetts		3020	13732.3	192100	GCMS (ASE)	108	(Allen *et al.*, 2008)
	Munich	Germany	36.5	438	1580	GCMS (SXH)	34	(Fromme *et al.*, 2009)
	Brisbane	Australia	219	527	3062	GCMS (ASE)	120	(Toms *et al.*, 2009)
	-	Kuwait	1.0	148.8	393	GCMS (SXH)	17	(Gevao *et al.*, 2006)
	Birmingham	United Kingdom	16.2	215.2	625.4	GCMS (SXH)	92	(Harrad *et al.*, 2006a)
Wastewater (ng L^{-1})	Cape Town	South Africa	5150	9910	15100	GCMS (LLE)	20	(Daso *et al.*, 2012)
	different locations	Canada	20	190	1000	GCMS (SPE)	120	(Kim *et al.*, 2013a)
	California	USA	-	29.02 ± 1.5	-	GCMS (LLE)	6	(North, 2004)
	Hong Kong	China	1	-	254	GCMS (SPE)	20	(Deng *et al.*, 2015)
	Guangzhou		13.3	-	2496.4	GCMS (UE)	9	(Peng *et al.*, 2009)
Sewage sludge/ Biosolids (ng.g^{-1} dry weight)	different locations	Canada	**primary sludge** (PS)			GCMS (SPE)	15	(Kim *et al.*, 2013b)
			230	990	82000			
			waste biological sludge (WBS)			GCMS (SPE)	10	
			530	1600	8800			
			treated biosolids			GCMS (SPE)	15	
			420	1900	6000			
	North Carolina	USA	37500	-	97400	GCMS (ASE)	n.d	(La Guardia *et al.*, 2007)
	California		-	3381	-	GCMS (LLE)	6	(North, 2004)
	Umm Haylaman	Kuwait	23.4	376.7	1599.8	GCMS (SXH)	18	(Gevao *et al.*, 2008)
	26 cities	China	5.1	94.0	1114.9	GCMS (SXH)	31	(Wang *et al.*, 2007b)
	Guangzhou		158	-	23750	GCMS (UE)	9	(Peng *et al.*, 2009)
	Shanghai		30.9	2430	35300	GCMS (SXH)	28	(Yang *et al.*, 2011)
	different locations	Spain	197	-	1185	GCMS (SXH)	n.d.	(Eljarrat *et al.*, 2008)
	different locations		57.5	488	2606	GCMS (ASE)	124	(De la Torre *et al.*, 2011)
	different locations	Sweden [c]	n.d.		450	GCMS (LLE)	116	(Öberg *et al.*, 2002)
	different urban locations	Australia	230	1308	4230	GCMS (ASE)	16	(Clarke *et al.*,

								2008)
	Mc Murdo and Scott (Antarctica)	USA and New Zealand	637	-	4690	GCMS (ASE)	4	(Hale *et al.*, 2008)
Groundwater (ng L^{-1})	Ontario	Canada	n.d.	12.6	94	GCMS (SPE)	26	(Levison *et al.*, 2012)
Surface water (ng L^{-1})	different locations	China	0.34	-	68	GCMS (UE)	96	(Guan *et al.*, 2007)
	San Francisco	USA	0.003	-	0.513	GCMS (ASE)	33	(Oros *et al.*, 2005)
	Lake Michigan	USA	Year 1997			n.d.	n.d.	(Stapleton *et al.*, 2001)
			-	0.031	-			
			Year 1999					
			-	0.158	-			
Aquatic biota (ng.g^{-1})	Bottlenose dolphins (Atlantic coasts)	USA	-	200	-	GCMS (SXH)	21	(Kuehl *et al.*, 1991)
	Fish and shellfish (Osaka bay)	Japan	-	14.6	-	GCMS (SE)	17	(Watanabe *et al.*, 1987)
	Different Biota (Fraser river)	Canada	4	-	2300	GCMS (SE)	32	(Ikonomou *et al.*, 2002)
	Fish (Viscan river)	Sweden	150	-	22000	GCECD (SE)	5	(Andersson *et al.*, 1981)
	Mountain whitefish (Washington)	USA	-	1250	-	GCAED (SXH)	18	(Johnson *et al.*, 2001)
	Rainbow trout (Washington)	USA	-	1.4	-			
Soil and Sediments (ng.g^{-1} wet weight)	British Columbia	Canada [c]	3.8	-	90.9	GCMS (SXH)	6	(Rayne *et al.*, 2003a)
	San Francisco	USA	n.d.	-	212	GCMS (ASE)	33	(Oros *et al.*, 2005)
	North Carolina	USA	-	132	-	GCMS (ASE)	11	(Hale *et al.*, 2002)
	Virginia	USA	-	52.3	-	GCELCD (ASE)	133	(Hale *et al.*, 2001b)
	different locations	South Korea	0.45	27.8	494	GCMS (SXH)	25	(Moon *et al.*, 2007)
	Guiyu	China	4434	9357	16088	GCMS (SXH)	5	(Luo *et al.*, 2007)
	Hangzhou *		n.d.	0.15	0.55	GCMS (SXH)	32	(Chen *et al.*, 2006)
	Dongjiang *		2.2	27.3	94.7	GCMS (SXH)	33	(Mai *et al.*, 2005)
	Antwerp *	Belgium	1.4	-	272	GCMS (SXH)	3	(Covaci *et al.*, 2005)
	River Schelde	Belgium	-	200	-	n.d.	n.d.	(Sellström *et al.*, 1998)
	River Mersey	UK	-	1700	-			
	different locations	Denmark	0.06	-	24.7	GCMS (SXH)	6	(Christensen *et al.*, 2001)
	Monzón	Spain	2.4	-	42	GCMS (SPLE)	23	(Eljarrat *et al.*, 2004b)
	Lombardy	Italy	2	-	19	GCMS (SXH)	70	(Guzzella *et al.*, 2008)
	different locations	Sweden	0.008	-	0.08	GCMS (SXH)	16	(Matscheko *et al.*, 2002)

n.d.: No data

*: ∑PBDE without BDE-209

AED: Atomic Emission Detection

SE: Solvent extraction

ELCD: Electrolytic conductivity detector

Table 5 Half-lives of PBDEs in the environment

Environmental compartments	Half life (h)		Reference
	Penta -- BDE (BDE-99)	Deca -- BDE (BDE-209)	
Air	467	7620	(Palm *et al.*, 2002)
Water	3600	3600	(Palm, 2001)
Sediments	14400	14400	(Palm, 2001)
Soil	3600	3600	(Palm, 2001)

Table 6: Typical methods for analysis of samples containing PBDEs

Stage	Options	Description	Reference
extraction	Soxhlet	Time consuming, requiring much	(Wang *et al.*, 2010)
	Centrifugation	Time consuming	(Covaci *et al.*, 2007)
	SPE	Time consuming, interference	(Covaci *et al.*, 2007)
	SPME	Limited to penta congeners, high	(Zhang *et al.*, 2011a)
	PLE	Sometimes low recovery, high	(Wang *et al.*, 2010)
	LLE	Limited selectivity, formation of	(Covaci *et al.*, 2007)
	MAE	Co-extraction of potential	(Beser *et al.*, 2014)
Cleanup	Florisil, alumina,	Time consuming	(Eljarrat *et al.*, 2004a)
	H_2SO_4 treatment	Destruction of several compounds	(Dufour *et al.*, 2016)
	GPC	High cost	(Gilson Inc, 2008)
Analysis	GC-MS(EI)	affected by PCBs interferences	(Thomsen *et al.*, 2002)
	GC-MS(ECNI)	affected by PBBs interferences	(Das, 2014)
	GC-ECD	limited selectivity	(Stapleton, 2006)

SPE: solid phase extraction

SPME: solid phase micro-extraction

PLE: pressurized liquid extraction

LLE: liquid-liquid extraction

MAE: microwave assisted extraction

GPC: gel permeation chromatography

MS: mass spectroscopy

EI: electron ionization

ECNI: electron capture negative ionization

ECD: electron capture detection

Table 7: Application of different treatment methods for PBDE contaminated matrices

PBDEs	Matrices	Process	Optimum operating conditions	Results and comments	Reference
Deca-BDE	Water	sewage sludge	T = 25°C, pH = 4.5, [BDE-209] = 2 mg.L^{-1}, [*T. versicolor*] = 3.5 g dw.L^{-1}, surfactant Tween 80 (500 mg.L^{-1})	degradation and removal of mixture after 7 days is respectively 73 ± 5%and 87 ± 6%, because Tween 80 increase the bioavailability	(Vilaplana *et al.*, 2015)
		Photolytic UV	[BDE-209] = 2.34 mg.L^{-1}, UV-B lamp (15 W, λ = 300-330 nm)	completely decomposed after 60 min, photodebromination occurred mostly at *para* position>*meta* position>*ortho* posi tion	(Shih *et al.*, 2009)
			[BDE-209] = 130 mg.L^{-1}, lamp Xenon(150W, λ = 200-400nm)	when λ = 228 nm, degradation was 80% after 4 min	(Agguine *et al.*, 2014)
		Photocatalytic	[TiO_2] = 1g L^{-1}(80% anatase, 20% rutile; surface area = 50 m^2 g^{-1}), [BDE-209] = 2 mg L^{-1}, [C_3H_8O] = 0.33 M, lamp Xenon (50 W, λ = 360 nm)	more than 90% of BDE209 disappeared after 7.5 min in anoxic conditions	(Sun *et al.*, 2009)
			pH = 5, [TiO_2] = 2 g L^{-1}(75% anatase, 25% rutile; surface area = 50 $m^2.g^{-1}$), [BDE-209] = 2 mg.L^{-1}, 6 lamps mercury (3080 µW $cm^{-2}.nm^{-1}$, λ_{max} = 365 nm), ratio C_4H_8O/ H_2O was 1:1,	Removal more than 98% after 4h and débromination ratio was greater than 80% in the pure water; while that ratio C_4H_8O/ H_2O was only 47.7% after after 11h	(Zhang *et al.*, 2014)
		Microscale of iron	T = 27°C, pH = 7, [MZVI] = 5 g L^{-1}(0.95 $m^2.g^{-1}$), [BDE-209] = 1.83 mg L^{-1}, ethyl acetate/methanol mixture (1:1, v/v)	70% was degraded after 34 day	(Peng *et al.*, 2013)
		Nanoscale of iron	T = 28±2°C, pH = 6.1, [S-ZNVI] = 6 g.L^{-1}(Fe^0, 35 $m^2.g^{-1}$, average sizes: 50-80 nm), [BDE-209] = 2 mg L^{-1}, THF/water = 6/4, v/v	removal efficiency were 100% after 24 h	(Fang *et al.*, 2011)
	sediments	Ozonation	T = 25°, Ph = 7.58, [BDE-209] = 1µg g^{-1}, [O_3] = 0.3 mg.L^{-1}, UV lamp vapor mercury (16W, λ = 300-400nm, 1.0 Mw.cm^{-2})	degradation was 99% on surface soil by ozone after 2h and 82% after 8h by UV-lamp irradiation	(Niu *et al.*, 2015)
		UV/H_2O_2	T = 28°C, [BDE-209] = 20 ng g^{-1}, [H_2O_2] = 4.41 Mm, low pressure mercury lamp (16W, 50W.cm^{-2}, λ_{max} =	only UV-photolysis giving 50% of removal and UV/H_2O_2 BDE-209	(Feo *et al.*, 2014)

PBDEs	Matrices	Process	Optimum operating conditions	Results and comments	Reference
			254 nm),	removal reached 90% after 10h	
	dust	photochemical	UVA-340 fluorescent lamp (λ = 290-385 nm, 17.5±1.5 W.m^{-2}), [BDE-209] = 8.12 µg.L^{-1}	half-life of 18.7±1.8 days	(Lagalante *et al.*, 2011)

THF: tetrahydrofuran

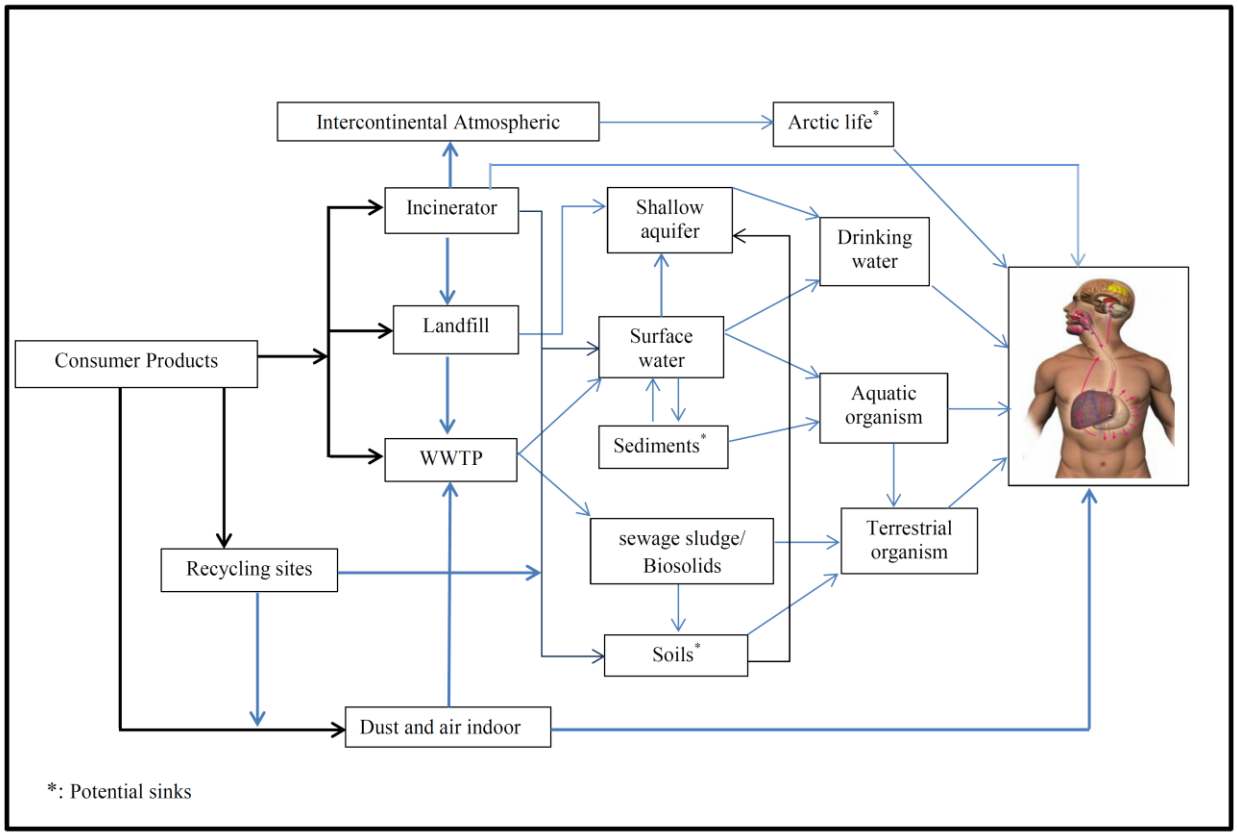


Fig 1: Schematic for transport of PBDEs in the environment