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Flame Retardancy in Consumer Products: An Overview of PBDE and Possible Alternatives

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ABSTRACT

Accelerated industrialization and urbanization, and unregulated disposal of waste of electric and electronic equipment (e-waste) and other consumer products in Nigeria have caused environmental pollution of brominated flame retardants (BFRs). Flame retardants (FRs) are a diverse group of chemicals used as additives in a wide range of products to inhibit, suppress, or delay ignition and to prevent the spread of fire. Halogenated FRs (HFRs) are widely used because of their low impact on other material properties and the low loading levels necessary to meet the required flame retardancy. In addition, Polybrominated diphenyl ethers (PBDEs) are a group of organobromine compounds that are used as flame retardants in many commonly used products. Their presence has been confirmed in various environmental matrices. Their usage in numerous consumer products has lent credence to their ability to retard flammable gas formation, hence their ubiquitous nature in the environment. PBDEs have been described as endocrine disrupting chemicals because of their interference with the endocrine system function in fish and other terrestrial animals. In spite of the progress in research over the years on PBDEs, full understanding of the environmental behaviour, fate of this contaminant and possible alternatives is still elusive. In this review, sources by which PBDEs enter the environment have been evaluated in conjunction with their levels, as well as their toxicity, and the transformation and transport of PBDEs in various environmental compartments. Health and environmental hazards associated with PBDEs have driven research for identifying safer alternatives. A variety of halogen-free FRs are available in the market, including organic (phosphorus and nitrogen based chemicals) and inorganic (metals) materials. Therefore possible alternatives to PBDEs such as organophosphorus compounds, nitrogen and silicon based, as well as nanocomposites (Multi-walled carbon nanotube) have all been critically discussed, with nanocomposite (CNTs) recommended as a more suitable alternative to PBDEs owing to their flame retardancy mechanism; ability to reduces the escape of volatile, combustible degradation products to the flame; as well as improve mechanical strength and electrical properties of the material.

Keywords: PBDEs, Flame retardants, congeners, MWCNT, BFR

1.0. Introduction

1.1. Flame Retardants

Flame retardants (FRs) are a large group of chemicals used in different materials to delay or prevent flaming (Zuiderveen *et al.*, 2020). Many are based on bromine, chlorine or phosphorus, or a mix of these, but others such as metal-based FRs and melamine also occur. They prevent flaming by quenching and cooling (metal-based FRs), by formation of solid phase char (melamine-based and phosphorus-based FRs), form a stable foam layer that acts as a barrier between the flames and the combustible material (intumescent FRs) (Horold, 2014), or inhibition by radical formation in the vapor phase, for which brominated FR (BFRs) are commonly used (Laoutid *et al.,* 2009). The production and application of BFRs have dramatically increased in the past thirty years (Liagkouridis *et al.*, 2015). Most BFRs have toxic properties and a negative impact (persistence, bioaccumulation) on the environment (Zuiderveen *et al.*, 2020). Polybrominated biphenyls (PBBs) were already restricted in 1984 (Directive 83/264/EEC) and their production ceased in 2000 (Kemmlein *et al.*, 2009). FRs are divided into reactive (chemically bound into the materials) and additive (integrated into the materials by physical mixing only) (Beard, 2013). They are usually classified based on their “active” chemical element – the main groups being products based on halogens (mostly bromine, but also chlorine), phosphorus, nitrogen, minerals such as aluminium and magnesium and to a lesser extend boron, zinc and carbon (Zuiderveen *et al.,* 2020). Recently, also nanomaterials (NMs) such as nanoclay and multi-walled carbon nanotubes (MWCNTs) have been used as FRs or synergists (Beyer, 2003; Kashiwagi *et al.,* 2005a; Aschberger *et al.,* 2017).

1.2. Mechanisms in flame retardancy of polymers

Some basic mechanisms of flame retardancy were recognised as early as 1947 when several primary principles were put forward (Lewin and Weil, 2001). These included the effect of the additive on the mode of the thermal degradation of the polymer in order to produce fuel-poor pyrolytic paths, external flame retardant coatings to exclude oxygen from the surface of the polymer, internal barrier formation to prevent evolution of combustible gases, inert gas evolution to dilute fuel formed in pyrolysis and dissipation of heat away from the flame front. Discovery of the flame-inhibiting effect of volatile halogen derivatives subsequently led to the postulation of the radical trap-gas-phase mechanism (Rosser *et al.,* 1959; Lewin and Weil, 2001). The gas-phase and the condensed-phase proposals have long been generally considered as the primary, though not the only, effective mechanism of flame retardancy.This situation is now being modified as new mechanisms of new flame-retarding systems, especially those based on physical principles, evolve and as new insights into the performance of flame retardants is being gained.

1.2.1. General considerations

Pyrolysis and combustion of polymers occur in several stages. The polymeric substrate heated by an external heat source is pyrolysed with the generation of combustible fuel. Usually, only a part of this fuel is fully combusted in the flame by combining with the stoichiometric amount of atmospheric oxygen (Lewin and Weil, 2001). The other part remains and can be combusted by drastic means, e.g. in the presence of a catalyst and by an excess of oxygen. A part of the released heat is fed back to the substrate and causes its continued pyrolysis, perpetuating the combustion cycle. Another part is lost to the environment. The energy needed to heat the polymer to the pyrolysis temperature and to decompose and gasify or volatilise the combustibles and the amount and character of the gaseous products determines the flammability of the substrate. A flame retardant acting via a condensed phase chemical mechanism alters the pyrolytic path of the substrate and reduces substantially the amount of gaseous combustibles, usually by favouring the formation of carbonaceous char and water. In this case the heat released in the combustion decreases with an increase in the amount of the flame-retarding agent (Lewin and Weil, 2001).

In the gas-phase mechanism the amount of combustible matter remains constant but the heat released in the combustion usually decreases with an increase in the amount of the flame-retarding agent. The amount of heat returned to the polymer surface is therefore also diminished and the pyrolysis is retarded or halted as the temperature of the surface decreases. The flame-retarding moiety has to be volatile and reach the flame in the gaseous form. Alternatively it has to decompose and furnish the active fraction of its molecule to the gaseous phase. The char remaining in the substrate will contain less of the active agent. The pyrolysis of the polymer should, in the limiting case, proceed as if there would have been no flame-retarding agent incorporated in it. In addition presence of the gas-phase active agent should not influence the composition of the volatiles reaching the flame (Lewin and Weil, 2001).

1.2.2. Gas-phase mechanisms

The gas-phase activity of the active flame retardant consists in its interference in the combustion train of the polymer. Polymers, like other fuels, produce upon pyrolysis species capable of reaction with atmospheric oxygen and produce the H_2–O_2 scheme which propagates the fuel combustion by the branching reaction (Lewin and Weil, 2001):

$H^{\bullet}+O_2=OH^{\bullet}+O^{\bullet}$ [1.1]

$O^{\bullet}+H_2=OH^{\bullet}+H^{\bullet}$ [1.2]

The main exothermic reaction which provides most of the energy maintaining the flame, is:

$OH^{\bullet}+CO=CO_2+H^{\bullet}$ [1.3]

To slow down or stop the combustion, it is imperative to hinder the chain-branching reactions [1.1] and [1.2]. The inhibiting effects of halogen derivatives, usually chlorine and bromine, is considered to operate via the gas-phase mechanism.

This effect in the first instance occurs either by releasing a halogen atom, if the flame-retardant molecule does not contain hydrogen, or by releasing a hydrogen halide:

$MX=M^{\bullet}+X^{\bullet}$ [1.4]

$MX=HX+M^{\bullet}$ [1.5]

where $M^{\bullet}$ is the residue of the flame-retardant molecule. The halogen atom reacts with the fuel, producing hydrogen halide:

$RH+X^{\bullet}=HX+R^{\bullet}$ [1.6]

The hydrogen halide is believed to be the actual flame inhibitor by affecting the chain branching:

$H^{\bullet}+HX=H_2+X^{\bullet}$ [1.7]

$OH^{\bullet}+HX=H_2O+X^{\bullet}$ [1.8]

Reaction [1.7] was found to be about twice as fast as [1.8] and the high value of the ratio H_2/OH in the flame front indicates that [1.7] is the main inhibiting reaction (Lewin and Weil, 2001) It is believed that the competition between reactions [1.7] and [1.1] determines the inhibiting effect. Reaction [1.1] produces two free radicals for each H atom consumed, whereas reaction [1.7] produces one halogen radical which recombines to become the relatively stable halogen molecule.

1.2.3. Comparing flame-retardant activity of halogen derivatives

Equation [1.7] represents an equilibrium with a forward reaction and a reverse reaction. The equilibrium constants of equation [1.7] for HBr and HCl are:

$$K_{HCl} = 0.583\exp(1097/RT);\ K_{HBr} = 0.374\exp(16760/RT)$$

The equilibrium constants decrease strongly with increase in temperature, which explains the decreasing effectivity of halogen derivatives in large hot fires (Lewin and Weil, 2001). Lewin (2001) calculated that in the temperature range 500–1500K the forward reaction predominates and KHBr is much higher than KHCl. Both are highly effective at the ignition temperature range of polymers. The flame retardant effectivity of the halogens was stated to be directly proportional to their atomic weights, i.e. F:Cl:Br: I = 1.0 : 1.9 : 4.2 : 6.7 (Larsen, 1980). On a volumetric basis 13% of bromine was found to be as effective as 22% of chlorine when comparing the tetrahalophthalic anhydrides as flame retardants for poly-esters (Lewin, 1984). A similar effect was found for Polypropylene (PP), Polystyrene (PS) and Polyacrylonitrile (PAN3) and when comparing NH4Cl to NH_4Br in cellulose (Lewin and Weil, 2001). The activity of the halogens is also strongly affected by the strength of the respective carbon-halogen bonds. The low bond strength of I–C and consequently the low stability of the iodine compounds virtually exclude their use. The high stability of the fluorine derivatives and the high reactivity of the fluorine atoms in reactions [1.7] and [1.8] will prevent the radical quenching processes in the flame. The lower bond strength and stability of the aliphatic compounds, their greater ease of dissociation as well as the lower temperature and earlier formation of the HBr molecules are responsible for their higher effectivity as compared to the aromatic halogen compounds. The higher stability of the latter along with their higher volatility allow these compounds to evaporate before they can decompose and furnish the halogen to the flame (Lewin and Weil, 2001).

1.2.4. Physical modes of action of halogenated flame retardants

The radical trap activity is not the only activity of the halogenated flame retardants (Lewin and Weil, 2001). The physical factors such as the density and mass of the halogen and its heat capacity, have a profound influence on the flame-retarding activity of the agent. In addition, its dilution of the flame which thus decreases the mass concentration of combustible gases present are effective. Lewin (2001) demonstrated the important role of the heat capacity of the flame retardant. In flame retardant polymer systems the halogens appear to work by reducing the heat evolved in the combustion of the gases given off by the decomposing polymer (low or zero fuel value plus action as a heat sink) such that to sustain burning the mass rate of gasification must be increased by the application of an increased external heat flux.

Other authors (Lewin and Weil, 2001), showed by thermochemical computation that most of the action of a wide variety of halocarbon flame inhibitors could be correlated to a combination of heat capacity and endothermic bond dissociation. A physical effect, often mentioned but rarely demonstrated or evaluated, is the ‘blanketing’ effect of excluding oxygen from the surface of the pyrolysing polymer. Ignition generally takes place in the vapour phase adjacent to the condensed phase, when an ignitable fuel–air mixture is reached. There is, however, evidence that the rate of pyrolysis may be affected by the oxygen getting to or into the condensed phase, and that in polyolefins surface oxidation may provide energy for pyrolysis. The rate of isothermal pyrolysis of cellulose was found to be higher in the presence of air as compared to vacuum pyrolysis by an order of magnitude. The rate of pyrolysis in the presence of air was also found to decrease linearily with increase in orientation of rayon fibres. Increase in chain orientation brings about a decrease in distance between chains and their more compact packing with consequent decreased penetrability and rate of diffusion of oxygen into the polymer resulting in a decreased rate of pyrolysis (Lewin and Weil, 2001). Although some doubt has been cast on the significance of the blanketing effect (Kashiwagi, 1984), it is self-evident that an outgoing stream of bulky halogen and other non-fuel molecules emitted from the pyrolysing polymer could retard the penetration of the oxygen into the polymer and slow down the pyrolysis.

2.0. Overview

2.1. PBDE Based Flame Retardants

Brominated flame retardants (BFRs) are used to reduce flammability mostly of polymer materials such as plastic in electric and electronic equipment (EEE) and wastes (WEEE), in polyurethane foams in furniture/vehicles or other synthetic fibres such as textiles (Alaee *et al.,* 2003; Sakai *et al*., 2001; Alcock *et al.,* 2003; Babayemi *et al.,* 2014). A range of BFRs is highly persistent and have been shown to be emitted to the environment from production plants, indoor environment from consumer products and from the end-of-life material flows (Allen *et al*., 2008; Imm *et al.*, 2009; Shaw *et al.*, 2010; Watanabe and Sakai 2003; Wong *et al.*, 2007). BFRs are global environmental contaminants and due to their bioaccumulation potential they are detected in biota and humans (Hale *et al.,* 2006; Shaw *et al.,* 2010). Moreover, a wide range of toxic effects have been demonstrated (De Wit *et al.,* 2010; Hale *et al.,* 2006; Shaw *et al.,* 2010). This includes the activation of several endocrine effects (Hamers *et al.,* 2006; Legler 2008) which are of particular concern for global health (WHO 2013).

In 2009, the first brominated flame retardants—commercial pentabromodiphenyl ether (c-PentaBDE) and certain congeners of commercial octabromodiphenyl ether (c-OctaBDE) and hexabromobiphenyl (HBB)—were included in the Stockholm Convention and are, therefore, officially recognised as persistent organic pollutants (POPs; Stockholm Convention 2009a, b). The production and use of c-PentaBDE and c- OctaBDE stopped approximately in 2004 (Stockholm Convention 2012a). Despite the ending of the production and use, large quantities of articles containing POP-PBDEs are still in use as well as in the recycling and end-of-life flows. This includes, for example, plastic in electronics and upholstery in transport and furniture or textiles (Stockholm Convention 2012a). These material flows must be managed in an environmentally sound manner to avoid environmental pollution and for the protection of human health which is the primary aim of the Stockholm Convention (2012b; UNEP 2010a, b). The assessment of the fate of these pollutant containing materials at various life cycle stages has revealed large challenges and widespread pollution (Shaw et al., 2010; Stockholm Convention 2012a, b; UNEP 2010a, b).To date, only one case has been assessed by substance flow analysis in a developing/transition country (Tien *et al.*, 2013; Babayemi *et al*., 2014).

A large volume of these materials is still in use and in the global recycling flow (e.g. plastic from waste electronics or polyurethane foam from transport and furniture) and are a major concern in this respect (UNEP 2010a, b; Secretariat of the Stockholm Convention 2012b). The Stockholm Convention has included an exemption for recycling of PBDE containing materials (Stockholm Convention 2012a, b). However, to minimize the risk to human and the environment, it is essential to closely monitor and control recycling of materials which may contain these substances (Babayemi *et al.*, 2014). The POPs Review Committee of the Stockholm Convention has, therefore, developed recommendations for risk reduction of POP-PBDEs from recycling (Stockholm Convention 2011). The intention is that the remaining stockpiles should be safeguarded, separated during recycling and subjected to environmentally sound management. This needs an understanding of the material and substance flows of POP-PBDEs in their major uses. For c-OctaBDE, the major use was in polymers in EEE—mainly for casings made from acrylonitrilebutadiene-styrene (ABS). These were used largely in casings of TVand PC cathode ray tubes (CRTs) and make up the largest share of POP-PBDE containing ABS (Choi *et al.*, 2009; Stockholm Convention 2012a).

A large share of PBDE containing articles have already been shipped or are still being shipped to developing and transition countries either as second-hand goods (e.g. as EEE or vehicles), as plastic/polymers for recycling or illegally as waste e.g. WEEE (Wong *et al*., 2007; Breivik *et al.*, 2011; Basel Convention 2011; Nnorom and Osibanjo 2008; UNEP 2010a, b). The end-of-life management and treatment of POPs pesticide stockpiles and PCBs has demonstrated the large challenges developing countries faced with POPs and little progresses has so far been made in the 10 years of Stockholm Convention implementation in this respect (Weber *et al.*, 2013; Vijgen *et al.*, 2013; World Bank 2013). Lack of resources, inadequate or non-existent treatment capacity and the difficulties in developing inventories have been the main causes of the failure to make progress (Babayemi *et al.,* 2014).

Human exposure to PBDEs can take place in all life cycle stages including the end of life stage (UNEP 2010a, b). There is also potential for additional releases (Hale *et al.,* 2006; Sepulveda *et al.*, 2010; Wong *et al.*, 2007) if inappropriate technologies are used for treatment (Nnorom and Osibanjo 2008) or wastes are burned in the open or using sub-standard technology (Stockholm Convention 2012b). Furthermore, the disposal of PBDE-containing materials over the last three decades has already created reservoirs in landfills/dumps which are partly released to the environment over time (Danon-Schaffer *et al.*, 2013; Odusanya *et al.*, 2009; Oliaei *et al*., 2002; Osako *et al.*, 2004; Weber *et al.*, 2011).

Nigeria has been a major importer of WEEE/EEE and a recent inventory has quantified the huge volumes imported since 2000 (Ogungbuyi *et al.*, 2012). However, information on the levels of pollutants, including PBDE/BFR, and the flow of

WEEE in the end of life and recycling phase along with the related risks to human health and the environment in Nigeria and other developing countries is scarce. Recent studies have shown that the flows of plastics from WEEE containing PBDEs/BFRs are largely uncontrolled and that this result in the presence of PBDEs/BFRs in recycled products—including sensitive uses such as children toys, household goods and even coffee cups (Chen *et al*., 2009, 2010; Samsonek and Puype 2013, Stockholm Convention 2012b). This demonstrates that the movement and the recycling flows of PBDE containing WEEE plastic need to be better understood and controlled (Babayemi *et al.,* 2014).

2.2. Production and applications of PBDEs

Generally, three known classes of PBDEs have been produced over the years in developed regions. However, there is little knowledge of their production in developing countries (BSEF2007). The total historical production of all PBDEs (including deca-BDE) based on the data compiled for POPs Reviewing Committee of the Stockholm Convention from 1970 to 2005 has been estimated to be between 1.3 million to 1.5 million tonnes (UNEP 2010a). Commercial penta-BDE, one of the most widely produced of the three congeners, is produced in Israel, Japan, USA, EU, and China (UNEP 2010a). Its production ceased in the EU in 1997. It is assumed that, since the start of the millennium, the production of penta-BDE has declined in proportion, and ceased entirely in 2004 (UNEP 2010b). Commercial octa-BDE has been produced in the Netherlands, France, USA, UK, Israel and Japan. Production ceased in the EU, USA and the Pacific Rim in 2004. Production of commercial deca-BDE, which initially was not listed as a POP, is estimated at above 1.1 million tonnes until 2005. It should be noted, however, that while the production of POPs c-penta-BDE and c-octa-BDE ended in 2004, the production of deca-BDE continued (Li *et al.,* 2015). The total amount of c-penta-BDE and c-octa-BDE global usage is estimated at around 100,000 tonnes and has remained at approximately the same level for about a decade. PBDEs have found applications in a wide variety of products over the years. The actual concentration applied to a product was based on several considerations such as the efficacy of the FR selected, the degree of the flame retardancy needed, whether it is applied in union with a synergist (e.g. antimony trioxide), the physical nature of the end products (e.g. colour, density and stability) and the specific application (European Chemicals Bureau 2000; Stubbings and Harrad 2014; Akortia *et al.,* 2016).

The major industrial sectors that have incorporated PBDEs in their products include the Electrical and Electronic Equipment (EEE) sector, manufacturers of textiles, carpets, furniture, and organobromine, as well as the transportation, construction and recycling industries (*SSC et al.,* 2012a). It is estimated that between 90 to 95% of c-penta-BDE was used in the treatment of PUF (Vyzinkarova and Brunner 2013), mainly for furniture upholstery (Sjodin *et al*., 2003) and automotive applications (European Chemicals Bureau 2000). The remaining minor uses (totaling 5%) include, printed circuit boards, insulation foam, lacquers, cable sheets, conveyor belts, and possibly oil drilling (UNEP 2007). The distribution of global c-penta-BDE use was approximately 36% in the transportation industry, 60% in the furniture industry, with the remaining 4% deployed in other articles (UNEP 2010b; Akortia *et al.,* 2016).

Historically, the prime use of c-octa-BDE was in acrylonitrile butadiene styrene (ABS) polymers (ca. 70% globally), accounting for about 95% of c-octa-BDE supplied in the EU (EC 2011). PBDE-enhanced ABS was predominantly used in casings of EEE, particularly for cathode ray tubes (CRTs) casings (TVs and Computer monitors), and office equipment such as photocopying machines and business printers. The remaining (ca. 5%) minor uses were deployed in high impact polystyrene (HIPS), polybutylene terephthalate (PBT), and polyamide polymers, with typical concentrations between 12 and 15%. Although the majority of these polymers were used in electronics, some have found application in the transportation sector as well. Other minor uses were in nylon, low density polyethylene, polycarbonate, phenolformaldehyde resins, and unsaturated polyesters (UPE), adhesives and coatings (UNEP 2010a, b). Owing to the relatively low cost and wide usage, deca-BDE (ca. 99%) was employed in the plastic modification industries for producing flame-retardant plastics. Out of these, about 70% have found use in EEE, refrigerator components (Park *et al*., 2013), and equipment casings. Ten percent is applied to fire resistant cables, including wire/cable insulation and switchgears. Additionally, about 10% is employed in the transportation sector, including automotive upholstery and plastic, while the remaining 10% is utilized in flame-retardant plastic used in mining and construction, such as conveyor belts, guard fences and ventilation ducts (Li *et al.,* 2015). The above underscores the extensive global use of PBDEs in a wide range of applications, and shows that while deployment in electronics is considerable, application in other sectors (soft furnishings, transportation and construction) are also extensive. Consequently, a considerable fraction of the PBDE inventory has either entered or is moving towards the disused phase, indicating that there is increasing attention directed towards the environmental implications of PBDE-containing articles (particularly, EEE) associated with waste streams (Akortia *et al.*, 2016).

2.3. Physical and Chemical Properties of PBDEs

There are 209 possible congeners, numbered using the same system as the long banned polychlorinated biphenyls (PCBs), and higher congeners are known to transform to lower congeners via biotic and abiotic processes (Ahn *et al.*, 2005; Gaul *et al.*, 2006; Clarke and Smith 2010). PBDE congeners can be divided into ten groups, classified by the number of bromine atoms substituted on the benzene rings, and may be anywhere from one to ten (Lober 2008; Chen *et al.*, 2012). The general chemical formula of a PBDE is $C_{12}H_{(x)}$ $Br_{(y)}$ O, with the sum of H and Br atoms always equal to 10. The general structure of PBDEs is shown in Figure 1.1.

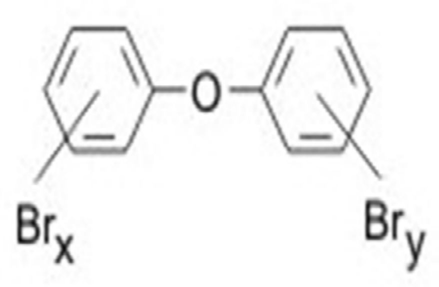

Figure 1.1, Structure of PBDE

The major technical products contain mainly penta-BDEs, octa-BDEs or deca-BDEs as well as other PBDEs and their composition is shown in Table Figure 1.1 The general formula for PBDEs.

1.1. Commercial PBDEs mostly found in environmental samples are quite resistant to physical, chemical and biological degradation . The boiling point of PBDEs is between 310 ° C and 450 ° C and has low vapour pressure at room temperature. PBDEs are hydrophobic (log K_{ow} range: 4.3- 9.9) and have very low water solubility properties, especially for the higher brominated compounds (deca-BDE), hence enables significant bioaccumulation in biota and humans. A summary of their physical and chemical properties is given in Table 1.2. Owing to the high octanol/water partition coefficient values, PBDEs entering the environment tend to bind to organic fraction of particulate matter, soils and sediments (Akortia *et al.,* 2016). For example, if PBDEs are released into water, the individual constituents would be expected to adsorb to sediment and suspended particulate matter, while a substantial proportion is likely to be bound to particles in water. PBDEs are able to partition between the gaseous and particulate phase in the atmosphere (Bennet *et al.* 2001). Lower brominated PBDEs (tetra- to hepta-BDEs) are slightly more soluble in water and have a greater tendency to volatilize and be easily transported in the atmosphere than more highly brominated PBDEs (Harner and Shoeib 2002). Hale *et al.*, (2003) reported that penta- BDE congeners tend to dominate in the atmosphere and aqueous media, while deca-BDE is more pronounced in soils, sediments and sludge (de Wit *et al.*, 2006; Law *et al.*, 2006; Wang *et al.*, 2007). Investigations by Chen *et al.*, (2006) have reported that BDE-28 was mostly present in the gas phase (approximately 96-98%), while BDE-209 was detected only in the solid particulate.

Table 1.1. General compositions of PBDE-based flame retardant commercial products in percent-BDE congeners.

Technical Product	Congener%						
	Tetra-BDEs	Penta-BDEs	Hexa-BDEs	Hepta-BDEs	Octa-BDEs	Nona-BDEs	Deca-BDE
Penta-BDE	24-38	50-60	4-8				
Octa-BDE			10-12	44	31-35	10-11	< 1
Deca-BDE						< 3	97-98

Source: de Wit 2002; Bocio *et al.,* 2003; Akortia *et al.,* 2016.

Table 1.2. Physical and chemical properties for some PBDE congener groups

Property/Congeners	Tetra-BDE	Penta-BDE	Octa-BDE	Deca-BDE
Chemical Formula	$C_{12}H_6OBr_4$	$C_{12}H_5OBr_5$	$C_{12}H_2OBr_8$	$C_{12}OBr_{10}$
Molecular mass	485.8	564.8	801.5	959.2
Vapour pressure (Pa)	$2.7\text{-}3.3E^{-4}$ (20 °C)	$2.9\text{-}7.3E^{-5}$ (20 °C)	$1.2\text{-}2.7E^{-7}$ (20 °C)	$< 1E^{-4}$ (25 °C)-670 (306 °C)
Melting point (°C)	79-82 (BDE-47)	92 (BDE-99) 97-98 (BDE-100)	~ 200	290-306
Boiling Point (°C)	-	>300 °C (decomposition)	-	Decomposition
Water solubility (µg L^{-1})	10.9 (25 °C)	0.0009 (20 °C)	-	-
Log Kow	5.9-6.2	6.5-7.0	8.4-8.9	10
Log Koa	10.53-11.31 (tetra- and penta-BDE)[a]	-	12.78-13.61 (hepta- and octa-BDE)[b]	14.44-15.27 (est. for nona- and deca-BDE)[b]

Source: Akortia *et al.*, 2016

2.4. Sources of PBDEs in the environment

The various means through which PBDEs are released into the environment can be classified into both point (localised) sources and non-point sources.

2.4.1. Point sources

Effluents from factories producing flame-retardant polymers, wastewater treatment plants as well as leachates from landfill sites are some important point sources of PBDE contaminants (Clarke *et al.*, 2008). Alcock *et al.*, (2003) identified some possible points through which PBDEs could be released into the environment. The combustion of waste containing PBDEs is one of the chief sources which release these chemicals as air pollutants into the atmosphere. Recycling of products containing PBDEs, emissions from the use of products containing PBDEs and blending of PBDEs within polymers and formation during textile manufacturing and finishing with PBDEs are also considerable point sources (Alcock *et al.*, 2003; Osako *et al.*, 2004). Other possible point sources of PBDEs into the environment are hospital waste and municipal or hazardous waste incinerators, facilities recycling plastics and metals from electronic devices and accidental fires (Watanabe *et al.*, 2003; Akortia *et al.*, 2016).

2.4.2 Non-point sources

One of the prominent non-point sources is the use of consumer products such as furniture, plastic and electronics in which PBDEs are incorporated. Atmospheric transport and deposition has also been identified as one of the pathways leading to the presence of PBDEs in rural and remote locations (Schure *et al.*, 2004a; Agrell *et al.*, 2004). The extent of quantifying impacts attributable to non-point sources is difficult to control due to their emission and redistribution in the environment (Akortia *et al.*, 2016).

2.4.2.1. Waste Electrical and Electronic Equipment (WEEE)

Electronic waste (e-waste) refers to electrical and electronic equipment that are obsolete and have been discarded by their original users. WEEE is becoming a major environmental concern, particularly in developing countries (UNEP 2006). Presently, e-waste is the most obvious environmental challenge, and the infrastructure to properly manage obsolete and unwanted WEEE is still poorly developed (Osibanjo and Nnorom 2007). There is greater concern that the current low-end management activities of WEEE in mostly developing countries in Africa (Nigeria, Ghana) as well as countries in transition like South Africa, may result in high levels of emissions of PBDEs into the environment. Unregulated e-waste recycling activities have led to the release of various hazardous chemicals, including PBDEs into the environment (Ahn *et al.*, 2005; Leung *et al*., 2007; Wang *et al.*, 2007; Chen *et al.*, 2009; Luo *et al.*, 2009). Products incorporated with PBDEs that have been dumped in landfills or in the open (e-waste dump sites) is probably the main source of PBDEs in the environment, when these products are incinerated. There is limited information on leaching of PBDEs from landfills, although PBDE-containing products are widespread, and leaching may be considered an important contaminating pathway in the long term (Darnerud *et al.*, 2001). For example, in Guiyu, South China, surface soils around acid treatment sites for e-waste are polluted by PBDEs with concentration levels of 2720- 4250 ng g^{-1} dry weight (d w) (Leung *et al*., 2007; Akortia *et al.*, 2016).

2.4.2.2. Sewage sludge

Many substances attributed to anthropogenic activities often end up in wastewater and

accumulate in sewage sludge. Widespread reports of sewage sludge and effluents derived from municipal waste treatment facilities also contribute to the environmental burdens of BFRs quite significantly (Song *et al.*, 2006; Vonderheide 2008). Like most hydrophobic organic contaminants, they tend to bind strongly with organic matter (Clarke *et al*., 2008). Sewage sludge, often generated by wastewater treatment plants (WWTPs) is disposed of through numerous methods that may further contaminate the environment in terms of formation of highly toxic chemical substances. These include incineration, land filling and agricultural land application (Sellstrom *et al.*, 2005).

The impact of wastewater irrigation on the distribution of persistent organic pollutants particularly PBDEs and PCBs on farm soils has been investigated (Wang *et al.*, 2010). Sewage sludge applied to agricultural areas could also contribute appreciably to the environmental burdens of brominated flame retardants particularly in soil (Sellstrom *et al*., 2005; Hale *et al.*, 2006). Eljarrat *et al.*, (2008) observed that sewage sludge amendment of agricultural soils significantly contributed to increased deca-BDE soil burdens. PBDEs were found in sludge samples in Germany (Knoth *et al.* 2007) at measurable concentrations (97- 2217 μg kg^{-1}; mean 256 μg kg^{-1}) at different stages of WWTP process as evidence of environmental contamination of PBDEs, particularly BDE-209. BDE-209 was found to be the dominant PBDE determined in Spanish sludge (n=6), comprising >95% of the PBDE burden (Fabrellas *et al.*, 2004). Evidence of sewage sludge as a source of PBDEs in the environment was similarly reported by Law *et al.*, (2006) in Swedish sludge, analyzed by the Swedish EPA, with concentrations ranging (5.6 - 1000 μg kg^{-1}). Investigations by Gorgy *et al*., (2011) on biosolids-amended soil confirmed that biosolids application is a non-point source of PBDE contamination for agricultural soils. PBDEs redistribution in the environment can also be influenced by precipitation and runoff phenomena on land-applied sludge (Goel *et al*., 2006). Globally, the contribution of other non-point sources of PBDEs to the overall environmental burden is highly significant (Akortia *et al*., 2016).

2.4.2.3 Incineration

PBDEs blended with polymer products may leach out during product usage and disposal and have been noted to produce toxic dioxins (PBDDs/Fs), especially during incineration which can become a persistent source contributing significantly to environmental PBDE burdens (WHO 1998; Soderstrom and Marklund 2002; Ebert and Bahadir 2003). The release of PBDEs into the atmosphere during crude burning of trash (often common in developing countries) could also contribute appreciably to environmental burdens of PBDEs (Shen *et al.*, 2006).

2.4.2.4 Dust and particulate matter

Dust in indoor environments, including homes and work places, may be significantly laden with flame retardant contaminants amongst other unknown brominated compounds (Leonards *et al.*, 2001; Cheng *et al*., 2009). PBDE-laden dust particles can emanate from hot electrical and electronic appliances as well as from carpets and furniture. However, the controls on indoor air concentrations are not clear, even though some research also ascertained that levels of PBDEs indoors may serve as a major source to outdoor concentrations (Harrad and Hunter 2006). Flame retardant contaminants are mostly bound to airborne particulates, which could be transported beyond their point of generation (Palm *et al*., 2002; de Wit *et al.*, 2006; Hale *et al.*, 2006; Gevao *et al.*, 2006; Abdallah *et al*., 2008). PBDE concentrations in indoor dust collected during computer usage have been found to be higher than when they are turned off, ascertaining the fact that increase in temperature facilitates the release of volatile PBDEs into the indoor environment (Cheng *et al.,* 2009).

2.4.2.5 Soil erosion

Another likely source of PBDEs contamination of the environment is through soil erosion (Zou *et al.* 2007), which these contaminants can be transported across environmental and political boundaries (Hale *et al*., 2006) and accumulate in sediments, floodplain agricultural soils (Sellstrom *et al*., 2005) and aquatic biota (Streets *et al.,* 2006; Akortia *et al.,* 2016).

2.4.2.6 Biota

Biota can also redistribute PBDEs throughout the environment following uptake and accumulation from abiotic media, occurring at regional and global scales owing to the long range migration and wide distribution of animals, particularly fish and birds (Blais *et al.,* 2007). Christensen *et al.,* (2005) estimated that approximately 70% of the PBDEs in bears originated from migratory salmon which picked up PBDE burdens from the ocean and transferred them into the terrestrial environment during spawning activities (Akortia *et al.,* 2016).

2.5. Levels of PBDEs in the environment

There is ample scientific evidence confirming the presence of PBDEs in most biotic and abiotic media over the years due to anthropogenic activities (Watanabe *et al.,* 1987; Sellstrom *et al.,* 1999; Hagmar *et al*., 2000; de Wit *et al*., 2006; Hazrati and Harrad 2006; Law *et al.,* 2006; Hale *et al.,* 2008; Sjodin *et al*., 2008; Clarke *et al.,* 2008; Polder *et al.,* 2008; Odusanya *et al.,* 2009). PBDEs began receiving attention as environmental contaminants in the early 1980s, when it was reported in the River Viskan (Anderson and Blomkvist 1981) and in the late 1990s when researchers detected an exponential increase of PBDE levels in Swedish mother's milk over a 25-year period, increasing from 0.07 ng g^{-1} lipid (1972) to 4.02 ng g^{-1} lipid (1997) (Meironyte *et al.*, 1999). Subsequently, PBDEs have been found in notable environmental and biotic compartments such as air (Strandberg *et al.,* 2001; Shoeib *et al.,* 2004; Toms *et al.*, 2009; Bennett *et al.*, 2015), soil (Wang *et al*., 2005; Wu *et al.,* 2015), sediment (Sellstrom *et al*., 1998; Sakai *et al*., 2002; de Boer *et al.,* 2003; Zheng *et al.,* 2004; Eljarrat *et al*., 2005; Olukunle *et al.,* 2012; Salvado *et al*., 2012; La Guardia *et al*., 2013) and water (Luckey *et al.,* 2001; Ikonomou *et al.,* 2002; de Boer *et al.,* 2003), as well as in biological samples (Akutsu *et al.* 2001; Herzke *et al.,* 2003) and human tissues (Sjodin *et al*., 1999; Ohta *et al.*, 2002; She *et al.,* 2002; Covaci *et al.,* 2002; Choi *et al.,* 2003; Dimitriadou *et al.,* 2016). Significant concentrations of PBDEs in matrices such as soil and vegetation (Wang *et al.,* 2011; Huang *et al.,* 2011), feral carp (Labandeira *et al*., 2007), birds (Voorspoels *et al.,* 2006; Malik *et al.*, 2011; Daso *et al*., 2015) and people (Hale *et al.,* 2006; Law *et al.,* 2006, 2008) have been reported. PBDEs have been known to potentially form polybrominated dibenzodioxins/furans (PBDD/Fs) during the processing of waste plastics containing flame retardants (Ebert and Bahadir 2003; Schlummer *et al.*, 2006; Kajiwara *et al.,* 2008; Wahl *et al*., 2008; Tang *et al*., 2013; Akortia *et al*., 2016).

Despite a decline in production and usage, PBDEs are still being detected in the environment, in several food items, marine species and terrestrial animals (Darnerud *et al.,* 2001; Hites, 2004; McDonald, 2005; Chen *et al.,* 2007). PBDEs are readily accumulated by soil organisms and show propensity to be bio-magnified in the food chain (Krauss *et al.,* 2000; Kelly *et al*., 2008). Existing reports show occurrence of PBDEs and other brominated flame retardants originating mostly from Europe (Mandalakis *et al.*, 2008b), North America (Harrad *et al.,* 2008b; Batterman *et al.,* 2009a) as well as Asia (Suzuki *et al*., 2006). PBDE levels found in America appear to be much higher than those from European countries (Sjodin *et al*., 2003). Reports indicating the occurrence of PBDEs in Africa are few (Polder *et al.,* 2008; Odusanya *et al.,* 2009; Asante *et al.,* 2011; Darnerud *et al.*, 2011; Kefeni *et al.,* 2012; Daso *et al*., 2012; Olukunle *et al*., 2012; La Guardia *et al.,* 2013). A summary of concentrations of some major BDE congeners detected in both abiotic and biotic matrices from around the world in the literature are shown in Tables 2.1a and 2.1b.

2.5.1 PBDE levels in abiotic matrices

A study by La Guardia *et al.,* (2013) reported concentrations ranging from 1850 to 25400 ng g^{-1} (mean 3240 ng g^{-1}) of PBDE, HBCD, TBB (2-ethylhexyl 2,3,4,5-tetrabromobenzoate) and other novel brominated flame retardants in both inland and coastal sediments collected in South Africa. The levels were comparable to that in the heavily impacted areas like the Pearl River Delta, China, which further depicts that PBDE contamination may not only be limited to the core production areas (Hale *et al.,* 2006; La Guardia *et al.,* 2013). PBDE congeners in leachate samples (n=13) collected from five landfill sites in Pretoria, South Africa reported mean concentrations ranging from not detected (ND) to 9793 pg L^{-1} which is evident of the fact that these contaminants are widespread (Odusanya *et al*., 2009).

PBDEs were measured in leachates, effluent and background water samples (ND - 867805 pg L^{-1}) across southern and northern Canada (Danon-Schaffer *et al*., 2014). Kefeni *et al*., (2014) measured Σ10PBDE concentrations in home dust samples collected in Pretoria, South Africa, and found a range of concentration from < 0.3 to 234 ng g^{-1} d w, with a median of 18.3 ng g^{-1} d w. Wang *et al*., (2005) examined PBDE levels in soil and sediment from an e-waste recycling facility in China, with concentrations ranging from as low as 0.26 ng g^{-1} to 824 ng g^{-1} d w.

In another study conducted on sediment from Buffalo River in the Great Lakes, USA, tetra-BDE accounted for 94 to 96% of the total PBDEs and was found to be bioaccumulative (Loganathan *et al*., 1995). Penta-BDE made up 3 to 5% and only 1% was hexa-BDE. However, deca-BDE was below the limit of detection (0.1 ng g^{-1} tissue). Luckey *et al*., (2002) measured total PBDE (mono- to hepta-BDEs) concentrations (~6 pg L^{-1}) in Lake Ontario surface waters in 1999. Similarly, Stapleton and Baker (2001) investigated PBDEs in water samples from Lake Michigan spanning a period of three years (1997-1999) and found that total PBDE concentrations (BDEs-47, 99, 100, 153, 154 and 183) ranged from 31 to158 pg L^{-1}. Penta-BDE congeners tend to dominate in the atmosphere and aqueous media whereas the prominence of BDE-209 in soils, sediments and sludge increases (Hale *et al.*, 2003, 2006; Law *et al.*, 2006; de Wit *et al*., 2006). Hale *et al.,* (2002, 2003) reported concentrations of total PBDEs (tetra- and penta-BDEs) of 76 ng g-1 d w in soil close to a polyurethane foam manufacturing facility in the U.S.A. and 13.6 ng g-1 d w in soil downwind from the same facility, which shows reduction in concentration by a little over fivefold magnitude. Kolic *et al*., (2003) investigated PBDE concentration in sewage sludge in southern Ontario and found total PBDE levels (mono- to deca-BDEs) ranging from 1414 to 5545 ng g^{-1} d w. An investigation by Eljarrat *et al*., (2008) on the fate of PBDEs (tetra- to deca-BDE) in surface soils, four years after biosolids application concluded that PBDEs are persistent. Rayne *et al*. (2003a) reported PBDE concentrations (Σ8 di- to penta-BDEs) ranging from 2.7 to 91 ng g^{-1} organic carbon (OC) in 11 surface sediments collected in 2001 from several sites along the Columbia River system in south eastern British Columbia (Rayne *et al.* 2003a). Dodder *et al.,* (2002) also measured concentrations of total tetra-, penta- and hexa-BDEs ranging from approximately 5 to 38 ng g^{-1} d w in sediment from a lake located near suspected PBDE sources in the northeastern United States and the Great Lakes region. Olukunle *et al.*, (2012) reported PBDE concentrations ranging from 0.92 to 6.76 ng g^{-1} d w in sediment samples collected from Jukskei River in South Africa. Table 2.1a shows a summary of concentrations of some major BDE congeners in abiotic matrices from across the world in the literature.

2.5.2 PBDE levels in Biota

Numerous studies have been published in the literature characterizing the exposure of biota to environmental contaminants in the ecosystem (Malik *et al.*, 2011; Mizukawa *et al*., 2013; Kim *et al.*, 2015). Some recent studies have been identified as novel, for example, research on exposure of bats to PBDEs by Kannan *et al*., (2010) and the study of pet cats (Guo *et al*., 2012) as indicators of BDE indoor contamination. Characterization of total PBDEs in most terrestrial animals have proved to be quite difficult, partly due to species specific differences and dietary preferences, which often reflect in the type of congeners that can be detected. However, in most thus far, BDEs-47, -99, -153, and -100 were more frequently detected and dominant. Birds and other wild animals have been useful as environmental sentinels because of their upper position in the food chain, providing integrative data on both pollutant exposure and biological effects (Malik *et al.*, 2011; Rios *et al.*, 2015). Among these animals, trout and egret species present several advantageous biological characteristics, (including being top consumers in the food web with potential to accumulate contaminants through bioaccumulation and biomagnification, a wide geographic distribution, ubiquitous and sensitive to environmental changes) (Malik *et al.*, 2011; Crimmins *et al.*, 2012; Akortia *et al.*, 2016).

Information derived from these animals may prove useful to the study of PBDE levels and distribution in the terrestrial and aquatic environment. In a previous study, Alaee *et al.,* (1999) measured average concentrations in the blubber of marine mammals from the Canadian Arctic as 25.8 ng g^{-1} lipid weight (l w) in female ringed seals (*Phoca hispida*), 50.0 ng g^{-1} l w in the blubber of male ringed seals, 81.2 ng g^{-1} l w in female belugas (*Delphinapterus leucus*) and 160 ng g^{-1} l w in male belugas. Hu *et al.,* (2008) reported PBDEs in wildlife tissues of a captive giant panda and a red panda from China ranging from 16.4 to 2158 ng g^{-1} l w (Hu *et al.*, 2008). Daso *et al.,* (2015) investigated the levels of eight PBDE congeners (BDEs-17, 47, 99, 100, 153, 154, 183 and 209) in egg shells of Southern Ground-Hornbill (SGH) (*Bucorvus leadbeateri*) and Wattled Crane (WC) (*Bugeranus carunculatus*) from different nesting sites in South Africa.

Table 2.1a. Summary concentrations of major PBDE congeners in various abiotic matrices from around the world in the literature

Matrix	**Country/ Location**	**n (Unit)**	**BDE47**	**BDE99**	**BDE100**	**BDE153**	**BDE154**	**BDE209**	**ΣPBDE**	**Reference**	**Comments**
Soil	China, Shanghai	37 ng g^{-1} dw	0.924(0.043-11.4)	1.03(0.022-17.5)	0.233 (ND-2.25)	0.201(ND-2.07)	0.162(0.010-1.14)	28.6 (3.55-141.4)	3.88(0.371-32.9)	Wu et al. (2015)	Reported mean and range of sum=13 PBDEs and BDE209
Soil	Pakistan	NS ng g^{-1}	0.049(0.006-0.498)	0.044(0.002-0.350)	0.042(ND-0.467)	0.037(0.003-0.250)	0.021(ND-0.121)		0.272(0.047-2.377)	Ali et al. (2015)	Reported mean and range of sum=8 PBDEs
Soil	Turkey, Kocaeli	49 µg kg^{-1} dw	1.1(0.05-1.35)	1.73(0.07-14.7)	0.36(0.03-2.05)	0.46(0.02-2.83)	0.35(0.02-1.96)	22.2(0.46-172)	26.3(0.70-203)	Cetin (2014)	BDE209 was the most dominant congener at all sites
Soil	USA, Michigan	10 ng g^{-1} dw	1.49	1.38	0.29	0.12	0.13	10.8	13.8	Yun et al. (2008)	Reported only mean values of sum=10 PBDEs
Road dust	China, Wen'an	31 ng g^{-1} dw	0.806(0.0004-7.74)	0.836(0.001-10.2)	0.311(0.002-3.14)	4.67(0.002-101.4)	2.82(0.002-39.9)	1430(2.67-10424)	1541(3.23-10640)	Tang et al. (2015)	BDE209 was the predominant congener in all road dust samples, Sum=21 PBDEs
Indoor dust(homes)	Nigeria, Makurdi	10 ng g^{-1} dw	42.5(26-51.1)	39.3(0.24-62)	38.8(0.1-55.6)	39.1(0.03-73.6)	34.8(0.03-72.1)	141(79-202)	397.2(144.2-601.7)	Olukunle et al. (2015)	Sum of PBDEs calculated for sum=7 PBDE congeners reported

Indoor dust(offices)	Nigeria, Makurdi	11	ng g^{-1} dw	51.6(35.8-84.76)	60.6(43.1-99.3)	56.1(38.1-92.7)	74.3(51.7-118)	64.7(46.7-110)	180(112-428)	559.3(328.4-1056.76)	Olukunle et al. (2015)	Sum of PBDEs calculated for sum=7 PBDE congeners reported
Car dust	Sweden	NS	ng g^{-1}	NS	NS	NS	NS	NS	NS	1400(54-30,000)[a]	Thuresson et al. (2012)	Reported median and range of sum=10 PBDEs including BDE209
Sediment	Pakistan	20	ng g^{-1}	0.6(ND-05)	0.4(ND-3.1)	0.1(ND-0.4)	1.7(ND-8.5)	0.1(ND-0.9)	640(1.0-2600)	640(1.0-2600)	Syed et al. (2013)	Reported mean and range of sum=8 PBDEs including BDE209
Sediment	Korea	25	pg g^{-1}	41.5	66.7	11	29.3	11.7	27419	NS	Moon et al. (2007)	Reported only mean values of BDE congeners detected
Sediment	USA, Michigan	28	ng g^{-1} dw	0.25	0.2	0.05	0.02	0.02	2.28	2.84	Yun et al. (2008)	Reported only mean values of BDE congeners detected
Sediment	China	NS	ng g^{-1} dw	0.031(0.013-0.069)[a]	0.016(0.006-0.091)[a]	0.024(0.010-0.088)[a]	0.004(ND-0.106)[a]	0.081(0.010-0.620)[a]	0.819(0.067-1.961)[a]	0.243(0.064-0.807)[a]	Wang et al. (2016)	Reported median and range of sum=7 PBDEs and BDE209

a= median values reported, ΣPBDE= sum of mean value of all BDEs measured in the literature, NS= not specified, ND= not detected, n= number of samples analysed, dw= dry weight, lw= lipid weight, ww= wet weight, BDE= bromodiphenyl ether, PBDE= polybrominated diphenyl ether. Source: Akortia et al., 2016

Table 2.1b Summary concentrations of major PBDE congeners in various biotic matrices from around the world in the literature

Matrix	Country/ Location	n	Unit	BDE47	BDE99	BDE100	BDE153	BDE154	BDE209	∑PBDE	Reference	Comments
Biotic matrices												
Fish(Various species)	UK	17	µg kg^{-1} ww	0.07-103.7	<0.01-6.13	NS	NS	NS	0.01-0.15	NS	Rose et al. (2015)	Reported range of concentrations of BDEs-47,-99, and -209
Yellow eels	Germany	30	ng g^{-1} lw	ND-6.5	NS	NS	NS	NS	NS	10.2	Sühring et al. (2013)	Reported range of concentrations of BDE-47 and sum PBDEs
Trout	Switzerland	9	ng g^{-1} lw	103	61	15	3.4	3.6	8.2	207	Cheaib et al. (2009)	Reported only mean values of BDE congeners detected
Cattle Egret	Pakistan, Punjab	NS	ng g^{-1}	NS	NS	NS	NS	NS	NS	1.91[a]	Malik et al. (2011)	Median concentration of sum=10 PBDEs were reported
Little Egret	Pakistan, Punjab	NS	ng g^{-1}	NS	NS	NS	NS	NS	NS	2.41[a]	Malik et al. (2011)	Median concentration of sum=10 PBDEs were reported
Human breast milk	Sweden, Uppsala	30	ng g^{-1} lw	0.46(0.10-2.1)[a]	0.07(0-0.48)	0.13(0.03-1.4)[a]	0.45(0.21-3.4)[a]	0.05(0.01-0.11)[a]	0.06(0.02-0.18)[a]	1.5(0.53-6.6)[a]	Darnerud et al. (2015)	Reported median and range of sum=10 PBDEs including BDE209
Human serum	Sweden, Uppsala	30	ng g^{-1} lw	0.36(0-2.1)[a]	0.05(0-1.1)[a]	0.18(0-1.7)[a]	0.72(0.40-6.6)[a]	0.12(0.01-0.21)[a]	0.90(0.35-2.3)[a]	2.8(1.0-11)[a]	Darnerud et al. (2015)	Reported median and range of sum = 10 PBDEs including BDE 209

a= median values reported, ∑PBDE= sum of mean value of all BDEs measured in the literature, NS= not specified, ND= not detected, n= number of samples analysed, dw= dry weight, lw= lipid weight, ww= wet weight, BDE= bromodiphenyl ether, PBDE= polybrominated diphenyl ether.
Source**:** Akortia *et a*l., 201**6**

The total PBDEs ranged between not detected (ND) to 264 µg g^{-1} l w in SGH and 5.98 to 7146 µg g^{-1} l w in WC. Concentrations of PBDEs were also determined in eggs of bird species from the Vaal River, which is situated downstream of the most industrialized area in South Africa, and reported sum PBDE concentration (396 ng g^{-1} l w) in eggs of an African sacred ibis (Polder *et al.,* 2008). Studies conducted in Europe provide evidence for the presence of deca-BDE in peregrine falcons eggs (*Falco peregrines*) from Sweden with concentrations ranging from 28 to 430 ng g^{-1} l w (Lindberg *et al.,* 2004). Malik *et al*., (2011) measured Σ10BDE in feathers of two colonial water bird species (cattle egret and little egret) in Pakistan and reported median concentrations of 1.91 and 2.41 ng g in cattle egret and little egret respectively, which were found to be lower than similar studies documenting BDE levels in feathers of various bird species in Belgium (Jaspers *et al.,* 2007a, 2009). These studies were characterized by the relative abundance of tetra- and pentabrominated congeners (BDEs-47, -99, and -100), which predominate in most biota studies, especially top predatory animals (Luo *et al*., 2009).

In rare cases, Kannan *et al.,* (2010) determined PBDEs in insectivorous brown bats from the USA, and the report showed penta-BDE (-47 and -99) dominated adipose sum BDE concentrations (118-8290 µg kg^{-1} l w), while BDE-28 was proportionately more pronounced in their brains than adipose tissues. Generally, PBDE congener specific levels are expected to be found in biological tissues such as liver (which is a major detoxification organ in vertebrates) than muscles, also due to the hydrophobicity of PBDEs. However, this correlation may depend also on the physiological status of the species. While some studies have demonstrated positive correlation of this pattern in fish species (Gewurtz *et al.,* 2011), others have found no clear correlation (Saele and Pittman 2010). Recently, structural analogues of PBDEs (hydroxylated- and methoxylated-BDE) have been receiving increasing attention following their detection in marine environment (Haraguchi *et al.,* 2011). Kim *et al*., (2015) investigated bioaccumulation and biotransformation of PBDEs, OHBDE and MeO-BDE in varying trophic level fresh water fishes. The concentrations of PBDEs and structural analogues were found to be preferentially distributed in the internal organs to different extents. PBDE concentrations in the muscle samples ranged from 0.15 to 9.4 ng g^{-1} w w, while OH-BDE and MeO-BDE concentrations were from 0.12 to 6.3 ng g^{-1} w w and 3.2 to 35 ng g^{-1} w w, respectively. A summary of concentrations of BDE congeners in some biotic matrices reported in the literature are shown in Table 2.1b.

2.5.3 PBDE levels in humans

Being lipophilic and persistent compounds, PBDEs are expected to preferentially accumulate in lipid-rich tissues such as breast milk, serum and human adipose tissues. Humans have been exposed to PBDEs and individual congeners mainly through diet. However, diet alone cannot explain the route through which human tissues have been contaminated by this endocrine disrupting chemical. Recently, research has shifted towards other sources of PBDE exposure to humans that were not considered hitherto, i.e. emissions from PBDE incorporated products such as TV sets and computers, household dust as well as occupational exposure. Data on PBDE human levels were reported mostly in Swedish studies (Lignell *et al.,* 2014; Darnerud *et al*., 2015). Studies have been conducted which measured PBDEs in human tissues and fluids such as breast milk, hair and nails, serum, umbilical cord blood and recently placental tissues (Asante *et al*., 2011; Zota *et al*., 2013; Nanes *et al*., 2014; Dimitriadou *et al*., 2016; Leonetti *et al.,* 2016; Akortia *et al.,* 2016). Levels of PBDEs in some human tissues/fluids are shown in Table 2.1b.

Variable concentrations were often detected among different countries probably due to varied concentrations in diet, especially food items bearing high contribution to total PBDE intake and different dietary patterns that pertain to each country. On a congener specific level, BDEs -47, - 99, -153, and -100 have been prominent in most human exposure studies (Lignell *et al.* 2013, 2014; Dimitriadou *et al.* 2016). Deca-BDE is poorly transferred to human tissues (e.g. milk), thus studies especially on human milk did not consider BDE-209. However, this can be a limiting factor in the determination of total PBDE exposure (Lignell *et al.,* 2013; Darnerud *et al.,* 2015). Direct exposure of humans to PBDEs from environmental matrices is quite low (except through occupational exposure), but direct exposure and subsequent bioaccumulation may occur through diet, mainly fatty foods from terrestrial and aquatic ecosystems. Of much concern is the increasing exposure of infants to PBDEs owing to increasing levels in mothers' milk during lactation (Asante *et al*., 2011), albeit considerably lower than levels of PCBs (Dimitriadou *et al*., 2016). While previous studies have reported a relationship between factors such as age and PCB levels in humans (Hassine *et al.*, 2012), maternal age did not show either a positive or a negative correlation (Dimitriadou *et al.,* 2016).

This is ascribed to the fact that human exposure to PBDEs is continuous, and there may be other factors controlling the variability of PBDE levels in breast milk. PBDE derivatives (MeO-BDE) were also determined in human milk samples in Tunisia, i.e. 6-MeO-BDE-47, 2-MeO-BDE-68, 4-MeO-BDE-49 and 5-MeO-BDE-100, and as such, 5-MeOBDE- 100 and 4-MeO-BDE-49 were the first to be determined in human milk thus far (Hassine *et al*., 2015). It was also observed from this study that age as a factor did not bear any significance to the levels of PBDE congeners nor their derivatives, and this concurs with other studies (Dimitriadou *et al.*, 2016; Akortia *et al.*, 2016).

In a recent study by Darnerud *et al.*, (2015) on human serum from Swedish mothers, BDE-209, rarely determined was found to record a mean level of 1.3 ng g-1 lipid. Inferring from their data, there was a decreasing time trend for BDEs-47, -99, -100, and an increase in BDE-153 levels. There was, however, a strong correlation between serum and milk levels of tetra- to hexabrominated congeners (r= 0.83-0.97) and a weak one for BDE-209 (r= 0.38). Inference can be drawn from the fact that, differences in PBDE congener transfer from blood to milk are probably related to molecular weight or size and not age. BDE-209 mean level (1.3 ng g-1 lipid) reported in Swedish mothers' serum by Darnerud and co-workers (2015) is about five orders of magnitude lower than observed in serum of Swedish dismantling plant workers by Sjodin *et al.*, (1999). This clearly points out decreasing trend in some specific congener levels as a result of the phase-out in production of the technical mixtures penta-, octa- and recently deca-BDE in consumer products, but does not rule out the possible leaching of products in service or disposed in landfills. Notwithstanding, occupational exposure may contribute significantly to human exposure to PBDEs.

A study within the framework of a French monitoring program measured tri- to deca-BDEs in maternal and cord serum, adipose tissues and breast milk samples collected from 93 women during caesarean deliveries (Antignac *et al.*, 2009). Seven major tri- to hepta-BDEs (28, 47, 99, 100, 153, 154 and 183) were detected in adipose tissue and breast milk with cumulated median values of 2.59 and 2.51 ng g^{-1} l w, while the remaining octa- to deca-BDEs (196, 197, 201, 202, 203, 206, 207, 208 and 209) reported cumulated median concentration of 2.73 and 3.39 ng g^{-1} l w in adipose tissue and breast milk respectively (Antignac *et al*., 2009). Toms *et al.* (2007) observed concentrations of BDE-47 in Australian mothers' breast milk, in the range of 2.8 to 9.6 ng g^{-1} fat, and a median of the sum of six individual PBDEs of 10.2 ng g^{-1} fat. Similarly, the concentrations of sum of five PBDEs in Canadian mother's milk reported a range of 2.4 to 22 ng g^{-1} milk fat (Hites 2004), and up to 38 ng g^{-1} plasma fat in human tissues in Mexico (Lopez *et al*. 2004).

2.5.4 Temporal trends

Reported concentrations of PBDEs over time in various locations show that PBDE levels have been reducing, but not consistently. Yang *et al.*, (2015) examined dated sediment cores from English lakes and reported an increasing trend in fluxes of penta-BDEs in the late-1990s and early-2000s at three out of seven lakes examined, and that fluxes in some UK lakes continued to increase. While the apparent declining trend at some locations may be credited to the introduction of EU control measures since 2004 (on production and usage of penta-BDE), the continuous surge in fluxes at other locations could be attributed to the latent impacts of the EU control measures on current production and usage of penta-BDEs. Concentrations of penta-BDE congeners were similarly compared with Scottish soils collected in three different surveys in 1990, 1999 and from 2007-09. The study showed that there was a large and significant increase in contamination between the period spanning 1990 to 1999, and while there appeared to be a further increase between 1999 and 2007-09, there was no significant peak in concentration observed over the latter period (Zhang *et al.*, 2014). Crosse *et al*., (2012a) examined temporal (1985-2007) and spatial trends in PBDE concentration in archived eggs of the sparrowhawk from England, UK. They found concentrations of penta- BDEs (-47, -99, -100, -153, and -154) to be more abundant and increased significantly from mid-'80s, peaking in the mid-late 1990s, after which point concentrations were sustained until 2007. It was however hypothesized that this trend could be explained by some debromination of deca- BDE that may have taken place over the period.

Temporal trend studies also examined not only penta-BDEs, but octa- and deca-BDEs since their emergence. For example, in the study of gannet eggs by Crosse *et al.*, (2012b), BDE-183 concentration was found to follow a similar trend to that of pent-BDE congeners measured in the same samples. They found concentrations to rise from the first samples in the 1980s, peaking in 1994, and then rapidly declining thereafter. Similarly, Crosse *et al.*, (2012b) reported long term trends in penta-BDE concentrations in gannet eggs from two UK colonies in the Western Atlantic and the North Sea, over a period of three decades (1977-2007). Penta-BDE and ΣPBDE concentrations in eggs from both colonies increased notably starting in the late 1980s, peaked in 1994, and then sharply declined such that concentrations in 2002 were similar to or lower than those in the 1970s and 1980s. In the marine environment, several studies (Law *et al.,* 2010; Trumble *et al*., 2012; Rotander *et al.,* 2012) have reported time trends in PBDEs in abiotic and biotic matrices. The time trends on concentration data indicate that PBDEs were introduced during the 1970s, and have increased in the late-1990s.

However, concentrations have continued to increase in some regions until recently, whereas in other regions, for example, in Europe, the levels stabilized at the start of the millennium, reflecting the effects of earlier restrictions on their production and usage. Gevao *et al.,* (2014) reported on the historical deposition of PBDEs using dated sediment cores (past ~60 years) collected from the entrance of Kuwait Bay. The historical record, reconstructed from a sediment core collected at the entrance of the Bay, showed that Σ_{11}PBDE concentrations were generally low in the deeper sediment sections. The concentrations began to increase above background levels in the mid-1950s, and surged rapidly, reaching a maximum of Σ_{11}PBDE concentration of approximately 1.1 ng g^{-1} d w in the late-1980s. Concentrations decreased thereafter until another pulse was observed in the early-2000s, followed by a decrease in subsequent years. The authors' best point explanation for the initial sharp increase in concentration in the late-1980s was possibly due to inputs from war related activities in the region. Rotander *et al.,* (2012) examined the temporal trends of PBDEs in seven species of marine mammals from the Arctic and the North Atlantic sampled during 1986 to 2009. The authors found high levels of PBDEs in samples from the late-1990s to the early-2000s. Similarly, Muir and de Wit (2010) examined temporal trends of select aquatic mammals (Arctic char, ringed seals, burbot, lake trout, and beluga whales), and concluded that evidence exists that environmental levels of PBDE congeners related to the penta-BDE commercial mixture were either leveling off or have started to decrease in samples taken from across the Arctic.

Regarding human dietary exposure, Mortimer *et al.,* (2013) reported on concentrations of penta-BDEs (-47 and -99) in 19 food group samples investigated as part of a total diet study (TDS) in the UK in 2003 and 2012. Data showed that the concentrations appear to have fallen since 2003, which reflects the effect of subsequent introduction of use restrictions on the penta-BDE in the mid-2000s. This study revealed UK exposure based on 2012 TDS samples to be approximately 50% lower than in 2003. This was further corroborated in a related study by Fernandes *et al.* (2014) who reported concentrations of ΣPBDEs (including 209) in 10 food group categories collected as part of the 2003, 2007 and 2012 TDSs. Their data also revealed a distinctive decline in ΣPBDE concentrations (dominated by penta-BDE congeners) between 2003 and 2012.

2.6. Toxicity of PBDEs

Many toxicological studies have demonstrated that exposure to PBDEs may result in adverse effects including carcinogenicity, neurotoxicity and endocrine disruption in laboratory animals and humans (Darnerud *et al*., 2003; Chen *et al.,* 2012; Costa *et al.*, 2014). Of particular concern is the neurobehavioral development that is apparent for penta-BDE mixture (Chen *et al*., 2012). These findings, however, raise particular concerns about potential risks to children (EPA 2006a; Akortia *et al*., 2016).

2.6.1. Human toxicity

Evidence in humans is suggestive of developmental effects of PBDEs, though research results are not always univocal and not completely understood to-date. Humans are exposed to low levels of PBDEs through ingestion of food and by inhalation of contaminated dust. Personnel associated with the manufacture of PBDE-containing products as well as recycling and repair plants are often exposed to high levels of PBDEs. People are also exposed to flame retardant chemicals in their domestic environments owing to incorporation in common household items. Perinatal exposure to BDE congeners is also of particular concern, especially with reports of latent alteration in cognitive function. Elevated PBDE levels in breast milk from a Taiwan study correlated with low birth weight and length, lower head and chest circumference and reduced body mass index, while a follow up study four years later reported developmental delays in cognition (Chao *et al.,* 2007, 2011). On the contrary, Harley *et al.,* (2011) found no association between prenatal exposure to PBDEs and reported birth defects in a study on Hispanic population in California. In a North Carolina cohort, lactational PBDE exposure correlated with increased activity/impulsivity behaviour in early childhood (Hoffman *et al.,* 2012), though a Spanish study found no association between PBDEs body-burden in 4 year old children and any motor or cognitive alteration (Gascon *et al*., 2011).

2.6.2. Ecosystem toxicity

Studies have been conducted on laboratory animals to gain insight of the potential health risks associated with PBDEs. Among commercially important PBDE congeners, penta and octa-BDEs have been reported as potential carcinogens, neurotoxic and disruptive to the endocrine system (Darnerud *et al.,* 2001; Birnbaum and Staskal 2004; Costa and Giordano 2007; Vonderheide *et al*., 2008). Herbstman *et al.,* (2010) reported neurodevelopmental effects in relation to cord blood PBDE concentrations. Several experimental investigations have also suggested that PBDE contaminants might have an impact on liver and kidney morphology (Costa *et al.*, 2008; Alonso *et al.*, 2010; Albina *et al.*, 2010). Exposure to penta-BDEs has been demonstrated to interfere with sexual development and decrease follicle formation (Lilienthal *et al.* 2006). Kuriyama *et al*., (2005) reported on the reduction in sperm counts where adult rats were exposed to BDE-99 at the prenatal stage. Research indicating similar findings in the female reproductivesystem was identified with BDE-47 (Talsness *et al.*, 2004). PBDE exposure has also been shown to result in cytotoxic effects, although such mechanisms occur at cellular level often affecting the associated organ (Vonderheide *et al.*, 2008). PBDEs have been reported to interfere by altering liver function, often leading to changes in thyroid hormones and vitamin A homeostasis, and further resulting in over elimination of plasma thyroxin (T4) (Ellis-Hutchings *et al.*, 2006).

Exposure to deca-BDEs has been noted to cause increase in liver weights and lactate levels in fish blood following 120 days of exposure (Kovacevic and O'Dell 2008). Janssen (2005) discovered trace amounts of PBDDs/Fs in PBDE mixtures that often prompt the toxicity of PBDEs. In addition, majority of the hydroxylated PBDE metabolites identified in in vitro studies have also been found in humans, with usually high levels in cord serum than in maternal blood (Athanasiadou *et al.*, 2008; Chen *et al*., 2013). Fernie *et al*., (2006) reported that decreased plasma thyroxine (T4) and vitamin A levels were observed in American kestrels after administering a dose of PBDE mixtures. Taken together, though study results in animals and humans are unequivocal, a strong pattern is emerging which shows that PBDE exposure may affect neurodevelopment in biota subjects.

2.7. Processes involved in the transformation of PBDEs

Every chemical in usage has the potential to persist in the surrounding environment, and any transformation products formed by abiotic or biotic processes can be identified in the environment (Hu *et al.*, 2009). Once introduced into the environment, PBDEs can be influenced by many processes, which determine its persistence, transport and ultimate destination. PBDEs and their transformation products can move vertically, for example, through the soil profile to groundwater or away from their point source. PBDEs have the potential to reach surface water through surface runoff, move into the atmosphere through volatilization, adsorption onto dust particles or as solid particles. Various microbes, plants, animals and even humans might pick up and biodegrade PBDEs to some extent. The possible pathways for any synthetic chemical in the environment are illustrated in Figure 2.1. The following processes have been identified to influence the fate of chemicals and its transformation products in the environment (Hu *et al.*, 2009). These are chemical degradation, biodegradation, volatilization and photodegradation (Akortia *et al.*, 2016).

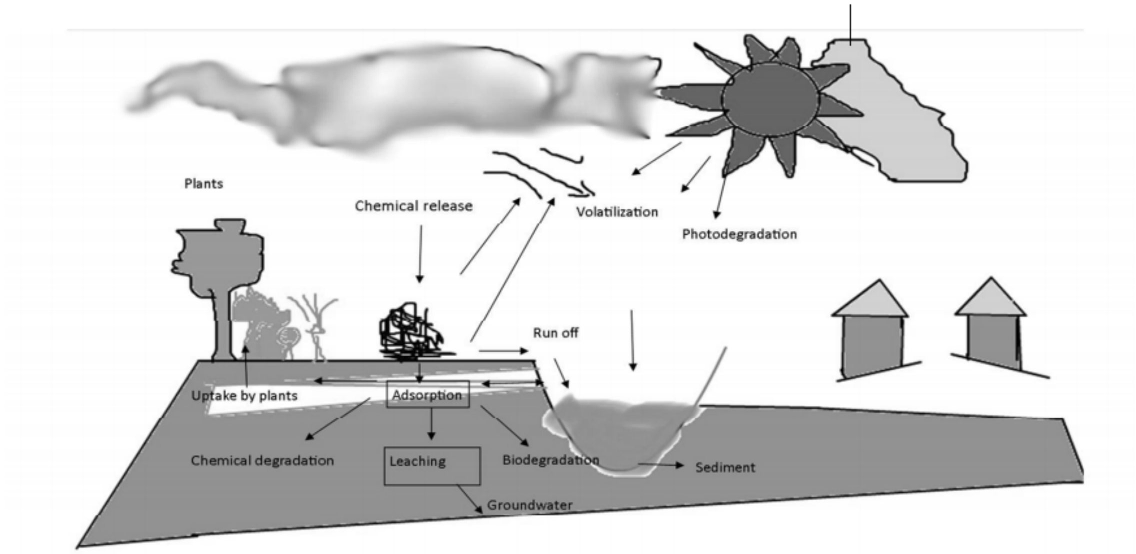

Figure 2.1. Environmental fate processes of a released chemical and its transformation products (Hu *et al.*, 2009).

2.7.1. Photochemical transformation of PBDEs

Photochemical degradation of chemicals in general plays a central role in determining the fate of large numbers of environmental contaminants (Eriksson *et al.,* 2004). Most organohalogen substances have been reported to undergo photolysis (interaction of one or more photons with a chemical compound or target molecule), both under experimental and natural conditions (Meallier 1999). PBDEs can be removed from the atmosphere by chemical reactions with OH and NO_3 radicals, O_3, and photolysis by ultra-violet (UV) light (Ueno *et al.,* 2008). Bieniek *et al.,* (1989) reported that photolysis possibly plays a key role in the environmental transformation of PBDEs. PBDEs have been shown to transform into hydroxylated metabolites (OH-PBDEs) in a similar manner as PCBs (Letcher *et al*., 2000; Hakk and Letcher 2003; Bastos *et al.,* 2008), because of their high lipophilicity (especially for the higher-brominated congeners) and high resistance to degradation processes. Bastos *et al*., (2008) investigated the resistance of PBDEs to oxidation and reported that oxidation transformation rates of PBDEs are slow compared to those for OHPBDEs.

However, there is paucity of information regarding their environmental fate, and more information is needed to appreciate environmental transformations of PBDEs. Ahn *et al.,* (2006) demonstrated that deca-BDE immobilized on specific soil/sediment and mineral aerosols yielded a number of penta- to tri-BDEs, via octa-BDE as an intermediate step, which invariably may pose further environmental concerns owing to the toxicity and bioaccumulation of lower brominated diphenyl ethers (Darnerud 2003). Photochemical degradation of PBDEs has been demonstrated in matrices such as soil, water, sediments and house dust under laboratory conditions (Eriksson *et al.,* 2004; Gerecke *et al.,* 2005; Vonderheide *et al*., 2006; He *et al.,* 2006; Stapleton and Dodder 2008). Ahn *et al.,* (2006b) found that BDE-209 is prone to abiotic degradation by metal oxides that are naturally occurring in soils and sediments. Soderstrom *et al*., (2004) undertook photodegradation studies in which deca-BDE was dissolved in toluene and then applied as a thin layer to silica gel, sand, soil or sediment substrates, and concluded that photodegradation of deca-BDE followed a stepwise debromination process, forming lower BDEs (nona- to hexa-) in the process. Similarly, Stapleton and Dodder (2008) reported debromination of BDE-209 to lower brominated congener in house dust that was experimentally exposed to sunlight. Raff and Hites (2007) reported that as much as 90% of lower brominated PBDE congeners that find way into the atmosphere may be removed by photochemical degradation before being deposited in soils and surface waters. Keum and Li (2005) investigated the debromination of PBDEs in contact with reducing agents, zero-valent iron, iron sulphide and sodium sulphide. The results demonstrated that deca-BDE undergoes reductive debromination in the presence of zero-valent iron. Soderstrom *et al.* (2004) also concluded that the lower BDEs (47, 154 and 183) found in the environment possibly originate mainly as emissions from the commercial penta-BDE and octa- BDE mixtures rather than deca-BDE photo transformation. The authors noted that, the most commonly found PBDEs in environmental samples (BDE-47, -99 and -100) were only formed to a minor degree under photolysis.

2.7.2 Thermal transformation of PBDEs

In spite of the fact that the use of BFRs guarantees higher fire safety, the presence of brominated compounds during accidental fires can result in the formation of undesirable by-products. Owing to the increasing usage of brominated flame-retardant products, it is expected that bromine concentrations will increase in waste streams (e.g. EEE waste plastics), hence brominated compounds becoming increasingly pertinent in thermal waste treatment (Weber and Kuch 2003). Bromine is primarily present in specific plastics in the form of BFRs, specifically brominated aromatic compounds which act as precursors for PBDDs/Fs formation (e.g. PBDEs) (Weber and Kuch 2003). Experiments using brominated aromatics that could be considered as precursors of PBDD/F often result in high yields of PBDDs/Fs (Buser 1986a; Dumler *et al.,* 1989a, b; Luijk *et al.,* 1991). The formation of PBDFs from PBDEs requires an inter-molecular elimination of Br_2 or HBr, Figure 2.2 (Ebert and Bahadir 2003). Luijk *et al.,* (1991) reported that PBDFs in higher yields resulting from low brominated PBDEs can be due to the energetically favourable elimination of HBr in lower BDEs, compared to the energetically less favourable elimination of two bromine substituents in highly brominated diphenyl ethers. Example of this reaction is shown in Figure 2.2 using deca-BDE.

Debromination/hydrogenation reactions have been noted to play a key role in the transformation of highly brominated deca-BDEs to PBDFs (Striebich *et al.,* 1991). Generally, debromination reactions are observed during thermal degradation of polybrominated aromatics above a temperature of 500 °C (Thoma *et al*. 1987a; Dumler *et al.*, 1989a). PBDEs environmental transformation has also been established through pyrolisis experiment conducted at high temperatures (400-800 °C) resulting in the formation of PBDF and PBDD (Rahman *et al.* 2001). PBDDs have also been found during thermal degradation of PBDEs, but their yields were quite lower compared to PBDFs in most investigated cases (Luijk and Govers 1992). Lenoir *et al.* (1994) reported that, the formation of PBDDs from deca-BDE in polybutylene terephthalate (500 °C) were increased in the presence of metals such as tin (Sn), iron (Fe), zinc (Zn) or cupper (Cu), to some extent yielding more than PBDFs. Research has indicated that the yield of PBDDs/Fs in pyrolytic residues decrease from penta-BDEs < octa-BDEs < deca-BDEs (Buser 1986a; Thoma *et al.*, 1987a; Luijk *et al.*, 1991). Studies have shown that the incomplete and uncontrolled incineration occurring in fire accidents in private residences can form high amounts of PBDDs/Fs, which can endanger the environment and persons in contact with fire residues (Ebert and Bahadir 2003).

2.7.3 Biotransformation of PBDEs

Once PBDEs are introduced to an organism, biotransformation can cause errors in interpreting biotic PBDE burdens, by masking differences between true accumulation/magnification of PBDEs and apparent patterns observed by most researchers in single time point samples (Riu *et al*., 2008). Studies have demonstrated the transformation of higher brominated PBDEs (e.g. hepta- to deca-BDEs) to lower brominated congeners (tetra- to hexa-BDEs), often associated with high levels of bioaccumulation. Research has shown that congeners of hepta-BDE and penta-BDE rapidly biotransform in the gut of carp (*Cyprinus carpio*), resulting in 10-12% debromination of congeners of hexa-BDE and tetra-BDE, respectively (Stapleton and Baker 2003; Stapleton *et al.*, 2004b, c). Similarly, approximately 0.4% of deca-BDE consumed by carp was shown to biotransform to penta- and octa-BDEs (Stapleton *et al.*, 2004a). PBDEs have been shown to be aerobically and anaerobically transformed by microorganisms, as indicated by recent studies on anaerobic biodegradation of PBDEs to less brominated congeners by a variety of anaerobic de-halogenating bacteria (Gerecke *et al.*, 2005; He *et al.*, 2006). Robrock *et al.*, (2009) investigated the ability of PCB degrading bacteria *Rhodococcus jostii* RHA1 and *Burkholderia xenovorans* LB400 to transform mono- through hexa-BDEs at parts per billion (ppb) levels. Tomy *et al.*, (2004) investigated the exposure of juvenile lake trout *Salvelinus namaycush* to three dietary concentrations (0, ~ 2.5 and ~ 25 ng g^{-1} per BDE congener) of 13 BDE congeners (tri- to deca-) in the laboratory for 56 days, followed by 112 days of clean food, to examine the bioaccumulation parameters and potential biochemical effects. They determined that the bioaccumulation of BDEs by the trout was highly influenced by biotransformation, via debromination, resulting in bioaccumulation parameters differing from that expected from PCBs. Bioaccumulation of up to 38000 ng g^{-1} (lipid normalized) total PBDEs by earthworms in sewage sludge amended agricultural soils indicates the potential for significant biomagnification in other terrestrial food webs (Sellstrom *et al.*, 2005).

Generally, experiments conducted in the laboratory have shown bioaccumulation of PBDEs, but varies widely for the congeners. For example, a laboratory study on blue mussels (*Mytilus edulis*) reported that BDEs 47, 99 and 153 had higher bioconcentration factors than PCB congeners with similar number of chlorines (Gustafsson *et al.*, 1999). PBDEs are typically metabolized in humans and other mammals through oxidative pathways, by producing hydroxylated PBDEs (OH-BDEs) (Chen *et al*., 2006; Stapleton *et al*., 2008). On the other hand, fish, unlike mammals demonstrated the ability to reductively de-brominate PBDEs both in vivo and in vitro (Stapleton *et al.*, 2004a).

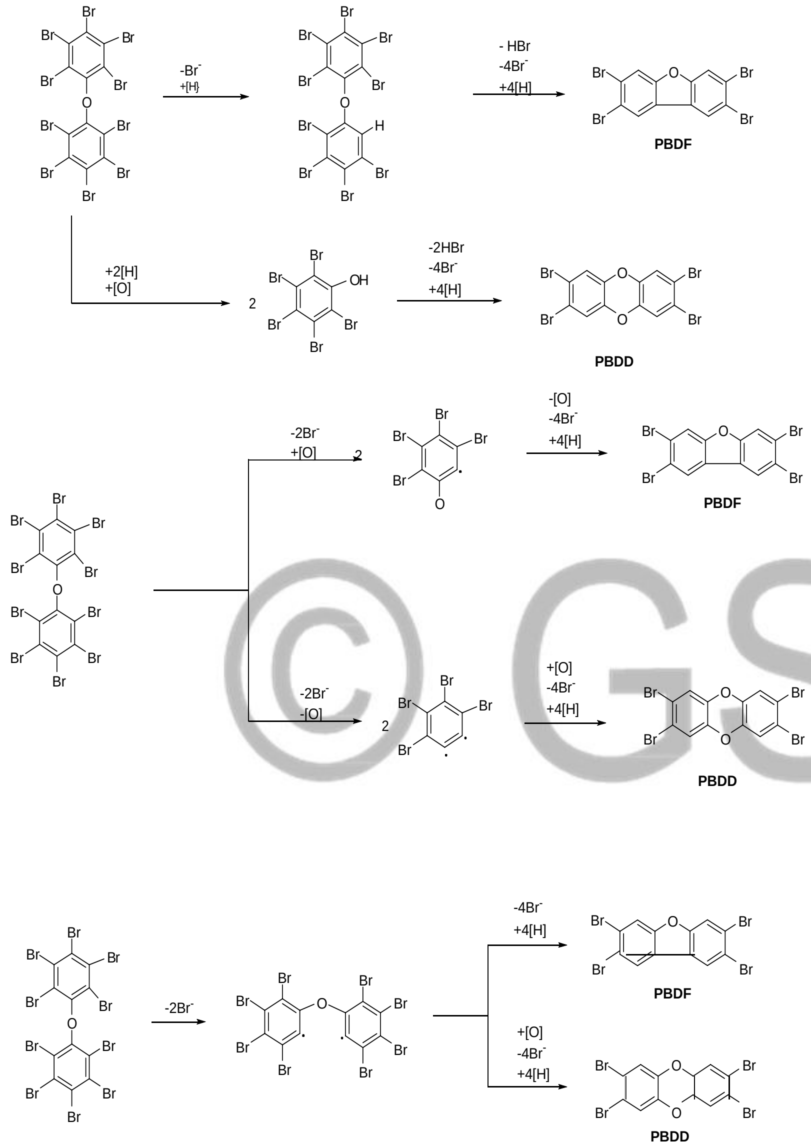

Figure. 2.2. Pathways for the formation of PBDDs/Fs from deca-BDE (Akortia *et al*., 2016).

2.8. Transport of PBDEs in the environment

Over the years, a surge in understanding the fate and transport of PBDEs in the environment has led to the development of several different analytical methods for measuring flame retardant-chemicals in environmental matrices. The transport or migration of organic contaminants in various environmental compartments is important in understanding their fate and behaviour as well as effects to humans and biota (Akortia *et al.,* 2016).

2.8.1 Air

Persistent organic pollutants such as lower congener PBDEs are generally known to undergo long-range atmospheric transport through air via volatilization from source materials. PBDEs can also be transported through diffusion process in a phenomenon known as 'halo-effect', thereby contaminating ambient regions. Fine soil aggregates or dust can be susceptible to erosion caused by strong winds, and PBDEs can be held on to particulates in air and hence deposited in nearby environmental compartments. Wang *et al.,* (2011) identified direct air deposition as responsible for high PBDE levels in wild plant samples from an e-waste burning site in South China.

2.8.2 Water

The transport of contaminants in the subsurface is often controlled by complex interaction between physical, chemical and biological processes. Once the contaminant such as PBDEs enters the regime of a water compartment, various processes including volatilization, air-water exchange, chemical reaction, and biologic interaction, often act to reduce the concentration, or sometimes degrade the chemical form (Schwarzenbach *et al.*, 1993). Depending upon temperature and dissolved oxygen content of water, PBDE contaminants will decrease downstream due to mass transfer to air in the form of volatilization. PBDE in subsurface water that is flowing and has turbulent activity is also expected to partition substantially into air from water, if the aqueous solubility of the contaminants (PBDEs) is proportionately low. However, PBDEs are insoluble in water, thus high levels are not contained in water. The few proportions of PBDEs that occur in water often hold on to particles and eventually settle to the bottom sediments. Sediments at the bottom of water bodies such as lakes and rivers then act as reservoirs of organic contaminants and can persist for longer periods.

Additionally, the reactivity and solubility of an organic chemical such as PBDEs in water may also affect its concentration, in the sense that it can be involved in a rapid, reversible transformation in the water phase. This often results in the overall rate of diffusive transport. Depending upon the presence or absence of polar and non-polar compounds in water, the organic chemical may bind to another compound and transform the chemical to another compound, become bound to another compound without altering its form, or may not bind but rather undergo other reactions or transformations (Schwarzenbach *et al.,* 1993).

2.8.3 Soil

Soil properties and types vary from place to place with differences in bedrock composition, climate and other factors such as the bulk density and organic matter. These are often affected by past land use, current activities and proximity to pollution sources. Soil consists of three size fractions (sand, silt and clay) as well as mixtures of these fractions, which have varied degrees of contaminant retention. Human activities have intentionally or unintentionally added contaminants such as PBDEs to soils and these contaminants may move through aggregates of soils differently. It is a known fact that soil generally represents a major sink for organic contaminants in the environment. It serves as a natural buffer for the movement of pollutants in different environmental compartments (Cetin 2014). Research on hydrophobic compounds similar in physicochemical properties to PBDEs, have demonstrated that they can sorb on particulate matter suspended in the aqueous phase and become mobilized in the soil phase (McCarthy and Zachara 1989). This can occur in soils used for agriculture, containing macropores due to wormholes and passages created by weathered roots. It has also been postulated that, suspended matter in percolating water can be transported to groundwater through these macropores in the unsaturated zone (Jarvis *et al.,* 1999; Kretzschmar *et al.,* 1999). To this end, few studies have comprehensively investigated the mechanism of PBDE transport in soils as well as their concentration at different depths.

The fate and transport of organic contaminants in soil and their possible migration to ground water often depends on various factors such as solubility, bulk density, hydrolysis, sorption, volatility, dissociation, rainfall and evaporation. An insoluble chemical such as PBDEs can be adsorbed in soil and slowly biodegradable. Sorption of organic contaminants including PBDEs to soil is an important process that bears great influence on their transport, bioavailability and fate in the natural environment (Walter and Weber 2002; Li *et al*., 2004). The sorption of an organic contaminant in a soil-water system is believed to be governed by a mechanism where the organic contaminant molecules (e.g. PBDEs) partitions into the soil organic matter (SOM) phase (Celis *et al.,* 1998). The higher the organic matter content of a soil, the more likely contaminants can easily percolate to the subsurface and invariably contaminate groundwater. Additionally, it can be noted that the presence of mixtures of hydrophobic organic contaminants and toxic metals in soils could be prominent. For instance, the presence of toxic metals in soil can sometimes restrain the biodegradation of organic contaminants (Maslin and Maier 2000).

Research has demonstrated that, most organic contaminants mainly interact with SOM, and heavy metallic cations can also be complexed by the organic molecules in soil solids or released into soil solution (Gao *et al.*, 2003; Zhang and Ke 2004). One major factor that aids contaminant transport in most soils is porosity. Additionally, bulk density (an indication of soil compaction) increases with soil depth, since subsurface layers are more compacted and have less organic matter and less aggregation. Soils that are more compacted such as clays often delay contaminant infiltration. Generally, loose, well-aggregated, porous soils as well as those rich in organic matter have lower bulk densities. Sandy soils exhibit relatively high bulk density, due to the fact that total pore space in sands is lower than silt or clay soils. PBDEs transport in soil can also be greatly affected by external environmental conditions such as precipitation, temperature and sunlight. For example, Matscheko *et al.*, (2002) reported that PBDE levels in agricultural soils sampled in spring turned out to be higher than in the autumn. This suggests the importance of limiting the effect of external factors on soils being investigated to obtain results with respect to PBDE distribution and fate in the environment. In view of this, laboratory investigations utilizing soil columns or leaching cells can contribute to understanding the fate of PBDEs in subsurface environments and also formulating transport models of PBDEs in soils, due to the complex nature of soils. Column experiments represent an established method for research purposes to monitor the fate and mobility of contaminants in the environment (Butler *et al*., 1999). For most organic compounds, column leaching experiments are the most appropriate methods of choice due to their simplicity and cost effectiveness. Columns made of suitable inert material (e.g. glass, stainless steel, aluminium) are usually packed with soil or suitable adsorbent and then saturated and equilibrated prior to the leaching process. To this end, column leaching studies with organic and inorganic contaminants have been performed in various regimes to elicit mobility information on a test substance and its transformation products that may not be available from batch experiments (Akortia *et al.*, 2016).

2.8.4. Interaction of PBDEs with other contaminants in soil

Soils may often be polluted with multiple contaminants in a manner which could result in possible chemical interaction with each other, thus affecting their determination in matrices as well; hence complex formation is a likely phenomenon in this regard. PBDEs may be engaged in chemical interactions with trace metals and anions on contaminated sites leading to the formation of coordination compounds. Most coordination compounds contain a metal atom or ion (Mn^+) as the central part of the structure and surrounded by molecules or ions referred to as ligands (i.e. “to bind”). Theoretically, PBDEs can form chemical (often reversible) reactions with a halogenated compound (e.g. HBr) which can result in the split of the PBDE structure (Figure 1.1) and form other metabolites as well as potential ligands that can be taken up by available trace metals present on the contaminated site (Figures 2.3a, b, and c).

Ligands can be either neutral (PBDEs) molecules or anions and are able to donate lone pairs of electrons,

which can easily be accepted by trace metals with empty d-orbital in order to form coordination compounds. It can result in the formation of other positively charged metabolites that may attract an anion (Figure 2.4) in order to be a stable or neutral ligand, thereby making the compound unavailable to allow for possible detection in a particular matrix. The formation of brominated phenol as well as possible formation of brominated benzene is a likely occurrence. The major metabolites formed (Figure 2.3a) is 2, 4, 5-tribromophenol (TBP), and an unstable radical which may further form brominated benzene (1, 2, 4, 5- tetrabromobenzene). However, 2, 4, 6-TBP, which is often the derivative formed is also found in the environment among marine species and in the ocean. The natural production of most brominated organic chemicals is common and variable in the marine environment, where the precursors for their biosynthesis are readily available. Consequently, these can be found in the terrestrial environment as a result of atmospheric deposition and sea spray activities. For example, the production and use of 2, 4, 6-TBP in the laboratory as a reactive flame retardant intermediate or as wood preservative may result in its presence in the environment through various waste streams (HSDB 2003). Most bromophenols have also been identified in vehicle emissions of leaded petrol (Muller and Buser 1986). They have been found to partition to soils and sediments, and are generally not biodegradable, hence persist in the environment for long periods. The presence of bromophenols can form coordination compounds with available trace elements especially in soil (Figure 2.3c and 2.4), which may result in enhancing or attenuating their toxicity.

3.0. Alternative FRs other than PBDEs

3.1. Why replace PBDEs?

Halogenated FRs (HFRs) have been the most commonly used compounds in many different applications as they can be added to plastics without altering the properties, while preserving the total colourability (commonly up to 5% in polyurethane foams in furniture and up to 20% in plastic of some electronic housings) (Aschberger *et al.*, 2017; Shaw *et al.,* 2010; American Chemical Council, 2016). They are also highly effective for reducing heat release rates of commodity polymers. Bromine interacts with the fire cycle in the gas phase to stop the chemical chain reaction that leads to flame formation and a self-sustaining fire. In essence, brominated FRs either prevent a fire fromstarting in the first place, or significantly slowit down. The future use of some brominated FRs (BFR) is however becoming highly questionable as they have been identified as global contaminants and are associatedwith adverse health effects including potential reproductive, developmental, and neurological effects (Aschberger *et al.*, 2017; Birnbaum and Staskal, 2004; ARCADIS, 2011). The most extensively used BFRs have been tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD) and three commercial mixtures of polybrominated diphenyl ethers (PBDEs): decabromo-diphenylether (deca-BDE), octabromodipheylether (octa-BDE) and pentabromo-diphenylether (penta-BDEs) (Shaw et al., 2010). PBDEs and polybrominated biphenyls (PBBs) have been restricted in the EU since 2004 (European Parliament and Council, 2011) and the production of penta- and octa- BDE has been phased out in the US since 2004 (US-EPA, 2008). Penta-BDE and octa-BDE have been identified as persistent organic pollutants (POP) (SFT, 2009), and Penta-BDE is already listed as a hazardous substance under the Water Framework Directive (WFD), while octa-BDE and deca-BDE are listed among the substances to be monitored (European Parliament and Council, 2000). Deca-BDE andHBCDwere included by the European Chemicals Agency (ECHA) in the list of candidates for Authorisation under REACH Article 57d as substances of very high concern (SVHC) based on PBT (persistent, bioaccumulating, toxic) properties. 1 TBBPA is registered under REACH and is currently not subject to any REACH restriction processes. Tris(2-chloroethyl) phosphate (TCEP) is a representative of the chlorinated FRs and has been included in Annex XIV of REACH (“Authorisation List”) because of concerns over its reproductive toxicity (Aschberger *et al.*, 2017).

Humans may be exposed to HFRs entering the environment through multiple pathways, such as emissions during manufacturing, from products in use, leaching from landfills, combustion or recycling at the end of the products' life. Due to their persistence HFRs can travel long distances and bioaccumulate; some were even found in human breastmilk (Shaw and Kannan, 2009; Fromme *et al.*, 2016). Children's exposure to HFRs through indoor air dust has also been indicated in the literature (Mizouchi *et al.*, 2015). Furthermore, HFRs are of concern because of their propensity to produce toxic fumes and acids (hydrobromic and hydrochloric acids, organo-irritants, dioxins/furans [PCDD/F]) during fire (Stec and Hull, 2010). These concerns have initiated a search for alternative flame-retardant additives with comparable FR performance but with less adverse effects (Aschberger *et al.,* 2017).

3.2. Possible Alternatives to PBDEs

3.2.1. Halogen based Flame retardant

This class includes organ chlorines such as chlorendic acid derivatives and chlorinated paraffin; organobromines such as decabromodiphenyl ether (decaBDE), decabromodiphenyl ethane (a replacement for deca BDE). Organo-halogen chemicals (including all BFRs) to be banned globally. The challenges of finding substitutes for banned halogen-containing flame retardants include:

- Lower flame retardancy: Only 10 wt% of BFRs is equivalent to about 30-50% by wt of inorganic FRs. High cost: Inorganic FRs is low-cost but require high loading. New HFFRs, on the other hand, are mostly costlier. The cost ratios (£) of BF-FR with phosphorous based and nonphosphorous based HFFR are about 1:6 and 1:2 respectively.
- Higher thermal stability: Many HFFRs decompose at higher temperature (about 400 °C) than their halogenated counterparts (about 3300C).
- Melt-dripping: Melt dripping occurs with most polymers e.g. polyethylene, polypropylene, PET, ABS and so on. Flammable drips act as secondary ignition sources. FRs should make drips non-flammable.
- Deterioration in Mechanical Properties: The deterioration of mechanical properties increase proportionately with the amount of FR. Therefore, the deterioration is more with less efficient FRs (Van der Veen and de Boer, 2012).

3.2.2. Organophosphorus compounds

This class includes organophosphates such as triphenyl phosphate (TPP), resorcinol bis (diphenylphosphate) (RDP), Bisphenol A diphenyl phosphate (BADP), and tricresyl phosphate (TCP); phosphonates such as dimethyl methyl phosphonate (DMMP) and phosphinates such as aluminum diethyl phosphonate (Weil and Levchik, 2009; Schartel, 2010). Phosphorus-containing flame retardants cover a wide range of inorganic and organic compounds and include both reactive products which are chemically bound into the polymer material as well as additive products which are integrated into the material by physical mixing only (Hollingbery and Hull, 2010). They have a broad range of applications, and a good fire safety performance. The most important phosphorus-containing flame retardants are phosphate esters, phosphonates and phosphinate. Phosphorus-containing flame retardants are widely used in standard and engineering plastics, polyurethane foams, thermosets, coatings, and textiles. Phosphate esters are mainly used as flame retardant plasticizers in polyvinylchloride (PVC, alkyl/aryl phosphates) and engineering plastics, particularly in polyphenylene oxide/high impact polystyrene (PPO/HIPS), polycarbonate/ acrylonitrile butadiene styrene (PC/ABS) blends and polycarbonate (PC, e.g. triphenylphosphate, resocinol-and bisphenol A-bis-(diphenyl) phosphate). The latter are widely used in IT housings requiring high fire safety levels. Other applications include phenolic resins and coatings. Phosphates, phosphonates and phosphinates are used as reactive phosphorus containing flame retardants in flexible polyurethane foams for automotive and building applications. Additive organic phosphinates are a new class of flame retardants for use in engineering plastics, particularly in polyamides. Specific reactive phosphorus flame retardants are used in polyester fibres and for wash resistant flame retardant textile finishes. Other reactive organophosphorus compounds can be used in epoxy resins in printed circuit boards. Flame retardant grades based on red phosphorus are mainly used in glass fibre reinforced polyamide 6 and 66. Further applications are in polyethylene and ethylene vinyl acetate (EVA), polyurethane foam, and thermosettings resins (unsaturated polyesters and epoxies). Ammonium polyphosphate grades are primarily used in intumescent coatings. They are also found in rigid and flexible polyurethane foams and polyolefins (injection moulded), in formulations for unsaturated polyesters, phenolics, epoxies and coatings for textiles (Jadhav, 2018).

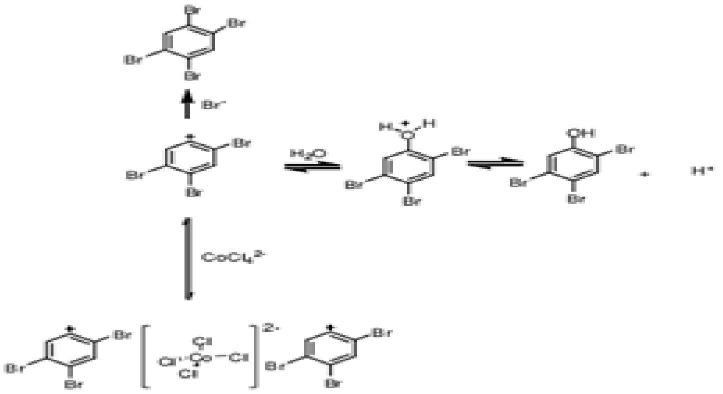

Figure. 2.4. An anionic complex formation of PBDE radical metabolite (Akortia *et al.,* 2016).

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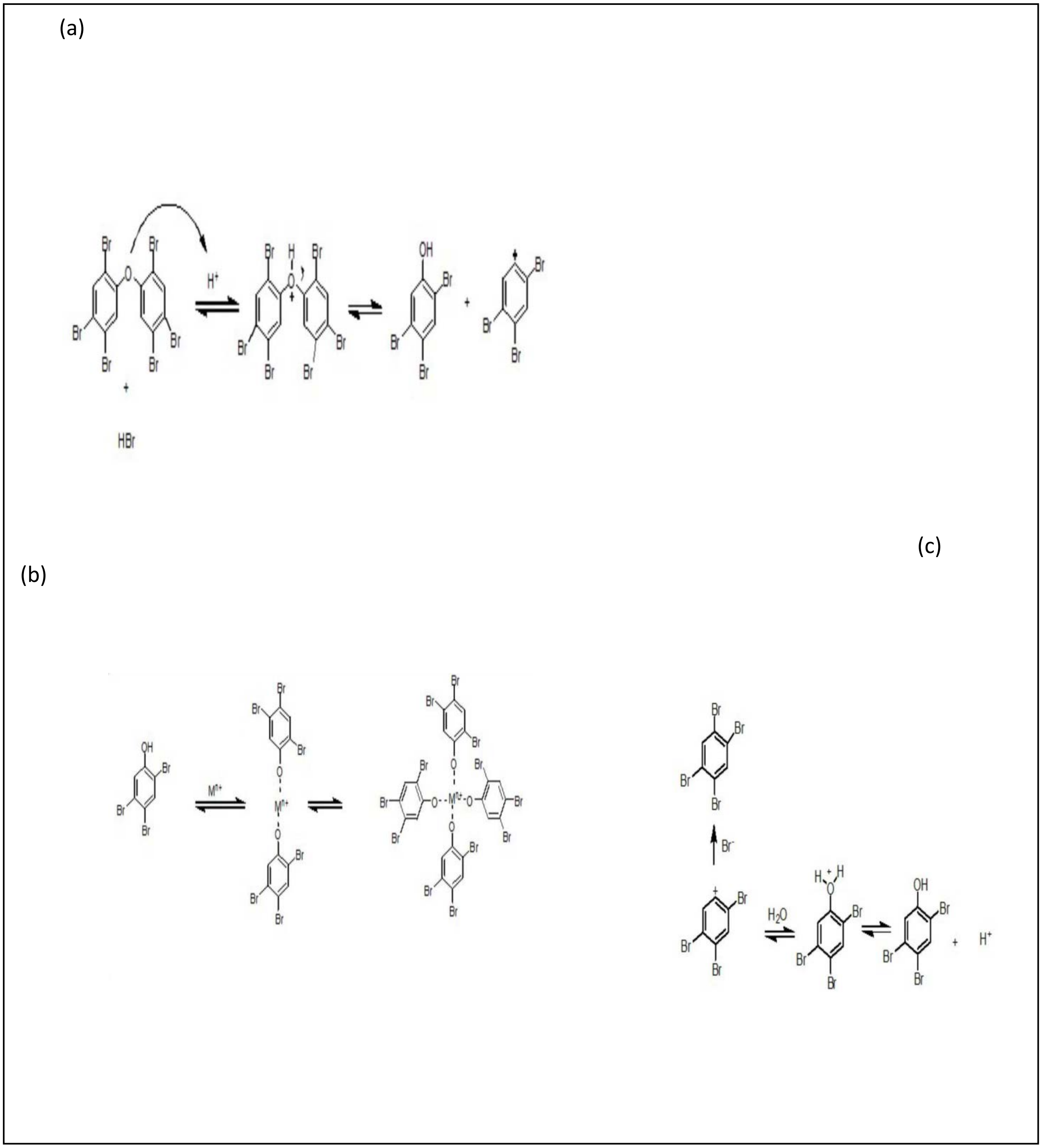

Figure 2.3. A chemical reaction between PBDE and a halogenated compound (HBr) [(a),(b)]; metal-Ligand interaction of a brominated phenol (c) (Akortia *et al.*, 2016).

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3.2.3. **Inorganic flame retardants**

The most common inorganic flame retardants are the hydroxides or aluminium and magnesium, huntite and Hydromagnesite (Hollingbery and Hull, 2010b; Hollingbery and Hull, 2012; US EPA 2005; Jadhav, 2018). Aluminium trihydroxide (ATH) is by far the most widely used flame retardant. It is very inexpensive, but usually requires higher loadings in polymers of up to more than 65%. Its mode of action is based on the release of water (Endothermic process) which cools the polymer and dilutes the flame zone. Magnesium hydroxide (MDH) is used in polymers which have higher processing temperatures, because it is stable up to temperatures of around 310 °C versus ATH which decomposes around 210 °C. Aluminum hydroxide flame retardants (white powder) for processing temperatures up to about 210 °C, for wire and cable, electronic and electrical components based on thermosets resins, building materials, mass transportation, paints and varnishes, paper and plaster with organic binder. Magnesium hydroxide flame retardants (white powder) for processing temperatures up to about 310 °C for wire and cable, electronic and electrical components based on polyamide resins, building materials. There are other minerals that show flame retarding effects and are used in commercial applications. Most of them are used as synergists i.e. they enhance the performance of other flame retardants or they are used for specific effects like the suppression of smoke formation, increasing char formation etc. For example, borates are used as mixtures of boric acids and borax as flame retardants for cellulose (cotton) and of zinc borate for PVC and other plastics like polyolefins, Elastomer, polyamides, or epoxy resins. In halogen-containing systems, zinc borate is used in conjunction with antimony oxide (mainly to reduce cost), while in halogen-free systems it is normally used in conjunction with ATH, MDH or red phosphorus. In some particular applications zinc borate can be used alone. Boron containing compounds act by stepwise release of water and formation of a glassy coating which protects the surface. Zinc compounds were initially developed as smoke suppressants for PVC (Zinc hydroxystannate) (Jadhav, 2018). Later it was found that they also act as flame retardants in certain plastics mainly by promoting char formation. Other inorganic fillers like talcum or chalk (calcium carbonate) are sometimes called flame retardants, their mode of action is simply by dilution, i.e. they they reduce the amount of polymer and hence the fire load (Jadhav, 2018).

3.2.4. Nitrogen based Flame Retardants

Nitrogen compounds are a small but rapidly growing group of flame retardants (FR) which are in the focus of public interest concerning environmentally friendly flame retardants. Today their main applications are melamine for polyurethane flexible foams, melamine cyanurate in nylons, melamine phosphates in polyolefins, melamine and melamine phosphates or dicyandiamide in intumescent paints, guanidine phosphates for textiles and guanidine sulfamate for wallpapers (Jadhav, 2018). Their main common advantages are their low toxicity, their solid state and, in case of fire, the absence of dioxin and halogen acids as well as their low evolution of smoke. Their efficiency lies between that of halogen compounds and that of aluminum trihydrate and magnesium hydroxide. The metallic hydroxides split off water and are environmentally friendly, but their low activity requires high concentrations which change the mechanical properties of the matrix that they are applied to. In contrast to many halogen compounds, flame retardants based on nitrogen do not interfere with the set of stabilizers added to every plastic material (Jadhav, 2018). Recyclability has become important as many plastics are recycled. Flame retarded materials based on nitrogen compounds are suitable for recycling as the nitrogen flame retardants have high decomposition temperatures. In the field of cable jacketing they evolve less corrosive gases during combustion and do not damage the electrical installations. Flame retardants based on nitrogen are environmentally friendly because they do not add any new element to those already present in the polymers such as polyurethanes, nylons and ABS. In regard to waste disposal they are comparable with fertilizers as they possess the same elements of importance, namely nitrogen and phosphorous. In comparison with metallic hydroxides they are more efficient and deteriorate the mechanical (Jadhav, 2018).

3.2.5. Silicon based flame retardants

Silicon-based materials are potential flame retardants as they produce protective surface coatings during a fire, caused by a low rate of heat released. Low levels of silicone in certain organic polymer systems have been reported to improve their LOI and UL-94 performance. Some compounded silicone (polydimethylsiloxane-type) contains dry powders with a variety of organic plastics. Particularly in PS, they showed that an additive level, as low as 1 to 3%, reduces the rate of heat released by 30 to 50%. They reported similar improvements in HIPS, PP, PS-blends EVA. These compounds can either be physically mixed with the base material (additive flame retardants) or chemically bonded to it (reactive flame retardants).Despite restrictions on further production in some countries, consumer products previously treated with banned retardants are still in use and continue to release toxic chemicals into the environment, and the worldwide use of organohalogens retardants continues to increase (Xiao *et al.,* 2014).

3.2.6. Intumescent Flame retardants

Intumescences is the result of a combination of charring and foaming at the surface of the burning polymer, which protects the underlying material from the action of the heat or flame. Intumescent FRs (IFRs) is often used for applications requiring high levels of flame retardancy (Jadhav, 2018). They are highly efficient and low toxic. They provide very robust fire safety and flame resistance performance. The carbon agent forms multicellular charred layers, the char may be soft or hard (Wang *et al.,* 2014). Soft char IFRs: composed of a carbon source pentaerythritol (PER), acid source (ammonium polyphosphate) and a gas-blowing additive (melamine) harder char IFRs: composed of sodium silicates and graphite. These are suitable for use in plastic pipe firestops as well as exterior steel fireproofing. PER is quite costly. A possible substitute is green carbon agent is chitosan (CS), obtained by the alkaline deacetylation of abundantly naturally occurring chitin. A good synergistic effect observed when chitosan/urea compound based phosphonic acid melamine salt (HUMCS), was added to an IFR system for polypropylene (PP) (Li *et al.*, 2014). A reactive, intumescent, HFFRs 2-({9-[(4, 6-diamino-1, 3, 5-triazin- 2-yl) amino]-3,9-dioxido-2,4,8,10-tetraoxa-3,9-diphosphaspiro [5.5] undecan-3-yl}oxy) ethyl methacrylate (EADP), synthesized from phosphorus oxychloride, pentaerythritol, hydroxyethyl methacrylate, and melamine. EADP (Figure 2) exhibited excellent thermal stability and char-forming ability without affecting tensile strength of polypropylene (Kim and Nguyen, 2008; Jadhav, 2018).

Rigid polyurethane foam (RPUF) is very flammable and releases toxic gases while burning. Traditional IFRs are mixtures, and are not compatible with the RPUF matrix (Wu *et al.*, 2014). A phosphorousnitrogen (P-N) containing IFR, toluidine spirocyclic pentaerythritol bisphosphonate (TSPB), exhibited better compatibility with RPUF and lesser negative influence on the mechanical properties of TSPB-RPUF forming compact and smooth char (Gu *et al.*, 2015). Waterborne polyurethane (WPU) has good applicability including fabric coating as against conventional solvent borne polyurethanes. Octahydro-2, 7-di (N, N-dimethylamino)-1, 6, 3, 8, 2, 7- dioxadiazadiphosphecine (ODDP), with bi-phosphonyl in a cyclic compound, was synthesized. ODDP reacted phosphorus-nitrogen synergistic HFFR waterborne PU (DPWPU) has excellent flame retardancy due to the presence of ODDP. The LOI value of DPWPU is 30.6% with UL-94, V-0 classification obtained at 15 wt % ODDP (Sinha *et al.*, 2003; Jadhav, 2018).

3.2.7. Synergist

The most widely used antimony synergist is antimony trioxide, antimony pentoxide and Sodium antimonate (Jadhav, 2018).

i. **Antimony Trioxide:** Approximately 20,000 metric tons of [1309-64-4] (commonly referred to as antimony oxide), Sb2O3, was used in the United States in 1990 to impart flame retardancy to plastics. Although antimony trioxide is found in nature, it is too impure to be used. Flame-retardant grades of antimony oxides are manufactured from either antimony metal or the sulfide ore by oxidation in air at 600-800 °C.

ii. **Antimony Pentoxide:** The second most widely used antimony synergist is antimony pentoxide [1313-60-9], Sb_2O_5, produced by the oxidation of the trioxide using either a peroxide or nitric acid. Antimony pentoxide is available as a nonpigmenting colloidal suspension in either water or organic media or as an agglomerated powder.

iii. **Sodium Antimonate:** Sodium antimonate [15593-75-6], Na_3SbO_4, another antimony synergist of commercial importance, has an antimony content of 61-63 wt % and a bulk density of 39.4-46.4 kg/m^3. It is made by oxidizing antimony trioxide using sodium nitrate and caustic.

3.2.8. Nanocomposites

Nanocomposites is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometres, or structures having nanoscale repeat distances between the different phases that make up the material. Polymer layered-silicate nanocomposites (PLSNs) with silicate enhance mechanical properties, increase heat-distortion temperatures, improve thermal stability, decrease gas/vapour permeability and reduce flammability (Gilman, 1999). Nanomaterials such as carbon nanotubes (CNTs) and nanoclays have been demonstrated to act as very effective/synergistic co-additive in some FR applications (Aschberger *et al.*, 2017; Beyer, 2003; Kashiwagi *et al.*, 2005a). When properly dispersed in polymer matrices they enable a reduction of the loading of other FRs and improve their fire performance (see Figure. 3.1) which is particularly interesting for HFFR. Polymer nanocomposites are also attractive because they have the potential to introduce true multifunctionality by improving other properties such as mechanical properties, conductivity and electromagnetic shielding (Aschberger *et al.*, 2017; Morgan and Wilkie, 2006).

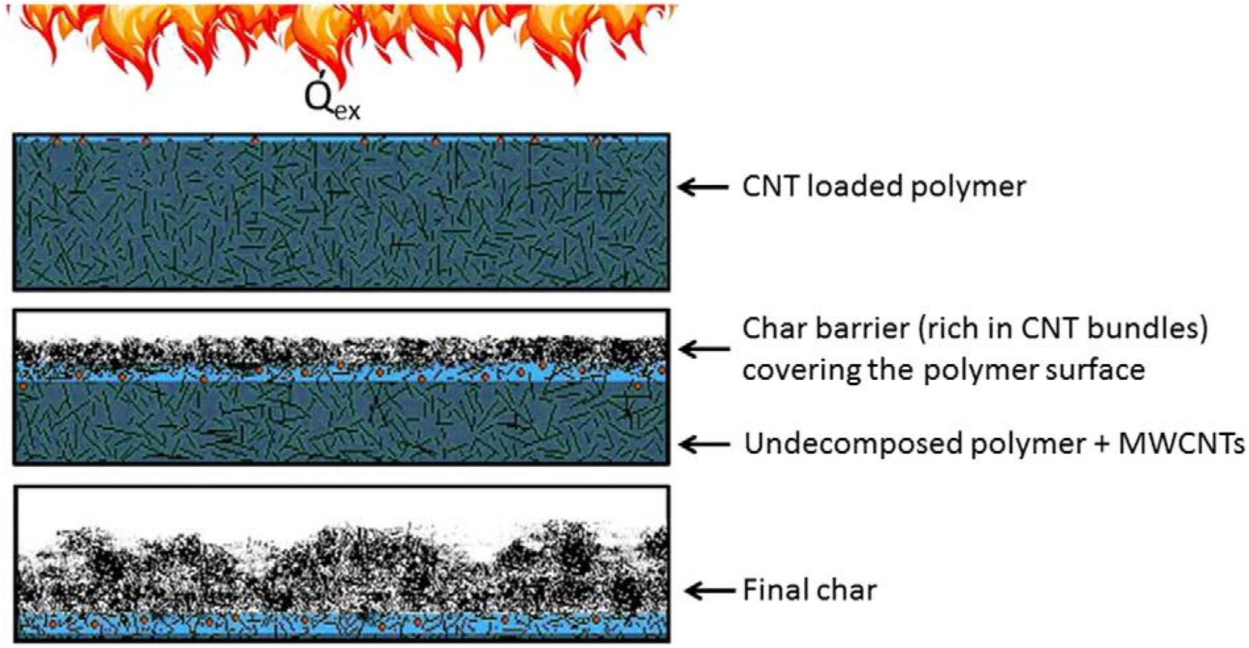

Figure. 3.1. MWCNTs as fire protection promoters (adapted from (Kashiwagi *et al.*, 2005b).

The use of P–N flame-retardant with montmorillonite (MMT) as a flame-retardant synergist for flame-resistant thermoplastics such as PP, PA6, and PA66 has been reported (Singla *et al.*, 2012). Chemically, montmorillonite is hydrated sodium calcium aluminium magnesium silicate hydroxide (Na, Ca) 0.33 (Al, Mg) 2 (Si4O10) (OH) 2 •nH2O. Montmorillonites swell or expand considerably more than other clays due to water penetrating the interlayer molecular spaces and concomitant adsorption. By exchanging sodium cations for organic cations the surface energy of MMT decreases and the interlayer spacing expands. The resulting material is called organoclay (Zhong *et al.*, 2014). Thermoplastic poly (ester ether) elastomers (TPEEs) are easily ignited and rapidly burned. TPEE nanocomposites with phosphorus-nitrogen (P-N) flame retardants and organic montmorillonite (o-MMT) were prepared by melt blending. A significant fire-retardant effect was induced in TPEE and rendered a V-0 classification in the UL 94 test (Bourbigot *et al.*, 2000). Organically treated layered silicates (clays), carbon nano-tubes/nano-fibres, or other submicron particles at low loading (1-10 wt%) are used for polymer nanocomposites. The polymer nanocomposites greatly lower the base flammability of a material. Recent research has suggested that combining nanoparticles with traditional fire retardants (e.g. intumescent) or with surface treatment (e.g. plasma treatment) effectively decreases flammability (Babushok and Tsang, 2000). When polymer nanocomposite is used, very little additive is needed (no great cost increase) and polymer dripping/flow while burning is reduced. The composite may have multifunctional performance (ex: electrical conductivity from carbon nanotubes) and a balance between flammability and mechanical properties may be maintained (Jafhav, 2020).

Therefore, for a country like Nigeria where e-wastes is poorly managed, it is imperative that nanocomposites additives are utilized in the manufacturing of most of the the consumers' products which requires the incorporation of flame retardancy because the main FR mechanism of nanomaterials like CNTs during thermal decomposition is that they promote the formation of a char layer covering the polymer surface, acting as an insulating barrier. This barrier limits heat transfer and diffusion of oxygen into the material and reduces the escape of volatile, combustible degradation products to the flame (Aschberger *et al.*, 2017; Kashiwagi *et al.*, 2005b; Kashiwagi, 2007). In addition CNTs can increase the strength of the material, make it more fatigue-resistant and improve its electrical properties. CNTs act synergistically to other FRs and have for example been suggested for application in textiles or polymer composites (Aschberger *et al.*, 2017; NANOCYL S.A., 2012; Nanotechproject, 2012; De Volder *et al.*, 2013; US-EPA, 2013).

4.0. Conclusion and Recommendations

This review reveals the occurrence of PBDEs in various consumer products and various possible alternatives to PBDEs have been evidentiated. However, to date, very little research has been conducted into synergistic interactions and effects from multi-contaminant exposure in various environmental media. Although many researchers have reported on the presence of PBDEs in various environmental compartments, comparatively little is known about their presence in aquatic ecosystems/marine environment. The greatest source of uncertainty regarding the movement and fate of PBDEs in abiotic matrices is the extent of degradation in these environments. As such, the degradation of BDE-209 is of particular importance as reports indicate its current usage, and its degradation may contribute substantially to the environmental enrichment of lower-brominated and more toxic congeners.

Toxicological end points have demonstrated that PBDEs are developmental neurotoxicants, that they disrupt the endocrine system functioning and that they are likely carcinogens. However, complete toxicological evaluation is currently lacking regarding any of the commercially available PBDE mixtures, as well as individual congeners. Much of the studies have been performed using commercial PBDEs with unspecified mixtures of congeners. Dose-response relationships concerning many PBDE congeners on aquatic species are not adequately established. Thus, toxicological studies with sentinel species such as birds, fish, carp, seals and otters are needed to derive threshold values for the harmful effects of PBDEs in marine ecosystems. As more novel brominated flame retardant chemicals are being marketed as replacements for PBDEs; nanocomposite (CNTs) are recommended as a more suitable alternative to PBDEs owing to their flame retardancy mechanism; ability to reduces the escape of volatile, combustible degradation products to the flame; as well as improve mechanical strength and electrical properties of the material.

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