

An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release

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Abstract

Brominated flame retardants (BFRs) are used in a variety of consumer products and several of those are produced in large quantities. These compounds have been detected in environmental samples, which can be attributed to the anthropogenic uses of these compounds. Brominated flame retardants are produced via direct bromination of organic molecules or via addition of bromine to alkenes; hence, an overview of the production and usage of bromine over the past three decades is covered. Production, application, and environmental occurrence of high production brominated flame retardants including Tetrabromobisphenol A, polybrominated biphenyls, Penta-, Octa-, Deca-brominated diphenyl ether (oxide) formulation and hexabromocyclododecane are discussed. Crown Copyright © 2003 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Brominated flame retardants; Usage; Application; Polybrominated biphenyls; Polybrominated diphenyl ethers; Tetrabromobisphenol A; Hexabromocyclododecane

1. Introduction

Advances in polymer science over the past 50 years has led to the introduction of a large number of polymers with different properties and applications. As a result, we are surrounded by a wide variety of polymers in clothing and furniture, to electronics, vehicles and computers. In fact modern cars contain in excess of 100 kg of various polymers. Most of these polymers are petroleum-based and hence are flammable. In order to meet fire safety regulations, flame retardants are applied to combustible materials such as plastics, wood, paper, and textiles. Flame retardants (FR) are materials added or applied to a material to increase the fire resistance of that product (EHC-192, 1997). A list of annual production figures of major polymers along with the brominated flame retardants (BFRs) commonly used to

increase their fire resistance is given in Table 1 (Arias, 2001).

With the increasing usage of polymeric materials in construction, electronic and computer equipment, global market demand for the use BFRs continues to grow substantially; for example the global market demand for BFRs in 1990 was 145 000 tonnes (Pettigrew, 1994), grew to over 310 000 tonnes in 2000 (BSEF, 2000), which represents a growth of over 100% over the past decade.

The idea of flame retardant materials dates back to about 450 BC, when the Egyptians used alum to reduce the flammability of wood. The Romans (about 200 BC) used a mixture of alum and vinegar to reduce the combustibility of wood (Hindersinn, 1990). Today, there are more than 175 chemicals classified as flame retardants. The four major groups are inorganic, halogenated organic, organophosphorus and nitrogen-based flame retardants which account for 50%, 25%, 20% and >5% of the annual production, respectively (EHC-192, 1997).

To understand the modes of action of flame retardants, it is essential to become familiar with the combustion process.

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Table 1
Global annual production of polymers in 2000 and their BFR content (Arias, 2001)

Polymer	BFR content (%)	Type of BFR	Annual production (1000 TPA)
Polystyrene foam	0.8–4	HBCDD	600
High-impact polystyrene	11–15	d-PBDE, Br PS	350
Epoxy resin	19–33	TBBPA	300
Polyamides	13–16	d-PBDE, Br PS	200
Polyolefins	5–8	d-PBDE, DBS	200
Polyurethanes	10–18	p-PBDE, Br Polyols	150
Polyterephthalate	8–11	Br PS, der-TBBPA	150
Unsaturated polyesters	13–28	TBBPA	150
Polycarbonate	4–6	Br PS, der-TBBPA	100
Styrene copolymers	12–15	o-PBDE, Br PS	50

HBCDD, hexabromocyclododecane; PBDE, polybrominated diphenyl ethers (d: deca, o: octa, and p: penta formulations); TBBPA, tetrabromobisphenol A, (der: derivative); Br PS, brominated polystyrene; DBS, propylene dibromo styrene; Br Polyols, esters of TBBPA; TPA, tonnes per annum (metric).

Combustion is a gas phase reaction involving a fuel source and oxygen. As illustrated in Fig. 1, the four steps involved in the combustion process are preheating, volatilization/decomposition, combustion and propagation (Troitzch, 1990).

Depending on the mode of action, flame retardants can act at any of the four steps involved in the combustion process, and prevent their occurrence. For example, at temperatures above 200 °C the dehydration of aluminum hydroxide takes place, which is an endothermic reaction resulting in diluting and lowering the temperature of the flame. Another effective method is to capture free radicals (highly oxidizing agents) that are produced during the combustion process; which are essential elements for the flame to propagate. Halogens are very effective in capturing free radicals, hence removing the capability of the flame to propagate. All four halogens are effective in eliminating free radicals, and the trapping efficiency increases with the size of the halogen (i.e., I>Br>Cl>F). Therefore, all organohalogen compounds could

be a good form of storage and delivery of halogens to be used as flame retardants. However, not all of the halogens are suitable for use in flame retardants. Fluorinated compounds are very stable and decompose at much higher temperatures than most organic matter burns, delivering their halogens too late to be effective as a FR. On the other hand, iodinated compounds are not stable and decompose at slightly elevated temperatures. Consequently, only organochlorine and organobromine compounds are used as flame retardants. With higher trapping efficiency and lower decomposing temperature, organobromine compounds have become more popular as a flame retardant than their organochlorine counterparts. Since bromine is the major component of a BFR, there is no particular restriction on the structure of the backbone. The main criteria for the usage of a compound as flame retardant are stability during the lifetime of the product and compatibility with the polymer. As a result, there are more than 75 different aliphatic, aromatic and cyclo-aliphatic compounds used as brominated flame retardants. Since bromine is the principle ingredient for BFRs, it is necessary to review the production and applications of bromine as an industrial chemical.

2. Bromine production and applications

Bromine is a member of group VII elements (halogens) and was discovered in 1826 by Antoine Balard. Bromine is a dense, mobile, dark red liquid at room temperature. Like other members of group VII, bromine is a reactive element, consequently, it is mostly found in the form of inorganic salts of the alkalis and alkaline earth metals mainly in seawater, saline lakes, and earth crust. Therefore, bromine is extracted from brines around the world. The production of bromine begins with the oxidation of bromide with chlorine followed by an absorption and purification process. Currently, there are a limited number of brines around the world that have high enough concentrations of bromide to make this process commercially viable. Arkansas brine wells with

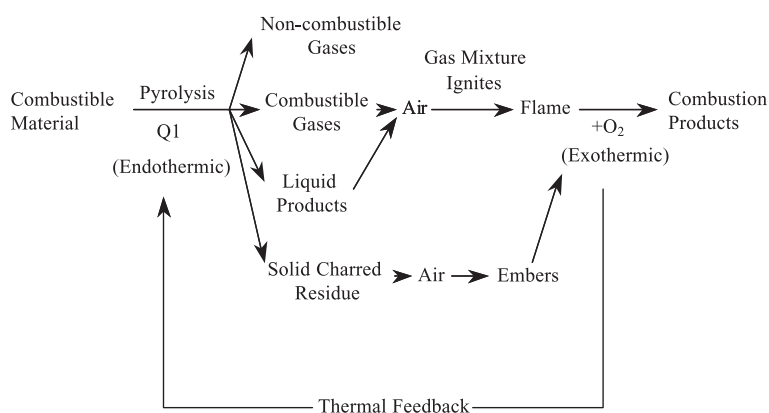


Fig. 1. The four steps of the combustion process (Troitzch, 1990).

0.38–0.5% bromide are the main source of bromine in the US produced by Great Lakes Chemicals and Albemarle Corporation (OECD Status Report, 1993). The annual bromine production in the US in 2000 was 229 000 tonnes. The Dead Sea with a bromide concentration of 0.5% is a viable source of bromine for the Dead Sea Bromine Corporation in Israel. The annual bromine production in Israel was 210 000 tonnes in 2000. China, with an annual production of 45 000 tonnes, is the third largest bromine producer in the world (Lyday, 2000). The majority of bromine production in EU countries takes place in the UK, i.e., 32 000 tonnes per year. Japan produces 20 000 tonnes of bromine mainly from seawater (Lyday, 2000). To a lesser extent, bromine is produced in the former USSR and India, with annual production of 5200 and 1500 tonnes, respectively. Due to its reactivity and toxicity, transport of bromine is subject to the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) regulating the transport of hazardous goods; hence, the manufacturing of organobromine compounds takes place in the vicinity of production sites.

Bromine is currently used in a large number of products; such as flame retardants, pesticides, gasoline additives, drilling fluids, and biocides (Fig. 2). In the 1960s and 1970s, the majority of bromine demand was for ethylene dibromide (1,2 dibromo ethane) [106-93-4], a gasoline additive used to prevent lead fouling. In the 1960s, gasoline additives accounted for 77% of the bromine consumption in US. The majority of bromine used for pesticides is in the form of methyl bromide, which is used as fumigant; however, methyl bromide is restricted under the Montreal protocol. Currently, the majority of the global production of bromine (38%) is used in the manufacturing of brominated flame retardants. Drilling fluids, biocides and miscellaneous applications, accounted for 10%, 9%, and 20%, respectively, of the global bromine production in 2000. A sum-

Table 2
Annual global production of bromine between 1976 and 2000 (Lyday, 2000)

	1976	1980	1986	1990	1995	2000
United States	234	189	141	177	218	229
Israel	23.1	48.7	105	135	130	210
European Union	55	49	48	50	31	32
Former USSR	70	74	65	60	5.1	5.2
China	nil	<1	??	15	41	45
Japan	13	13	15	15	15	20
India	0.5	0.4	1.2	1.3	1.5	1.5

All values in 1000 metric tonnes.

mary of the global bromine demand between 1976 and 2000 is given in Table 2.

3. Brominated flame retardants

BFRs are divided into three subgroups depending on the mode of incorporation of these compounds into the polymers: brominated monomers, reactive and additive. A brominated monomer such as brominated styrene or brominated butadiene is used in the production of brominated polymers, which are then blended with nonhalogenated polymers or introduced into the feed mixture prior to polymerization, resulting in a polymer containing both brominated and non-brominated monomers. Reactive flame retardants, such as tetrabromobisphenol A (TBBPA), are chemically bonded into the plastics. Additive flame retardants, which include polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) are simply blended with the polymers, and are more likely to leach out of the products (Hutzinger and Thoma, 1987).

Various bromofluoromethanes including dibromodifluoromethane [75-61-6] and bromotrifluoromethane [75-

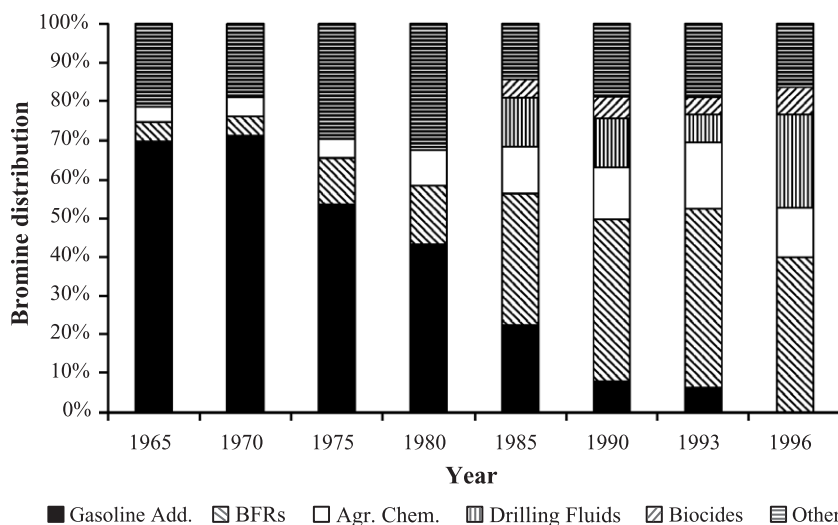


Fig. 2. Consumption distribution of bromine in the final product, all values in Grinbaum and Feiberg (2002).

63–8] have been used as fire-extinguishing agents. These types of FRs are not further addressed here.

4. Polybrominated biphenyls

Polybrominated biphenyls (PBBs) were introduced as flame retardants in the early 1970s. The commercial production of PBBs in the form of Firemaster® in the United States continued until 1976 and approximately 6071 tonnes of PBBs were produced during those 6 years. In 1973, Firemaster BP-6® and FF-1® were unintentionally mixed into cattle feed at a production site and distributed in rural Michigan. The widespread contamination of Michigan farm products that resulted from this accident led to the ban of hexabromobiphenyl flame retardants in the USA in 1974 (EHC-152, 1994). Nevertheless, the production of octabromobiphenyl and decabromobiphenyl formulations continued until 1979. In Europe, a mixture of highly brominated PBBs was in production in Germany until 1985, and in France, Deca-BB (Adine 0102) (EHC-152, 1994) was in production until 2000 (Hardy, 2000).

5. Tetrabromobisphenol A

Tetrabromobisphenol A (TBBPA) [79-94-7] is a reactive flame retardant with a global consumption of 210 000 tonnes, which makes TBBPA the highest volume BFR on the market. TBBPA is produced via bromination of bisphenol A in an organic solvent.

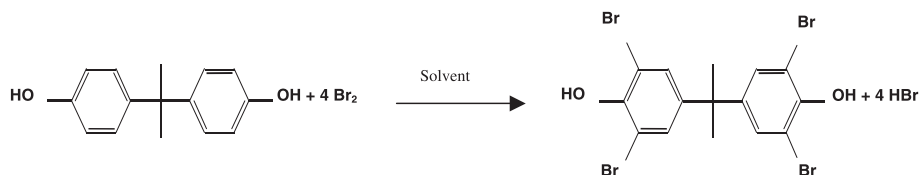
Approximately 90% of TBBPA is used as a reactive intermediate in the production of epoxy and polycarbonate resins. The main application of epoxy resins is in the manufacturing of printed circuit boards that contain approximately 20% bromine. The remaining 10% of TBBPA is transformed into derivatives such as dimethyl TBBPA and used as additive BFR in acrylonitrile-butadiene-styrene (ABS) resin and high-impact polystyrene. Bis (2-hydroxyethyl ether) TBBPA, another TBBPA derivative, is used as a flame retardant for paper and textile adhesives and coatings. Despite the primary use of TBBPA as a reactive flame retardant (covalently bond to the polymer), TBBPA has been observed in the environment. TBBPA has been detected in sewage sludge from three different sewage treatment plants in Sweden. The concentrations of TBBPA ranged between 3.6 and 45 ng/g (Sellström, 1999); similar

results have been observed in Canada (Lee and Peart, 2002). The key concern with TBBPA is its similarity in chemical structure to thyroxine (T4); Meerts et al. (2000), in *in vitro* T4-TTR assay showed that TBBPA has stronger affinity for binding with the thyroid hormone transport protein transthyretin (TTR) than the natural ligand T4. Currently, there is no regulation on the usage of TBBPA, however, a review of TBBPA is currently underway in the EU.

6. Polybrominated diphenyl ethers

Polybrominated diphenyl ethers (PBDEs) are additive flame retardants and the next highest production group of BFRs currently in use. PBDEs are produced by bromination of diphenyl ether in the presence of a Friedel–Craft catalyst (i.e., AlCl₃) in a solvent such as dibromomethane. Diphenyl ether molecules contain 10 hydrogen atoms, any of which can be exchanged with bromine, resulting in 209 possible congeners. The structure of PBDEs is similar to that of PCBs, hence the nomenclature proposed by Ballschmiter and Zell (1980) is also used for PBDEs. The reaction conditions for the bromination of diphenyl ether by various manufacturers are not disclosed. PBDEs are however, typically produced at three different degrees of bromination, i.e., Penta-BDE, Octa-BDE and Deca-BDE, and classified according to their average bromine content. Chromatograms of the three commercial products are presented in Fig. 3 (Sjödin, 2000). The global market demand for Deca-, Octa-, and Penta-BDEs in 1999 was 54 800, 3825, and 8500 tonnes, respectively; detailed historical usage along with regional breakdowns is provided in Table 3.

The bromination of diphenyl ether is rather specific due to the directing properties of the oxygen and steric hindrance, and consequently, resulting in a limited number of PBDE congener formation. For example in the commercial Penta-BDE (BromKal 70-5DE® [BK70]; Chemische Fabrik Kalk [Köln, Germany]), more than 70% of the product by weight is represented by only two major congeners, i.e., 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99) (Sjödin et al., 1998), cf., Fig. 3. Two tribrominated compounds, 2,2',4-tri-BDE (BDE-17) and 2,4,4'-tri-BDE (BDE-28) are also present in commercial Penta-BDE, but the levels of these congeners are very low in the commercial product (<0.2% by weight in Penta-BDE). These tri-BDEs are precursors in the formation of one of the



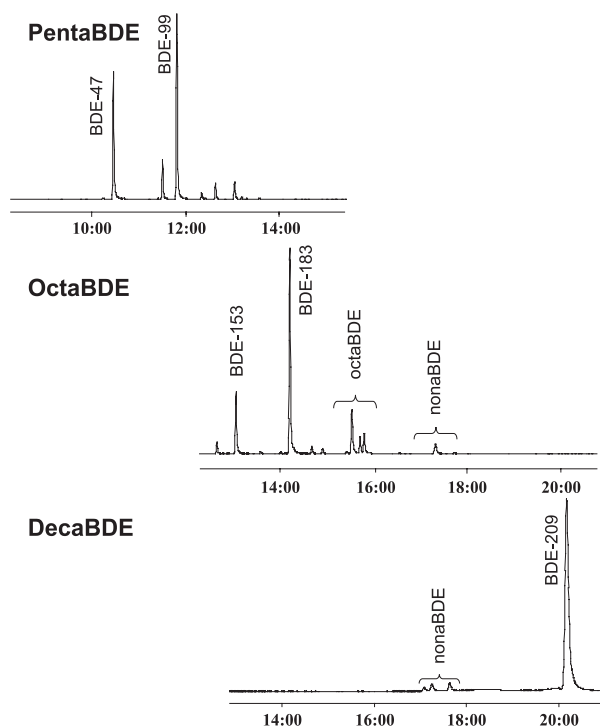


Fig. 3. Chromatograms of three PBDE commercial products (Sjödin, 2000).

major congeners in penta-BDE, i.e., BDE-47. Continued bromination of BDE-47 yields mainly 2,2',4,4',5-penta-BDE (BDE-99) and to a lesser extent 2,2',4,4',6-penta-BDE (BDE-100). The percentages of BDE-99 and BDE-100 in BK70[®] are 35% and 6.8%, respectively. The favored formation of BDE-99 might result from the *ortho/para* directing property of the bromine atoms in BDE-47 and/or steric hindrance. This initial selectivity in the bromination of diphenyl ether, up to tetra- and penta-BDEs, limits the number of congeners that may be formed by continued conventional bromination. Hence, further bromination yields 2,2',4,4',5,5'-hexaBDE (BDE-153) and 2,2',4,4',5,6'-hexaBDE (BDE-154), that also are present in commercial Penta-BDE. Still further bromination yields 2,2',3,4,4',5',6-heptaBDE (BDE-183), which is the major congener found in currently produced Octa-BDE (Great Lakes Chemical), cf., Fig. 3. Also found in Octa-BDE products are octa- and nona-BDEs of which only 2,2',3,4,4',5,5',6-octaBDE (BDE-203)

Table 3
Global production of BFRs between 1989 and 1999

	1989 ^a	1994 ^b	1999 ^c
Europe	28.0	32.5	30.9
Asia	28.7	38.5	113.9
United States	50.0	65	58.7
Total	106.7	136	203.5

All values in 1000 metric tonnes.

^a From Flame Retardants Specialty Updated program 1990.

^b Estimated values from Pettigrew (1994).

^c From BSEF (2000).

has been structurally identified (Sjödin, 2000). Commercially produced Deca-BDE contains mainly 2,2',3,3',4,4',5,5',6,6'-decaBDE (BDE-209) and only low levels of nona-BDEs, cf. Fig. 3.

Deca-BDE [1163-19-5] is a white powder, with 83% bromine content by weight. Deca-BDE formulation consists mainly of BDE-209 (97–98%), with a small amount of nona-BDEs (0.3–3%). Deca-BDE is a general purpose flame retardant and is used in virtually any type of polymer including: polycarbonates, polyester resins, polyolefins, ABS, polyamides, polyvinyl chloride, and rubber. Deca-BDE combined with antimony oxide is used in processes that require high-temperature processing such as high-impact polystyrene used in TV and computer monitor cabinets (Larsen, 1978). BDE-209 is the main congener observed in sediments and sewage sludge from various locations (Zegers et al., 2000; de Boer et al., 2000a; Allchin et al., 1999; Hale et al., 2001). BDE-209 has been detected in human blood serum from Sweden and the US (Sjödin et al., 1999, 2001), and recently BDE-209 has been detected in peregrine falcon eggs in Sweden (Sellström et al., 2001) and Norway (Herzke et al., 2001). Currently, there is no regulation for the usage and disposal of Deca-BDE; however, recently European Parliament announced “a deferred ban on Deca-BDE applicable no later than 1 January 2006, unless the final result of the risk assessment currently in progress show that this substance gives no cause for concern” (EP, 2002).

Octa-BDE [32536-52-0] is a white powder which contains 79% bromine; the degree of bromination is controlled either through stoichiometry or reaction kinetics; as a result, product composition varies from batch to batch. Octa-BDE is produced in the lowest quantity and is mainly used in ABS resins. BDE-183 has been observed in human blood serum (Sjödin et al., 1999) and biota (Luross et al., 2002; Rice et al., 2002). Octa-BDE was also detected in sediment samples from the UK (Allchin et al., 1999). Recently, the EU announced an immediate ban on marketing of Octa-BDE and expressed the European Parliament's wish to introduce the ban of Octa-BDE into the ongoing legislative procedure (EP, 2002).

Penta-BDE [32534-81-9] formulation is a viscous liquid, which contains 70% bromine by weight, consists of 41–42% tetra-BDEs (mainly BDE-47), 44–45% Penta-BDEs (predominantly BDE-99 and to a lesser extent BDE-100), and 6–7% Hexa-BDEs, (BDE-153 and -154). In addition to these congeners, Sjödin et al. (1998) identified six addi-

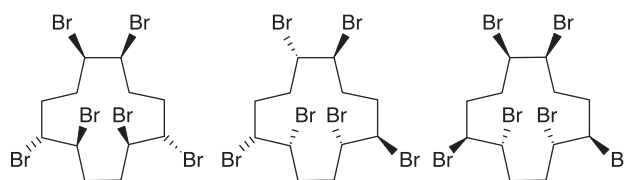


Fig. 4. Structures of α , RR SR RS [134237-5-6] (left), β , RR RS RS [134237-51-7] (middle) and γ , RS SS SR, [169102-57-2] (right) HBCDD.

tional congeners (BDE-17, -28, -66, -85, -138, and -183) as minor components of Bromkal 70-DE®. Penta-BDE is mainly used in polyurethane foam and textile. Penta-BDE formulation contains the three predominant congeners (BDE-47, -99, -100) the same found in biological matrices including human tissue (de Wit, 2002). The majority (>97%) of Penta-BDE formulation is used North America, where the concentrations of these compounds in biota and breast milk are on the rise (Luross et al., 2000; She et al., 2002; Ikononou et al., 2002; Norstrom et al., 2002; Ryan et al., 2002). The use of Penta-BDE was voluntarily withdrawn from the Japanese market (Watanabe and Sakai, 2001) and has been banned in Europe as of 2003 (EU, 2001; EP, 2002).

7. Hexabromocyclododecane

Hexabromocyclododecane (HBCDD) [25637-99-4] is a white crystalline powder, with 74.7% bromine. HBCDD is a cyclic compound produced from bromination of cyclododecatriene (a butadiene trimer), which results in the formation of three isomers (α , β and γ), with the γ isomer being the predominant product. The structures of the three isomers of HBCDD are presented in Fig. 4 (Chemical Abstracts, 1996). HBCDDs are susceptible to thermal degradation (Barontini et al., 2001). Furthermore, these congeners are not resolvable with gas chromatography techniques; however, they can be resolved using liquid chromatographic techniques (ACC, 2001). The main application of HBCDD is in polystyrene foam that is used in building construction. HBCDD has been detected in various environmental compartments including arctic air and biota (de Wit, 2002).

8. Additional information

This manuscript has provided an overview of the use and application of BFRs. Additional information on BFRs is available in a number of reports prepared by the World Health Organization, a general overview is presented in Environmental Health Criteria 192 (EHC-192, 1997), and on specific BFRs such as TBBPA and derivatives, PBBs and PBDEs are presented in Environmental Health Criteria 172 (EHC-172, 1995), 152 (EHC-152, 1994), and 162 (EHC-162, 1994), respectively. Recent reviews by de Wit (2002) and de Boer et al. (2000b) cover the environmental levels and trends.

Acknowledgements

The authors acknowledge editorial assistance provided by Mrs. Sue Quade from the University of Guelph and Mr. Richard Jones from CDC.

References

- ACC. HPV, Data summary and test plan for hexabromocyclododecane. American Chemistry Council, Brominated Flame Retardant Industry Panel (BFRIP), 1300 Wilson Blvd., Arlington, VA, December 20; 2001. 23 pp.
- Allchin CR, Law RJ, Morris S. Polybrominated diphenylethers in sediments and biota downstream of potential sources in the UK. *Environ Pollut* 1999;105:197–207.
- Arias P. Brominated flame retardants—an overview. The Second International Workshop on Brominated Flame Retardants. Stockholm: AB Firmatryck, 2001. p. 17–9.
- Ballschmiter KH, Zell M. Analysis of polychlorinated biphenyls (PCBs) by glass capillary gas chromatography. *Fresenius Z Anal Chem* 1980; 302:20–31.
- Barontini F, Cozzani V, Petrea L. Thermal stability and decomposition of hexabromocyclododecane. *Ind Eng Chem Res* 2001;40:3270–80.
- BSEF. Bromine Science and Environmental Forum, Brussels, Belgium. Data reported at http://205.232.112.21/bsef/docs/Major_Brominated.doc; 2000.
- Chemical Abstracts. 13th Collective Formula Index, 1992–1996; 1996.
- de Boer J, van der Horest A, Wester P. PBDEs and PBBs in suspended particulate matter, suspended sediment, sewage treatment plant in- and effluents and biota from the Netherlands. *Organohalogen Compd* 2000a; 47:85–8.
- de Boer J, de Boer K, Boon JP. Polybrominated biphenyls and diphenyl ethers. In: Paasivirta J, editor. The handbook of environmental chemistry. Part K, New Types of Persistent Halogenated Compounds, vol. 3. Berlin, Germany: Springer-Verlag; 2000b. p. 62–95. Chapter 4.
- de Wit C. An overview of brominated flame retardants in the environment. *Chemosphere* 2002;46:583–624.
- EHC-152. Polybrominated biphenyls. International Program on Chemical Safety, World Health Organization, Geneva, Switzerland; 1994.
- EHC-162. Brominated diphenyl ethers. International Program on Chemical Safety, World Health Organization, Geneva, Switzerland; 1994.
- EHC-172. Tetrabromobisphenol A and derivatives. International Program on Chemical Safety, World Health Organization, Geneva, Switzerland; 1995.
- EHC-192. Flame-retardants: a general introduction. International Program on Chemical Safety, World Health Organization, Geneva, Switzerland; 1997.
- EP. European Parliament Report A5-0437/2002; 2002.
- EU. European Union press release, January 30; 2001.
- Grinbaum B, Feiberg M. Bromine. Kirk–Othmer encyclopedia of chemical technology. 4th ed. New York: Wiley; 2002. Article online posting date: January 25, 2002.
- Hale RC, LaGuardia MJ, Harvey E, Gaylor MO, Mainor TM, Duff WH. Flame retardants: persistent pollutants in land-applied sludges. *Nature* 2001;412:141–2.
- Hardy M. Results presented at BSEF workshop on polybrominated diphenyl ethers. In: de Boer J, Leonard PEG, Boon JP, Law RJ, editors. IJmuiden, The Netherlands: The Netherlands Institute for Fisheries Research (RIVO); 2000.
- Herzke D, Kallenborn R, Nygard T, Sandanger T. Species dependent distribution of polybrominated biphenyls and diphenyl ethers in eggs of Norwegian bird of prey. The Second International Workshop on Brominated Flame Retardants. Stockholm: AB Firmatryck, 2001. p. 321–4.
- Hindersinn RR. Historical aspects of polymer fire retardance. In: Nelson GL, editor. Fire and polymers hazard identification and prevention. American Chemical Society Symposium Series, vol. 415. New York: American Chemical Society; 1990.
- Hutzinger O, Thoma H. Polybrominated dibenzo-*p*-dioxins and dibenzofurans: the flame retardant issue. *Chemosphere* 1987;16:1877–80.
- Ikononou MG, Rayne S, Addison RF. Exponential increase in brominated flame retardants, polybrominated diphenyl ethers in Canadian Arctic from 1981 to 2000. *Environ Sci Technol* 2002;36:1886–92.

- Larsen ER. Flame retardants, halogenated fire retardants. 3rd ed. Kirk–Othmer encyclopedia of chemical technology, vol. 10. New York: Wiley; 1978. p. 373–94.
- Lee HB, Peart TE. Organic contaminants in Canadian municipal sewage sludge: Part I. Toxic or endocrine-disrupting phenolic compounds. *Water Qual Res J Can* 2002;37:681–94.
- Luross JM, Alaee M, Sergeant DB, Whittle DM, Solomon KR. Spatial and temporal distribution of polybrominated diphenyl ethers in lake trout from the Great Lakes. *Organohalog Compd* 2000;47:73–6.
- Luross JM, Alaee M, Sergeant DB, Whittle DM, Solomon KR, Muir DCG. Spatial distribution of polybrominated diphenyl ethers and polybrominated biphenyls in lake trout from the Great lakes. *Chemosphere* 2002; 45:665–72.
- Lyday PA. Bromine, Mineral Information, United States Geological Survey, 988 National Center Reston, VA 20192. <http://minerals.usgs.gov/minerals/pubs/commodity/bromine/index.html>; 2000.
- Meerts IATM, van Zanden JJ, Luijckx EAC, van Leeuwen-Bol I, Marsh G, Jakobsson E, et al. Potent competitive interactions of some brominated flame retardants and related compounds with human transthyretin in vitro. *Toxicol Sci* 2000;56:95–104.
- Norstrom RJ, Simon M, Moisey J, Wakeford B, Weseloh DVC. Geographical distribution (2000) and temporal trends (1981 to 2000) of brominated diphenyl ethers in Great Lakes herring gull eggs. *Environ Sci Technol* 2002;36:4783–9.
- OECD. Brominated flame retardants: draft status report. Paris, France: Organization for Economic Cooperation and Development; 1993.
- Pettigrew A. Halogenated flame retardants. 4th ed. Kirk–Othmer encyclopedia of chemical technology, vol. 10. New York: Wiley; 1994. p. 954–76.
- Rice CP, Chernyak SM, Begnoche L, Quintal R, Hickey J. Comparisons of PBDE composition and concentration in fish collected from the Detroit River, MI and Des Plaines River, IL. *Chemosphere* 2002;49:731–7.
- Ryan JJ, Patry B, Mills P, Beaudoin N. Recent trends in levels of brominated diphenyl ethers (BDEs) in human milk from Canada. *Organohalog Compd* 2002;58:173–7.
- Sellström U. Determination of some polybrominated flame-retardants in biota, sediment and sewage sludge. PhD Dissertation, Stockholm University, Stockholm, Sweden; 1999.
- Sellström U, Lindberg P, Hågberg L, de Wit C. Higher brominated PBDEs found in eggs of peregrine falcons (*Falco peregrinus*) breeding in Sweden. The Second International Workshop on Brominated Flame Retardants. Stockholm: AB Firmatryck, 2001. p. 159–62.
- She J, Petreas M, Winkler J, Visita P, McKinney M, Kopec D. PBDEs in the San Francisco Bay area: measurements in harbor seal blubber and human breast adipose tissue. *Chemosphere* 2002;46:697–708.
- Sjödén A. Occupational and dietary exposure to organohalogen substances, with special emphasis on polybrominated diphenyl ethers. PhD Thesis. Stockholm University, Stockholm, Sweden; 2000.
- Sjödén A, Jakobsson E, Kierkegaard A, Marsh G, Sellström U. Gas chromatographic identification of polybrominated diphenyl ethers in a commercial product, Bromkal 70-5DE. *J Chromatogr, A* 1998;822:83–9.
- Sjödén A, Hagmar L, Klasson-Wehler E, Kronholm-Diab K, Jakobsson E, Bergman A. Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. *Environ Health Perspect* 1999;107: 643–8.
- Sjödén A, Patterson D, Bergman Å. Brominated flame retardants in serum from US blood donors. *Environ Sci Technol* 2001;35:3830–3.
- Troitzch JH. International plastics flammability handbook: principles, regulations, testing and approval. 2nd ed. Munich, Germany: Hanser Publishers; 1990.
- Watanabe I, Sakai S. Environmental release and behavior of brominated flame-retardants—an overview. *Organohalog Compd* 2001;52:1–4.
- Zegers BN, Lewis WE, Boon JP. Levels of some polybrominated diphenyl ether (PBDE) flame retardants in dated sediment cores. *Organohalog Compd* 2000;47:229–32.