5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

The commercial production of PBDEs generally involves bromination of diphenyl oxide to varying degrees. The degree of bromination is controlled either through stoichiometry or through control of reaction kinetics (Pettigrew 1993).

The commercial production of PBDEs began in late 1970s (WHO 1994a). There are no current manufacturers of technical PBDEs in the United States. About 98% of the global demand for the technical pentaBDE mixture resided in North America (Hale et al. 2003). PentaBDE and octaBDE mixtures were voluntarily withdrawn from the U.S. marketplace by their manufacturers at the end of 2004, leaving only decaBDE being marketed for use in commercial products in the United States (EPA 2010). In December of 2009, the two remaining U.S. producers of decaBDE, Albemarle Corporation and Chemtura Corporation (formerly known as the Great Lakes Chemical Corporation), and the largest U.S. importer, ICL Industrial Products, Inc., announced commitments to phase out manufacture and importation of decaBDE for most uses in the United States by December 31, 2012, and to end manufacture and import for all uses by the end of 2013 (EPA 2013j). In 2003, the EU passed a Directive to ban the marketing and use of penta- and octaBDE that took effect in 2004. In 2008, the use of decaBDE was restricted by an EU Directive on the Restriction of the use of certain Hazardous Substances (RoHS) (EC 2014; EPA 2010).

Table 5-1 lists the facilities in each state that manufactured or processed technical decaBDE in 2014, the intended use, and the range of maximum amounts of technical decaBDE that are stored on-site (TRI14 2016). The data from the Toxics Release Inventory (TRI) listed in Table 5-1 should be used with caution, however, since only certain types of facilities were required to report. The TRI is not an exhaustive list. Facilities are only required to report to the TRI if they manufacture or process more than 25,000 pounds of a TRI listed chemical during the year, or otherwise use more than 10,000 pounds, and have the equivalent of more than 10 full-time employees. According to the EPA, TRI data have certain limitations. TRI data reflect releases and other waste management of chemicals, and not exposures of the public to those chemicals. TRI data alone are not sufficient to determine exposure or calculate potential adverse effects on human health and the environment.

Table 5-1. Facilities that Produce, Process, or Use Decabromodiphenyl Ether

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AR	2	1,000	99,999	7
CA	1	10,000	99,999	2, 3, 7, 8, 10
CT	1	10,000	99,999	8
GA	3	1,000	99,999	7, 8
IL	3	10,000	99,999	7
IN	1	50,000,000	99,999,999	2, 3, 4, 8
KS	1	1,000	9,999	8
MA	2	10,000	999,999	7
MS	1	10,000	99,999	7, 8
NH	1	Not reported	Not reported	Not reported
NJ	1	10,000	99,999	7
NV	1	10,000	99,999	7
NY	1	1,000	9,999	7
OH	4	1,000	99,999	2, 3, 7, 8
PA	3	100,000	999,999	1, 3, 7, 8
SC	5	10,000	99,999	7, 8
TX	2	1,000	9,999	7
VA	3	0	99,999	7

[a] Post office state abbreviations used.
[b] Amounts on site reported by facilities in each state.
[c] Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses
14. Process Impurity

Source: TRI14 2016 (Data are from 2014)

5.2 IMPORT/EXPORT

Production and importation of the final commercial PBDE, decaBDE, ended on December 31, 2013.

5.3 USE

PBDEs were used as additive flame retardants in thermoplastics. Additive flame retardants are physically combined with the polymer material being treated rather than chemically combined (as in reactive flame retardants). This means that there is a possibility that the flame retardant may diffuse out of the treated material to some extent. PBDEs were used in different resins, polymers, and substrates at levels ranging from 5 to 30% by weight (EU 2001).

The commercial pentaBDE product was used predominantly (95–98%) for flame retardant purposes as an additive in consumer products manufactured by the furniture industry (ENVIRON 2003a). It was used almost exclusively to flame retard flexible polyurethane foam (FPUF), which is used in bed mattresses and cushioning in upholstered products. The commercial pentaBDE was typically used in FPUF as an additive mixture with aromatic phosphate esters (e.g., mixture of 75% pentaBDE and 25% aromatic phosphate esters). Mattress FPUF contains approximately 2–3% flame retardant mixture and cushion FPUF contains 3–5% flame retardant mixture (ENVIRON 2003a). Scrap materials from both industries have been used as padding beneath carpets, and as a result, carpet padding likely contained 3–5% flame retardant mixture. However, not all of the FPUF found in cushion, mattress, and carpet padding products were treated with commercial pentaBDE. Approximately 7.5% of the more than 2.1 billion pounds of FPUF produced annually in the United States used the commercial pentaBDE product as a flame retardant additive (ENVIRON 2003a). The majority of FPUF products treated with the commercial pentaBDE product were sold in California, the only state requiring by law that upholstered products achieve a prescribed level of ignition resistance (ENVIRON 2003a). A small percentage of pentaBDE was used in commercial adhesive products. Other former uses of commercial pentaBDE included coatings for specialty textiles, printed circuit board components, hydraulic and oilfield completion fluids, and rubber products. In the past, automotive and airplane seating cushions contained FPUF with commercial pentaBDE. However, this use was discontinued in the early 1990s. Prior to approximately 1990, the commercial pentaBDE product may have been used in small quantities as a flame retardant in specialty fire-resistant clothing using polyurethane treatment and in polyurethane coatings in carpets (ENVIRON 2003a). Commercial pentaBDE product was used in rigid polyurethane elastomers for instrument casings, and applied in printed circuit boards and microprocessor packaging previously (Betts 2006;

Hazrati and Harrad 2007). Electronic equipment containing pentaBDE produced in other countries (principally Asian) could also find its way into the United States (EU 2001).

The commercial octaBDE was used by the plastics industry as an additive flame retardant for manufactured products. It was used almost exclusively to flame retard ABS terpolymers used in computer casings and monitors (ENVIRON 2003b). In the EU, approximately 95% of the total commercial octaBDE product sold to the electronics and plastics industries was used in ABS before it was banned (EU 2003a). Although data are not available in the United States, similar volumes were likely (ENVIRON 2003b). The commercial octaBDE product formerly used in ABS products was 12–18% weight loadings of flame retardant. OctaBDE was always used as a flame retardant in conjunction with antimony trioxide. Other minor uses for octaBDE, were high impact polystyrene (HIPS), polybutylene terephthalate (PBT), and polyamide polymers (EU 2003a). Other former applications of octaBDE included use as additive flame retardant in polycarbonate, phenol-formaldehyde resins, and unsaturated polyesters (EU 2003a).

The commercial decaBDE product was an additive flame retardant used in a variety of polymer applications. Industry information indicates that decaBDE was used at loadings of 10–15% weight in polymers and always in conjunction with antimony trioxide (EU 2002). The major application for decaBDE was in HIPS, which is used in the television industry for cabinet backs. It was also used for a large number of other polymers with end-uses in electrical and electronic equipment (e.g., computers, connectors, electrical boxes, wire, cable, etc.). Examples include polypropylene (for electronics), acetate copolymers (ethylene-vinyl acetate [EVA] and other copolymers for wire and cable), ethylene-propylene-diene terpolymer (EPDM) and thermoplastic elastomers (for wire and cable), and polyester resins (for electronics). Other minor uses included styrenic rubbers, polycarbonates, polyamides, and terephthalates, and small amounts are reported to be used in hot-melt adhesives (EU 2002).

5.4 DISPOSAL

PBDEs were used as flame retardants in a wide range of consumer products (see Section 5.3). In the United States, waste disposal of PBDE-containing consumer products is described as transfers to disposal (landfill), recycling, energy recovery (incineration), or publicly owned treatment works (POTWs) (Darnerud et al. 2001). No other information was located on the past or present volumes of PBDE-containing consumer products disposed of by each method of waste transfer.

Landfill disposal of plastic consumables containing pentaBDE (e.g., polyurethane foams), octaBDE (e.g., computer monitors), and decaBDE (e.g., televisions) to landfills is likely to increase in the United States due to their limited useful lifespan. Given that all PBDEs have low water solubility (see Table 4-4), the potential for leaching of PBDE from landfills appears to be small (EU 2002). Well-designed landfills will include measures to minimize leaching and those measures would also be effective in minimizing the leaching of any PBDE particulates present (EU 2002). PBDEs have been detected in landfill leachate and landfill related aqueous samples worldwide (Daso et al. 2013; Kwan et al. 2013; Odusanya et al. 2009; Oliaei et al. 2010; Stubbings and Harrad 2014). The presence of hydrophobic compounds like PBDEs in leachate is expected to be a result of enhanced leachability due to the presence of other constituents present in the leachate (Stubbings and Harrad 2014). Mass transfer evaluation of PBDEs from e-waste solids found that lower pH conditions resulted in higher transfer of PBDEs to the aqueous phase, with the highest concentration of PBDEs detected at pH 5 and 25°C (Danon-Schaffer et al. 2013). The levels of PBDEs in the aqueous phase did show a trend with temperature at the temperature range evaluated, 10–25°C.

Incineration of waste materials containing PBDEs is thought to be a potential source of PBDFs and/or PBDDs. The formation of PBDFs/PBDDs as a result of uncontrolled landfill fires is also a possibility, although no data are available on the scale of this source. The results of pyrolysis experiments showed that PBDEs can form PBDFs and PBDDs (in much smaller quantities) under a wide range of heating conditions. If chlorine is present, mixed halogenated furans/dioxins can be formed (Oberg et al. 1987; Zier et al. 1991). Unless sufficiently high temperatures and long residence times are maintained, PBDFs/PBDDs can be generated during the incineration of products containing PBDEs. When heavy metals are present, the concentration of PBDDs and PBDFs are higher than when no metals are present. Sakai et al. (2001) measured residues of PBDFs/PBDDs in effluents from a municipal incineration plant burning domestic waste materials. Flue gases, fly ash, and bottom ash reportedly contained PBDFs/PBDDs at concentration ranges of 0.28–3.3 ng/N m^3, 0.082–13 ng/g, and 0.0058–27 ng/g, respectively. However, modern, properly operated municipal waste incineration should not emit significant quantities of PBDFs/PBDDs, regardless of the composition of municipal waste (WHO 1994a).

In the United States, waste disposal of industrial by-products containing PBDEs may also be described as transfers to disposal (landfill), recycling, energy recovery (incineration), industrial treatment works, or POTWs. The types of waste transfer may be different for manufacturing versus processing sectors, and also from within different types of processing. Waste disposal from manufacturing processes is predominantly to secure chemical landfills (e.g., those built with liners and leachate collection). Plastic processors typically transfer most waste to disposal (landfill), recycling, energy recovery (incineration), and industrial treatment works, while minimal releases are to POTWs. In contrast, textile processors typically transfer most waste to POTWs. This difference in waste transfers between the plastic and textile sectors is because textile processors use water in their processing operation and other processors (e.g., processors of plastic) do not.

Recycling of plastic materials containing PBDEs is a common practice in industry. It has been demonstrated that decaBDE-containing resins can be successively recycled without generation of PBDDs/PBDFs (Brenner and Knies 1990; Donnelly et al. 1987; McAllister et al. 1990). For example, virgin HIPS resins (containing antimony trioxide [Sb_2O_3] and decaBDE) and repeatedly ground and injected molded (e.g., “recycled”) HIPS/decaBDE/Sb_2O_3 resins both met the requirements of the German Chemicals Banning Ordinance with respect to 2,3,7,8-substituted PBDD/PCDF congeners. These resins were at least 1 order of magnitude below the regulated limit values for PBDDs/PCDFs (1 ppb for the sum of four congeners, 5 ppb for the sum of all eight regulated congeners).