United States
Environmental Protection
Agency

Technical Fact Sheet – Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Biphenyls (PBBs)

January 2014

At a Glance

- ❖ Classes of brominated hydrocarbons that serve as flame retardants for electrical equipment, electronic devices, furniture, textiles and other household products.
- ❖ Structurally similar and exhibit low to moderate volatility. Lower brominated congeners of PBDE tend to bioaccumulate more than higher brominated congeners.
- ❖ May act as endocrine disruptors in humans and other animals. Exposure in rats and mice caused neuro-developmental toxicity and other symptoms.
- ❖ The EPA has developed oral reference doses for decaBDE, octaBDE, tetraBDE, hexaBDE and pentaBDE.
- ❖ The U.S. Department of Health and Human Services states that PBBs are reasonably anticipated to be human carcinogens.
- ❖ According to the EPA, evidence of carcinogenic potential is suggested for decaBDE.
- ❖ The EPA has calculated screening levels for PBBs in air, soil and tap water.
- ❖ Detection methods include gas chromatography, mass spectrometry and liquid chromatography.
- ❖ Potential treatment methods being evaluated at the laboratory scale include debromination using zero-valent iron (ZVI) and nanoscale ZVI, activated carbon treatment and enhanced biodegradation.

Introduction

This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Federal Facilities Restoration and Reuse Office (FFRRO), provides a summary of the contaminants polybrominated diphenyl ethers (PBDE) and polybrominated biphenyls (PBB), including physical and chemical properties; environmental and health impacts; existing federal and state guidelines; detection and treatment methods; and additional sources of information. This fact sheet provides basic information on PBDEs and PBBs to site managers and other field personnel who may encounter these contaminants at cleanup sites.

The manufacture of PBB was banned in the United States in 1976 after an agricultural contamination episode in 1973 when PBB was accidentally mixed into animal feed, exposing millions of Michigan residents to contaminated dairy products, eggs and meat (ATSDR 2004; DHHS 2011). In contrast, PBDEs have been used widely in the United States since the 1970s; however, there is growing concern about their persistence in the environment and their tendency to bioaccumulate in the food chain (ATSDR 2004; EPA 2009). Since PBDEs and PBBs belong to the same class of brominated hydrocarbons and their chemical structures are similar, they are both discussed in this fact sheet.

What are PBDE and PBB?

- ❖ PBDE and PBB are classes of brominated hydrocarbons, also referred to as brominated flame retardant (BFR) chemicals. They are structurally similar, containing a central biphenyl structure surrounded by up to 10 bromine atoms (ATSDR 2004).
- ❖ PBBs were formerly used as additive flame retardants in synthetic fibers and molded plastics. They are no longer used in the United States (ATSDR 2004; DHHS 2011).
- ❖ PBDEs are used as flame retardants in a wide variety of products, including plastics, furniture, upholstery, electrical equipment, electronic devices, textiles and other household products (ATSDR 2004; EPA 2009).
- ❖ At high temperatures, PBDEs and PBBs release bromine radicals that reduce both the rate of combustion and dispersion of fire (Hooper and McDonald 2000).

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What are PBDE and PBB? (continued)

- PBDEs exist as mixtures of distinct chemicals called congeners with unique molecular structures. The PBDE congeners may differ in the total number or position of bromine atoms attached to the ether molecule. Congeners with equal numbers of bromine atoms are known as homologs (ATSDR 2004; EPA 2009)
- There are three types of commercial PBDE homologs, including pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE) and decabromodiphenyl ether (decaBDE). DecaBDE is the most widely used PBDE globally (ATSDR 2004; EPA 2009).
- The production of octaBDE and pentaBDE in the United States ceased at the end of 2004 after the voluntary phase-out of these chemicals by the only U.S. manufacturer. In addition, the two U.S. producers and the main U.S. importer of decaBDE have announced plans to phase out the compound by the end of 2013 (EPA 2012; EPA 2013a).
- PBBs also exist as mixtures of congeners. They were produced as three primary homologs: hexabromobiphenyl (hexaBB), octabromobiphenyl (octaBB) and decabromobiphenyl (decaBB) (ATSDR 2004; DHHS 2011).
- Production of PBBs in the United States was banned in 1976 after an agricultural contamination episode in 1973 (ATSDR 2004).
- There are no known natural sources of PBDEs and PBBs, except for a few marine organisms that produce some forms of PBDEs (ATSDR 2004).
- Both PBDE and PBB are structurally similar to polychlorinated biphenyls (PCBs). Both PBDE and PBB are fat-soluble and hydrophobic (DHHS 2011; Hooper and McDonald 2000).

Exhibit 1: Physical and Chemical Properties of PBDEs and PBBs
(ATSDR 2004; HSDB 2012a, b)

Property	PBDEs		
	PentaBDE	OctaBDE	DecaBDE
Chemical Abstracts System (CAS) Numbers	32534-81-9	32536-52-0	1163-19-5
Physical description (physical state at room temperature)	Pale yellow liquid	Off-white powder	Off-white powder
Molecular weight (g/mol)	564.69	801.47	959.22
Water solubility at 25 ^{O}C (µg/L)	13.3 (commercial)	Less than 1 (commercial)	Less than 1
Boiling point (^{O}C)	Over 300	Over 330 (decomposes)	Over 320 (decomposes)
Melting point (^{O}C)	-7 to -3 (commercial)	85 to 89 (commercial)	290 to 306
Vapor pressure at 25 ^{O}C (mm Hg)	2.2×10^{-7} to 5.5×10^{-7}	9.0×10^{-10} to 1.7×10^{-9}	3.2×10^{-8}
Octanol-water partition coefficient (log K_{ow})	6.64 to 6.97	6.29 (commercial)	6.265
Soil organic carbon-water coefficient (log K_{oc})	4.89 to 5.10 [a]	5.92 to 6.22 [a]	6.80 [a]
Henry's Law Constant at 25 ^{O}C (atm-m^3/mol)	1.2×10^{-5} [a]	7.5×10^{-8} [a]	1.62×10^{-6} [a]
Property	**PBBs**		
	HexaBB	**OctaBB**	**DecaBB**
CAS Numbers	36355-01-8	27858-07-7	13654-09-6
Physical description (physical state at room temperature)	White solid	White solid	White solid
Molecular weight (g/mol)	627.4	785.2	943.1
Water solubility at 25 ^{O}C (µg/L)	11	20 to 30	Insoluble
Boiling point (^{O}C)	Not available	Not available	Not available
Melting point (^{O}C)	72	200 to 250	380 to 386
Vapor pressure (mm Hg)	5.2×10^{-8} (at 25 ^{O}C)	7×10^{-11} (at 28 ^{O}C)	Not applicable
Octanol-water partition coefficient (log K_{ow})	6.39	5.53	8.58
Soil organic carbon-water coefficient (log K_{oc})	3.33 to 3.87 [a]	Not available	Not available
Henry's Law Constant at 25^{o}C (atm-m^3/mol)	3.9×10^{-6}	Not available	Not available

Abbreviations: g/mol – gram per mole; µg/L – micrograms per liter; ^{O}C – degrees Celsius; mm Hg – millimeters of mercury; atm-m^3/mol – atmosphere-cubic meters per mole.
[a] – Estimated value

What are the environmental impacts of PBDE and PBB?

- PBDEs may enter the environment through emissions from manufacturing processes, volatilization from various products that contain PBDEs, recycling wastes and leachate from waste disposal sites (ATSDR 2004; EU 2001).
- PBBs may enter the environment through disposal of contaminated animal feed and animal products, accidental spills during transport and disposal of PBB-containing wastes from manufacturing sites (ATSDR 2004).
- PBDEs and PBBs have been detected in air, sediments, surface water, fish and other marine animals (ATSDR 2004; EPA 2009).
- Lower brominated congeners of PBDE tend to bioaccumulate more than higher brominated congeners and are more persistent in the environment (ATSDR 2004).
- Higher brominated congeners of PBDE tend to bind to sediment or soil particles more than lower brominated congeners (ATSDR 2004).
- PBDEs and PBBs do not dissolve easily in water and bind strongly to soil or sediment particles, which reduces their mobility in soil, sediment and groundwater, but increases their mobility in the atmosphere, where they are attached to airborne particulate matter (ATSDR 2004).
- Volatilization from soil surfaces is expected to be low to moderate, depending on the number of bromine atoms. Homologs with the highest numbers of bromine atoms tend to exhibit the lowest volatilities (DHHS 2011; EPA 2009).
- Even though PBDEs and PBBs are relatively stable, they are susceptible to photolytic debromination when they are exposed to ultraviolet light (Birnbaum and Staskal 2004; DHHS 2011; EPA 2009).
- As of 2004, PBBs had been identified at more than nine sites on the EPA National Priorities List (NPL) (HazDat 2004).
- As of 2004, PBDEs were not identified at any of the current or former hazardous waste sites on the NPL; however, the number of sites evaluated for PBDEs is not well documented. As more NPL sites are evaluated, there is a possibility that PBDE contamination may be discovered at these sites (HazDat 2004).

What are the routes of exposure and the health effects of PBDE and PBB?

- Routes of potential human exposure to PBBs and PBDEs are ingestion, inhalation or dermal contact (DHHS 2011).
- Since PBBs are no longer produced or used in the United States, the general population will be exposed to PBBs only from historical releases (ATSDR 2004).
- Traces of PBDEs have been detected in samples of human tissue, human blood and breast milk (EPA 2009; He and others 2006)
- The EPA has not classified PBBs for carcinogenicity.
- The U.S. Department of Health and Human Services (DHHS) states that PBBs are reasonably anticipated to be human carcinogens based on sufficient evidence of carcinogenicity from experimental animal studies (DHHS 2011).
- The International Agency for Research on Cancer (IARC) classified PBBs as “probably carcinogenic to humans” (IARC 2013).
- Neither the DHHS nor the IARC has classified the carcinogenicity of any PBDEs.
- According to the EPA, evidence of carcinogenic potential is suggested for decaBDE (EPA 2009; EPA IRIS 2008a).
- Studies on mice and rats have shown that exposure to PBDEs and PBBs causes neuro-developmental toxicity, weight loss, toxicity to the kidney, thyroid and liver and dermal disorders (ATSDR 2004; Birnbaum and Staskal 2004; EPA 2009).
- Studies on animals and humans have shown that some PBBs and PBDEs can act as endocrine system disruptors and also tend to deposit in human adipose tissue (ATSDR 2004; Birnbaum and Staskal 2004; DHHS 2011; He and others 2006).
- A study has indicated that octaBDE may be a potential teratogen (a prenatal developmental toxin) (Darnerud and others 2001; He and others 2006).

Are there any existing federal and state guidelines and health standards for PBDE and PBB?

- The EPA has not derived chronic oral reference doses (RfD) for PBBs; however, the it has established the following RfDs for PBDEs (EPA IRIS 2008a,b,c, d; 1990a,b):
  - 7 x 10^{-3} milligrams per kilogram per day (mg/kg/day) for the 2,2',3,3',4,4',5,5',6,6' decaBDE-209 congener;
  - 3 x 10^{-3} mg/kg/day for the octaBDE homolog;
  - 2 x 10^{-3} mg/kg/day for the pentaBDE homolog;
  - 1 x 10^{-4} mg/kg/day for the 2,2',4,4' - tetrabromodiphenyl ether (tetraBDE-47) congener;
  - 2 x 10^{-4} mg/kg/day for the 2,2',4,4',5,5' - hexabromodiphenyl ether (hexaBDE-153) congener; and
  - 1 x 10^{-4} mg/kg/day for the 2,2',4,4',5 - pentaBDE-99 congener.
- For decaBDE-209, EPA has assigned an oral slope factor for carcinogenic risk of 7 x 10^{-4} mg/kg/day and a drinking water unit risk of 2.0 x 10^{-8} micrograms per liter (µg/L) (EPA IRIS 2008a).
- EPA risk assessments indicate that the drinking water concentration representing a 1 x 10^{-6} cancer risk level for decaBDE-209 is 50 µg/L (EPA IRIS 2008a).
- EPA has calculated a residential soil screening level (SSL) of 1.6 x 10^{-2} milligrams per kilogram (mg/kg) and an industrial SSL of 5.7 x 10^{-2} mg/kg for PBBs. [1]
- For PBBs in tap water, EPA has calculated a screening level of 2.2 x 10^{-3} µg/L (EPA 2013b).[2]
- EPA has also calculated a residential air screening level of 2.8 x 10^{-4} micrograms per cubic meter (µg/m^3) and an industrial air screening level of 1.4 x 10^{-3} µg/m^3 (EPA 2013b).
- EPA issued a Significant New Use Rule (SNUR) in 2006 to phase out pentaBDE and octaBDE. According to this rule, no new manufacture or import of these two homologs is allowed after January 1, 2005, without a 90-day notification to EPA for evaluation (EPA 2013a).
- On March 20, 2012, EPA proposed to amend the 2006 SNUR by: (1) designating processing of any combination of the six PBDE congeners contained in pentaBDE or octaBDE for any use that is not ongoing, as a significant new use; (2) designating manufacturing, importing, or processing of decaBDE for any use that is not ongoing (as of December 31, 2013), as a significant new use; and (3) designating the manufacture, import or processing of any PBDE-containing article as a significant new use (EPA 2013a).
- In December 2009, the two U.S. producers and the main U.S. importer of decaBDE committed to end production, import and sales of the chemical for all consumer, transportation and military uses by the end of 2013 (EPA 2012).
- The American Industrial Hygiene Association (AIHA) has developed a workplace environmental exposure level of 5 milligrams per cubic meter (mg/m^3) for decaBDE, with ongoing air monitoring required if dust levels of pentaBDE and octaBDE exceed 5 mg/m^3 (AIHA 2013; ATSDR 2004).
- The Occupational Safety and Health Administration (OSHA) has not established occupational exposure limits for PBDEs or PBBs (OSHA 2006).
- The Agency for Toxic Substances and Disease Registry (ATSDR) has established a minimal risk level (MRL) of 0.01 mg/kg/day for acute-duration (14 days or less) oral exposure to PBBs and a MRL of 10 mg/kg/day for intermediate-duration (15 to 364 days) oral exposure to decaBDE (ATSDR 2013).
- For lower brominated PBDEs, ATSDR has established an MRL of 0.006 mg/m^3 for intermediate-duration inhalation exposure. In addition, ATSDR has established an MRL of 0.03 mg/kg/day for acute-duration oral exposure and 0.007 mg/kg/day for intermediate-duration oral exposure (ATSDR 2013).
- Several states including California, Hawaii, Illinois, Maine, Maryland, Michigan, Minnesota, New York, Rhode Island, Oregon and Washington have banned pentaBDE and octaBDE. States such as Washington, Maine, Maryland and Oregon have also introduced legislation that bans the sale of certain products containing decaBDE (EPA 2009; Lowell 2013).

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[1] Screening Levels are developed using risk assessment guidance from the EPA Superfund program. These risk-based concentrations are derived from standardized equations combining exposure information assumptions with EPA toxicity data. These calculated screening levels are generic and not enforceable cleanup standards but provide a useful gauge of relative toxicity.

[2] Tap water screening levels differ from the Integrated Risk Information System (IRIS) drinking water concentrations because the tap water screening levels account for dermal, inhalation and ingestion exposure routes; age-adjust the intake rates for children and adults based on body weight; and time-adjust for exposure duration or days per year. The IRIS drinking water concentrations consider only the ingestion route, account only for adult-intake rates, and do not time-adjust for exposure duration or days per year.

Are there any existing federal and state guidelines and health standards for PBDE and PBB? (continued)

- The California Environmental Protection Agency (Cal/EPA) has proposed a No Significant Risk Level of 0.02 µg per day for PBBs (Cal/EPA 2013).

What detection and site characterization methods are available for PBDE and PBB?

- Analytical methods used for PBDE detection include gas chromatography (GC)-mass spectrometry (MS) for air, sewage, fish and animal tissues; capillary column GC/electron capture detector (ECD) for water and sediment samples; GC/high resolution MS (HRMS) for fish tissue; and liquid chromatography (LC)-GC-MS/flame ionization detector (FID) for sediments (ATSDR 2004).
- Analytical methods for PBB detection include GC-ECD for commercial samples, soil, plant tissue, water, sediment, fish, dairy and animal feed; high resolution GC (HRGC)/HRMS for fish samples; GC-FID/ECD for soil; and LC-GC-MS/FID for sediment (ATSDR 2004).
- EPA Method 1614 uses isotope dilution and internal standard HRGC/HRMS to detect PBDEs in water, soil, sediment and tissue (EPA 2007).

What technologies are being used to treat PBDE and PBB?

- Research is being conducted at the laboratory scale on potential treatment methods for media contaminated with PBDEs and PBBs.
- A laboratory study investigated the degradation of a mixture of decaBDE and octaBDE using anaerobic bacteria (He and others 2006).
- Another laboratory study investigated zero valent iron (ZVI) as a treatment method for decaBDE. Secondary treatment using cationic surfactants may be required to increase the availability of PBDE molecules for reactions with ZVI (Keum and Li 2005).
- Laboratory studies are also evaluating the use of bimetallic nanoparticles (BNPs) and nanoscale ZVI (nZVI) for the treatment of PBDEs. Sequential treatment with nZVI and aerobic biodegradation and treatment with iron silver BNPs coupled with microwave energy were both shown to effectively degrade PBDEs (Kim and others 2012; Luo and others 2012).
- Bench-scale experiments indicate that electrokinetic remediation may be effective for the treatment of PBDEs in soil (Chun and others 2012).
- The use of activated carbon has also been investigated in a laboratory study for the treatment of PDBE in sediment (Choi and others 2003).

Where can I find more information about PBDE and PBB?

- Agency for Toxic Substances and Disease Registry (ATSDR). 2004. “Toxicological Profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers.” www.atsdr.cdc.gov/toxprofiles/tp68.pdf.
- ATSDR. 2013. “Minimal Risk Levels (MRLs).” www.atsdr.cdc.gov/mrls/index.html#bookmark02
- American Industrial Hygiene Association (AIHA). 2013. “2013 EPRG/WEEL Handbook.” AIHA Guideline Foundation.
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- California Environmental Protection Agency (Cal/EPA) Office of Environmental Health and Hazard Assessment. 2013. “Proposition 65 No Significant Risk Levels for Carcinogens and Maximum Allowable Dose Levels for Chemicals Causing Reproductive Toxicity.” http://oehha.ca.gov/prop65/pdf/022813safeharbor.pdf
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Where can I find more information about PBDE and PBB? (continued)

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- EPA. 2008a. "2,2',3,3',4,4',5,5',6,6' -Decabromodiphenyl ether (BDE-209) (CASRN 1163-19-5)." www.epa.gov/IRIS/subst/0035.htm
- EPA IRIS. 2008b. "2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153) (CASRN 68631-49-2)." www.epa.gov/iris/subst/1009.htm

Where can I find more information about PBDE and PBB? (continued)

- EPA IRIS. 2008c. “2,2',4,4',5-Pentabromodiphenyl ether (BDE-99) (CASRN 60348-60-9).” www.epa.gov/iris/subst/1008.htm
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