Technical Fact Sheet – Polybrominated Diphenyl Ethers (PBDEs)

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TECHNICAL FACT SHEET – PBDEs

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.
- Exposure in rats and mice caused thyroid hormone bioactivity, neuro-developmental toxicity and other symptoms.
- According to EPA, evidence of carcinogenic potential is suggested for decaBDE.
- 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 contaminant groups polybrominated diphenyl ethers (PBDEs), 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 to site managers and other field personnel who may encounter these contaminants at cleanup sites.

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 (ATSDR 2015; EPA 2009).

What are PBDEs?

- PBDEs are brominated hydrocarbons in which 2-10 bromine atoms are attached to the molecular structure (ATSDR 2015).
- 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 2015; EPA 2009).
- At high temperatures, PBDEs release bromine radicals that reduce both the rate of combustion and dispersion of fire (Hooper and McDonald 2000).
- PBDEs exist as mixtures of distinct chemicals called congeners with unique molecular structures (ATSDR 2015; EPA 2009).
- There are three types of commercial PBDE mixtures, including pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE) and decabromodiphenyl ether (decaBDE). DecaBDE is the most widely used PBDE globally (ATSDR 2015; 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 2009, the two U.S. producers and the main U.S. importer of decaBDE announced plans to phase out the compound by the end of 2013 (EPA 2013).

- In 2014, EPA identified 29 potentially functional, viable alternatives to decaBDE for use in select polyolefins, styrenics, engineering thermoplastics, thermosets, elastomers, or waterborne emulsions and coatings (EPA 2014).
- There are no known natural sources of PBDEs, except for a few marine organisms that produce forms of PBDEs that contain higher levels of oxygen (ATSDR 2015).
- PBDEs are structurally similar to polychlorinated biphenyls (PCBs). PBDEs are fat-soluble and hydrophobic (Hooper and McDonald 2000; NTP 2014).

Exhibit 1: Physical and Chemical Properties of PBDEs
(ATSDR 2015)

Property	PBDEs		
	PentaBDE	OctaBDE	DecaBDE
Chemical Abstracts System (CAS) number	32534-81-9	32536-52-0	1163-19-5
Physical description (physical state at room temperature)	Clear, amber to pale yellow liquid	Off-white powder	Off-white powder
Molecular weight (g/mol)	Mixture	Mixture	959.22
Water solubility at 25°C (µg/L)	13.3 (commercial)	Less than 1 (commercial)	Less than 1
Boiling point (°C)	Over 300	Over 330 (decomposes)	Over 320 (decomposes)
Melting point (°C)	-7 to -3 (commercial)	85 to 89 (commercial)	290 to 306
Vapor pressure at 25°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°C (atm-m^3/mol)	1.2×10^{-5} [a]	7.5×10^{-8} [a]	1.62×10^{-6} [a]

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

Existence of PBDEs in the environment

- 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 2015; EU 2001).
- PBDEs have been detected in air, sediments, surface water, fish and other marine animals (ATSDR 2015; EPA 2009).
- Based on a very limited number of studies, biodegradation does not appear to be significant for PBDEs (ATSDR 2015).
- Higher brominated congeners of PBDE tend to bind to sediment or soil particles more than lower brominated congeners (ATSDR 2015).
- PBDEs do not dissolve easily in water and bind strongly to soil or sediment particles. This reduces their mobility in soil, sediment, surface and groundwater, but increases their mobility in the atmosphere, where they are attached to airborne particulate matter (ATSDR 2015).
- Volatilization from soil surfaces is expected to be low to moderate, depending on the number of bromine atoms. More brominated congeners (higher numbers of bromine atoms) tend to exhibit lower volatilities (EPA 2009; NTP 2014).
- Even though PBDEs are stable, they are susceptible to photolytic debromination when they are exposed to ultraviolet light (ATSDR 2015).
- As of 2016, PBDEs were not identified at any of the current or former hazardous waste sites on the EPA National Priorities List (NPL); however, the number of sites evaluated for PBDEs is not well documented (EPA 2016).

What are the routes of exposure and the potential health effects of PBDEs?

- Routes of potential human exposure to PBDEs are ingestion, inhalation or dermal contact (NTP 2014).
- Traces of PBDEs have been detected in samples of human tissue, human blood and breast milk (EPA 2009; He and others 2006)
- According to EPA, evidence of carcinogenic potential is suggested for decaBDE (EPA 2009; EPA IRIS 2008).
- Neither the U.S. Department of Health and Human Services (DHHS) nor the International Agency for Research on Cancer (IARC) has classified the carcinogenicity of any PBDEs (IARC 2016; NTP 2014). However, the National Toxicology Program (NTP) evaluated a pentabromodiphenyl ether mixture in a rodent bioassay and concluded there was clear evidence of carcinogenicity in each species/sex tested (NTP 2014).
- Studies in rats and mice show that PBDEs cause neurotoxicity, developmental neurotoxicity, reproductive toxicity, thyroid toxicity, immunotoxicity, liver toxicity, pancreas effects (diabetes) and cancer (penta and decabromodiphenyl ether). There may be differences in the severity of effects depending on bromination level (ATSDR 2015; Birnbaum and Staskal 2004; EPA 2009).
- Studies on animals and humans show that some PBDEs can act as endocrine system disruptors and tend to deposit in human adipose tissue (ATSDR 2015; Birnbaum and Staskal 2004; He and others 2006; NTP 2014).
- Studies indicate that octaBDE is a 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 PBDEs?

- EPA has established the following chronic oral reference doses (RfDs) for PBDEs (EPA 2017):

PBDE Congener	Milligrams per kilogram per day (mg/kg/day)
2,2',3,3',4,4',5,5',6,6' decaBDE-209 congener	7×10^{-3}
octaBDE congener	3×10^{-3}
pentaBDE congener	2×10^{-3}
2,2',4,4' - tetrabromodiphenyl ether (tetraBDE-47) congener	1×10^{-4}
2,2',4,4',5,5' - hexabromodiphenyl ether (hexaBDE-153) congener	2×10^{-4}
2,2',4,4',5 - pentaBDE-99 congener	1×10^{-4}

- For decaBDE-209, EPA has assigned an oral slope factor for carcinogenic risk of 7×10^{-4} (mg/kg/day)$^{-1}$ and a drinking water unit risk of 2.0×10^{-8} micrograms per liter (µg/L) (EPA IRIS 2008).
- EPA risk assessments indicate that the drinking water concentration representing a 1×10^{-6} cancer risk level for decaBDE-209 is 50 µg/L (EPA IRIS 2008).
- EPA has calculated the following screening levels for residential soil, industrial soil and tap water (EPA 2017):

Chemical	Residential Soil (mg/kg)	Industrial Soil (mg/kg)	Tap Water (µg/L)
decaBDE-209	440	3,300	110
octaBDE	190	2,500	61
pentaBDE	160	2,300	40
tetraBDE-47	6.3	82	2.0
hexaBDE-153	13	160	4.0
pentaBDE-99	6.3	82	2.0

- For lower brominated PBDEs, the Agency for Toxic Substances and Disease Registry (ATSDR) has established a minimal risk level (MRL) of 0.006 milligrams per cubic meter for intermediate-duration inhalation exposure. In addition, ATSDR established an MRL of 6×10^{-5} mg/kg/day for acute-duration oral exposure and 3×10^{-6} mg/kg/day for intermediate-duration oral exposure (ATSDR 2016).
- Some states, including California, Hawaii, Illinois, Maine, Maryland, Michigan, Minnesota, New York, Oregon, Rhode Island and Washington, have banned pentaBDE and octaBDE. States such as Maine, Maryland, Oregon and Washington have also introduced legislation that bans the sale of certain products containing decaBDE (EPA 2009).

- 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 congeners is allowed after January 1, 2005, without a 90-day notification to EPA for evaluation (EPA 2013).
- 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 2014). However, based on 2012 industry comments to EPA, there may be ongoing uses for decaBDE.

What detection and site characterization methods are available for PBDEs?

- 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 2015).
- EPA Method 1614 uses isotope dilution and internal standard high resolution GC (HRGC)/HRMS to detect PBDEs in water, soil, sediment and tissue (EPA 2007).

What technologies are being used to treat PBDEs?

- Research is being conducted at the laboratory scale on potential treatment methods for media contaminated with PBDEs.
- Anaerobic bacteria may be utilized to partially degrade higher brominated PBDE, but may lead to the formation of less-brominated, more toxic congeners (He and others 2006; Lee and He 2010).

  Secondary treatment using cationic surfactants may be required to increase the availability of PBDE molecules for reactions with zero valent iron (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, 2014; Luo and others 2012).
- A 2016 laboratory study indicates a tourmaline catalyzed Fenton-like reaction can remove PBDEs from soil (Li and others 2016).
- 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 PBDE in sediment (Choi and others 2003).

Where can I find more information about PBDEs?

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Where can I find more information about PBDEs? (continued)

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