

Polybrominated Diphenyl Ethers (PBDEs)

TIER 3
MODERATE
CONCERN

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Quick Summary

PBDEs are flame retardants once common in foam furniture, electronics, and many other products. Bans and phase-outs are eliminating these chemicals from new goods, but they remain present in products in use today and in the wastestream. PBDEs have been extensively monitored in San Francisco Bay water, sediment, and wildlife. In wildlife, levels appear to be declining over time, likely a response to the chemical bans. Preliminary research indicates concentrations in Bay harbor seals may be present at harmful levels, but those found in bird eggs do not appear to be problematic. Levels of PBDE contamination in sport fish do not pose risks to people who eat them. However, there is little information about the effects of contamination on the health of the fish themselves. California's unusually strict flammability standards have resulted in widespread use of chemical flame retardants in products. An effort is underway to revise these standards to provide fire safety while reducing the need for added flame retardants.

What Are They?

- A class of synthetic bromine-containing chemicals.
- Used as flame retardants in polyurethane foam, plastics, and textiles.
- Produced in three commercial mixtures named for the average number of bromines in each: PentaBDE, OctaBDE, and DecaBDE.
- Structurally similar to PCBs, a class of legacy pollutants that are persistent, bioaccumulative, highly toxic, and commonly found in the Bay.

What Are They Used For?

- Chemical flame retardants like PBDEs are often added to products to meet the unusually strict flammability standards set by the state of California. Most furniture sold in the US meets California flammability standards.
- PentaBDE, composed primarily of PBDEs containing four and five bromines (e.g., BDE-47 and BDE-99), was commonly used as a flame retardant in polyurethane foam in furniture cushions, car seats, and mattresses. It was also used in foam-based packaging and carpet padding.
- OctaBDE, composed primarily of PBDEs containing six, seven, and eight bromines (e.g., BDE-183, BDE-197, and BDE-203), was used as a flame retardant in plastic housings for electrical and electronic equipment.
- PentaBDE and OctaBDE are no longer manufactured or added to new products in the US. They were banned in California in 2006. However, they are still found in many consumer goods made before the ban went into effect.
- DecaBDE, composed primarily of BDE-209, is a flame retardant used with virtually any type of polymer, including plastics, textiles, and back-coatings of consumer electronics.

- By the end of 2013, DecaBDE will no longer be manufactured in the US. Because this phase-out is voluntary, DecaBDE may still be present in imported products.
- If California's existing flammability standards are not revised, manufacturers of consumer goods will likely simply substitute new chemical flame retardants for PBDEs. Some of these alternative flame retardants are potentially harmful to human health or wildlife and have already been detected in the Bay (PAGE 67).
- The California bureau charged with consumer product fire safety has proposed revised flammability standards that will provide fire protection without requiring the use of added chemical flame retardants in many consumer goods.

How Are They Getting into the Bay?

- PBDEs are not chemically bound to the polymers or products that contain them, so they can escape via volatilization to the air or on loose particles. They are a major contaminant of indoor dust.
- Discharges of treated wastewater from municipal wastewater treatment facilities are considered the major pathway for BDE-47 (one of the most abundant PBDEs) to enter the Bay.
- On the other hand, urban stormwater is considered the major pathway for BDE-209 (another abundant PBDE, and the primary component of DecaBDE) to enter the Bay.
- Flows from the Delta and direct atmospheric deposition are minor PBDE pathways to the Bay.

Polybrominated Diphenyl Ethers (PBDEs)

What Happens to Them in the Bay?

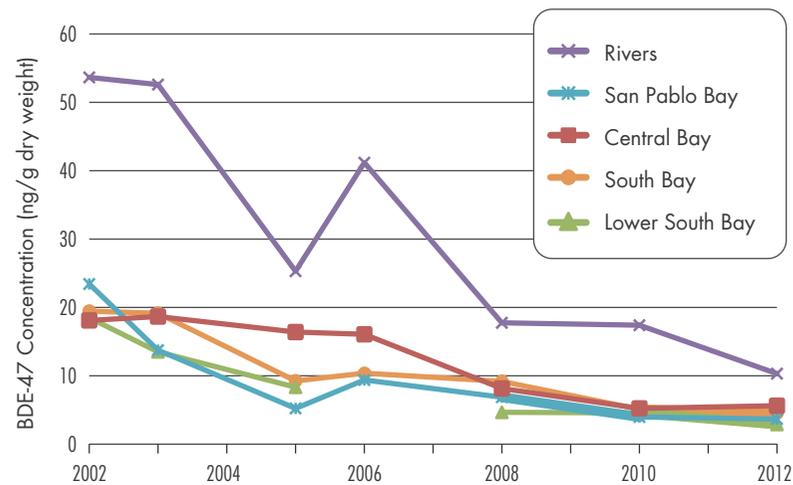
General Properties

- Individual PBDEs have different chemical properties depending on the number of bromine atoms they contain. This range of chemical properties affects how individual PBDEs behave in the environment.
- PBDEs tend to associate with sediment particles, and those with more bromine atoms show a stronger particle affinity. Bay sediment tends to contain a large proportion of all PBDEs, especially BDE-209, which has ten bromine atoms. BDE-47, with four bromine atoms, is the dominant PBDE found in Bay water, though it is still mainly found in sediment.
- PBDEs are generally lipophilic (“fat-loving”), and many accumulate in organisms. However, the most lipophilic, BDE-209, is not often detected in Bay wildlife. It may be too strongly bound to sediments to be transferred to organisms. It may also be too large to pass readily through an organism’s cell membranes.
- PBDEs are generally persistent chemicals in the environment. However, PBDEs with larger numbers of bromine atoms can be debrominated via microbial and metabolic processes or exposure to sunlight, forming PBDEs with fewer bromines.
- Debromination of BDE-209 can result in formation of less-brominated PBDEs with higher toxicity and greater tendency to bioaccumulate.

Patterns of Occurrence in the Bay and in Other Aquatic Ecosystems

- PBDEs are common in Bay sediment (PAGE 37). The dominant PBDE found in sediment is BDE-209 (PAGE 37), the major component of the DecaBDE commercial mixture.
- In 2011 and 2012, most sediment samples contained PBDE levels totaling 52 parts per billion (ppb) or less. Levels are similar to those found in other areas, such as the coastal regions of Southern California and Canada (Grant et al. 2011, Dodder et al. 2012).

PBDEs in Bay Bivalves



Footnote: River bivalves are resident clams, while Bay bivalves are primarily mussels deployed for 90 days and then collected for monitoring. The higher levels present in river bivalves are likely due to their longer exposure time.

FIGURE 1

PBDE levels in Bay bivalves have declined over the last decade, likely a result of both the nationwide phase-out and state ban of PentaBDE and OctaBDE. BDE-47 is the dominant form of PBDEs in wildlife and is graphed here as an indication of overall PBDE levels. BDE-47 is a major component of the PentaBDE mixture.

- However, sediment from two contamination “hotspot” sites located in the margins of the Bay (San Leandro Bay and Mission Creek), contained more than four times the maximum amount reported for more typical Bay locations (220 and 240 ppb, respectively).
- In Bay water samples, BDE-47 is the dominant PBDE detected. The Baywide average level of BDE-47 was 43 picograms per liter (pg/L) in 2011 (PAGE 36).
- PBDEs are detected in all Bay wildlife monitored by the RMP. The dominant PBDE in wildlife samples is BDE-47. BDE-209 is rarely detected.
- Bay mussels are widely contaminated with PBDEs. The National Oceanic and Atmospheric Association considers Bay mussels highly contaminated relative to other parts of the US (Kimbrough et al. 2009). However, RMP measurements from 2002 to 2012 show levels have begun to decline (FIGURE 1).
- Bay sport fish also contain PBDEs, with concentrations that vary widely by species. Levels in shiner surfperch,

a fish that tends to feed over a relatively small territory, indicate regional variation in contamination, along with an overall decline in PBDEs from 2003 to 2009 (FIGURE 2).

- A tern egg collected from the Bay in 2002 contained the highest level of PBDEs ever measured in an organism at that time, 63,300 ppb lipid weight (nanograms of PBDE per gram of lipid [or fat] in the sample) (She et al. 2008).
- The RMP analyzed tern eggs in 2009 and found a maximum value of 2,400 ppb lipid weight (lw); the eggs averaged 1,400 ppb lw.
- Cormorant eggs collected by the RMP from three different locations also generally show declining levels of PBDE contamination from 2002 to 2009 (FIGURE 3).
- A decade ago, a California Environmental Protection Agency study showed PBDE levels in Bay harbor seal blubber samples were as high as 8,300 ppb lw and were doubling every 1.8 years (She et al. 2002). Recent results suggest that contamination in adult harbor seals may have stabilized or begun to decline.

Polybrominated Diphenyl Ethers (PBDEs)

Trends in the Bay and Nationally

- PBDE levels are generally declining in Bay wildlife. Over the last ten years, RMP monitoring of bivalves, fish, and bird eggs consistently indicates falling levels of pollution (FIGURES 1, 2, and 3).
- Other studies have identified potential PBDE declines, including osprey eggs in the Pacific Northwest (Henny et al. 2009), sockeye salmon from the northeast Pacific Ocean (Ikonou et al. 2011), and trout in the Great Lakes (Crimmins et al. 2012).
- BDE-47 levels in sediment also appear to have declined over the past 10 years (PAGE 37).
- Concern remains despite evident declines, as PBDEs present in existing products can be sources of continuing contamination of the environment over time.

Is There a Risk of Harm in the Bay?

- Bay sport fish do not contain PBDE levels that would make them unfit for human consumption based on comparison to thresholds developed by the California Office of Environmental Health Hazard Assessment (Klasing and Brodberg 2011).
- PBDEs also appear unlikely to affect the reproduction and development of Bay birds, according to a recent study of the toxicity of PentaBDE to tern embryos (Ratner et al. 2011).
- Current levels of PBDE contamination may be harmful to Bay harbor seals (Neale et al. 2005), though further research is needed to investigate these potential health impacts.
- There are few studies on the effects of PBDEs on fish. One study (Arkoosh et al. 2010) documented increased susceptibility to pathogenic microorganisms in young Chinook salmon at a PBDE concentration that has been exceeded in some Bay fish samples. Bay fish samples from 2009 had lower levels of PBDEs than in prior years.
- PBDE levels are declining, so any risk of harm should decline as well.

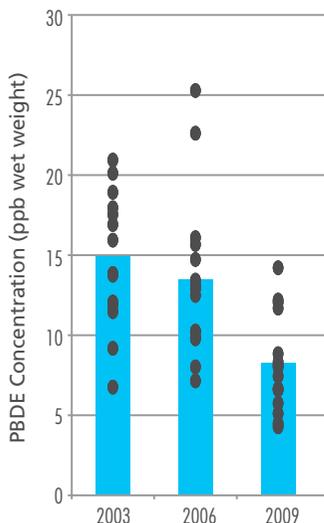


FIGURE 2
PBDE concentrations in shiner surfperch, a popular Bay sport fish, were significantly lower in 2009 as compared to previous years. This decline is likely due to the nationwide phase-out and state ban of PentaBDE and OctaBDE. All sport fish examined in the Bay contained PBDE levels below 100 ppb, meaning an adult person can safely eat up to three servings per week according to the California Office of Environmental Health Hazard Assessment (Klasing and Brodberg 2011).

Footnote: Bars indicate average concentrations. Points represent composite samples. The RMP examined eight sport fish species in 2009; shiner surfperch had the highest levels of contamination, and therefore represent the worst-case exposure.

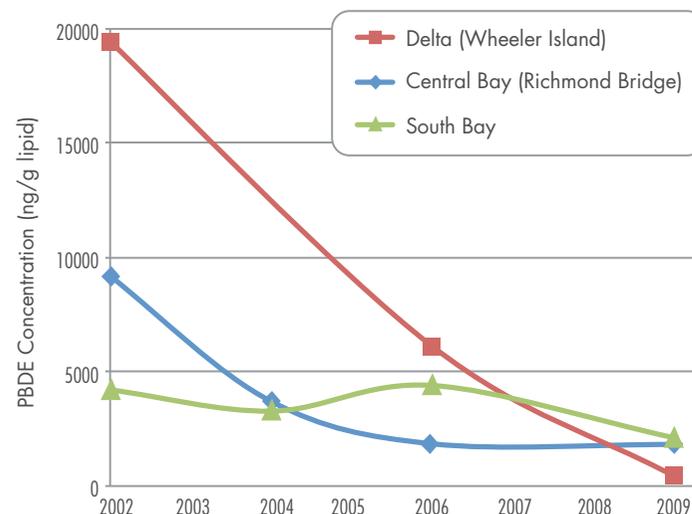


FIGURE 3
PBDE levels in cormorant eggs show general declines from 2002 to 2009, likely a result of both the nationwide phase-out and state ban of PentaBDE and OctaBDE. Cormorants are piscivores and prefer to forage in open Bay waters.

Footnote: Each value is an average of two or three composite samples. Each composite sample is made up of the contents of seven to ten eggs.

Polybrominated Diphenyl Ethers (PBDEs)

Key Information Gaps

- The impact of current levels of contamination on Bay harbor seals and fish.
- Characterization of PBDE levels in Bay water, sediment, and biota in the margins of the Bay, where localized “hotspots” of contamination are likely.
- Degradation and debromination rates for BDE-209, the primary component of DecaBDE.
- Toxicity assessment of lower-brominated congeners created through environmental debromination processes and not found in commercial mixtures.

Management Timeline

2004

In response to pressure from the US Environmental Protection Agency (USEPA), the major manufacturer of PentaBDE and OctaBDE agrees to stop producing the compounds in 2004.

2006

The state of California bans production, use, and sale of products containing PentaBDE and OctaBDE. USEPA issues a Significant New Use Rule for PentaBDE and OctaBDE, allowing the agency to review and regulate any new uses for these compounds.

2013

In response to pressure from USEPA, the major manufacturers of DecaBDE agree to stop producing this mixture by the end of 2013.

The California state agency responsible for flammability standards (www.bearhfti.ca.gov) proposes new standards that will eliminate the need for added chemical flame retardants in many consumer goods (www.bhfti.ca.gov/about/laws/propregs.shtml).

2005

2007

2008

2009

2010

2011

2012

