NOAA NATIONAL STATUS & TRENDS

MUSSEL WATCH PROGRAM

An Assessment of Polybrominated Diphenyl Ethers (PBDEs) in Sediments and Bivalves of the U.S. Coastal Zone

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Citation for this Report

Kimbrough, K. L., W. E. Johnson, G. G. Lauenstein, J. D. Christensen and D. A. Apeti. 2009. An Assessment of Polybrominated Diphenyl Ethers (PBDEs) in Sediments and Bivalves of the U.S. Coastal Zone. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 94. 87 pp.

An Assessment of Polybrominated Diphenyl Ethers (PBDEs) in Sediments and Bivalves of the U.S. Coastal Zone

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Background

NOAA's Mussel Watch Program was designed to monitor the status and trends of chemical contamination of U.S. coastal waters, including the Great Lakes. The Program began in 1986 and is one of the longest running, continuous coastal monitoring programs that is national in scope. NOAA established Mussel Watch in response to a legislative mandate under Section 202 of Title II of the Marine Protection, Research and Sanctuaries Act (MPRSA) (33 USC 1442). In addition to monitoring contaminants throughout the Nation's coastal shores, Mussel Watch stores samples in a specimen bank so that trends can be determined retrospectively for new and emerging contaminants of concern.

In recent years, flame retardant chemicals, known as polybrominated diphenyl ethers (PBDEs), have generated international concern over their widespread distribution in the environment, their potential to bioaccumulate in humans and wildlife, and concern for suspected adverse human health effects. The Mussel Watch Program, with additional funding provided by NOAA's Oceans and Human Health Initiative, conducted a study of PBDEs in bivalve tissues and sediments.

This report, which represents the first national assessment of PBDEs in the U.S. coastal zone, shows that they are widely distributed. PBDE concentrations in both sediment and bivalve tissue correlate with human population density along the U.S. coastline. The national and watershed perspectives given in this report are intended to support research, local monitoring, resource management, and policy decisions concerning these contaminants.

Acknowledgements

The Mussel Watch Team would like to thank those who through their hard work made this document possible. As a result of their efforts, this report has been greatly enhanced.

Ken Buja	National Oceanic and Atmospheric Administration
Theresa Goedeke	National Oceanic and Atmospheric Administration
Treda Smith-Grayson	U.S. Environmental Protection Agency
Chris Jeffrey	Consolidated Safety Services, Inc.
Tom McDonald	Texas A&M University
Kevin McMahon	National Oceanic and Atmospheric Administration
Terry McTigue	National Oceanic and Atmospheric Administration
Keith Maruya	Southern California Coastal Water Resources Project
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Mussel Watch Program Background

- Approximately 300 active monitoring sites are located in the continental U.S., Alaska, Puerto Rico, and Hawaii.
- Stations are 10 to 100 km apart along the entire U.S. coastline.
- Approximately 150 contaminants are monitored in resident bivalve populations including: polycyclic aromatic hydrocarbons (69), polychlorinated biphenyls (40), organotins (4), metals and metalloids (15), and historic and contemporary use pesticides and selected transformation products (20).
- Special assessments are used to determine the environmental impacts of new contaminants, extreme events, and oil spills.

Program Background

NOAA's Mussel Watch Program monitors the status and trends of chemical contamination of U.S. coastal waters. The Program began in 1986 and is one of the longest running, continuous coastal monitoring programs that is national in scope. The Program is based on annual collection and analysis of oysters and mussels. These bivalves are stationary organisms that filter particles from water; thus, contaminant levels in their tissue are a good indicator of local contamination. Mussel Watch data are useful for characterizing the environmental impact of new and emerging contaminants, measuring effects of extreme events (hurricanes and oil spills), and for assessing the effectiveness of legislation, management decisions, and remediation of coastal contamination. As a result of monitoring all major estuaries for chemical contamination, Mussel Watch results can be used to identify geographic areas of concern and potential human exposures to elevated levels in seafood.

NOAA established Mussel Watch in response to a legislative mandate under Section 202 of Title II of the Marine Protection, Research and Sanctuaries Act (MPRSA) (33 USC 1442), which called on the Secretary of Commerce to, among other activities, initiate a continuous monitoring program "to assess the health of the marine environment, including monitoring of contaminant levels in biota, sediment and the water column." As part of the NOAA Authorization Act of 1992, the overall approach and activities of NOAA's National Status and Trends Program (NS&T), including Mussel Watch, were codified under provisions of the National Coastal Monitoring Act (Title V of the MPRSA).

In 1986, the inaugural year of the Mussel Watch Program, 145 sites were sampled. Today, Mussel Watch is comprised of approximately 300 monitoring sites, where about 150 chemical contaminants, chosen through consultation with experts and scientists from academia and government, are measured. Many of these contaminants are listed as Environmental Protection Agency (EPA) Priority Pollutants (Keith and Teillard, 1979). Legislation has been passed to regulate most of the organic contaminants analyzed by the Mussel Watch Program

Program Goal

To support ecosystem-based management through an integrated nationwide program of environmental monitoring, assessment, and research to describe the status and trends of contaminants in our Nation's estuaries and coasts.

(http://NSandT.noaa.gov). The majority are toxic to aquatic organisms, and some are taken up and stored in animal tissues with the potential to be transferred through food webs to humans.

This report utilizes Mussel Watch PBDE measurements of mussels, oysters, and sediment to provide a summary of national PBDE levels, and is intended for use by resource managers, policy makers, scientists, legislators, and concerned citizens. The bivalve mollusks measured included species of the genus *Mytilus* (blue mussels), species of the genus *Dreissena* (zebra mussels), and species of the genus *Crassostrea* (oyster). Some of these species are edible, but no PBDE threshold levels for the protection of human health have been promulgated by the U.S. Food and Drug Administration. This report compares the status of PBDEs at the national level to those found locally or regionally. Comparisons can be used to determine if the concentrations are high relative to the rest of the Nation. Site specific measurements can be found in Appendix 1. More detailed program information can be accessed at http://NSandT.noaa.gov.

Highlight

Many Mussel Watch sites are coincident with the 1976-1978 EPA Mussel Watch sites.

Program staff consulted with state officials, academic professionals and others when sites were established.

Some sites are located in or near NOAA-managed areas (National Estuarine Research Reserves, National Marine Sanctuaries).

Sites were selected in shellfish beds large enough for repeated sampling.

Samples are only collected from natural substrates; caged mussels are not used.

Chemical Description

- Production of PBDEs in the U.S. began in the 1970s and peaked in the late 1990s.
- PBDEs are ubiquitous in the U.S. coastal environment.
- In the U.S., PBDE levels in humans have been rising over the past 30 years and are generally 10-100 times higher than levels measured in Europe and Asia. Current concentrations in humans may be leveling off or decreasing.

Chemical Description

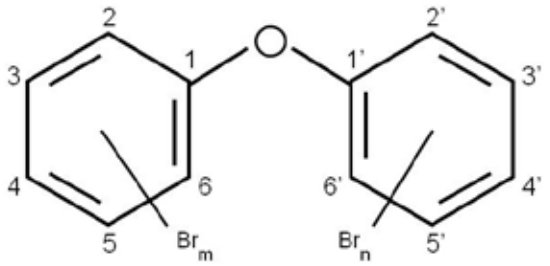

Figure 1. Chemical structure of polybrominated diphenyl ethers.

Polybrominated diphenyl ethers are persistent man-made aromatic chemicals composed of two phenyl rings linked by an oxygen bridge (ether linkage). Bromine atoms can replace up to ten hydrogen atoms on the phenyl rings (Figure 1). Theoretically, 209 unique PBDE structures (congeners) are possible. Congeners with the same number of bromine atoms are referred to as a homologue, and thus, there are ten homologues ranging from mono- to decaBDE. For example, a PBDE with ten bromines, is called decaBDE; five bromines is a pentaBDE (Tables 1 and 2).

The chemical structure of PBDEs are similar to that of polychlorinated biphenyls (PCBs), another class of globally distributed environmental contaminants that the U.S. banned from production in 1976 (ATSDR, 2001). PBDEs have been referred to as the new PCBs. Consumer product manufacturers have begun using alternative flame retardants; but, in the short term, the current load of PBDEs in buildings, vehicles, and consumer products assures continued release and exposure for years to come.

Manufacture and Regulation

The industrial production of brominated diphenyl ethers primarily yields a mixture of tetra, penta, hexa, hepta, octa, nona, and deca homologues in various percentages (Siddiqi et al., 2003). Three generic commercial formulations: Penta, Octa, and DecaBDE, were produced (ATSDR, 2004) under a variety of product names (e.g., DE-71, Bromkal 70-5DE, DE-79, Bromkal 790-8DE, Saytex 102E, and Bromkal 82-0DE). Commercial formulations are mixtures of specific homologues. The relative homologue composition of these three generic formulations is shown in Table 1. The predominant congeners found in the environment are the main congeners found in commercial mixtures.

Flame retardants save lives by inhibiting ignition and subsequent burning of consumer products. Laws and regulations require that consumer products meet minimum fire safety standards. Hence, human exposure to products containing flame retardant chemicals is practically unavoidable.

Production of PBDEs in the U.S. began in the 1970s and peaked in late 1990s (Hardy, 2002a). Global demand for brominated flame retardants doubled during the 1990s (Alaee et al., 2003). In 2004, the European Union (EU) banned the use of PentaBDE and OctaBDE commercial mixtures (BSEF, 2006) and the U.S. chemical manufacturers voluntarily ceased production. Subsequently, the EU banned DecaBDE in 2008, but it continues to be produced and used in the U.S.

Commercial PentaBDE was used mainly in polyurethane foam (mattresses and padding beneath carpets and furniture). Commercial OctaBDE was predominantly used in casings for electronic products (computers, monitors, plastics). Commercial PentaBDE, OctaBDE, and DecaBDE mixtures were also used in nylon, textiles, and adhesives. Today, commercial DecaBDE is used primarily in TV casings.

Chemical Description

Table 1. Percent composition of commercial PBDE flame retardant mixtures. Commercial products contain more than one homologue in a specific range (WHO, 1994).

Product	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
Penta				24-38	50-60	4-8				
Octa						10-12	44	31-35	10-11	<1
Deca									<3	>97

Table 2. Unique PBDE congeners measured in this Mussel Watch Program assessment.

Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
BDE-1	BDE-7	BDE-17	BDE-47	BDE-85	BDE-138	BDE-181			
BDE-2	BDE-8	BDE-25	BDE-49	BDE-99	BDE-153	BDE-183			
BDE-3	BDE-10	BDE-28	BDE-66	BDE-100	BDE-154	BDE-190			
	BDE-11	BDE-30	BDE-75	BDE-116	BDE-155				
	BDE-12	BDE-32	BDE-77	BDE-118	BDE-166				
	BDE-13	BDE-33		BDE-119					
	BDE-15	BDE-35		BDE-126					
		BDE-37							

Not measured for this study

Exposure and Toxicity

Human exposure to PBDEs occurs through inhalation of contaminated household (Jones-Otazo et al., 2005) and workplace dust (Julander et al., 2005), and eating contaminated food (Schecter et al., 2006; Hale et al., 2001; Hayward et al., 2007).

Women in the U.S. were found to have some of the highest levels of PBDEs in breast milk (Schecter et al., 2003; Norén and Meronyté, 2000), blood (Schecter et al., 2005; Sjödin et al., 2008), and body fat (Johnson-Restrepo et al., 2005a; She et al., 2002). Levels in the U.S. have been rising over the past 30 years, but appear to be leveling off or decreasing (Sjödin et al., 2008). Generally, in the U.S., levels in human samples are 10-100 fold higher than levels measured in Europe, Asia, and New Zealand. Recent evidence suggests that PBDEs can be transferred from mother to fetus and from breast milk to infants (Hooper et al., 2000).

Occupational exposure may be important for some workers. The highest reported concentrations of PBDEs in human blood serum were measured in workers at an electronic waste dismantling facility in China (Qu et al., 2007).

There is a growing body of research describing the toxicology of PBDEs in animals and humans. Thorough reviews on the subject include Darnerud et al., 2001; Hardy, 2002b; and Darnerud, 2003. Toxicological studies in animals indicate that liver, thyroid, and neurobehavioral development may be impaired by these contaminants. The human health effects from exposure to PBDEs are not well documented; however, based on the structural similarity of PBDEs to PCBs, there is reason for concern. The most sensitive populations are likely to be pregnant women, developing fetuses, and infants (McDonald, 2002). Human prenatal and neonatal exposure to PBDEs is being carefully studied

and a recent report suggests an association of reduced thyroxine levels with prenatal exposure to PBDEs and PCBs (Herbstman et al., 2008).

Environmental Fate and Transport

PBDEs are widely distributed in marine sediments (Wurl and Obbard, 2005; Oros et al., 2005; Allchin et al., 1999) and biota (Environment Canada, 2006; Hites, 2004; de Wit et al., 2004). The major sources of PBDEs to the environment are homes and household dust (Stapleton et al., 2005; Jones-Otazo et al., 2005; Butt et al., 2004), releases during the manufacturing and use of commercial products, and releases during the recycling and disposal of products containing PBDEs. Subsequently, PBDEs may be distributed throughout the environment by atmospheric transport (Stranderg et al., 2001), runoff, industrial point sources, and sewage outflows (Litten et al., 2003). PBDEs are detected in remote places, such as the Arctic (Ikonomou et al., 2002; de Wit et al., 2004), representing further evidence of atmospheric transport and deposition. Other diffuse PBDE pathways include leaching from aging consumer products, incineration of municipal waste, land application of sewage sludge as biosolids, industrial discharge, and accidental spills (EPA, 2008; Hale et al., 2001; ATSDR, 2004).

Relatively high concentrations of PBDEs have been detected in sediments and biota in areas close to industrial sources (Shen et al., 2006; Liu et al., 2005). At high temperatures, PBDEs may form a volatile mixture of polybrominated dibenzodioxins (PBDD) and polybrominated dibenzofurans (PBDF), making the incineration of municipal waste containing plastic and upholstery a source of atmospheric PBDEs, dioxins, and furans (ATSDR, 2004).

PBDEs have low vapor pressures, very low water solubility, and high octanol-water partition coefficients (log K_{ow}) values (Environment Canada, 2006); therefore, they behave like many other persistent organic contaminants that accumulate in biota and sediment. In the environment they are more likely to be associated with particles than dissolved in the water.

In addition to being found in fish (Johnson and Olson, 2001; Hites et al., 2004) and shellfish (Hoenicke et al., 2007; Booij et al., 2002; Oros et al., 2005), PBDEs have been measured in foxes, grizzly bears (Christensen et al., 2005), seals (Ikonomou et al., 2008; Ikonomou et al., 2002), sea lions (Stapleton et al., 2006), polar bears (Verreault et al., 2005; Kannan et al., 2005), porpoises, whales (Weijs et al., 2009; Ross, 2006), land and sea birds (Lindberg et al., 2004; McKinney et al., 2006; Voorspoels et al., 2006; Jaspers et al., 2005; Verreault et al., 2005; Bustnes et al., 2008), and bird eggs (Herzke et al., 2005; Braune et al., 2007).

Since the 1970s, levels of PBDEs in sediments and wildlife, including aquatic species, have increased substantially (Ikonomou et al., 2002). Studies of PBDEs in marine foodwebs (Wan et al., 2008; Xia et al., 2008; Bragigand et al., 2006; Johnston-Restrepo et al., 2005a; Haglund et al., 1997) provide evidence of biomagnification. PBDEs in the environment may be transformed by debromination processes (removal of bromine atoms), including photo-transformation during exposure to sunlight (Stapleton and Dodder, 2008).