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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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.

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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

Zebra Mussels

Oysters

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.

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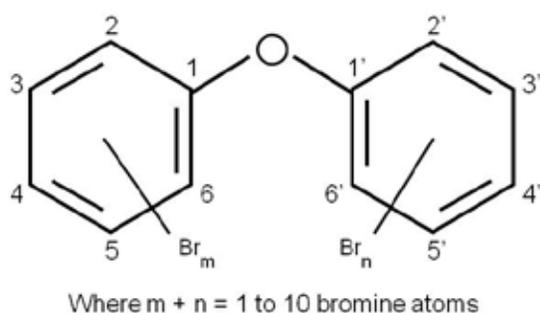
Figure 1. Chemical structure of polybrominated diphenyl ethers.

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.

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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	Not measured for this study		
	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							

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

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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).

▼ Methods

- Mussel Watch sites were selected to represent coastal areas that can be used to construct a nationwide assessment.

- Approximately half the sites are visited each year.

- Sediment samples are collected from Mussel Watch sites approximately once every 10 years, when new sites are established, or during special sampling events such as oil spills.

- Bivalve collection includes blue mussels in the Northeast Atlantic, and West Coast; oysters in the Middle Atlantic, Southeast Atlantic, Gulf of Mexico, Hawaii, and Puerto Rico; and zebra mussels in the Great Lakes.
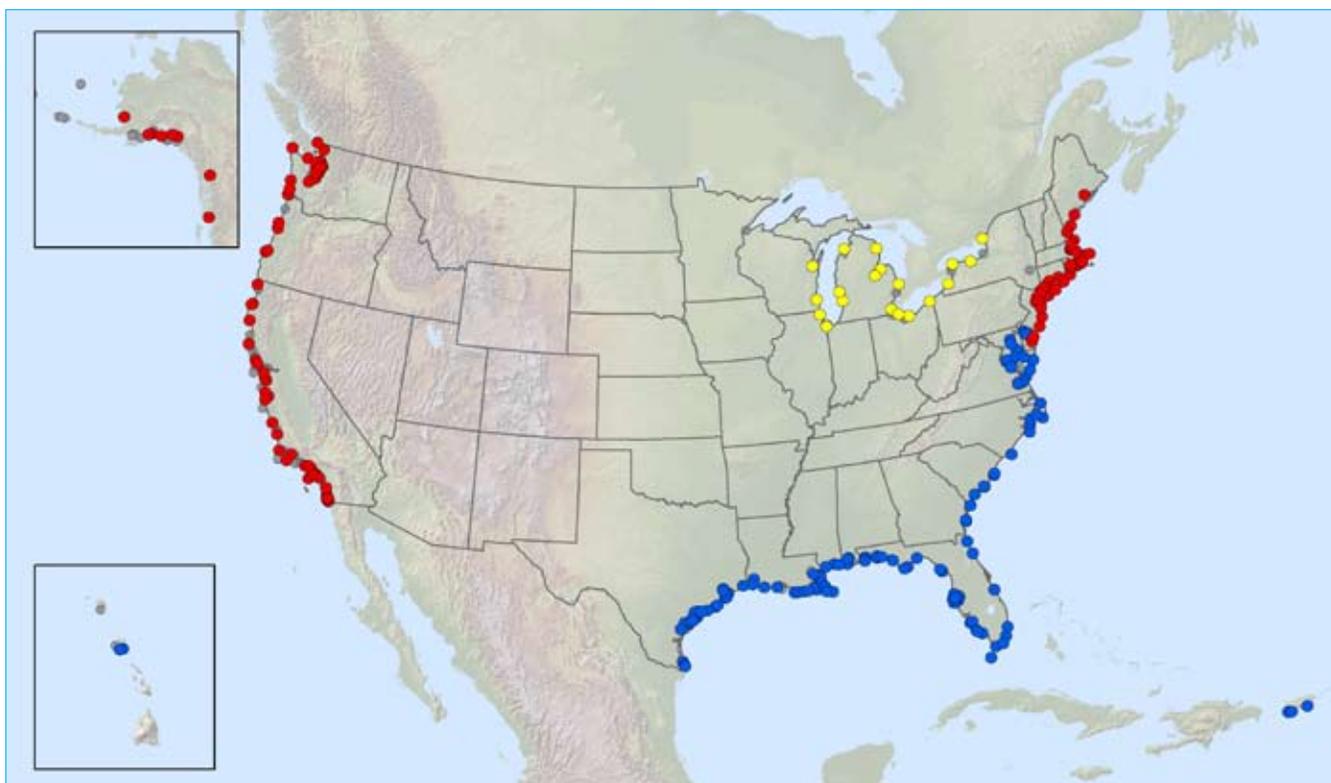
Figure 2. Distribution of ● zebra mussels, ● oysters, and ● mussels collected and measured as part of the Mussel Watch Program PBDE assessment. Mussel Watch Program sites not measured as part of this study (●).

Species and Sites

Mussels and oysters are widely distributed along the coasts. They are integrators of contaminants where they live, and their use as indicators minimizes the problems inherent in comparing data from markedly different species (Berner et al., 1976; Farrington et al., 1980; Farrington, 1983; Tripp and Farrington, 1984). They are good indicators of environmental quality because contaminant levels in their tissue respond to changes in the ambient environment and accumulate with little metabolic transformation (Roesijadi et al., 1984; Sericano, 1993).

Mussel Watch sites were selected to represent coastal areas that can be used to construct a nationwide assessment. Sites selected for monitoring are generally 10 to 100 km apart along the entire U.S. coastline, including the Great Lakes, Puerto Rico, and Hawaii. Where possible, sites were selected to coincide with historic mussel and oyster monitoring locations from other programs, such as the U.S. EPA's Mussel Watch sites that were sampled from 1976 to 1978 (Goldberg et al., 1983), and to complement sites sampled through state programs, such as the California Mussel Watch Program (Martin, 1985).

Because one single species of mussel or oyster is not common to all coastal regions, a variety of species are collected to gain a national perspective. A target species is identified for each site based on abundance and ease of collection. Mussels (*Mytilus*

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Methods

Table 3. Bivalves species used to assess national coastal PBDE concentrations.

Target Species	Name used in this report
Mytilus edulis, Mytilus californianus, Mytilus galloprovincialis, and *Mytilus trossulus*	Mussels
Crassostrea virginica, Ostrea sandvicensis, Crassostrea rhizophorae, and *Chama sinuosa**	Oysters
Dreissena polymorpha and *Dreissena bugensis*	Zebra mussels

* smooth-edge jewelbox collected from one site in the Florida Keys

species) are collected from the North Atlantic (Maine to Delaware) and Pacific coasts. Oysters are collected from Delaware Bay southward and along the Gulf Coast (*Crassostrea virginica)*, Hawaii (*Ostrea sandvicensis)*, and Puerto Rico *(Crassostrea rhizophorae)*. *Chama sinuosa* is collected from the Florida Keys and is classified along with oysters for this report. Zebra and quagga mussels (*Dreissena species*) are invasive species collected from the Great Lakes (Table 3; Figure 2). Oysters and *Mytilus* species range in size from 7 to 10 cm and 5 to 8 cm, respectively. Zebra mussels are smaller, typically 2 to 4 cm. Previous comparisons of contaminant accumulation between mussels and oysters showed large differences for trace metals, particularly zinc and copper, but the differences in organic contaminants were determined to be minor and not likely to affect comparison between species (O'Connor, 1992).

Although the U.S. coastline is extensive, relatively few species are currently required to determine a national contaminant perspective. It is possible to make spatial comparisons of organic contaminant concentrations across all sites, because Mussel Watch species bioaccumulate organic contaminants similarly (O'Connor, 1992).

Oysters and mussels are collected by hand or dredged from intertidal to shallow subtidal zones, brushed clean, packed in iced containers, and shipped to analytical laboratories within two days of collection. Approximately 20 oysters or 30 mussels are composited for each site from three stations. The bivalves are shucked, soft tissue is homogenized, and approximately 15 grams of wet tissue is extracted. Sample collection, preparation, and extraction protocols are described in detail in McDonald et al., (2006); Lauenstein et al., (1997); Lauenstein and Cantillo, (1993a-d and 1998).

Mussel Watch sites are sampled biennially with approximately half the sites visited in any one year. Annual collections are spatially distributed to provide a national snapshot (Figure 2). To provide a historical perspective and a current assessment, Mussel Watch samples from 1996 and 2004-2007 were measured respectively. Samples collected between 2004 and 2007 were aggregated and called 200X (Figure 3). Hence, 200X is a designation for samples collected from 2004 through 2007.

Sediment Sites

Sediment samples are collected from Mussel Watch sites approximately once every 10 years, when new sites are established, or following extreme events such as oil spills. Bivalve and sediment sites are taken from areas in close proximity to one another. The top 3 cm of sediments, representing recent deposition, are used in this analysis. Three sediment grabs are collected from three

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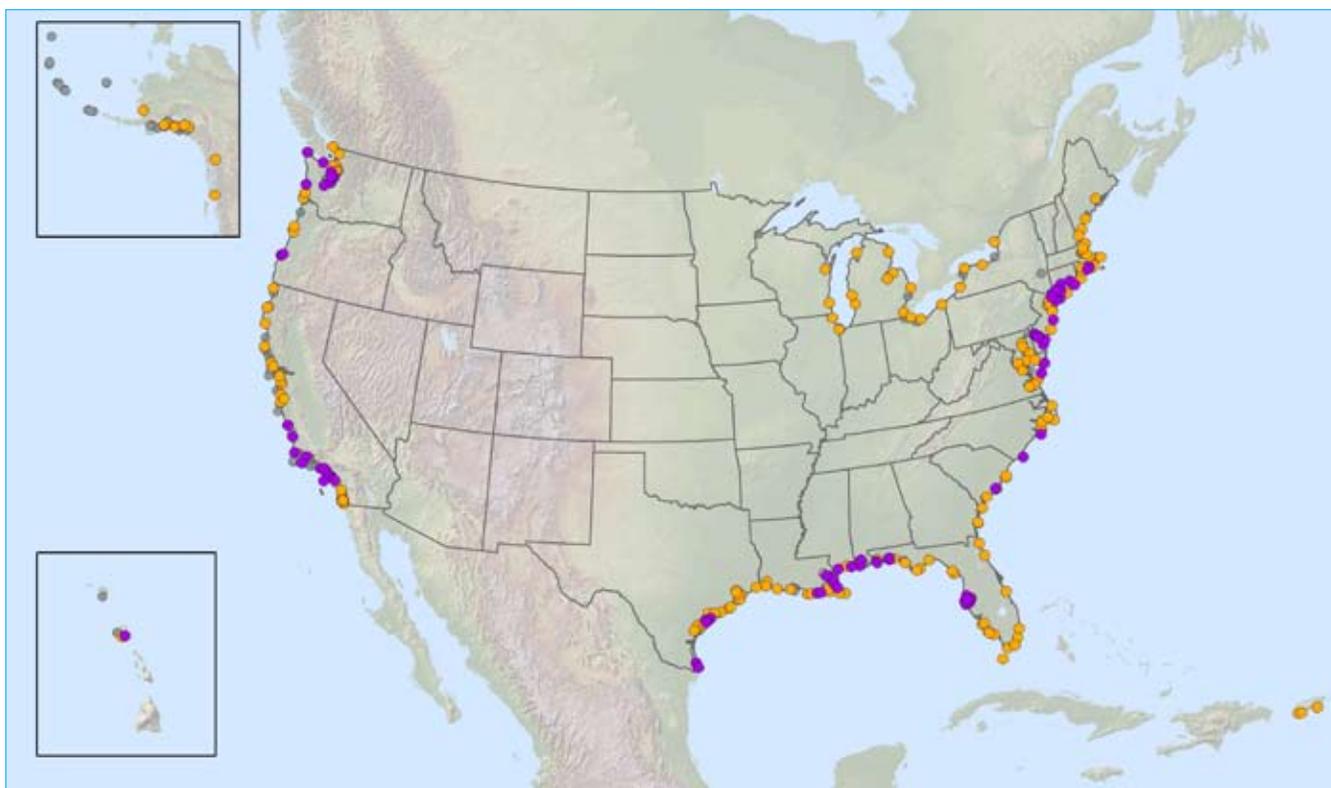
Figure 3. Number of biennial measurements taken at each of the 254 sites sampled in 1996 and 200X. Sites shown have one year (●) or two years (●) of data. Mussel Watch Program sites not measured as part of this study (●).

stations and composited. Sediment collection sites are located as near as possible to, but generally not more than, 2 km from the bivalve site, and located in low energy depositional areas.

Analytical Methods

Analytical methods used by the Mussel Watch Program are provided in Appendix 2 and available online at http://NSandT.noaa.gov. Of the 209 possible PBDE congeners, 38 were analyzed for this report (Table 2) as a result of available standards, methodology and predominant congeners (Appendix 2). The co-eluting congeners 49 and 71 are labeled in this document as 49.

Higher substituted PBDEs, such as the octa,

nona, and deca homologues that were not measured in this study, appear to accumulate preferentially in sediment. Other homologues, those measured in this study, more frequently accumulate in tissue (Zhu and Hites, 2005). Hence, this presentation provides a partial picture of the sediment-tissue relationship.

While PBDE's occur at ten different bromination levels, it was standard in early analyses to quantify the concentration of the first seven homologues. The more highly brominated forms or homologues (octa-, nona-, and deca-) were not generally measured because a standardized procedure for doing so did not readily exist. As the use of Deca, the most highly brominated form became the industry standard, the need to measure its presence in the environment

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Methods

became increasingly important. A procedure for measuring high molecular weight PBDE's was developed for use in the NS&T and was implemented as a part of our protocols in 2007. Archived Mussel Watch samples have not yet been reanalyzed for these heavier compounds but could be should the need arise.

Statistical Analysis

Results from a Shapiro-Wilk W test for tissue (W = 0.233, prob < W =0.001) and sediment (W = 0.257, prob < W = 0.001) show that Mussel Watch chemistry data were not normally distributed; thus, nonparametric tests were used for statistical analyses.

All measurements below detection limits were considered to be zero. Maps for each year show the sum of all 38 PBDE (Table 2) congeners measured for this study. Mussel Watch sites were classified into three groups. Sites below detection limit were categorized as low. Sites above the detection limit were categorized as either medium or high through cluster analysis. Clustering was performed using Ward's Minimum Variance technique. The concentration in each cluster group was then tested using Wilcoxon analysis to ensure that medium and high categories were significantly different at the α = 0.05 level. Statistical outliers were reanalyzed to ensure measurements were correct and then combined within the high category. Here, clustering was used to partition site-specific PBDE concentrations into a fixed number of "closely related" subsets. For purposes of highlighting regions with elevated PBDEs, clustering was limited to 2 subsets: high and medium.

Spearman's nonparametric statistical test was used to test for correlation between PBDE concentrations and human population.

Population was derived from 2000 census data and represents population within a radius of 20 km of each site. Tests were considered significant at the α = 0.05 level.

To evaluate overall PBDE contamination levels in watersheds throughout the Nation, a 2-way clustering (statistical classification) procedure was performed using paired sediment and tissue concentrations simultaneously. This procedure provided a descriptive yet objective technique to consider PBDE contamination levels as a function of the two measurements. Sediment and tissue concentrations from all sites within each unique watershed were averaged to develop the 2-way classification.

The Wilcoxon analysis was used to compare sediment and tissue concentrations from the watershed comparison analysis, significance was achieved at the α = 0.05 level. To ensure comparable dimensions the dry weight measurements for sediment and tissue were used.

Mussels

▼ Results and Discussion

- The highest PBDE concentrations were measured at industrial and urban locations.
- Sediment and tissue PBDE concentrations were correlated with human population within 20 km of a site.

Tissue

The national distribution of PBDEs is presented as the sum of all 38 congeners. The majority of tissue measurements above detection limits had concentrations between 1 and 270 ppb lipid weight and were categorized as medium (Figure 4 - 6). Eight percent of tissue samples (1996 and 200X) had all 38 congener measurements below detection limits.

Anaheim Bay, CA, located in an industrialized area that includes a military base, had the highest measurement in the Nation (8202 pbb lipid weight). Elevated PBDE concentrations were also found in several other developed and industrialized areas; the most high measurements occurred in the Hudson-Raritan Estuary (Figures 5 and 6; Table 4).

The highest percentage of low and high measurements occur in oysters and mussels respectively (Figure 4). As discussed earlier, the species differences are not thought to reflect uptake rate variability, rather local contaminant conditions (O'Connor, 1992). Hence, species-based distributions of PBDE bivalve body burdens are not presented.

Using Spearman's nonparametric statistical test (Figure 7), human population within 20 km of a site was found to be positively correlated with tissue concentrations (Rho = 0.555, prob <0.001). However, sites located in the same region (e.g. Southern California) exhibited both increasing and decreasing decadal results (Figure 8). This is evidence that, like many contaminants, local sources are key in determining environmental concentrations.

Temporal changes were assessed using the following categories: increasing, decreasing, or no significant change (Figure 8). The highest increase occurred at Anaheim Bay, CA; the largest decrease occurred at a Buzzards Bay, MA location.
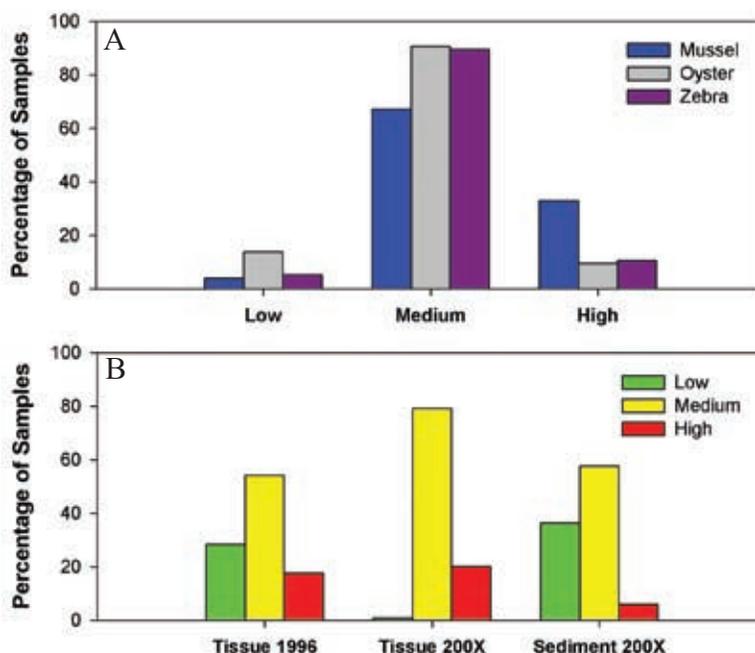
Figure 4. Percentage bar charts by species, tissue and sediment: (A) species mussel n = 161, oyster n = 158, and zebra n = 20; (B) tissue (1996 n = 85, 200X n = 254) and sediment (200X n = 122) measurements, where 200X = 2004 through 2007. Categories low (●), medium (●), and high (●) were determined by cluster analysis.

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Results and Discussion
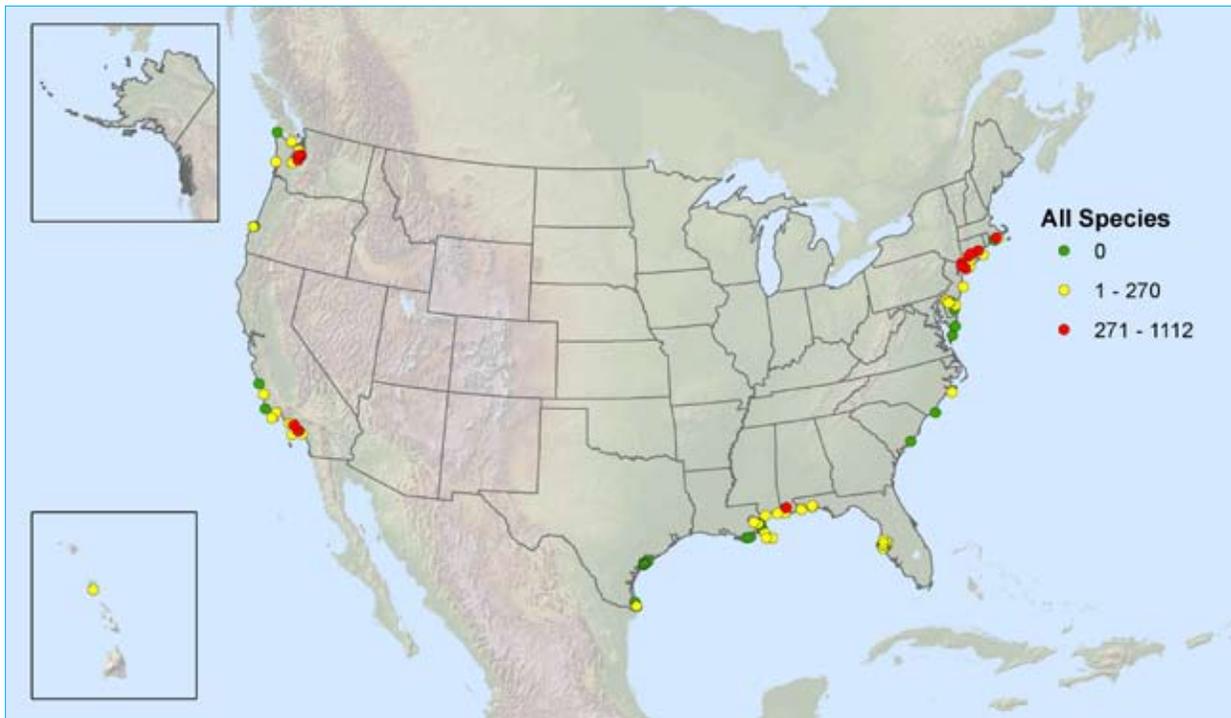
Figure 5. National distribution of 1996 PBDE tissue concentration in ppb lipid weight. Categories low (●), medium (●), and high (●) were determined by cluster analysis.
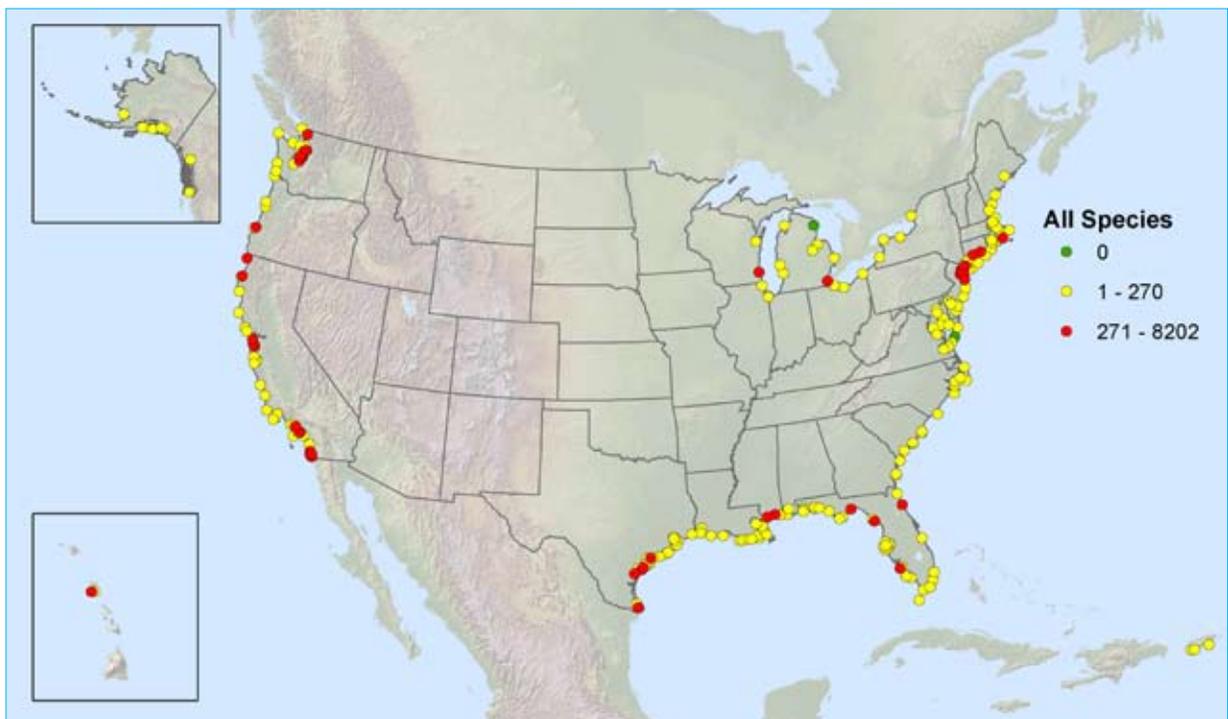
Figure 6. National distribution of 200X tissue concentration in ppb lipid weight (where 200X = 2004 through 2007). Categories low (●), medium (●), and high (●) were determined by cluster analysis.

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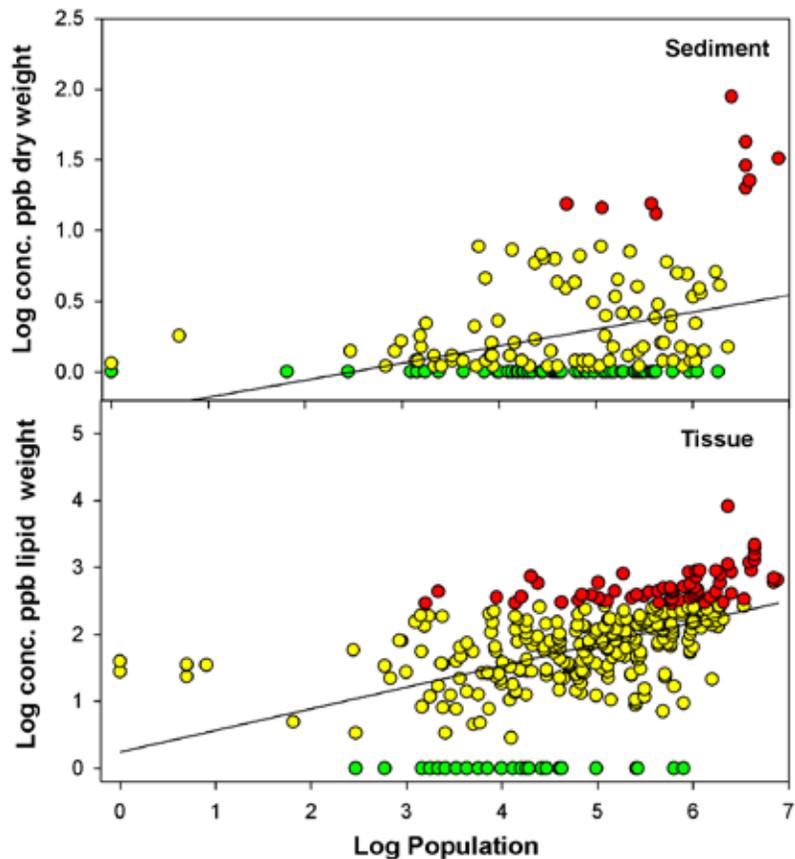
Figure 7. Tissue and sediment concentration vs population correlation analysis. Spearman's correlation tests for tissue ($\rho = 0.555$, prob <0.001) and sediment ($\rho = 0.283$, prob < 0.01) were both significant. Colors representing low (●), medium (●), and high (●) were determined by cluster analysis.

Figure 8. National change in tissue concentration in ppb lipid weight, where change = 1996 - 200X and where 200X = 2004 through 2007.

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Results and Discussion

Table 4. Location of sites with elevated PBDE tissue concentrations (ppb lipid weight), where 200X = 2004 through 2007.

State	General Location	Specific Location	Tissue 1996	Tissue 200X
CA	Anaheim Bay	West Jetty	1112	8202
NY	Hudson River	Governor's Island		2189
NY	Hudson River	Battery Park		1946
NY	Hudson River	Shore Road		1550
NY	Hudson River	Fort Wadsworth		1287
NY	Hudson/Raritan Estuary	Lower Bay		1191
CA	San Francisco Bay	Dumbarton Bridge		900
NY	Hudson/Raritan Estuary	Jamaica Bay		899
CA	Marina Del Rey	South Jetty	404	855
CA	Imperial Beach	North Jetty		846
NJ	New York Bight	Sandy Hook		784
CA	San Francisco Bay	San Mateo Bridge		731
TX	Aransas Bay	Long Reef		728
MA	Waquoit Bay	Estuarine Reserve		720
NY	Long Island Sound	Throgs Neck	601	697
NY	Hudson/Raritan Estuary	Upper Bay		653
NY	Hudson/Raritan Estuary	Raritan Bay		594
WA	San Francisco Bay	Yerba Buena Island		585
CA	Crescent	Point St. George		581
WA	Puget Sound	Edmonds Ferry		567
CA	La Jolla	Point La Jolla		514
CA	Point Loma	Lighthouse		498
CT	Long Island Sound	New Haven	333	495
NJ	New York Bight	Shark River		439
MS	Mississippi Sound	Biloxi Bay		438
FL	Cedar Key	Black Point		436
CA	Long Beach	Breakwater	883	432
WA	Commencement Bay	Tahlequah Point	342	427
NJ	New York Bight	Long Branch		426
WA	Elliott Bay	Four-Mile Rock	895	405
MS	Mississippi Sound	Pass Christian		389

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Table 4. Continued.

State	General Location	Specific Location	Tissue 1996	Tissue 200X
WA	Elliott Bay	Duwamish Head	453	389
TX	Corpus Christi	Nueces Bay		387
CA	Eureka	Samoa Bridge		383
WI	Lake Michigan	Milwaukee Bay		374
FL	Apalachee Bay	Spring Creek		361
TX	Matagorda Bay	Carancahua Bay		355
FL	Charlotte Harbor	Bird Island		352
CT	Long Island Sound	Connecticut River	590	350
WA	Puget Sound	Mukilteo		345
NY	Long Island Sound	Hempstead Harbor		334
FL	Matanzas River	Crescent Beach		322
HI	Honolulu Hrb.	Keehi Lagoon		319
WA	Bellingham Bay	Squalicum Marina Jet.		316
MI	Lake Erie	Stony Point		310
OR	Coos Bay	Russell Point		299
CA	San Diego Bay	Harbor Island		296
WA	Puget Sound	Everett Harbor		296
TX	Lower Laguna Madre	Port Isabel		293
TX	Mesquite Bay	Ayres Reef		292
WA	Sinclair Inlet	Waterman Point	456	287
AL	Mobile Bay	Dog River	374	
CT	Long Island Sound	Housatonic River	493	
MA	Buzzards Bay	Angelica Rock	804	
NY	Long Island	Jones Inlet	360	
NY	Long Island Sound	Mamaroneck	300	

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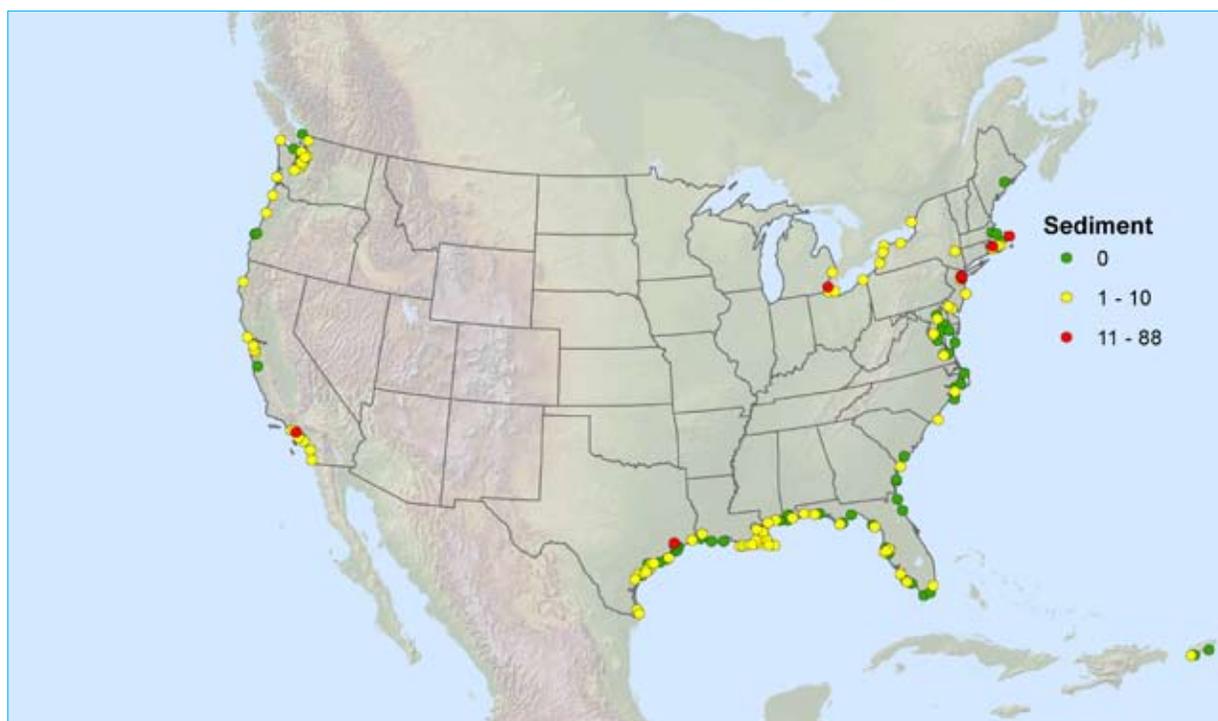
Figure 9. National distribution of 200X sediment concentration in ppb dry weight, where 200X = 2004 through 2007. Categories low (●), medium (●), and high (●) were determined by cluster analysis.

Sediment

Sediments were collected for PBDE quantification in 2004-2007. Sums ranged from below detection limit to 88 ppb dry weight (Figure 9). Thirty six percent of sediment samples had all 38 congener measurements below detection limits. As with tissue samples, cluster analysis was used to categorize like concentrations. A majority of sediment sites were categorized as medium with a small percentage of high measurements (Figure 4).

Elevated sediment concentrations (1 to 88 ppb dry weight) were found in urbanized or industrialized bays and estuaries (Figure 9; Table 5). However, a statistically significant correlation between sediment PBDE concentrations and population was weak in comparison to tissue (Figure 9). The relatively low correlation between population and sediment concentration may be caused by the large number of measurements that were below detection.

The highest sediment measurements observed were taken from an urbanized location, Marina del Rey, CA (88 ppb dry weight). Several high measurements were found in the Hudson-Raritan Estuary in addition to other areas (Figure 9; Table 5). Sediment PBDE concentrations were generally lower than concentrations found in tissues.

Location	State	Sediment	Tissue
Albemarle Sound	NC	0.00	26.92
Pensacola Bay	FL	0.10	29.60
Savannah River	GA	0.10	30.00
Atchafalaya/Vermilion Bays	LA	0.15	26.67
Sabine Lake	LA	0.10	26.02
Terrebonne/Timbalier Bays	LA	0.17	24.31
Big Cypress Swamp	FL	0.00	45.87
Mermentau	LA	0.00	47.83
Monie Bay	MD	0.00	37.37
St. Catherines/Sapelo Sounds	GA	0.00	37.14
Bogue Sound	NC	0.00	21.14
North Ten Thousand Islands	FL	0.00	20.17
Crystal-Pithlachascotee	FL	0.20	15.66
Pamlico Sound	NC	0.03	15.16
Rookery Bay	FL	0.20	9.50
Barataria Bay	LA	0.73	79.65
Choctawhatchee Bay	FL	0.75	76.00
Yaquina Bay	OR	0.70	91.67
San Antonio Bay	TX	0.46	64.72
Willapa Bay	WA	0.60	64.60
Tampa Bay	FL	0.24	62.99
Breton/Chandeleur Sound	LA	0.70	33.43
Buzzards Bay	MA	0.88	52.76
Puerto Rico	PR	1.47	42.10
Eastern Lower Delmarva	VA	0.00	0.00
Florida Bay	FL	0.00	2.90
Altamaha River	GA	0.00	64.29
Calcasieu Lake	LA	0.05	69.85
Dungeness-Elwha	WA	0.00	70.27
Mullica-Toms	NJ	0.10	74.89
East Mississippi Sound	MS	0.00	78.66
Mobile Bay	AL	0.00	87.97
Monterey Bay	CA	0.00	83.33
Austin-Oyster	TX	0.20	136.07
Los Angeles	CA	0.20	129.71
Bass Island	SC	0.00	103.75
Chesapeake Bay	VA/MD	0.10	104.25
Lower Laguna Madre	TX	0.20	105.63
Brazos River	TX	0.00	151.06
St. Johns River	FL	0.00	152.50
Massachusetts Bay	MA	0.00	159.38
Penobscot Bay	ME	0.00	143.33
Coos Bay	OR	0.00	170.78
Matagorda Bay	TX	0.06	206.00
Biscayne Bay	FL	0.60	136.25
Puget Sound	WA	0.74	224.53
Strait of Georgia	WA	0.40	185.39
Tomales Bay	CA	0.30	220.00
Apalachee Bay	FL	0.00	361.11
Daytona-St. Augustine	FL	0.00	322.00
Aransas Bay	TX	0.05	397.71
Humboldt Bay	CA	0.20	383.33
Suwannee River	FL	0.15	294.11
San Diego Bay	CA	0.40	296.30
Apalachicola Bay	FL	3.35	25.19
Chautauqua-Connaut	NY/OH	3.10	28.81
Cape Fear River	NC	5.40	28.77
Irondequoit-Ninemile	NY	5.00	72.66
Oak Orchard-Twelvemile	NY	5.80	56.83
Cape Cod	MA	14.40	31.82
St. Lawrence River	NY	3.60	6.73
Cedar-Portage	OH	6.30	184.76
Narragansett Bay	RI	4.87	135.83
Charlotte Harbor	FL	6.10	351.67
Corpus Christi Bay	TX	1.60	386.67
San Louis Rey-Escondido	CA	1.40	268.33
San Francisco Bay	CA	2.00	738.70
Delaware Bay	DE/NJ	1.95	135.02
Newport Bay	CA	2.60	126.20
Galveston Bay	TX	2.42	181.94
West Mississippi Sound	MS/LA	2.36	186.80
San Pedro Bay	CA	2.33	2961.90
Hudson River/Raritan Bay	NY	18.70	812.50
Ottawa-Stony	MI	13.50	310.24
Santa Monica Bay	CA	44.00	499.46

Cluster 1
Avg. Sed. = 0.29 (L)
Avg. Tis. = 37.5 (L)

Cluster 2
Avg. Sed. = 0.13 (L)
Avg. Tis. = 175.4 (H)

Cluster 3
Avg. Sed. = 5.9 (H)
Avg. Tis. = 35.8 (L)

Cluster 4
Ave. Sed. = 7.9 (H)
Ave. Tis. = 520.0 (H)

Figure 10. Cluster analysis of paired sediment (ppb dry weight) and tissue (ppb lipid weight) contamination measurements.

Results and Discussion

Table 5. Location of sites with elevated PBDE sediment concentrations (ppb dry weight), where 200X = 2004 through 2007.

State	General Location	Specific Location	Sediment 200X
CA	Marina del Rey	South Jetty	88
NY	Hudson-Raritan Estuary	World Trade Center	41
NY	Hudson-Raritan Estuary	Upper Bay	31
NY	Hudson-Raritan Estuary	Holland Tunnel	28
NY	Hudson-Raritan Estuary	Lower Bay	22
NY	Hudson-Raritan Estuary	Ellis Island	19
TX	Galveston Bay	Ship Channel	15
MA	Cape Cod	Nauset Harbor	14
OH	Lake Erie	Stony Point	14
RI	Narragansett Bay	Dyer Island	12

Regional and Local Analysis

Using the Wilcoxon statistical test, tissue PBDE concentrations were found to be significantly higher than sediment measurements taken at the same site (χ^2 = 211, prob < 0.001). To ensure comparable dimensions, the dry weight measurements for sediment and tissue were used during comparisons of the two matrices. No correlation was found between tissue and sediment measurements (prob = 0.135).

Two-way clustering of paired data provides a detailed view of paired concentration values, and groups of similar character (Figure 10). The cluster "map" is color-coded to represent concentration values, with dark red indicating elevated concentrations, light red and green indicating moderately elevated concentrations, and dark green indicating low concentrations. Cluster 4 stands out as a unique group with high concentrations of PBDEs in both tissue and sediment. These levels may also be reflected in humans. For example, the Hudson-Raritan Estuary is surrounded by the highest density population

in the Nation, which probably contributes to the elevated PBDE levels observed there (Figure 5 and 6; Tables 4 and 5). A study by Johnston-Restrepo et al., (2005b) indicates that levels of PBDEs in adipose tissue of New Yorkers is orders of magnitude higher than levels found in Europeans.

Hoh and Hites, (2005) measured air samples from Lake Michigan through the Midwest to the Gulf of Mexico and detected residues of PBDE in remote areas. Their results suggest that concentrations in particles are 3 to 6 times higher in urban areas. While this finding corroborates the link between PBDE concentrations and human population density, it also highlights the potential of PBDEs to be transported through the atmosphere to remote locations. The highest concentrations occur in areas with high population; however, even in some densely populated areas, the median concentration was not always in the elevated range.

The distribution of congeners measured in this study is in the range of what has been reported globally for mussels and sediment

(Hoenicke et al., 2007; Oros et al., 2005; Hites, 2004; Christensen and Platz, 2001; de Wit, 2002). Sediment concentrations reported globally from highly polluted industrial locations had congener concentrations for 47, 99, and 153 on the order of 1000 ppb dry weight (Luo et al., 2007).

Industrial sources have also been identified in other studies as a source for the highest levels of PBDEs (Luo et al., 2007; de Wit, 2000). Studies have found that PBDE concentrations in urban areas are elevated but not to the level of industrial locations

(Hoenicke et al., 2007; Oros et al., 2005; Hites, 2004; Christensen and Platz, 2001; de Wit, 2002). Mussel Watch sampling does not specifically collect industrial and point sources; as a result, mean sediment concentrations reported in this study were lower than what had been reported for industrial point sources.

Future assessments by the National Status and Trends Program will include higher brominated homologues, providing a more complete characterization of PBDEs in the U.S. coastal zone.

▼ Societal Relevance

- In the environment major PBDE and PCB congeners have similar concentration ranges.
- Proper disposal of consumer goods is critical to limiting environmental releases of PBDEs.
- Societal benefits must be weighed against toxicity when determining the value of flame retardants.

PBDEs readily accumulate in organisms, including humans, and magnify upwards through marine food chains (Wan et al., 2008). Some of the highest PBDE levels measured in humans are from occupational exposures (Qu et al., 2007); however, PBDE levels in the general population result from exposure to contaminated indoor dust and food (Hites, 2004).

PBDEs have been called "the new PCBs," and while there are some similarities, a major difference between them is the source of exposure. PCBs were primarily point source industrial contaminants, while PBDEs are primarily found in consumer goods.

A comparison of Mussel Watch PCB data (Kimbrough et al., 2008) and Mussel Watch PBDE data (this report) suggests environmental concentrations of major PBDE and PCB congeners have a similar concentration range. With the continued use of DecaBDE and the current pool of consumer goods that contain PBDEs, environmental concentrations of PBDEs could surpass that of PCBs in certain locations.

Chemical flame retardants clearly save

lives and property, but the costs and benefits of using some of these compounds are hotly debated with respect to consumer health and safety, and the environment. The U.S. Consumer Product Safety Commission (CPSC, 2008) estimates losses from residential fire. They reported that the combined fire related deaths from upholstered furniture and mattress bedding fires (which exceeded all other categories) decreased from a high of 2,200 deaths in 1980 to 930 deaths in 1998 (CPSC, 2000) partly due to the use of flame retardants, including PBDEs.
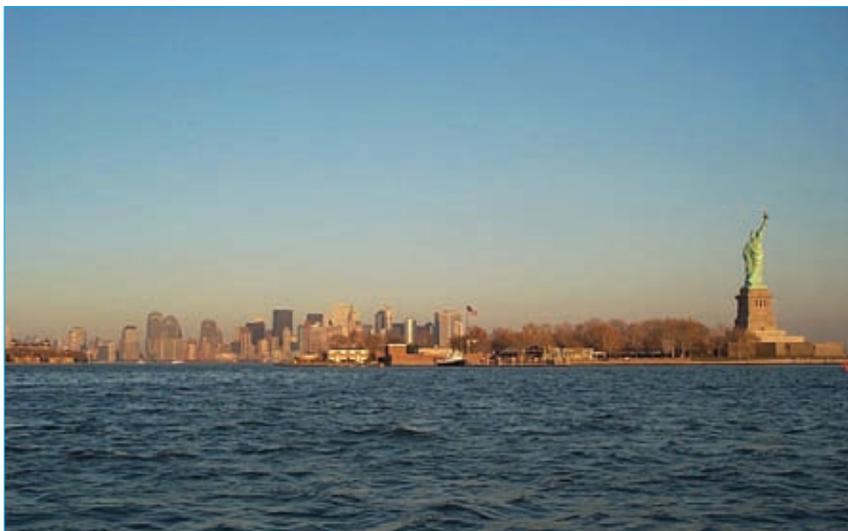
Flame retardant manufacturers in the U.S. voluntarily stopped producing the PentaBDE and OctaBDE formulations in 2004. Thus, upholstered furniture and mattress manufactures had to seek alternative flame retardants to meet fire safety standards, some of these new retardants have already been measured in house dust samples (Stapleton et al., 2008). Unfortunately, alternative chemical flame retardants may be toxic while

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others have very limited toxicity data. For example, chlorinated tris, a flame retardant, is a known carcinogen. Other brominated chemicals, such as tetrabrominated benzoate and tetrabrominated phthalate, have incomplete toxicity data (SFEI, 2008).

As with many persistent organic pollutants, PBDEs are distributed by atmospheric transport (Hoh and Hites, 2005). Even with a global reduction in PBDE use, the continued release of PBDEs into the environment is inevitable for years to come due to their persistant nature. Therefore, the proper disposal of consumer products such as furniture, mattresses, televisions, and computers is critical (Bogdal et al., 2008; Strandberg et al., 2001). Consumer products that contain PBDEs fill homes across the country. Hence, care must be taken to prevent further release of PBDEs into the environment when these products are discarded or recycled. Proper disposal methods must be developed and implemented.

Improper electronic waste recycling and disposal can cause significant environmental degradation (Luo et al., 2007) and may have negative occupational health ramifications (Qu et al., 2007). Proper disposal would curtail

local releases to the environment and limit atmospheric transport, thereby mitigating the threat to coastal areas, remote regions, and marine food chains. Elevated levels of PBDEs found in municipal sewage is evidence of an increased threat to the environment from land based sources (Song et al., 2006; de Wit, 2002).

The toxicity and ecosystem effects of PBDEs on marine biota have not been well studied. Laboratory toxicity studies show potential for adverse human health effects. Until such time as these questions are satisfactorily resolved, ongoing monitoring for these contaminants should continue.

This report clearly shows that PBDEs are ubiquitous in coastal sediments and bivalves. NOAA's NS&T Program will continue to monitor and report on PBDEs in sediment and tissue. In addition, NOAA staff are working with Federal and State agencies, and non-governmental organizations to identify other emerging contaminants of concern, including alternative flame retardants.

An Assessment of PBDEs in Sediment and Bivalves of the U.S. Coastal Zone

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Appendix 1

Alabama

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
MBWE	30.3867	-87.8320	Mobile Bay	Weeks Bay	AL	O
MBDR	30.5917	-88.0398	Mobile Bay	Dog River	AL	O
MBHI	30.5633	-88.0750	Mobile Bay	Hollingers Is. Chan.	AL	O
MBCP	30.3155	-88.1338	Mobile Bay	Cedar Point Reef	AL	O

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
MBWE					● 0.6
MBDR	● 374	38.5	● 149	22.0	● 0.0
MBHI	● 136	24.6			● 0.0
MBCP	● 29	3.6	● 27	3.8	● 0.0

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
KTMP	55.2938	-131.5480	Ketchikan	Mountain Point	AK	M
CINK	59.3580	-151.9300	Kachemak Bay	Nanwalek	AK	M
NBES	59.4533	-135.3365	Nahku Bay	East Side	AK	M
CIHS	59.6145	-151.4442	Cook Inlet	Homer Spit	AK	M
RBNR	60.1021	-149.3642	Resurrection Bay	Nash Road	AK	M
RBMF	60.1130	-149.3740	Resurrection Bay	Mud Flats	AK	M
UISB	60.9608	-147.6460	Unakwit Inlet	Siwash Bay	AK	M
PVMC	61.1328	-146.4610	Port Valdez	Mineral Creek Flats	AK	M
NGEK	58.7961	-158.5325	Nushagek Bay	Nushagek Bay	AK	M

Low ●, Medium ●, and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
KTMP			● 32	3.2	
CINK			● 2	0.3	
NBES			● 79	7.9	
CIHS			● 150	9.0	
RBNR			● 35	4.5	
RBMF			● 17	1.6	
UISB			● 34	1.7	
PVMC			● 46	4.1	
NGEK			● 15	1.5	

Appendix 1

California

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
IBNJ	32.5877	-117.1335	Imperial Beach	North Jetty	CA	M
PLLH	32.6805	-117.2488	Point Loma	Lighthouse	CA	M
SDCB	32.6865	-117.1592	San Diego Bay	Coronado Bridge	CA	M
SDHI	32.7247	-117.1947	San Diego Bay	Harbor Island	CA	M
MBVB	32.7675	-117.2420	Mission Bay	Ventura Bridge	CA	M
LJLJ	32.8515	-117.2738	La Jolla	Point La Jolla	CA	M
OSBJ	33.2017	-117.3937	Oceanside	Municipal Beach Jetty	CA	M
SCBR	33.4517	-118.4873	South Catalina Island	Bird Rock	CA	M
NBWJ	33.5910	-117.8900	Newport Beach	West Jetty	CA	M
SPFP	33.7067	-118.2742	San Pedro Harbor	Fishing Pier	CA	M
PVRP	33.7170	-118.3227	Palos Verdes	Royal Palms State Pk.	CA	M
LBBW	33.7232	-118.1735	Long Beach	Breakwater	CA	M
ABWJ	33.7335	-118.1010	Anaheim Bay	West Jetty	CA	M
RBMJ	33.8320	-118.3928	Redondo Beach	Municipal Jetty	CA	M

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
IBNJ			● 846	77.0	
PLLH			● 498	29.9	
SDCB			● 236	30.2	
SDHI			● 296	32.0	● 0.4
MBVB			● 153	13.8	
LJLJ			● 514	36.0	
OSBJ			● 268	16.1	● 1.4
SCBR	● 63	3.1	● 21	1.4	
NBWJ	● 228	13.2	● 126	7.6	● 2.6
SPFP			● 252	24.1	● 2.4
PVRP	● 234	17.8	● 154	12.0	
LBBW	● 883	47.7	● 432	37.4	● 4.1
ABWJ	● 1112	93.4	● 8202	840.8	● 0.5
RBMJ	● 253	17.7	● 264	22.2	

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
MDSJ	33.9618	-118.4580	Marina del Rey	South Jetty	CA	M
PDPD	34.0010	-118.8088	Point Dume	Point Dume	CA	M
TBSM	34.0390	-118.5972	Las Tunas Beach	Santa Monica Bay	CA	M
SCFP	34.0580	-119.9203	Santa Cruz Island	Fraser Point	CA	M
SBSB	34.3957	-119.7275	Point Santa Barbara	Point Santa Barbara	CA	M
PCPC	34.4438	-120.4570	Point Conception	Point Conception	CA	M
SLSL	35.1607	-120.7558	San Luis Obispo Bay	Point San Luis	CA	M
SSSS	35.6347	-121.1947	San Simeon Point	San Simeon Point	CA	M
PGLP	36.6272	-121.9165	Pacific Grove	Lovers Point	CA	M

Low ●, Medium ●, and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996			Tissue 200X			Sediment 200X	
		Lipid	Dry		Lipid	Dry		Dry
MDSJ	●	404	37.6	●	855	75.2	●	87.8
PDPD	●	236	13.7	●	130	9.8	●	0.2
TBSM	●	117	13.7	●	144	11.7	●	0.2
SCFP	●	22	2.6	●	34	2.1		
SBSB	●	62	3.2	●	96	7.0		
PCPC	●	0	0.0	●	33	2.7		
SLSL	●	71	5.8	●	77	12.2		
SSSS	●	0	0.0	●	26	1.9		
PGLP				●	170	11.9		

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Appendix 1

California cont'd

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
MBML	36.8012	-121.7897	Monterey Bay	Moss Landing	CA	M
MBES	36.8098	-121.7852	Monterey Bay	Elkhorn Slough	CA	M
MBSC	36.9542	-122.0247	Monterey Bay	Point Santa Cruz	CA	M
SFDB	37.5027	-122.1213	San Francisco Bay	Dumbarton Bridge	CA	M
SFSM	37.5780	-122.2537	San Francisco Bay	San Mateo Bridge	CA	M
SFYB	37.8152	-122.3715	San Francisco Bay	Yerba Buena Island	CA	M
TBSR	38.1495	-122.9040	Tomales Bay	Spenger's Residence	CA	M
BBBE	38.3050	-123.0660	Bodega Bay	Bodega Bay Entrance	CA	M
PALH	38.9530	-123.7430	Point Arena	Lighthouse	CA	M
PDSC	40.0225	-124.0733	Point Delgada	Shelter Cove	CA	M
HMBJ	40.7642	-124.2375	Eureka	Humboldt Bay Jetty	CA	M
EUSB	40.8215	-124.1713	Eureka	Samoa Bridge	CA	M
SGSG	41.7478	-124.2077	Crescent	Point St. George	CA	M

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
MBML			● 139	11.1	
MBES			● 83	10.0	● 0.0
MBSC			● 162	9.7	
SFDB			● 900	63.0	● 2.9
SFSM			● 731	65.8	● 1.2
SFYB			● 585	58.5	● 1.9
TBSR			● 220	17.6	● 0.3
BBBE			● 117	18.7	
PALH			● 183	11.0	
PDSC			● 190	11.4	
HMBJ			● 134	9.4	
EUSB			● 383	23.0	● 0.2
SGSG			● 581	46.5	

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
LICR	41.2667	-72.3417	Long Island Sound	Connecticut River	CT	M
LINH	41.2542	-72.9393	Long Island Sound	New Haven	CT	M
LIHR	41.1673	-73.1083	Long Island Sound	Housatonic River	CT	M
LISI	41.0527	-73.4173	Long Island Sound	Sheffield Island	CT	M

Low ●, Medium ● , and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
LICR	● 590	36.6	● 350	21.1	
LINH	● 333	25.0	● 495	26.6	
LIHR	● 493	42.9	● 210	17.2	
LISI	● 68	2.5	● 74	7.1	

Appendix 1
Delaware

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
DBKI	39.2032	-75.3590	Delaware Bay	Kelly Island	DE	O
DBCH	38.7835	-75.1205	Delaware Bay	Cape Henlopen	DE	M

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site		Tissue 1996			Tissue 200X		Sediment 200X
		Lipid	Dry		Lipid	Dry	Dry
DBKI	●	12	1.8	●	18	1.7	
DBCH	●	0	0.0	●	14	1.0	

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
SJCB	30.3810	-81.4400	St. Johns River	Chicopit Bay	FL	O
MRCB	29.7640	-81.2618	Matanzas River	Crescent Beach	FL	O
IRSR	27.8295	-80.4743	Indian River	Sebastian River	FL	O
NMML	25.9377	-80.1497	North Miami	Maule Lake	FL	O
BBGC	25.5333	-80.3232	Biscayne Bay	Gould's Canal	FL	O
BHKF	24.6612	-81.2730	Florida Keys	Bahia Honda	FL	O *
FBJB	25.2122	-80.5340	Florida Bay	Joe Bay	FL	O
FBFO	25.1412	-80.9237	Florida Bay	Flamingo	FL	O
EVFU	25.9023	-81.5123	Everglades	Faka Union Bay	FL	O
RBHC	26.0270	-81.7388	Rookery Bay	Henderson Creek	FL	O
NBNB	26.1118	-81.7852	Naples Bay	Naples Bay	FL	O
CBFM	26.5583	-81.9228	Charlotte Harbor	Fort Meyers	FL	O

* BHKF is classified as O; however, it is the smooth-edged jewelbox.

Low ●, Medium ●, and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
SJCB			● 153	6.1	● 0.0
MRCB			● 322	16.1	● 0.0
IRSR			● 199	29.9	
NMML			● 138	16.5	
BBGC			● 136	10.9	● 0.6
BHKF			● 9	0.8	
FBJB			● 2	0.3	● 0.0
FBFO			● 4	0.6	● 0.0
EVFU			● 20	2.3	● 0.0
RBHC			● 10	1.2	● 0.2
NBNB			● 46	5.0	● 0.0
CBFM			● 166	13.3	

Florida Cont'd

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
CBBI	26.5143	-82.0345	Charlotte Harbor	Bird Island	FL	O
TBHB	27.8548	-82.3947	Tampa Bay	Hillsborough Bay	FL	O
TBKA	27.9097	-82.4538	Tampa Bay	Peter O. Knight Airport	FL	O
TBCB	27.6810	-82.5177	Tampa Bay	Cockroach Bay	FL	O
TBPB	27.8443	-82.6115	Tampa Bay	Papys Bayou	FL	O
TBOT	28.0237	-82.6328	Tampa Bay	Old Tampa Bay	FL	O
TBMK	27.6208	-82.7265	Tampa Bay	Mullet Key Bayou	FL	O
TBNP	27.7872	-82.7540	Tampa Bay	Navarez Park	FL	O
CKBP	29.2067	-83.0695	Cedar Key	Black Point	FL	O
SRWP	29.3292	-83.1742	Suwannee River	West Pass	FL	O
AESP	30.0633	-84.3220	Apalachee Bay	Spring Creek	FL	O

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
CBBI			● 352	21.1	● 6.1
TBHB	● 24	3.8	● 22	3.2	● 0.6
TBKA	● 196	46.5	● 220	26.4	● 0.5
TBCB	● 0	0.0	● 9	1.0	● 0.0
TBPB	● 0	0.0	● 8	1.1	● 0.1
TBOT	● 53	6.2	● 55	7.9	● 0.0
TBMK	● 8	1.5	● 10	1.2	
TBNP	● 0	0.0	● 16	1.6	● 0.2
CKBP			● 436	43.6	● 0.3
SRWP			● 152	13.7	● 0.0
AESP			● 361	32.5	● 0.0

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
APCP	29.7242	-84.8842	Apalachicola Bay	Cat Point Bar	FL	O
APDB	29.6725	-85.0657	Apalachicola Bay	Dry Bar	FL	O
SAWB	30.1425	-85.6322	St. Andrew Bay	Watson Bayou	FL	O
CBSR	30.4120	-86.2037	Choctawhatchee Bay	Off Santa Rosa	FL	O
CBPP	30.4823	-86.4793	Choctawhatchee Bay	Postil Point	FL	O
CBJB	30.4108	-86.4908	Choctawhatchee Bay	Joe's Bayou	FL	O
PBIB	30.5167	-87.1117	Pensacola Bay	Indian Bayou	FL	O
PBSP	30.3498	-87.1547	Pensacola Bay	Sabine Point	FL	O
PBPH	30.4137	-87.1913	Pensacola Bay	Public Harbor	FL	O

Low ●, Medium ●, and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996 Lipid	Dry	Tissue 200X Lipid	Dry	Sediment 200X Dry
APCP			25	3.5	0.0
APDB			25	3.3	6.7
SAWB			59	8.2	
CBSR			27	3.8	0.0
CBPP	27	2.9	33	4.7	
CBJB	62	8.1	125	14.3	1.5
PBIB			30	4.6	0.1
PBSP	24	1.8	23	2.0	
PBPH	48	5.9	53	6.7	

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Appendix 1

Georgia

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
SRTI	32.0165	-80.8825	Savannah River Estuary	Tybee Island	GA	O
SSSI	31.3928	-81.2880	Sapelo Sound	Sapelo Island	GA	O
ARWI	31.3242	-81.3108	Altamaha River	Wolfe Island	GA	O

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
SRTI			● 30	2.7	● 0.1
SSSI			● 37	2.6	● 0.0
ARWI			● 64	4.5	● 0.0

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
HHKL	21.3167	-157.8858	Honolulu Hrb.	Keehi Lagoon	HI	O
HHKB	21.4118	-157.7788	Hawaii	Kaneohe Bay	HI	O

Low ●, Medium ● , and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site		Tissue 1996			Tissue 200X		Sediment 200X
		Lipid	Dry		Lipid	Dry	Dry
HHKL				●	319	35.1	
HHKB	●	139	11.1	●	65	6.0	

Illinois-Indiana

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
LMNC	42.3047	-87.8273	Lake Michigan	North Chicago	IL	ZM
LMHM	41.6987	-87.5083	Lake Michigan	Hammond Marina	IN	ZM
LMCB	41.7272	-87.4950	Lake Michigan	Calumet Breakwater	IN	ZM

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996			Tissue 200X		Sediment 200X
	Lipid	Dry		Lipid	Dry	Dry
LMNC			●	6	0.5	
LMHM			●	189	18.7	
LMCB			●	20	1.4	

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
MRPL	29.0895	-89.0748	Mississippi River	Pass A Loutre	LA	O
MRTP	29.1450	-89.4273	Mississippi River	Tiger Pass	LA	O
BSSI	29.4057	-89.4838	Breton Sound	Sable Island	LA	O
BSBG	29.5980	-89.6208	Breton Sound	Bay Gardene	LA	O
LBMP	29.8670	-89.6785	Lake Borgne	Malheureux Point	LA	O
LBGO	29.9448	-89.8353	Lake Borgne	Gulf Outlet	LA	O
BBMB	29.2767	-89.9420	Barataria Bay	Middle Bank	LA	O
BBSD	29.4048	-89.9988	Barataria Bay	Bayou Saint Denis	LA	O
LPNO	30.0363	-90.0413	Lake Pontchartrain	New Orleans	LA	O
BBTB	29.5112	-90.0833	Barataria Bay	Turtle Bay	LA	
TBLF	29.2642	-90.3982	Terrebonne Bay	Lake Felicity	LA	O
TBLB	29.2595	-90.5943	Terrebonne Bay	Lake Barre	LA	O
CLCL	29.2532	-90.9267	Caillou Lake	Caillou Lake	LA	O
ABOB	29.2555	-91.1362	Atchafalaya Bay	Oyster Bayou	LA	O

Low ●, Medium ●, and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
MRPL	● 33	5.3			● 0.8
MRTP	● 80	5.5			● 0.4
BSSI	● 22	3.2	● 55	7.9	● 0.3
BSBG	● 0	0.0	● 12	1.5	● 1.1
LBMP	● 0	0.0	● 17	1.9	● 1.3
LBGO	● 14	1.7	● 11	1.3	● 0.5
BBMB			● 133	12.8	● 0.8
BBSD			● 26	2.7	● 0.7
LPNO	● 250	48.8	● 79	9.9	● 3.9
BBTB					● 0.2
TBLF	● 0	0.0	● 39	3.3	● 0.2
TBLB	● 0	0.0	● 13	1.6	● 0.2
CLCL			● 21	2.2	● 0.1
ABOB			● 27	3.0	● 0.2

Louisiana cont'd

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
VBSP	29.5795	-92.0510	Vermilion Bay	Southwest Pass	LA	O
JHJH	29.6368	-92.7668	Joseph Harbor Bayou	Joseph Harbor Bayou	LA	O
CLLC	30.0587	-93.3075	Calcasieu Lake	Lake Charles	LA	O
CLSJ	29.8290	-93.3840	Calcasieu Lake	St. Johns Island	LA	O
SLBB	29.7908	-93.9063	Sabine Lake	Blue Buck Point	LA	O

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
VBSP			● 39	5.2	● 0.0
JHJH			● 57	6.0	● 0.0
CLLC			● 67	7.5	● 0.1
CLSJ			● 73	8.0	● 0.0
SLBB			● 26	3.2	● 0.1

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
PBSI	44.4567	-68.8832	Penobscot Bay	Sears Island	ME	M
MSSP	43.7578	-69.9977	Merriconeag Sound	Stover Point	ME	M
CAKP	43.3453	-70.4743	Cape Arundel	Kennebunkport	ME	M

Low ●, Medium ● , and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996			Tissue 200X		Sediment 200X
	Lipid	Dry		Lipid	Dry	Dry
PBSI			●	143	17.2	● 0.0
MSSP			●	21	2.1	
CAKP			●	54	4.3	

Appendix 1

Maryland

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
CBBO	39.1573	-76.4048	Chesapeake Bay	Bodkin Point	MD	O
CBHP	38.9695	-76.4147	Chesapeake Bay	Hackett Point Bar	MD	O
CBCP	38.6073	-76.1200	Chesapeake Bay	Choptank River	MD	O
CBHG	38.3123	-76.3978	Chesapeake Bay	Hog Point	MD	O
PRSP	38.2817	-76.9337	Potomac River	Swan Point	MD	O
CBMB	38.2030	-75.8812	Chesapeake Bay	Monie Bay	MD	O

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
CBBO			● 185	24.1	● 0.0
CBHP			● 94	10.3	● 0.3
CBCP			● 88	8.8	● 0.0
CBHG			● 43	8.2	● 0.0
PRSP			● 78	8.6	● 0.1
CBMB			● 37	7.1	● 0.0

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
CAGH	42.6577	-70.5973	Cape Ann	Gap Head	MA	M
SHFP	42.5135	-70.8442	Salem Harbor	Folger Point	MA	M
MBNB	42.4198	-70.9072	Massachusetts Bay	Nahant Bay	MA	M
BHDI	42.3573	-70.9730	Boston Harbor	Deer Island	MA	M
BHDB	42.3022	-71.0363	Boston Harbor	Dorchester Bay	MA	M
BHHB	42.2760	-70.8833	Boston Harbor	Hingham Bay	MA	M
MBNR	42.1603	-70.7425	Massachusetts Bay	North River	MA	M
DBCI	42.0137	-70.6365	Duxbury Bay	Clarks Island	MA	M
CCNH	41.7958	-69.9462	Cape Cod	Nauset Harbor	MA	M

Low ●, Medium ●, and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
CAGH			● 70	4.9	
SHFP			● 125	7.5	
MBNB			● 160	11.2	
BHDI			● 159	14.3	
BHDB			● 130	9.1	● 0.0
BHHB			● 64	5.1	
MBNR			● 189	15.1	● 0.0
DBCI			● 102	6.1	
CCNH			● 32	3.5	● 14.4

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Massachusetts cont'd

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
BBCC	41.7402	-70.6157	Buzzards Bay	Cape Cod Canal	MA	M
BBWF	41.6067	-70.6528	Buzzards Bay	West Falmouth	MA	M
BBAR	41.5797	-70.8590	Buzzards Bay	Angelica Rock	MA	M
WBER	41.5507	-70.5479	Waquoit Bay	Estuarine Reserve	MA	M
BBRH	41.5397	-70.9283	Buzzards Bay	Round Hill	MA	M
BBNI	41.5142	-70.7397	Buzzards Bay	Naushon Island	MA	M
BBGN	41.4817	-71.0373	Buzzards Bay	Goosebury Neck	MA	M

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
BBCC			● 44	5.2	● 0.0
BBWF			● 22	1.8	
BBAR	● 804	107.7	● 109	12.6	● 0.0
WBER			● 720	57.6	
BBRH			● 48	5.7	● 3.5
BBNI	● 36	3.5			● 2.1
BBGN	● 0	0.0	● 11	1.0	● 0.0

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Michigan

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
LMMU	43.2258	-86.3470	Lake Michigan	Muskegon	MI	ZM
LMHB	42.7732	-86.2150	Lake Michigan	Holland Breakwater	MI	ZM
TBLL	45.2057	-85.5368	Traverse Bay	Leelanau State Park	MI	ZM
SBSR	43.6735	-83.8367	Saginaw Bay	Saginaw River	MI	ZM
LHTB	44.9222	-83.4135	Lake Huron	Thunder Bay	MI	ZM
SBSP	43.9098	-83.4002	Saginaw Bay	Sandpoint	MI	ZM
LESP	41.9587	-83.2330	Lake Erie	Stony Point	MI	ZM
LSAB	42.6492	-82.7110	Lake St. Clair	Anchor Bay	MI	
LHBR	43.0443	-82.4387	Lake Huron	Black River Canal	MI	ZM

Low ●, Medium ● , and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
LMMU			● 80	12.8	
LMHB			● 128	24.5	
TBLL			● 54	4.0	
SBSR			● 115	9.0	
LHTB			● 0	0.0	
SBSP			● 24	2.1	
LESP			● 310	39.4	● 13.5
LSAB					● 3.0
LHBR			● 73	6.1	

Appendix 1
Mississippi

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
MSPB	30.3360	-88.5892	Mississippi Sound	Pascagoula Bay	MS	O
MSBB	30.3925	-88.8575	Mississippi Sound	Biloxi Bay	MS	O
MSPC	30.3023	-89.3272	Mississippi Sound	Pass Christian	MS	O

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
MSPB	● 71	7.2	● 79	8.6	● 0.0
MSBB			● 438	52.4	● 0.5
MSPC	● 40	5.1	● 389	42.2	● 5.6

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
GBDP	43.1207	-70.8265	Great Bay	Dover Point	NH	M

Low ●, Medium ● , and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
GBDP			● 167	15.0	

New Jersey

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
NYSH	40.4875	-74.0333	New York Bight	Sandy Hook	NJ	M
NYLB	40.2948	-73.9787	New York Bight	Long Branch	NJ	M
NYSR	40.1870	-74.0090	New York Bight	Shark River	NJ	M
BIBL	39.7617	-74.0950	Barnegat Inlet	Barnegat Light	NJ	M
DBHC	39.4267	-75.4933	Delaware Bay	Hope Creek	NJ	
DBAP	39.3833	-75.4500	Delaware Bay	Arnolds Point Shoal	NJ	O
AIAC	39.3672	-74.4112	Absecon Inlet	Atlantic City	NJ	M
DBBD	39.2523	-75.3028	Delaware Bay	Ben Davis Pt. Shoal	NJ	O
DBFE	39.2117	-75.1917	Delaware Bay	False Egg Island Point	NJ	O
DBCM	38.9822	-74.9613	Delaware Bay	Cape May	NJ	M

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
NYSH			● 784	49.6	
NYLB			● 426	31.1	
NYSR			● 439	30.3	
BIBL	● 103	8.2	● 75	5.5	● 0.1
DBHC					● 4.9
DBAP	● 60	4.2	● 102	7.3	● 3.3
AIAC			● 168	11.9	
DBBD	● 77	12.8	● 168	16.2	● 0.6
DBFE	● 0	0.0			
DBCM	● 13	1.1	● 111	7.0	

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
HRCI	42.0338	-73.9293	Hudson River	Cruger Island	NY	
LIGB	40.9982	-72.1162	Long Island	Gardiners Bay	NY	M
LIPJ	40.9573	-73.0937	Long Island Sound	Port Jefferson	NY	M
LIMR	40.9418	-73.7032	Long Island Sound	Mamaroneck	NY	M
LIHU	40.9220	-73.4285	Long Island Sound	Huntington Harbor	NY	M
LIHH	40.8558	-73.6753	Long Island Sound	Hempstead Harbor	NY	M
LITN	40.8167	-73.7983	Long Island Sound	Throgs Neck	NY	M
MBTH	40.7767	-72.7558	Moriches Bay	Tuthill Point	NY	M
HRHT	40.7263	-74.0148	Hudson-Raritan	Holland Tunnel	NY	
HRWT	40.7127	-74.0170	Hudson-Raritan	World Trade Center	NY	
HRBP	40.7046	-74.0183	Hudson-Raritan	Battery Park	NY	M
HREI	40.6993	-74.0426	Hudson-Raritan	Ellis Island	NY	
HRGI	40.6933	-74.0190	Hudson-Raritan	Governor's Island	NY	M

Low ●, Medium ●, and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
HRCI					● 6.7
LIGB	● 28	1.0	● 23	1.5	
LIPJ	● 119	10.8	● 111	7.4	
LIMR	● 300	19.5	● 169	11.0	
LIHU	● 106	8.5	● 96	6.6	
LIHH	● 264	23.2	● 334	26.3	
LITN	● 601	55.3	● 697	60.2	
MBTH			● 112	8.6	
HRHT					● 27.9
HRWT					● 41.3
HRBP			● 1946	130.4	
HREI					● 19.0
HRGI			● 2189	194.8	

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New York cont'd

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
HRUB	40.6893	-74.0432	Hudson-Raritan	Upper Bay	NY	M
LIFI	40.6252	-73.2795	Long Island	Fire Island Inlet	NY	M
HRFW	40.6150	-74.0614	Hudson-Raritan	Fort Wadsworth	NY	M
HRSR	40.6081	-74.0348	Hudson-Raritan	Shore Road	NY	M
LIJI	40.5955	-73.5867	Long Island	Jones Inlet	NY	M
HRJB	40.5667	-73.8953	Hudson-Raritan	Jamaica Bay	NY	M
HRLB	40.5660	-74.0508	Hudson-Raritan	Lower Bay	NY	M
HRRB	40.5190	-74.1845	Hudson-Raritan	Raritan Bay	NY	M
LEDK	42.5292	-79.2777	Lake Erie	Dunkirk	NY	ZM
NRNF	43.0468	-78.8920	Niagara River	Niagara Falls	NY	
LOOC	43.3553	-78.6867	Lake Ontario	Olcott	NY	ZM
LORC	43.2578	-77.4953	Lake Ontario	Rochester	NY	ZM
LOCV	44.1442	-76.3247	Lake Ontario	Cape Vincent	NY	ZM

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996			Tissue 200X			Sediment 200X	
		Lipid	Dry		Lipid	Dry		Dry
HRUB				●	653	96.6	●	31.4
LIFI	●	71	4.4	●	140	9.0		
HRFW				●	1287	118.4		
HRSR				●	1550	145.7		
LIJI	●	360	18.0	●	154	11.9		
HRJB				●	899	62.7		
HRLB				●	1191	70.5	●	21.6
HRRB				●	594	36.9	●	3.1
LEDK				●	33	3.3	●	2.9
NRNF							●	4.0
LOOC				●	57	7.9	●	5.8
LORC				●	73	10.1	●	5.0
LOCV				●	7	0.7	●	3.6

North Carolina

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
RSJC	35.8898	-75.6337	Roanoke Sound	John Creek	NC	O
PSWB	35.4123	-76.0397	Pamlico Sound	Wysocking Bay	NC	O
PSPR	35.2960	-76.4392	Pamlico Sound	Pungo River	NC	O
PSCH	35.2028	-75.7162	Pamlico Sound	Cape Hatteras	NC	O
PSNR	35.0897	-76.5290	Pamlico Sound	Neuse River	NC	O
BIPI	34.7183	-76.6755	Beaufort Inlet	Pivers Island	NC	O
CFBI	33.9158	-78.0035	Cape Fear	Battery Island	NC	O

Low ●, Medium ● , and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
RSJC			● 27	3.5	● 0.0
PSWB			● 35	5.2	● 0.0
PSPR			● 7	1.2	● 0.0
PSCH			● 11	0.8	
PSNR			● 4	0.6	● 0.1
BIPI	● 37	5.6	● 21	1.7	● 0.0
CFBI	● 0	0.0	● 29	2.1	● 5.4

Ohio

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
LERB	41.6745	-83.2262	Lake Erie	Reno Beach	OH	
SBPP	41.6597	-82.8250	Lake Erie	Peach Orchard Pt.	OH	ZM
LELR	41.4612	-82.2070	Lake Erie	Lorain	OH	ZM
LEAB	41.9247	-80.7183	Lake Erie	Ashtabula	OH	ZM

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
LERB					● 5.3
SBPP			● 185	19.4	● 6.3
LELR			● 45	5.5	
LEAB			● 24	1.7	● 3.3

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
CBCH	43.3500	-124.3308	Coos Bay	Coos Head	OR	M
CBRP	43.4313	-124.2212	Coos Bay	Russell Point	OR	M
YBOP	44.5752	-123.9890	Yaquina Bay	Oneatta Point	OR	M
YHFC	44.8370	-124.0520	Yaquina Bay	Fogarty Creek	OR	M
TBHP	45.5472	-123.9075	Tillamook Bay	Hobsonville Point	OR	
CRSJ	46.2287	-124.0232	Columbia River	South Jetty	OR	M

Low ●, Medium ●, and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
CBCH	● 22	1.7	● 42	3.1	● 0.0
CBRP	● 0	0.0	● 299	18.8	● 0.0
YBOP			● 92	5.5	● 0.7
YHFC			● 41	3.3	
TBHP					● 0.2
CRSJ			● 255	20.4	

Puerto Rico

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
PRBB	18.0078	-67.1752	Puerto Rico	Bahia de Boqueron	PR	O
PRBM	17.9710	-66.9895	Puerto Rico	Bahia Montalva	PR	O
PRBJ	17.9392	-66.1813	Puerto Rico	Bahia de Jobos	PR	O

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
PRBB			● 89	4.8	● 4.4
PRBM			● 25	1.7	● 0.0
PRBJ			● 13	0.5	● 0.0

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
NBPI	41.6523	-71.3567	Narragansett Bay	Patience Island	RI	M
NBDI	41.6048	-71.3052	Narragansett Bay	Dyer Island	RI	M
NBDU	41.5013	-71.3928	Narragansett Bay	Dutch Island	RI	M
BIBI	41.1982	-71.5922	Block Island Sound	Block Island	RI	M

Low ●, Medium ●, and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
NBPI			● 216	17.3	● 0.0
NBDI			● 140	14.0	● 12.2
NBDU			● 51	4.1	● 2.4
BIBI			● 36	2.5	

Appendix 1

South Carolina

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
WBLB	33.2433	-79.1972	Winyah Bay	Lower Bay	SC	O
SRNB	33.1683	-79.2417	Santee River	North Bay	SC	O
CHSF	32.7735	-79.9122	Charleston Harbor	Shutes Folly Island	SC	O
CHFJ	32.7505	-79.9003	Charleston Harbor	Fort Johnson	SC	O
ABBI	32.4894	-80.5283	Ace Basin	Bass Island	SC	O

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996			Tissue 200X		Sediment 200X
	Lipid	Dry		Lipid	Dry	Dry
WBLB			●	13	1.0	
SRNB			●	4	0.4	
CHSF	● 0	0.0	●	41	3.0	
CHFJ			●	73	6.0	
ABBI			●	104	8.3	● 0.0

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
GBHR	29.4803	-94.7418	Galveston Bay	Hanna Reef	TX	O
GBOB	29.2840	-94.8363	Galveston Bay	Offatts Bayou	TX	O
GBTD	29.5030	-94.8960	Galveston Bay	Todd's Dump	TX	O
GBCR	29.2633	-94.9163	Galveston Bay	Confederate Reef	TX	O
GBSC	29.7045	-94.9930	Galveston Bay	Ship Channel	TX	O
GBYC	29.6220	-94.9958	Galveston Bay	Yacht Club	TX	O
BRFS	28.9212	-95.3395	Brazos River	Freeport Surfside	TX	O
BRCL	28.8580	-95.4647	Brazos River	Cedar Lakes	TX	O
MBEM	28.7112	-95.8833	Matagorda Bay	East Matagorda	TX	O
MBTP	28.6663	-96.2335	Matagorda Bay	Tres Palacios Bay	TX	O
MBCB	28.6650	-96.3830	Matagorda Bay	Carancahua Bay	TX	O
ESBD	28.4118	-96.4490	Espiritu Santo	Bill Days Reef	TX	O
MBGP	28.5788	-96.5630	Matagorda Bay	Gallinipper Point	TX	O
MBLR	28.6603	-96.5845	Matagorda Bay	Lavaca River Mouth	TX	O

Low ●, Medium ●, and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
GBHR			● 66	7.8	● 0.0
GBOB			● 269	30.1	● 0.0
GBTD			● 119	14.6	● 0.0
GBCR			● 166	14.9	● 0.0
GBSC			● 246	31.7	● 14.5
GBYC			● 227	25.4	● 0.0
BRFS			● 136	8.3	● 0.2
BRCL			● 151	14.2	● 0.0
MBEM			● 187	14.8	● 0.0
MBTP			● 202	20.8	● 0.2
MBCB			● 355	38.3	● 0.1
ESBD	● 0	0.0	● 11	1.4	● 1.2
MBGP			● 126	14.8	● 0.0
MBLR			● 160	15.0	● 0.0

Appendix 1

Texas

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
ESSP	28.2982	-96.6220	Espiritu Santo	South Pass Reef	TX	O
SAPP	28.2323	-96.7082	San Antonio Bay	Panther Point Reef	TX	O
SAMP	28.3440	-96.7123	San Antonio Bay	Mosquito Point	TX	O
MBAR	28.1730	-96.8350	Mesquite Bay	Ayres Reef	TX	O
ABLR	28.0548	-96.9512	Aransas Bay	Long Reef	TX	O
CBCR	28.1420	-97.1280	Copano Bay	Copano Reef	TX	O
LMSB	26.0432	-97.1760	Lower Laguna Madre	South Bay	TX	O
LMPI	26.0748	-97.1995	Lower Laguna Madre	Port Isabel	TX	O
LMAC	26.2825	-97.2853	Lower Laguna Madre	Arroyo Colorado	TX	O
CCNB	27.8522	-97.3598	Corpus Christi	Nueces Bay	TX	O

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
ESSP	● 0	0.0	● 16	1.1	● 0.1
SAPP	● 0	0.0	● 2	0.3	● 0.4
SAMP	● 0	0.0	● 2	0.5	● 0.1
MBAR			● 292	22.8	● 0.5
ABLR			● 728	55.3	● 0.0
CBCR			● 68	10.1	● 0.1
LMSB	● 0	0.0	● 17	1.1	● 0.3
LMPI	● 13	1.0	● 293	14.4	● 0.0
LMAC	● 0	0.0	● 7	0.7	● 0.3
CCNB			● 387	23.2	● 1.6

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
PRMC	38.2233	-76.9615	Potomac River	Mattox Creek	VA	O
CBCI	37.9385	-75.3758	Chincoteague Bay	Chincoteague Inlet	VA	O
RRRR	37.9020	-76.7878	Rappahannock River	Ross Rock	VA	O
QIUB	37.5250	-75.7138	Quinby Inlet	Upshur Bay	VA	O
CBCC	37.2845	-76.0153	Chesapeake Bay	Cape Charles	VA	O
CBDP	37.0983	-76.2948	Chesapeake Bay	Dandy Point	VA	O
CBJR	37.0653	-76.6322	Chesapeake Bay	James River	VA	O

Low ●, Medium ● , and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
PRMC			● 78	8.6	● 0.1
CBCI	● 0	0.0	● 11	1.2	
RRRR			● 82	9.8	● 0.0
QIUB	● 0	0.0	● 0	0.0	● 0.0
CBCC			● 106	14.8	
CBDP			● 120	13.2	● 0.0
CBJR			● 170	8.5	● 0.4

Appendix 1

Washington

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
WBNA	46.4992	-124.0272	Willapa Bay	Nahcotta	WA	M
GHWJ	46.9097	-124.1177	Gray's Harbor	Westport Jetty	WA	M
SSBI	47.0993	-122.8942	South Puget Sound	Budd Inlet	WA	M
CBTP	47.3312	-122.5043	Commencement Bay	Tahlequah Point	WA	M
PSSS	47.5233	-122.3937	Puget Sound	South Seattle	WA	
SIWP	47.5852	-122.5708	Sinclair Inlet	Waterman Point	WA	M
EBDH	47.5958	-122.3867	Elliott Bay	Duwamish Head	WA	M
EBFR	47.6388	-122.4138	Elliott Bay	Four-Mile Rock	WA	M
PSEF	47.8140	-122.3823	Puget Sound	Edmonds Ferry	WA	M
PSHC	47.8318	-122.6883	Puget Sound	Hood Canal	WA	M
WIPP	47.9053	-122.3770	Whidbey Island	Possession Point	WA	M
PSMF	47.9497	-122.3016	Puget Sound	Mukilteo	WA	M
PSEH	47.9727	-122.2303	Puget Sound	Everett Harbor	WA	M
PSPT	48.1047	-122.7780	Puget Sound	Port Townsend	WA	M

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
WBNA			● 65	4.9	● 0.6
GHWJ	● 102	8.5	● 86	7.2	
SSBI	● 223	19.6	● 226	25.6	● 1.6
CBTP	● 342	33.2	● 427	38.3	● 1.5
PSSS					● 0.4
SIWP	● 456	37.4	● 287	29.1	● 1.1
EBDH	● 453	36.7	● 389	28.0	● 0.0
EBFR	● 895	56.4	● 405	29.8	● 0.2
PSEF			● 567	50.4	
PSHC	● 28	2.4	● 26	1.7	● 0.0
WIPP			● 85	7.3	● 0.2
PSMF			● 345	19.0	
PSEH			● 296	20.7	● 2.0
PSPT			● 53	8.2	● 0.4

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
PSPA	48.1397	-123.4202	Puget Sound	Port Angeles	WA	M
PSCC	48.1752	-122.4784	Puget Sound	Cavalero County Park	WA	M
JFNB	48.3743	-124.6160	Strait of Juan de Fuca	Neah Bay	WA	
JFCF	48.3825	-124.7280	Strait of Juan de Fuca	Cape Flattery	WA	M
BBSM	48.7522	-122.4978	Bellingham Bay	Squalicum Marina Jet.	WA	M
PRPR	48.9903	-123.0883	Point Roberts	Point Roberts	WA	M

Low ●, Medium ●, and High ●
Concentrations Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996		Tissue 200X		Sediment 200X
	Lipid	Dry	Lipid	Dry	Dry
PSPA	● 87	7.4	● 70	6.5	● 0.0
PSCC			● 100	6.3	
JFNB					● 0.2
JFCF	● 0	0.0	● 7	0.6	
BBSM			● 316	24.7	● 0.8
PRPR			● 54	2.8	● 0.0

Appendix 1

Wisconsin

Mussels (M), Zebra Mussels (ZM), Oysters (O)

Site	Latitude	Longitude	General Location	Specific Location	State	Bivalve
LMMB	43.0322	-87.8952	Lake Michigan	Milwaukee Bay	WI	ZM
GBBS	44.6370	-87.8082	Green Bay	Bayshore Park	WI	ZM

Low ●, Medium ●, and High ●
Concentrations: Lipid = ppb lipid weight, Dry = ppb dry weight, 200X = 2004 through 2007

Site	Tissue 1996			Tissue 200X			Sediment 200X
	Lipid	Dry		Lipid	Dry		Dry
LMMB			●	374	68.0		
GBBS			●	36	2.8		

Appendix 2

QUANTITATIVE DETERMINATION OF POLYBROMINATED DIPHENYL ETHERS USING SELECTED ION MONITORING GAS CHROMATOGRAPHY/MASS SPECTROMETRY 1999 – 2006

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ABSTRACT

Selected polybrominated diphenyl ethers (PBDEs) are detected using a gas chromatograph/ mass spectrometer in selected ion monitoring mode. This method is capable of detecting ppb concentrations of PBDEs in complex matrices such as tissues and sediments.

1.0   INTRODUCTION

A gas chromatograph/mass spectrometer (GC/MS) in selected ion mode (SIM), coupled to a capillary column, is used to resolve and detect polybrominated diphenyl ethers in tissues and sediments at ppb. Samples are injected into a temperature-programmed GC/MS, operated in splitless mode. The capillary column is a DB-XLB (30 m x 0.25 mm ID and 0.1 μm film thickness). The mass spectrometer is capable of scanning from 35 to 500 AMU every second or less and uses 70 electron volts energy in electron impact ionization mode. The data acquisition system continuously acquires and stores all data for quantitation.

2.0   APPARATUS AND MATERIALS

2.1   EQUIPMENT

- Gas chromatograph, split/splitless injection port and electronic pressure control, Agilent Technologies 5890-II
- Mass spectrometer, capable of scanning from 35 to 500 AMU, utilizing 70 electron volts of energy in impact ionization mode, Agilent Technologies 5972-MSD
- Data acquisition system, Agilent Technologies ChemStation, capable of continuous acquisition and storage of all data during analysis
- Autosampler, capable of making 1 to 5 μL injections
- Capillary column, Agilent Technologies DB-XLB (30 m x 0.25 mm ID and 0.10 μm film thickness)
- Micropipetters, calibrated, 1% accuracy, disposable tips

2.2   REAGENTS

- Dichloromethane (CAS 75-09-02), pesticide grade or equivalent purity
- Helium (CAS 7440-59-7), 99.8% purity

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2.3   STANDARDS

2.3.1   SURROGATE SPIKING SOLUTION

Surrogate spiking solution is prepared from aliquots of pure compounds (Wellington Laboratories) that are diluted with dichloromethane to a final concentration of 1.0 µg/mL. The surrogate spiking solution includes 2,4,4'-TriBDE (13C12) and 2,2'3,4,4',6-HexaBDE (13C12). The surrogate spiking solution (100 µL) is added to all samples and quality control samples prior to extraction. Surrogate compounds are resolved from, but elute in close proximity to, the analytes of interest. Individual surrogate recoveries are used to correct specific analyte concentrations based on retention time.

2.3.2   INTERNAL STANDARD SOLUTION

The internal standard solution is made from a solution purchased from a commercial vendor (Wellington Laboratories, Guelph, Ontario, Canada) and diluted with dichloromethane to a final concentration of 1.0 µg/mL. The internal standard solution includes 2,2'4,4'-TetraBDE (13C12). The internal standard compound is resolved from, but elutes in close proximity to, the analytes of interest. The internal standard solution (100 µL) is added to all samples and quality control samples just prior to instrument analysis. Internal standards are used to calculate relative response factors and specific analyte concentrations based on retention time.

2.3.3   MATRIX SPIKING SOLUTION

A certified solution containing tri to deca PBDE compounds is purchased from a commercial vendor (Cambridge Isotope Laboratories, Inc. Andover, MA) and diluted with dichloromethane to prepare the matrix spiking solution (Table 1). The matrix spiking solution is diluted to approximately 10 times the method detection limit (MDL) and is added to all matrix spike samples.

2.3.4   CALIBRATION SOLUTION

Calibration solutions are prepared at 5 concentrations ranging from approximately 0.05 to 1 µg/mL (Table 2) by diluting a commercially available certified solution (Cambridge Isotope Laboratories, Inc.) containing the analytes of interest.

Appendix 2

Table 1. Polybrominated Diphenyl Ethers Contained in the Matrix-Spiking Solution.

Analyte CAS Spiking Solution Concentration (µg/mL)

Analyte	CAS	Spiking Solution Concentration (µg/mL)
2,2'4-TriBDE (BDE-17)	NA	1.00
2,4,4'-TriBDE (BDE-28)	41318-75-6	1.00
2,2',4,4'-TetraBDE (BDE-47)	5436-43-1	1.00
2,3'4,4'-TetraBDE (BDE-66)	NA	1.00
2,3',4',6-TetraBDE (BDE-71)	NA	1.00
2,2'3,4,4'-PentaBDE (BDE 85)	182346-21-0	1.00
2,2'4,4',5-PentaBDE (BDE-99)	60348-60-9	1.00
2,2'4,4',6-PentaBDE (BDE-100)	189084-64-8	1.00
2,2'3,4,4'5'-HexaBDE (BDE-138)	NA	1.00
2,2'4,4'5,5'-HexaBDE (BDE-153)	68631-49-2	1.00
2,2'4,4'5,6'-HexaBDE (BDE-154)	NA	1.00
2,2'3,4,4'5',6-HeptaBDE (BDE-183)	NA	1.00
2,3,3'4,4'5,6-HeptaBDE (BDE-190)	68928-80-3	1.00

Table 2. Polybrominated Diphenyl Ethers Contained in Calibration Solutions and their Approximate Concentrations.

Compounds Contained in Calibration Solutions	CAS	Level 1 (µg/mL)	Level 2 (µg/mL)	Level 3 (µg/mL)	Level 4 (µg/mL)	Level 5 (µg/mL)
Internal Standards						
2,2'4,4'-TetraBDE (13C12)	NA	0.1	0.1	0.1	0.1	0.1
Surrogates						
2,4,4'-TriBDE (13C12)	NA	0.05	0.10	0.25	0.50	1.0
2,2'3,4,4',6-HexaBDE (13C12)	NA	0.05	0.10	0.25	0.50	1.0
Analytes						
2,2'4-TriBDE (BDE-17)	NA	0.05	0.10	0.25	0.50	1.0
2,4,4'-TriBDE (BDE-28)	41318-75-6	0.05	0.10	0.25	0.50	1.0
2,2',4,4'-TetraBDE (BDE-47)	5436-43-1	0.05	0.10	0.25	0.50	1.0
2,3'4,4'-TetraBDE (BDE-66)	NA	0.05	0.10	0.25	0.50	1.0
2,3',4',6-TetraBDE (BDE-71)	NA	0.05	0.10	0.25	0.50	1.0
2,2'3,4,4'-PentaBDE (BDE 85)	182346-21-0	0.05	0.10	0.25	0.50	1.0
2,2'4,4',5-PentaBDE (BDE-99)	60348-60-9	0.05	0.10	0.25	0.50	1.0
2,2'4,4',6-PentaBDE (BDE-100)	189084-64-8	0.05	0.10	0.25	0.50	1.0
2,2'3,4,4'5'-HexaBDE (BDE-138)	NA	0.05	0.10	0.25	0.50	1.0
2,2'4,4'5,5'-HexaBDE (BDE-153)	68631-49-2	0.05	0.10	0.25	0.50	1.0
2,2'4,4'5,6'-HexaBDE (BDE-154)	NA	0.05	0.10	0.25	0.50	1.0
2,2'3,4,4'5'6-HeptaBDE (BDE-183)	207122-16-5	0.05	0.10	0.25	0.50	1.0
2,3,3'4,4'5,6-HeptaBDE (BDE-190)	68928-80-3	0.05	0.10	0.25	0.50	1.0

Appendix 2

3.0   QUANTITATIVE DETERMINATION OF PBDES BY GC/MS-SIM

3.1   MASS SPECTROMETER TUNING

Prior to calibration, the MS is autotuned to perfluorotributylamine (PFTBA) using criteria established by the instrument manufacturer.

3.2   INITIAL CALIBRATION

A 5-point relative response factor (RRF) calibration curve is established for analytes of interest prior to the analysis of samples and quality control (QC) samples. A RRF is determined, for each analyte, for each calibration level using the following equation:

$$RRF = \frac{(A_A)(C_{IS})}{(A_{IS})(C_A)}$$

Where:

A_A = the area of the characteristic ion for the analyte to be measured
A_{IS} = the area of the characteristic ion for the specific internal standard
C_A = the known concentration of the analyte in the calibration solution (µg/mL)
C_{IS} = the known concentration of the internal standard in the calibration solution (µg/mg)

The response factors determined for each calibration level are averaged to produce a mean relative response factor ($\overline{RRF_i}$) for each analyte. The percent relative standard deviation (%RSD) for the 5 response factors must be less than or equal to 15%, for each analyte.

$$\%RSD = \frac{\text{Standard Deviation of the RRFs}}{\text{Average of the RRFs}} \times 100$$

Where:

$$\text{Standard Deviation} = \sqrt{\frac{\sum\limits_{i=1}^{n}(X_i - \overline{X})^2}{(n-1)}}$$

x_i = each RRF value used to calculate the mean RRF

$\overline{X}$ = the mean of n values

n = total number of values (5)

3.3   CONTINUING CALIBRATION

A mid-level calibration standard is analyzed at the beginning and end of each analytical set or every 10 samples (whichever is more frequent). The daily relative response factor for each compound is compared to the mean relative response factor from the initial calibration curve and the average relative percent difference (RPD) of all analytes must be less than 25%. If the calibration check does not meet this criterion then the initial five-point calibration is repeated.

$$RPD = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where:

$\overline{RRF_i}$ = mean relative response factor from the most recent initial calibration (meeting technical acceptance criteria)

$\overline{RRF_c}$ = relative response factor from the continuing calibration standard

3.4   GC/MS-SIM ANALYSIS

The initial calibration of the GC/MS must meet the previously described criteria prior to sample analysis. Samples are analyzed in analytical sets that consist of standards, samples and QC samples. Quality control samples are method blanks, laboratory duplicates, blank spikes, and matrix spikes. An autosampler is used to inject 1 or 2 µL of all samples, standards and QC samples into the capillary column of the GC using the following instrument conditions. Slight modifications may be necessary depending upon the analysis.
Inlet: Splitless
Carrier gas: Helium, 1 mL/min

Temperatures
Injection port: 300°C/ splitless
Transfer line: 290°C

Oven program
Initial oven temp: 60°C
Initial hold time: 0 minutes
Ramp rate: 7°C/min
Final oven temp: 315°C
Final hold time: 22 minutes
Total run time: 56 minutes

Appendix 2

The effluent from the GC capillary column is routed directly into the ion source of the MS. The MS is operated in the selected ion monitoring mode (SIM) and includes the quantitation masses for the PBDEs listed in Table 3.

3.5 ANALYTE IDENTIFICATION

The extracted ion current profiles of the primary m/z and the confirmatory ion for each analyte must meet the following criteria:

- The characteristic masses of each analyte of interest must be in the same scan or within one scan of each other. The retention time must fall within +/- 5 seconds of the retention time of the authentic compound determined by the analysis of the daily calibration check or PBDE Reference solution.
- The relative peak heights of the primary mass ion, compared to the confirmation or secondary mass ion, must fall within +/-30 percent of the relative intensities of these masses in a reference mass spectrum (Table 3). The reference mass spectrum is obtained from the continuing calibration solution. In some instances, a compound that does not meet secondary ion confirmation criteria may still be determined to be present in a sample after close inspection of the data by a qualified mass spectrometrist. Supportive data includes the presence of the confirmation ion, but at a ratio different then that indicated in Table 3.
- Data not meeting the criteria established in this section are appropriately qualified or re-analyzed.

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Table 3. Target Analyte Parameters.

Analyte	CAS	Reference to	Ion
Internal Standard and Surrogate			
2,2'4,4'-TetraBDE (13C12) (I-1)	NA	I-1	338.0
2,4,4'-TriBDE (13C12) (S-1)	NA	S-1	418.0

Analyte	CAS	Reference to	**Ion**
BDE 2 (3-MonoBDE)	6876-00-2	I-1, S-1	248.0
BDE 3 (4-MonoBDE)	101-55-3	I-1, S-1	248.0
BDE 4 (2,2'-DiBDE)	NA	I-1, S-1	248.0
BDE 7 (2,4-DiBDE)	NA	I-1, S-1	327.9
BDE 8 (2,4'-DiBDE)	147217-71-8	I-1, S-1	327.9
BDE 10 (2,6-DiBDE)	NA	I-1, S-1	327.9
BDE 11 (3,3'-DiBDE)	6903-63-5	I-1, S-1	327.9
BDE 12 (3,4-DiBDE)	NA	I-1, S-1	327.9
BDE 13 (3,4'-DiBDE)	83694-71-7	I-1, S-1	327.9
BDE 15 (4,4'-DiBDE)	2050-47-7	I-1, S-1	327.9
BDE 17 (2,2',4-TriBDE)	NA	I-1, S-1	405.8
BDE 25 (2,3',4-TriBDE)	NA	I-1, S-1	405.8
BDE 28 (2,4,4'-TriBDE)	41318-75-6	I-1, S-1	405.8
BDE 30 (2,4,6-TriBDE)	NA	I-1, S-1	405.8
BDE 32 (2,4',6-TriBDE)	NA	I-1, S-1	405.8
BDE 33 (2',3,4-TriBDE)	NA	I-1, S-1	405.8
BDE 35 (3,3',4-TriBDE)	NA	I-1, S-1	405.8
BDE 37 (3,4,4'-TriBDE)	NA	I-1, S-1	405.8

Appendix 2

Table 3 cont'd.

Analyte	CAS	Reference to	Ion
BDE 47 (2,2',4,4'-TetraBDE)	5436-43-1	I-1, S-1	485.7
BDE 49/71 (2,2',4,5'-TetraBDE/2,3',4',6-TetraBDE)	NA/NA	I-1, S-1	485.7
BDE 66 (2,3',4,4'-TetraBDE)	NA	I-1, S-1	485.7
BDE 75 (2,4,4',6-TetraBDE)	NA	I-1, S-1	485.7
BDE 77 (3,3',4,4'-TetraBDE)	93703-48-1	I-1, S-1	485.7
BDE 85 (2,2',3,4,4'-PentaBDE)	182346-21-0	I-1, S-1	563.6
BDE 99 (2,2',4,4',5-PentaBDE)	60348-60-9	I-1, S-1	563.6
BDE 100 (2,2',4,4',6-PentaBDE)	189084-64-8	I-1, S-1	563.6
BDE 116 (2,3,4,5,6-PentaBDE)	NA	I-1, S-1	563.6
BDE 118 (2,3',4,4',5-PentaBDE)	NA	I-1, S-1	563.6
BDE 119 (2,3',4,4',6-PentaBDE)	NA	I-1, S-1	563.6
2,2'3,4,4',6-HexaBDE (13C12) (S-2)	NA	S-2	496.0
BDE 126 (3,3',4,4',5-PentaBDE)	NA	I-1, S-2	563.6
BDE 138 (2,2',3,4,4',5'-HexaBDE)	NA	I-1, S-2	643.5
BDE 153 (2,2',4,4',5,5'-HexaBDE)	68631-49-2	I-1, S-2	643.5
BDE 154 (2,2',4,4',5,6'-HexaBDE)	NA	I-1, S-2	643.5
BDE 155 (2,2',4,4',6,6'-HexaBDE)	NA	I-1, S-2	643.5
BDE 166 (2,3,4,4',5,6-HexaBDE)	NA	I-1, S-2	643.5
BDE 181 (2,2',3,4,4',5,6-HeptaBDE)	NA	I-1, S-2	563.6
BDE 183 (2,2',3,4,4',5',6-HeptaBDE)	207122-16-5	I-1, S-2	563.6
BDE 190 (2,3,3',4,4',5,6-HeptaBDE)	68928-80-3	I-1, S-2	563.6

(I-#) = Internal reference number
(S-#) = Surrogate reference number

4.0   QUANTITATION CALCULATIONS

Sample analyte concentrations are calculated based on the concentration and response of the internal standard compounds (Table 2). The equations in Section 3.2 are used to calculate the RRF of each analyte relative to the concentration and area of the internal standard in the initial calibration. Response factors for target analytes not contained in the initial calibration solution are presumed equal to the response factor of a respective similar PBDE compound.

The mass (MA) of each target analyte (ng) is calculated using the following equation:

$$MA = \frac{(A_A \, M_{IS})}{(A_{IS} \, \overline{RRF}_i)}$$

Where:

A_A = the area of the characteristic ion for the analyte measured
A_{IS} = the area of the characteristic ion for the specific internal standard
M_{IS} = mass of internal standard added to the extract (ng)

$\overline{RRF}_i$ = average relative response factor for the analyte from the current calibration

The concentration of each target analyte in a sample (ng/g) is calculated using the following equation:

$$C = \frac{(M_A \, DF)}{(W)}$$

Where:

DF = the dilution factor applied to the extract

$$DF = \frac{\text{Volume of Extract (µL)}}{\text{Volume of Extract used to make dilution (µL)}}$$

W = the sample weight (g)

Analyte concentrations are reported as corrected for individual surrogate recoveries. The corrections for each compound are based on the surrogates referenced in Table 3. Percent surrogate recoveries (SURecovery) for each surrogate are calculated using the following equation:

$$SU_{Recovery} = \frac{C_{ESU}}{C_{SU}} \times 100$$

Where:
CESU = calculated surrogate concentration in the extract
CSU = known concentration of surrogate added to extract

Appendix 2

Analyte concentration corrections (corrected for surrogate recovery) are calculated using the following equation:

$$C_{Corrected} = \frac{C}{SU_{Recovery}} \times 100$$

5.0   QUALITY CONTROL (QC)

Samples are analyzed in analytical batches consisting of 19 samples or fewer and QC samples. The QC samples are a method blank, laboratory duplicate, matrix spike, and matrix spike duplicate. A method blank is a reagent blank prepared in the laboratory. A duplicate is a sample for which a second aliquot is analyzed. Matrix spikes are samples that are spiked with known concentrations of known analytes.

The validity of the data is monitored using defined QC criteria. The following QC criteria are used to evaluate analytical batches:

1) Calibration
*   The calibration criteria (Section 3.2) must be met prior to data analyses. If the calibration criteria are not met, then the run is aborted and the instrument re-calibrated before further sample analysis.

2) Method Blank
*   No more than two target analytes exceed 3 times the concentration of the MDL. Exceptions are that if an analyte detected in the method blank exceeds 3 times the concentration of the MDL, but is not present in the associated samples or if a sample analyte concentration is greater than 10 times that analyte concentration in the method blank, the result is qualified and reported.
*   If a method blank exceeds these criteria then the source of contamination is determined and corrective action is taken before further sample analysis.

3) Matrix Spikes
*   Analytes spiked into a matrix are considered valid only if they are spiked at concentrations equivalent to levels found in the sample.
*   The average recovery for all valid spiked analytes in a matrix spike is between 60% and 120%. No more than two individual spiked analyte (valid) recoveries may exceed 40%-120%.
*   If the QC criteria are not met then the matrix spike sample failing the criteria will be re-

analyzed and if the re-analyzed spike meets the criteria then the data are reported. If an analyte exceeds the criteria and is not present in the associated samples analyzed with the analytical batch, the result is qualified and reported.

- If upon re-analysis, QC criteria are still not met, the entire batch of samples is reanalyzed. If sufficient sample is unavailable to re-extract the matrix-spike, another sample may be selected or a blank-spike may be substituted.
- The average RPD for a valid matrix spike/matrix spike duplicate or blank spike/blank spike duplicate pair is 30%. No more than two individual analyte RPDs may exceed 35%.

4) Duplicate
- The average RPD between the duplicate and original sample, for analytes greater than 10 times the concentration of the MDL, is 30%. The RPD for no more than two individual analytes may exceed 35%.
- If the QC criteria are not met then the sample pair failing the criteria will be re-analyzed and if the re-analyzed samples meet the criteria then the data are reported.
- If an analyte exceeds the criteria and is not present in the associated samples analyzed with the analytical batch, the result is qualified and reported.
- If upon re-analysis, QC criteria are still not met, the entire batch of samples is reanalyzed. If sufficient sample is unavailable to re-extract the duplicate pair, another sample may be selected.

5) Surrogates
- The average recovery of surrogate compounds is between 50% and 150%.
- Exceptions are analytical interferences with the surrogates and diluted samples.
- If the average recovery of surrogates exceeds the criteria, and calculation and analytical errors are eliminated, the sample is re-analyzed. If sufficient sample is unavailable for re-extraction, the data are qualified and reported.

6) Method Detection Limit
- The method detection limit (MDL) is determined following the procedures outlined in Federal Register (1984), Vol. 49, No. 209: 98-199.