PBDEs in San Francisco Bay

Conceptual Model/Impairment Assessment

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July 31, 2007

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been used as flame retardants for about 30 years and were first detected in environmental samples in 1979. Marketed in three commercial mixtures identified as PentaBDE, OctaBDE, and DecaBDE, they are found in products used in homes, offices, automobiles, and airplanes, and they have been widely used in fire-prone California. Evidence suggests that PBDEs may pose risks to human health, similar to the risks posed by polychlorinated biphenyls (PCBs). At the same time, studies have found elevated levels of PBDEs in Bay Area wildlife and humans that are among the highest reported in the world.

This report reviews the current status of PBDEs in San Francisco Bay. It is one of several Conceptual Model/Impairment Assessment (CM/IA) reports that have been prepared for San Francisco Bay. The general objectives of the CM/IA reports are:

- Evaluate the current level of **impairment** of beneficial uses, including descriptions of standards or screening indicators and relevant data.
- Develop a **conceptual model** that describes the current state of knowledge for the pollutant of concern, including sources, loads, and pathways into and out of the Bay and its water, sediment, and biota.
- Identify **potential studies** that might reduce uncertainties associated with the report's conclusions.

PBDEs in the Bay are a relatively new concern, and this report will not fully meet the general objectives for CM/IAs. Rather, the report should be viewed as a tool for planning and a framework for understanding additional information as it is developed.

This introduction presents overviews of the conditions that have led to our concern, the regulatory status, the San Francisco Bay setting and its designated beneficial uses, and chemistry and toxicology of PBDEs.

1.1 Understanding the Problem

Although PBDEs have been used since the 1970s, until recently, they were unregulated and rarely included in environmental assessments. During the 1980s and 1990s, there began to be reports, mostly from northern Europe and Canada, of PBDEs in fish and human milk and blood.

In 2002, San Francisco was identified as a global PBDE "hot spot." She et al. (2002) found levels of PBDEs in harbor seal blubber in the low ng/g to µg/g fat range (equivalent to parts per billion to part per million). Especially alarming, the

data suggested that concentrations of PBDEs in seal blubber had doubled every 1.8 years throughout the 1990s (Figure 1-1), with levels among the highest ever reported in tissue samples.

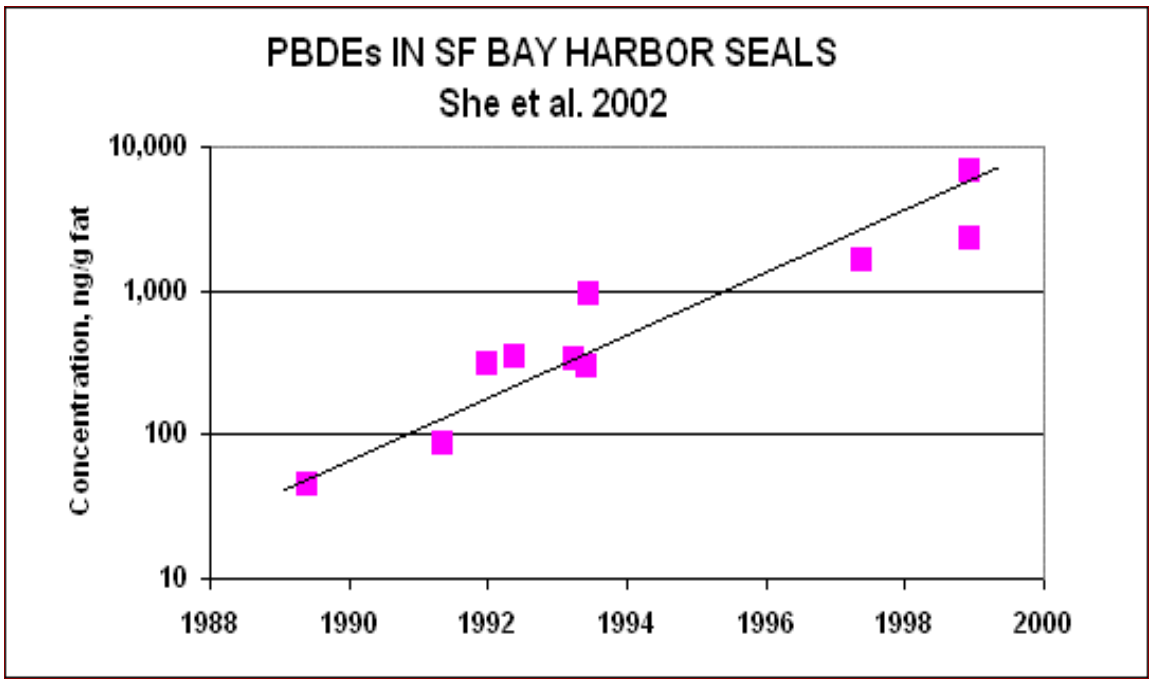

Figure 1-1. Total PBDEs in harbor seal blubber from San Francisco Bay (She et al., 2002)

She et al. (2002) also reported alarmingly high concentrations of PBDEs in human tissue samples from 23 Bay Area women. Concentrations in breast adipose tissue ranged from 17 to 462 ng/g lipid, averaging 86 ng/g lipid, the highest concentrations that had ever been reported in human tissues (Figure 1-2) and at or near levels thought to be of concern for human health. The average concentration of the most common congener was about ten times greater than blood serum from Germany and human milk from Canada, three times higher than tissue samples from Sweden, and 25 times higher than human tissues from Spain.

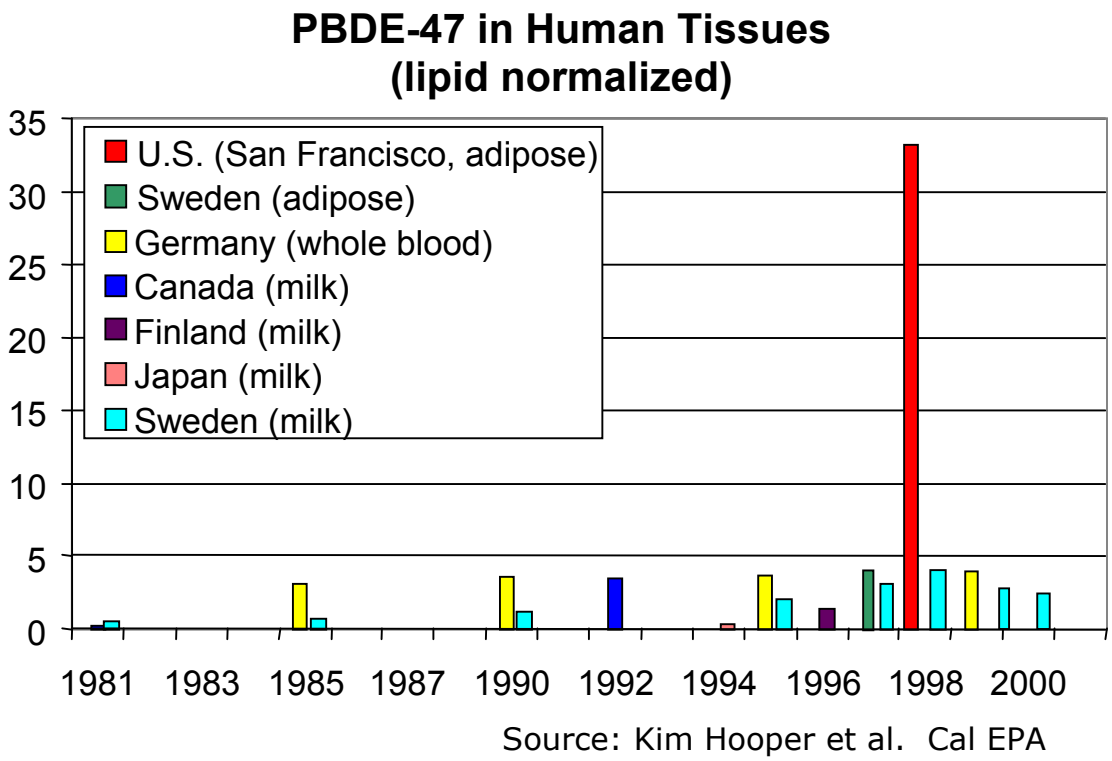

Figure 1-2. PBDEs in human tissues (figure from Kim Hooper, Cal EPA; San Francisco data from She et al., 2002)

Some encouraging news has been reported from Sweden, where levels of PBDEs in human breast milk have declined following bans of some commercial PBDE formulations (Figure 1-3, top). However, even at their highest points, the levels measured in Sweden have not approached those measured in human samples from the United States (Figure 1-3, bottom).

The high and rapidly increasing levels of PBDEs in marine mammals and humans from the Bay Area were particularly alarming, because it seemed the PBDEs could become the next "PCB-like problem" for San Francisco Bay. Twenty-five years after banning polychlorinated biphenyls (PCBs), concentrations in sport fish remain more than ten times higher than levels of concern, and even as clean-up continues, recovery is expected to be very slow. Thus, one major question for this CM/IA report is how PBDEs compare with PCBs. Therefore, where appropriate, this document compares the status of PBDEs in the Bay to that of PCBs. Though instructive, the comparison is not perfect—PBDEs and PCBs have had different uses, they have different toxicities, and the historical patterns of use have differed. However, the comparisons are made because they put the relatively new concerns about PBDEs in the environment into a context of a much better-known environmental problem.

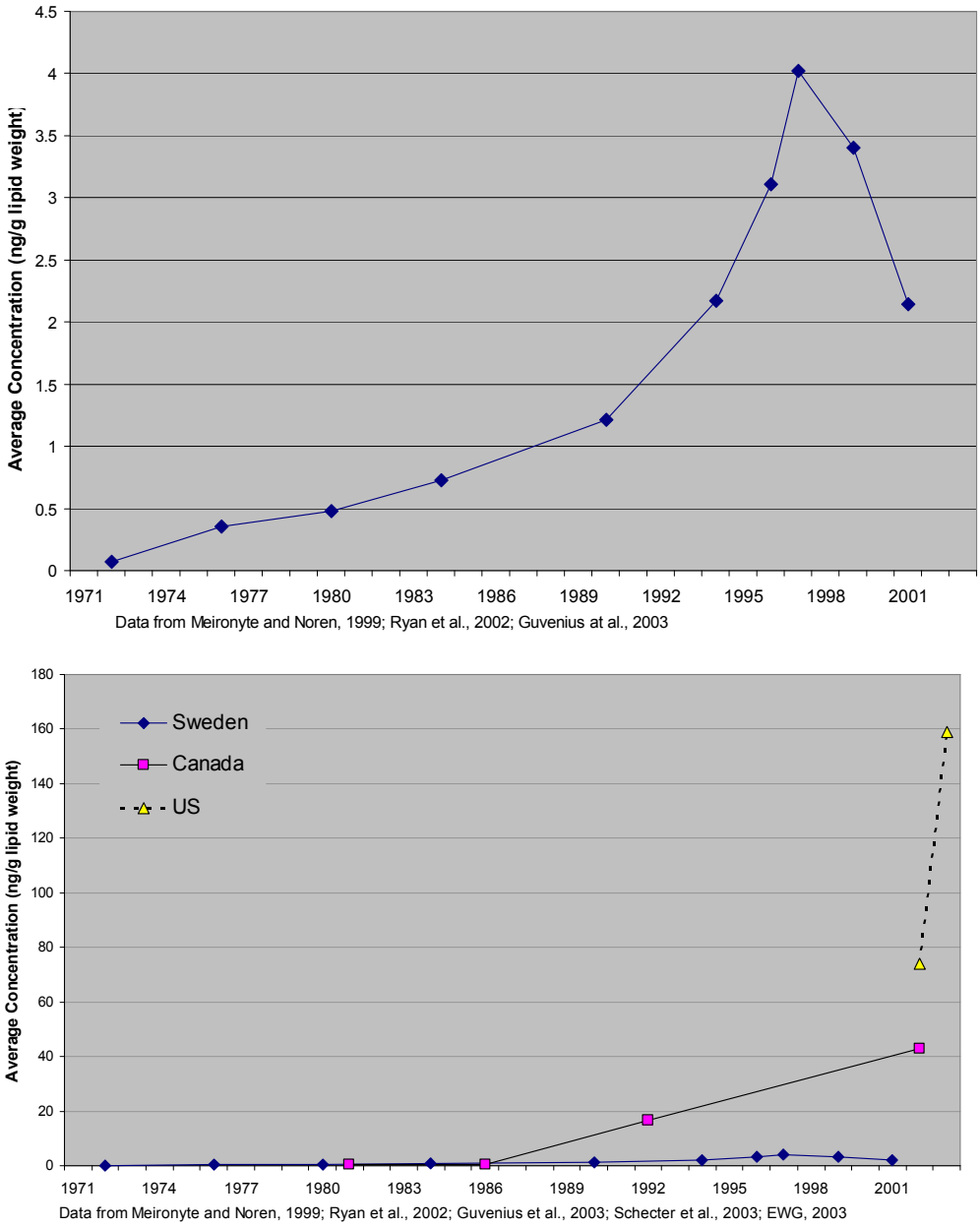

Figure 1-3. Top: concentrations of PBDEs in human breast milk in Sweden; Bottom: the same data, plotted with similar information from Canada and the United States

1.2 Regulatory Status

The federal Clean Water Act (CWA) provides protection to the surface waters of the United States. Section 303(d) requires states to compile lists of water bodies that do not meet water quality standards and to develop plans (known as total maximum daily loads or TMDLs) for achieving the standards. In California, Section 13001 of the California Water Code identifies the California State Water Resources Control Board and Regional Water Quality Control Boards (Water Board) as the principal agencies responsible for controlling water quality.

The state has not listed any segment of San Francisco Bay as impaired by PBDEs. The state has, however, taken unusual steps to regulate PBDEs, steps that would be important mitigating factors if impairment of the beneficial uses of the Bay has occurred. Recognizing that PBDEs were ubiquitous, that Europeans had limited their use (Table 1-1), and that concentrations found in humans were increasing, in 2003, California passed legislation aimed at phasing out use of two commercial formulations of PBDEs, PentaBDE and OctaBDE.

In February 2006, a multi-agency California work group issued recommendations to reduce PBDE exposure in California (Cal/EPA Workgroup, 2006), and in June 2006, California began to phase-out use of PentaBDE and OctaBDE. As of June 1, 2006, manufacture, distribution, and processing of products containing PentaBDE and OctaBDE were prohibited. No regulatory actions concerning the more commonly used formulation, known as DecaBDE, were undertaken, as its components, primarily the fully brominated congener, BDE-209, were understood to be less bioavailable than the congeners that make up the other mixtures. (As of January 1, 2007, Sweden became the first nation to ban DecaBDE.)

Banning PentaBDE and OctaBDE was an important step, and inventories of those contaminants may be expected to decline. However, there remains a large reservoir of the contaminants in manufactured products and the environment, so declines could be slow. Since the components of DecaBDE can degrade to more bioavailable or toxic compounds, its continued use will continue to affect the Bay.

Table 1-1. Regulatory status of PBDEs in Europe, Japan, and the United States.

Political Unit	Regulatory Status
European Union	Published risk assessments on PentaBDE in 2000, OctaBDE in 2003, and DecaBDE in 2002. A draft updated risk assessment for DecaBDE was published in 2004, and it is expected to be finalized soon. Banned PentaBDE and OctaBDE in 2004. Sweden unilaterally bans DecaBDE as of January 1, 2007.
Japan	Requires reporting of DecaBDE imports, volumes used, and quantities released into the environment.
Hawaii	Legislation to phase out PentaBDE and OctaBDE signed in 2004.
Illinois	Legislation to ban manufacture of PentaBDE and OctaBDE and to study DecaBDE signed in 2005.
Maryland	Legislation to prohibit manufacturing, processing, sale, and distribution of new products containing PentaBDE and OctaBDE and to report on DecaBDE by 2007 signed in 2005.
Maine	Bill to phase out products containing PentaBDE and OctaBDE signed in 2004, effective 2006.
Michigan	Ban on manufacture, processing, and distribution of PentaBDE and OctaBDE effective in 2005.
New York	Manufacture of products containing more than 0.1 percent PentaBDE and OctaBDE prohibited as of 2006.
Oregon	Use of PentaBDE and OctaBDE curtailed as of 2006.
Washington	Executive Order required development of action plan in 2004.
California	Manufacture, distribution, and processing of products containing PentaBDE and OctaBDE prohibited in 2006.

1.3 San Francisco Bay

San Francisco Bay is the largest estuary on the West Coast of the United States, draining a watershed of 60,000 square miles. Much of the Bay is shallow, and the average depth is only about 14 feet. At its deepest, however, the Bay is more than 300 feet deep.

The federal and state regulatory bodies divide San Francisco Bay into eight segments: Sacramento /San Joaquin River Delta, Suisun Bay, Carquinez Strait, San Pablo Bay (including Castro Cove), Richardson Bay, Central San Francisco Bay (including Oakland Harbor and San Leandro Bay), Lower San Francisco Bay, and South San Francisco Bay (Figure 1-4).

The Bay is a popular for sport fishing and is visited by thousands of anglers every year. The Bay is also important habitat for wildlife, including birds and marine mammals. The Bay is a staging and wintering area for approximately one million migratory waterfowl and one million shorebirds and also provides breeding habitat for many bird species. The Bay also supports a significant resident breeding population of Pacific harbor seals.

The Water Quality Control Plan for the region (San Francisco Regional Water Quality Control Board, 1995) lists the beneficial uses for the Bay (Table 1-2).

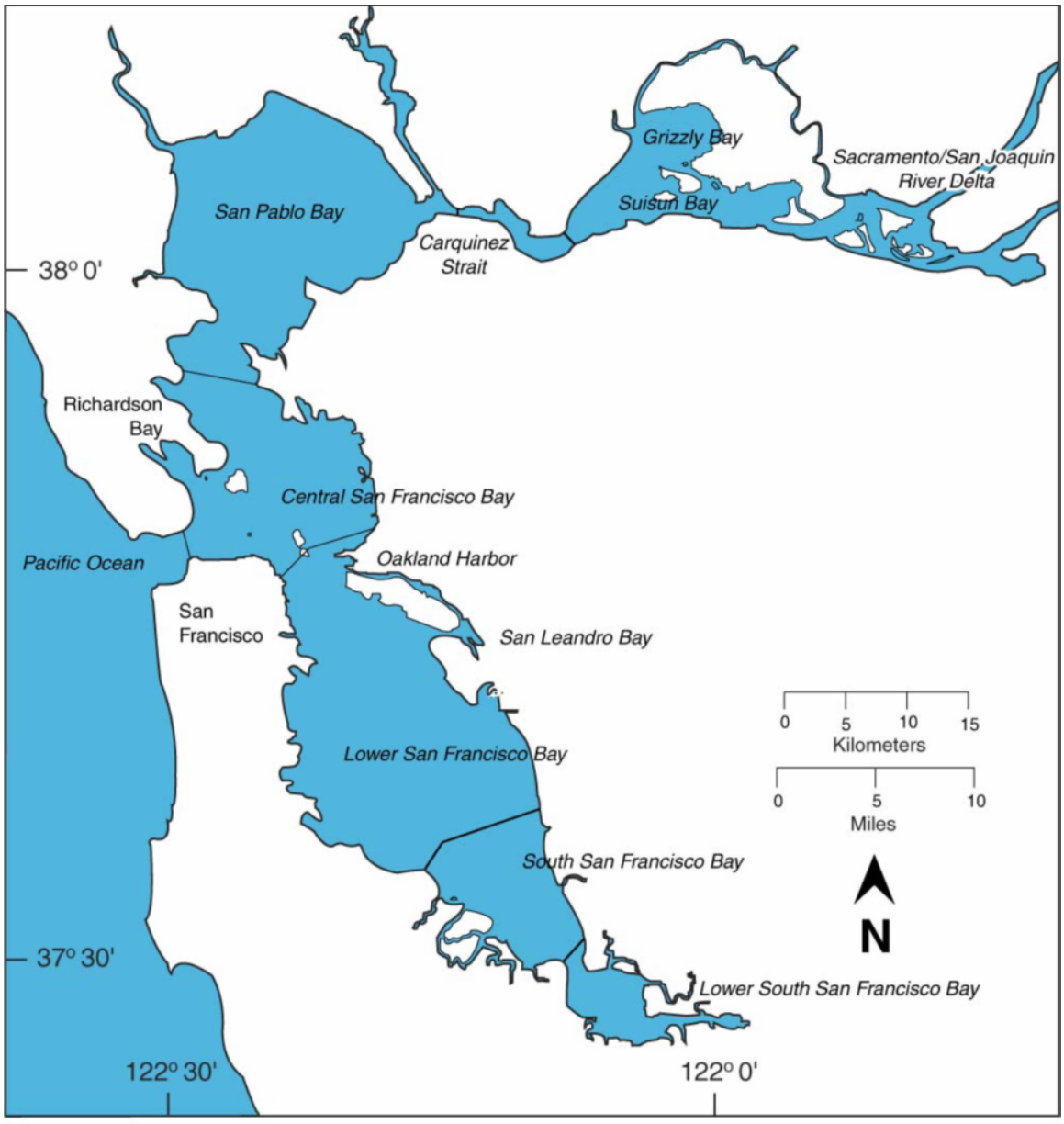

Figure 1-4. San Francisco Bay

Table 1-2. Beneficial uses of San Francisco Bay (All beneficial uses do not apply to all Bay segments.)

Use	Abbreviation	Definition
Ocean, commercial, and sport fishing	COMM	Uses of water for commercial or recreational collection of fish, shellfish, or other organisms in oceans, bays, and estuaries, including but not limited to, uses involving organisms intended for human con
Estuarine habitat	EST	Uses of water that support estuarine ecosystems, including, but not limited to, preservation or enhancement of estuarine habitats, vegetation, fish, shellfish, or wildlife (*e.g.*, estuarine mammals, waterfowl, shorebirds), and the propagation, sustenance, and migration of estuarine organisms.
Industrial service supply	IND	Uses of water for industrial activities that do not depend primarily on water quality, including, but not limited to, mining, cooling water supply, hydraulic conveyance, gravel washing, fire protection, and oil well repressurization
Fish migration	MIGR	Uses of water that support habitats necessary for migration, acclimatization between fresh water and salt water, and protection of aquatic organisms that are temporary inhabitants of waters within the region.
Navigation	NAV	Uses of water for shipping, travel, or other transportation by private, military, or commercial vessels.
Industrial process supply	PRO	Uses of water for industrial activities that depend primarily upon water quality.
Preservation of rare and endangered species	RARE	Uses of waters that support habitats necessary for the survival and successful maintenance of plant of animal species established under state and/or federal law as rare, threatened, or endangered.
Water contact recreation	REC1	Uses of water for recreational activities involving body contact with water where ingestion of water is reasonably possible. These uses included, but are not limited to, swimming, wading, water-skiing, skin and scuba diving, surfing, whitewater activities, fishing, and uses of natural hot springs.
Noncontact water recreation	REC-2	Uses of water for recreational activities involving proximity to water, but not normally involving contact with water where ingestion is reasonably possible. These uses include, but are not limited to, picnicking, sunbathing, hiking, beachcombing, camping, boating, tide pool and marine life study, hunting, sightseeing, or aesthetic enjoyment in conjunction with the above activities.
Shellfish harvesting	SHELL	Uses of water that support habitats suitable for the collection of crustaceans and filter-feeding shellfish (*e.g.*, clams, oysters, and mussels) for human consumption, commercial, or sport purposes.
Fish spawning	SPWN	Uses of water that support high quality aquatic habitats suitable for reproduction and early development of fish
Wildlife habitat	WILD	Uses of waters that support wildlife habitats, including, but not limited to, the preservation and enhancement of vegetation and prey species used by wildlife, such as waterfowl

1.4 Polybrominated Diphenyl Ethers (PBDEs)

PBDEs are members of a class of organic compounds with one to ten bromine atoms. They are added to foams and plastics because they retard the ignition and growth rates of fire. The basic chemical structure of PBDEs is similar to those of dioxins, furans, and PCBs (Figure 1-5), and their chemical nomenclature is also similar. That is, there are specific forms or congeners with varying numbers of bromine atoms, which for convenience, have been given International Union of Pure and Applied Chemistry (IUPAC) numbers (Table 1-3). Theoretically there are 209 congeners, but not all possible variants are manufactured or present in the environment. There are few or no known natural sources.

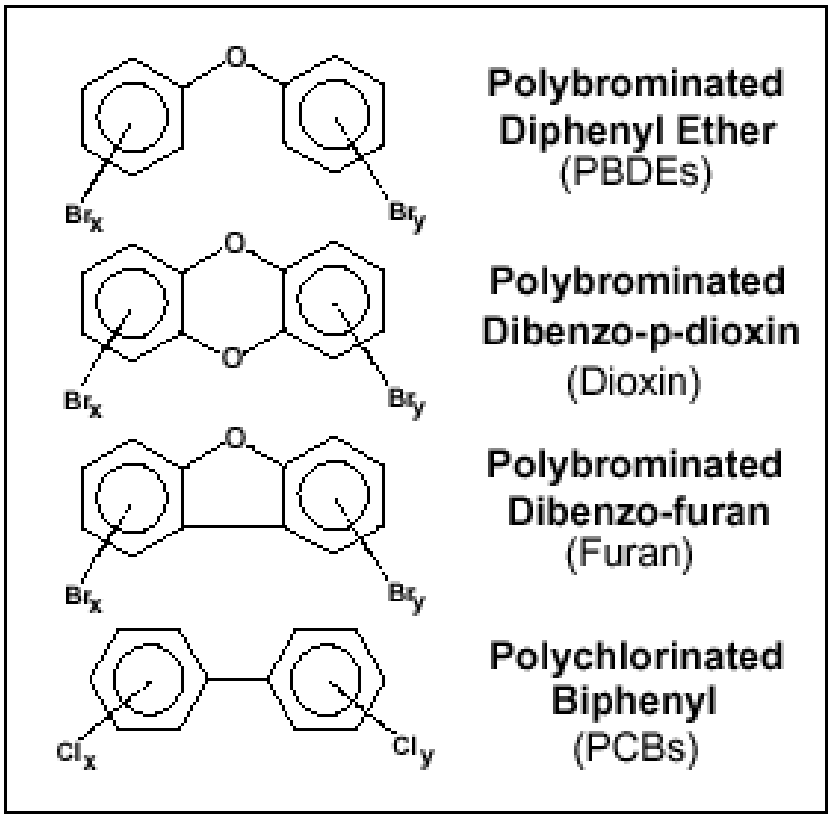

Figure 1-5. Chemical structure of PBDEs, compared to dioxins, furans, and PCBs (from Madsen et al., 2003)

Table 1-3. PBDE congeners that have been reported in environmental samples

PBDE Congener	IUPAC No.		PBDE Congener	IUPAC No.
2,4-DiBDE	BDE-7		2,2',3,4,4'-PeBDE	BDE-85
2,4'-DiBDE	BDE-8		**2,2',4,4',5-PeBDE**	**BDE-99***
2,6-DiBDE	BDE-10		**2,2',4,4',6-PeBDE**	**BDE-100***
3,3'-DiBDE	BDE-11		2,3,3',4,4'-PeBDE	BDE-105
3,4-DiBDE	BDE-12		2,3,4,5,6-PeBDE	BDE-116
3,4'-DiBDE	BDE-13		2,3',4,4',6-PeBDE	BDE-119
4,4'-DiBDE	BDE-15		2,3',4,5,5'-PeBDE	BDE-120
2,2',4-TrBDE	BDE-17		3,3',4,4',5-PeBDE	BDE-126
2,3',4-TrBDE	BDE-25		2,2',3,3',4,4'-HxBDE	BDE-128
2,4,4'-TrBDE	**BDE-28***		2,2',3,4,4',5'-HxBDE	BDE-138
2,4,6-TrBDE	BDE-30		2,2',3,4,4',6'-HxBDE	BDE-140
2,4',6-TrBDE	BDE-32		**2,2',4,4',5,5'-HxBDE**	**BDE-153***
2',3,4-TrBDE	BDE-33		**2,2',4,4',5,6'-HxBDE**	**BDE-154***
3,3',4-TrBDE	BDE-35		2,2',4,4',6,6'-HxBDE	BDE-155
3,4,4'-TrBDE	BDE-37		2,3,4,4',5,6-HxBDE	BDE-166
2,2',4,4'-TeBDE	**BDE-47***		2,2',3,4,4',5,6-HpBDE	BDE-181
2,2',4,5'-TeBDE	BDE-49		**2,2',3,4,4',5',6-HpBDE**	**BDE-183***
2,2',4,6'-TeBDE	BDE-51		2,3,3',4,4',5,6-HpBDE	BDE-190
2,3',4,4'-TeBDE	BDE-66		2,2',3,4,4',5,5',6-OcBDE	BDE-203
2,3',4',6-TeBDE	BDE-71		2,2',3,3',4,4',5,5',6-NoBDE	BDE-206
2,4,4',6-TeBDE	BDE-75		2,2',3,3',4,4',5,6,6'-NoBDE	BDE-207
3,3',4,4'-TeBDE	BDE-77		2,2',3,3',4,5,5',6,6'-NoBDE	BDE-208
3,3',4,5'-TeBDE	BDE-79		**2,2',3,3',4,4',5,5',6,6'-DeBDE**	**BDE-209***

*** BDE congeners of "Primary Interest"** as defined by USEPA Method 1614.

Chemical concentrations may be reported by individual congener, by level of bromination (for example, total tetrabrominated biphenyl ethers or TrBDE), or as the sum of concentrations of all identified congeners (total PBDEs).

There are three commercial PBDE mixtures, named for the dominant chemical forms in the mixtures and having had somewhat differing uses. Conventions for writing the names of the commercial mixtures and specific chemical forms vary. In this report, the names of the commercial mixtures are capitalized. For example, "PentaBDE" refers to a commercial mixture made up of congeners having three to seven bromine atoms, while "pentaBDE" or "PeBDE" refers to just the congeners with five bromine atoms. PentaBDE is primarily composed of five congeners with four or five bromine atoms and has been used in foam furniture cushions, automobile seats, and carpet padding. One of the most common forms of PBDE found in environment samples, BDE-47, is a major constituent of PentaBDE. OctaBDE, made up of several congeners with six to eight bromine atoms, has been used in automobiles and plastics for computers and kitchen appliances. DecaBDE is the most common mixture; it is mostly

composed of the fully brominated congener, 2,2',3,3',4,4',5,5',6,6'-DeBDE or PDE-209, and is used in consumer electronics, the backs of television sets, wire insulations, and upholstery. (PBDEs have not been used in flame-resistant children's sleepwear.)

There are few long-term records of PBDE production or use, and the available production and use data are insufficient for estimating inputs of PBDEs from various sources or inventories of PBDE compounds into California. An industry organization, the Bromine Science and Environmental Forum, has published some data on global market demand, suggesting a market demand of approximately 73 million pounds in 2001, with the U.S. using almost all the PentaBDE in production at that time (Table 1-4). Total production was estimated to have peaked in 1990 at an estimated 88 million lbs/year, a similar level as peak PCB production (86 million lbs/year in 1970). Total production of PBDEs remained steady through the 1990s, although there was a shift from the lower-brominated mixtures to the more highly brominated formulations. As of 2003, PBDE mixtures were being produced in the U.S. by the Great Lakes Chemical Corporation (now Chemtura) of El Dorado, Arkansas and the Albemarle Corporation in Magnolia, Arkansas (ATSDR, 2004). Great Lakes Chemical Corporation was the only domestic producer of PentaBDE and OctaBDE until it voluntarily ceased production at the end of 2004.

Table 1-4. Global market demand of PBDEs in 2001 (Bromine Science and Environmental Forum, www.bsef.com).

PBDE Mixture	Global Market Demand 2001 (million lbs/year)	Percent Used by United States	Major Uses
PentaBDE	16	95	Flexible polyurethane foam for furniture, auto seats, carpet pads, and mattresses
OctaBDE	3	40	Automobiles, computer casings, appliances
DecaBDE	54	44	High-impact polystyrene television set cabinets and other electronics, upholstery fabrics

PentaBDE is a thick liquid, and OctaBDE and DecaBDE are white or light-colored solids. They do not evaporate into the air or readily dissolve. Air-borne PBDEs are associated with dust particles, and PBDEs in the water column are usually associated with suspended solid material. PBDEs are known to persist in the environment, bioaccumulate, and biomagnify. Physical properties of the commercial mixtures were summarized in European Union risk assessment reports (European Chemicals Bureau, 2000, 2002, 2003, 2004; Table 1-5).

Table 1-5. Physical properties of commercial PBDEs (European Chemicals Bureau, 2000, 2002, 2003, 2004)

Property	PentaBDE	OctaBDE	DecaBDE
Physical state at normal temperature at pressure	Amber, viscous liquid or semi-solid	Off-white powder or flaked material	Fine crystalline powder
Melting point	-7 to -3°C	Varying by specific commercial product:	300-310°C
Boiling point	Decomposes at >200°C	Decomposes at >330°C	Decomposes at 320°C
Vapor pressure	4.69×10^{-5} Pa at 21°C	6.69×10^{-5} Pa at 21°C	4.63×10^{-6} Pa at 21°C
Water solubility	13.3 µg/L at 25°C	0.5 µg/L at 25°C	<0.1 µg/L at 25°C
Log octanol-water partition coefficient	6.57	6.29	6.27
Estimated atmospheric half-life	12.6 days	76 days	94 days

PBDEs can be degraded when exposed to light, in the water or sediments, and in biological organisms. They may be debrominated, producing more bioaccumulative or toxic PBDE compounds with fewer bromine atoms. They may be hydroxylated, a phenomenon also known in PCBs, and of concern because the hydroxylated compounds are often more toxic than the parent compounds. Degradation rates in water and sediments, especially important in addressing water quality concerns for San Francisco Bay, have not been measured.

Despite their chemical similarities to other organic pollutants, there was little interest in the environmental or health effects of PBDEs until they began to be detected in environmental samples. Consequently, the toxicity of PBDE mixtures and specific congeners is only beginning to be understood. A summary of existing information is included in the U.S. Environmental Protection Agency Project Plan for PBDEs (U.S. Environmental Protection Agency, 2006; selected results shown in Table 1-6). In humans, there are concerns about liver and thyroid toxicity and developmental effects. Constituents in the DecaBDE have been considered to be less toxic than those in the PentaBDE and OctaBDE formulations, as they are not readily bioaccumulated, particularly BDE-209 which is the primary constituent. However, DecaBDE has been classified as a possible human carcinogen; the carcinogenic potentials of PentaBDE and OctaBDE have not been evaluated.

Table 1-6. Selected toxicological information about PBDEs

Taxonomic Group	Study Results	Reference
Aquatic plants	PentaBDE not toxic to freshwater alga exposed to concentrations ranging from 1.7 to 26 µg/L in acute toxicity test.	European Chemicals Bureau, 2000
	DecaBDE in concentrations up to 1 µg/L had no effect on growth of three marine algae.	Walsh et al., 1987
Invertebrates	BDE-47, BDE-99, and BDE-100 at low microgram per liter concentrations affect larval development and growth of copepod *Nitocra spinipes*.	Breitholtz and Wollenberger, 2003
	BDE-28, BDE-47, BDE-99, and BDE-100 in low microgram per liter concentrations inhibit larval development of copepod *Acartia tonsa*.	Wollenberger et al., 2005
Fish	Commercial mixtures of PentaBDE, OctaBDE, and DecaBDE had low or no acute toxicity to Japanese medaka and rainbow trout, even when a carrier solvent was used to increase solubility.	European Chemicals Bureau, 2000; Hardy, 2002
	BDE-47, BDE-85, and BDE-99 not toxic in rainbow trout egg-injection test with great sensitivity in detecting dioxin-like toxicity.	Hornung et al., 1996
	DecaBDE increased liver weight and plasma lactate levels and decreased number of lymphocytes in rainbow trout fed 10 mg for up to 120 days.	Kierkegaard et al., 1999
	Three-spined sticklebacks fed 861 and 1630 mg/kg lipid PentaBDE exhibited fat accumulation in liver and reduced spawning success.	Holm et al., 1993
	Rainbow trout fed 21 mg/kg over 22 days BDE-47 or 19.5 mg/kg BDE-99 exhibited reduced glutathione reductase activity, hemocrit, and blood glucose levels	Tjarnlund et al., 1998
Mammals	Hepatic effects, such as liver enlargement, observed in rodents exposed to 5-10 mg/kg/day in food. Effects more severe for PentaBDE and OctaBDE than DecaBDE.	U.S. EPA, 2006, interpretation of several studies
	Dioxin-like induction of cytochrome P450 enzyme CYP1A apparently due to non-PBDE component of commercial mixtures	
	Developmental and neurotoxic effects observed in rodents treated with 0.6 mg/kg/day for 15 days (BDE-99), single 60 µg/k doses (BDE-99), and 31 days of exposure to 30 mg/kg/day PentaBDE.	
	Effects on thyroid system from exposure to 3 mg/kg/day or single dose of 0.8 mg/kg PentaBDE and 3200mg/kg/day DecaBDE.	
	Reproductive effects at 30 mg/kg/day PentaBDE for 5 days.	
	Some evidence that DecaBDE is carcinogenic, for example increased hepatic neoplastic nodules in male rats fed 1120 and 2240 mg/kg/day and female rates fed 2550 mg/kg/day.	

In an analysis of PBDEs in human food sources and consumption patterns, Schecter et al. (2006) found that fish was the food source that was highest in PBDE concentrations but that meat accounted for greater total intake (Figure 1-6). Overall, they determined that dietary exposure does not account for high body burdens of PBDEs in humans, and that indoor air and dust may be more important exposure pathways. (The total PBDE concentrations that they measured in fish ranged from 37 to 480 ng/g lipid, and many of the fish from San Francisco Bay have levels that are twice as high.)

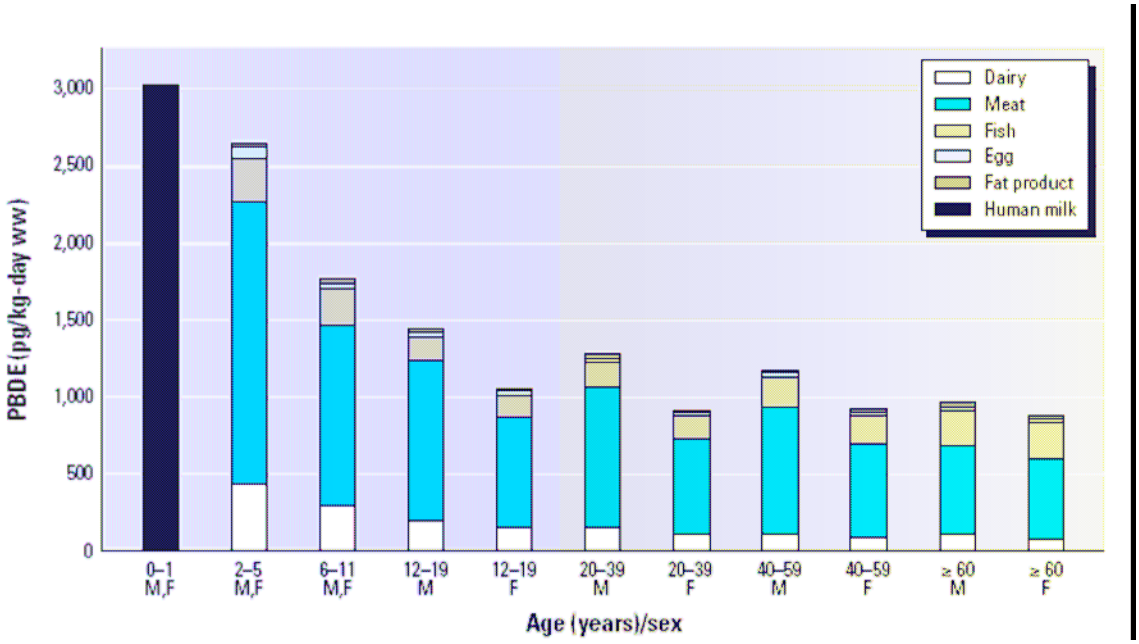

Figure 1-6. Daily PBDE dietary intake of the U.S. population by age and gender (Schecter et al., 2006). (The high level of intake for infants results from high levels in human milk and the authors' simplifying assumption that human milk was the only food consumed.)

2. Impairment Assessment

This section of the report will review the basis for a potential impairment listing for San Francisco Bay. Typically, CM/IA documents review the available data to determine whether there is a weight of evidence indicating:

- **No impairment:** The available data demonstrate no negative effect on beneficial uses of the Bay, and there is sufficient information to make the finding.
- **Impairment unlikely:** The data indicate that PBDEs cause no impairment to the Bay. However, there is some uncertainty, due to lack of sufficient information or disagreement about how to interpret the data.
- **Possible impairment:** There is some suggestion of impairment, but the uncertainties preclude making a definitive judgment.
- **Definite impairment:** The data clearly demonstrate a negative effect on the beneficial uses of the Bay.
- **Unable to determine impairment:** There is insufficient information to make any determination.

For PBDEs, this task is especially difficult. There are no local, state, or federal criteria, standards, or screening levels for PBDEs in water, sediment, fish, or wildlife tissues. Because of suspected threats to human health and the environment, regulation of PBDE use in California and other areas has proceeded in advance of complete toxicological studies. Although these actions did not result specifically or solely because of concerns for impairment of the beneficial uses of the Bay, they did recognize concerns.

This assessment focuses on the two greatest concerns: concentrations in sport fishes and concentrations in wildlife, as these measures are the greatest concerns for PCB impairment. Information is also available on concentrations in water, sediments, and bivalve mollusks and is presented as part of Section 3, Conceptual Model.

2.1 Sport Fishing

One of the beneficial uses of the Bay is ocean, commercial, and sport fishing (abbreviated as COMM). This use of the Bay is currently considered impaired, primarily because of high concentrations of PCBs and mercury in sport fish.

The Regional Monitoring Program for Trace Substance (RMP) has collected fishes and bivalve shellfish for analysis of contaminant concentrations at three-year intervals since 1997. The program has sampled jacksmelt (*Atherinopsis californiensis*), shiner surfperch (*Cymatogaster aggregata*), white croaker (*Genyonemus lineatus*), striped bass (*Morone saxatilis*), California halibut

(*Paralichthys californicus*), leopard shark (*Triakis semifasciata*), and white sturgeon (*Acipenser transmontanus*). The species are all residents of the estuary and do not migrate. Fish fillets are prepared for analysis using methods commonly used to prepare, cook, and consume each species (SFEI, 2000). Within each species, samples are composited for analysis.

The program did not include PBDEs on its list of analytes until 2000, when they were discovered as large peaks in the electron capture detection gas chromatography results (Greenfield et al., 2003). This discovery was unanticipated, and the analysis was considered to be only semi-quantitative. Subsequently, the Environmental Working Group in Oakland California arranged for archived samples from 1997 to be analyzed for PBDEs by the California Department of Toxic Substances Controls Hazardous Materials Laboratory (HML) (Lunder and Sharp, 2003). Every sample was found to contain the seven most common PBDEs, with total concentrations ranging from 1 to 62 ng/g (part per billion) wet weight (Lunder and Sharp, 2003). Total concentrations were highest in white croaker fillets and lowest in leopard shark and jacksmelt. The single most contaminated fish was a white croaker from the Richmond Inner Harbor.

The most recent available data were collected by the RMP in 2003 (Davis et al., 2006a). PBDEs were detected in every species except for California halibut (Figure 2-1, top). The highest concentration, 79 ng/g, was detected in a white sturgeon sample from the South Bay with unusually high lipid content. Median concentrations of PBDEs in white croaker, often regarded as a good indicator species, were 28 ng/g.

In contrast, PCB concentrations were about ten times higher than PBDEs (Figure 2-1, bottom). However, normalized for lipid content, the highest concentrations of PBDEs in fishes from San Francisco Bay were as high as the many of the highest reported for other regions of the U.S. and abroad (Figure 2-2). Similarly, concentrations of BDE-47 (a major component of the PentaBDE formulation) and the sums of all measured PBDEs were higher in San Francisco Bay fishes than in fishes from the Baltic Sea and Japan (summarized in de Witt, 2002). (The comparison is limited, however, because information about concentrations in fishes from other part of the world is largely for migratory rather than resident fishes.)

Whether these levels constitute impairment is impossible to determine until there are defined standards, such as the screening values against which concentrations of PCBs in sport fish are compared.

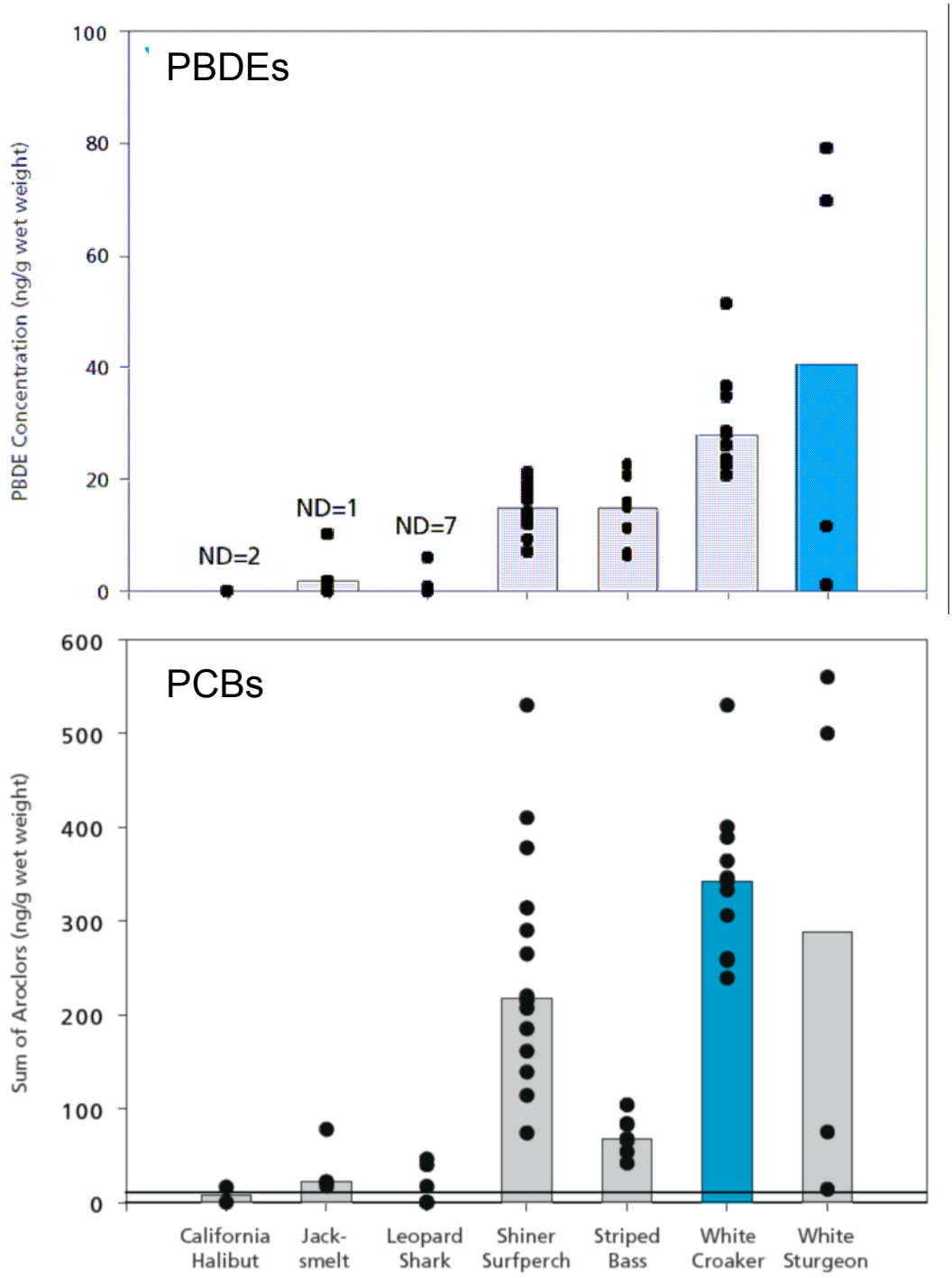

Figure 2-1. PBDE (top) and PCB (bottom) concentrations in sport fish from the Bay in 2003. Note the differences in scale. The horizontal line on the PCB graph denotes the screening value that is being applied in the PCB TMDL, 10 ng/g.

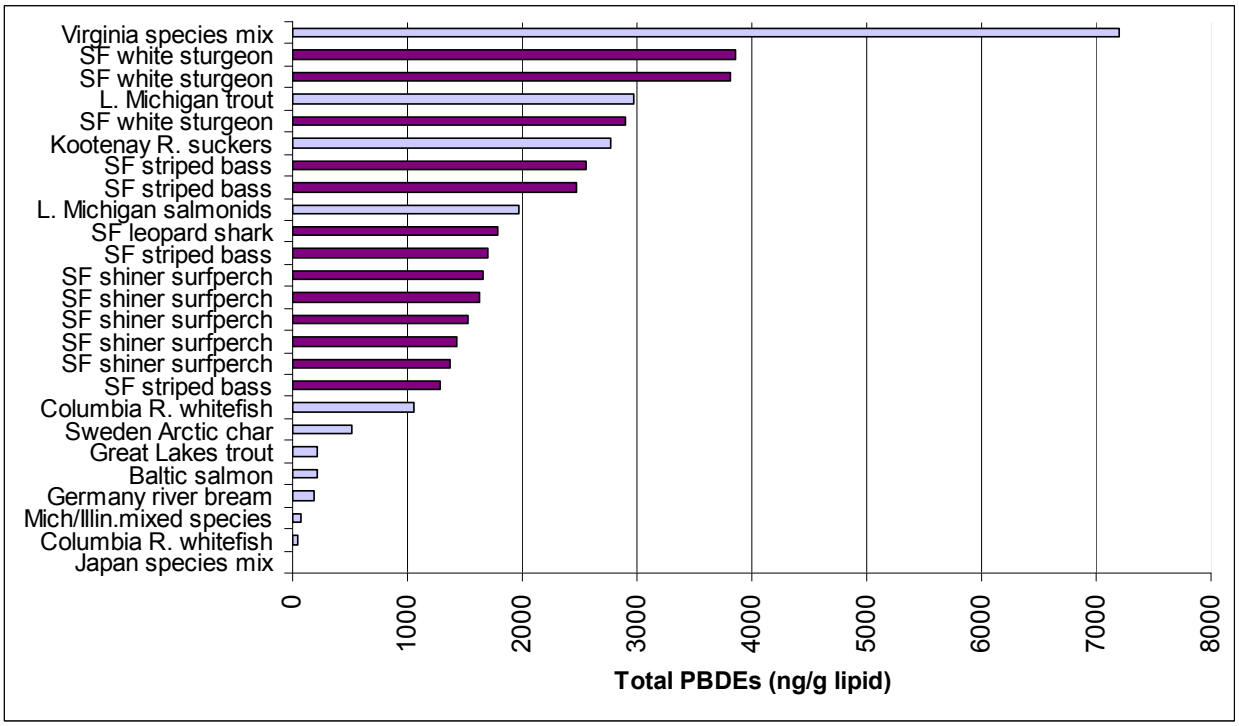

Figure 2-2. Concentrations of PBDEs in fish from San Francisco Bay (fish labeled SF are 2003 RMP data for the samples with the highest concentrations) compared to fish from other regions (non-RMP data are from Hites, 2004)

2.2 Wildlife

There are several designated beneficial uses of San Francisco Bay that relate to wildlife: preservation of rare and endangered species (RARE), estuarine habitat (EST), wildlife habitat (WILD), and fish spawning (SPWN). There are no numeric standards for these uses for any contaminants.

If concentrations of PBDEs are high enough to affect wildlife, as is the situation for PCBs, fish-eating species are the most likely group to be affected. PBDE concentrations have been measured in the eggs of two types of fish-eating birds from San Francisco Bay, terns and cormorants, and in harbor seals.

She et al. (2004) measured PBDE levels in 45 individual tern eggs, representing three species—Caspian (*Sterna caspia*), Forster's (*Sterna forsteri*), and California Least (*Sterna antillarum brownie*) terns—collected in 2003 from nesting sites throughout the Bay Area. A major finding of the study was that Forster's Tern eggs had the highest levels of PBDEs ever reported in wildlife, with a maximum level of 63 mg/kg lipid (parts per million, equivalent to 63,000 ng/g or parts per

billion, the unit of measure used to describe concentrations in fish tissue). Mean concentrations ranged from 5,870 ng/g lipid in Least Tern eggs to 9,420 ng/g lipid in Forster's Tern eggs.

In comparison, the highest concentration of PCBs measured in the study was about six times higher than the highest concentration of PBDEs and found in the same sample. Overall, levels of PCBs were three to seven times the PBDE levels (Figure 2-3).

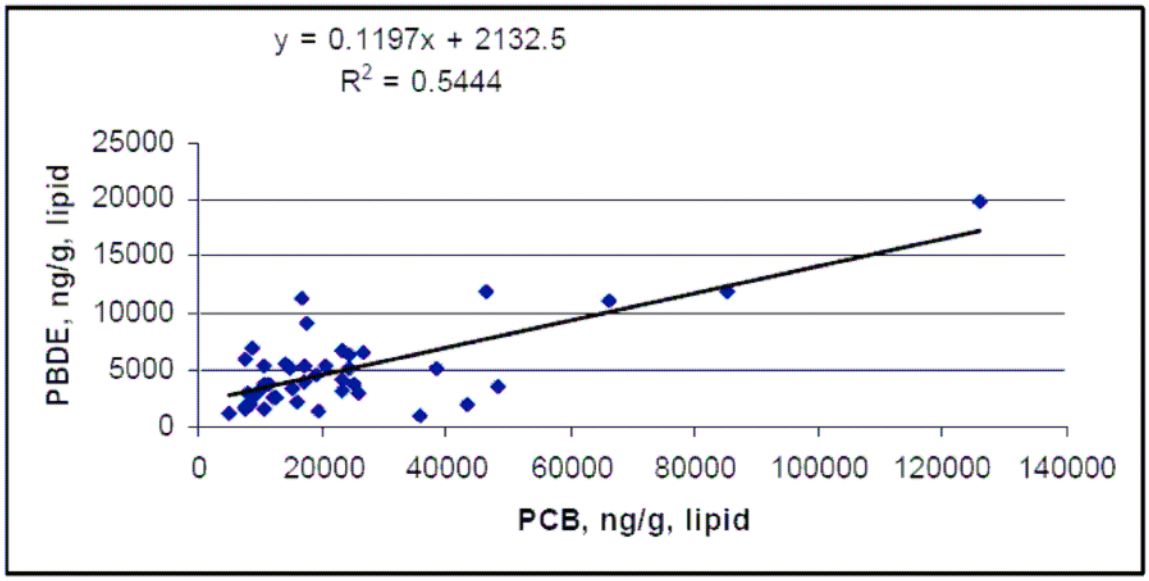

Figure 2-3. Correlation between total PCBs and PBDEs in tern eggs (She et al., 2004)

PBDEs have been measured in Double-crested Cormorant eggs as part of an RMP study (Davis et al., 2006b). Sampling was conducted at three locations in 2002 and 2004: Wheeler Island located just below the confluence of the Sacramento and San Joaquin rivers, the Richmond Bridge close to the boundary between San Pablo and Central San Francisco bays, and the Don Edwards San Francisco Bay National Wildlife Refuge in the South Bay. At each location, two composites of 10 randomly selected eggs were sampled. PBDE concentrations were variable over space and time, with concentrations up to 960 ng/g fresh wet weight (fww) or 24,000 ng/g lipid, approximately the same range as found in tern eggs. The data suggest a possible decline in concentrations between 2002 and 2004, but a longer time series will be necessary to determine whether there is a real trend (Figure 2-4).

Similar to the findings in terns, concentrations of PCBs in the cormorant eggs were as much as five times higher than concentrations of PBDEs, ranging from 1200 to 4500 ng/g fww (or 30,000 to 100,000 ng/g lipid) over a five-year period (Figure 2-4).

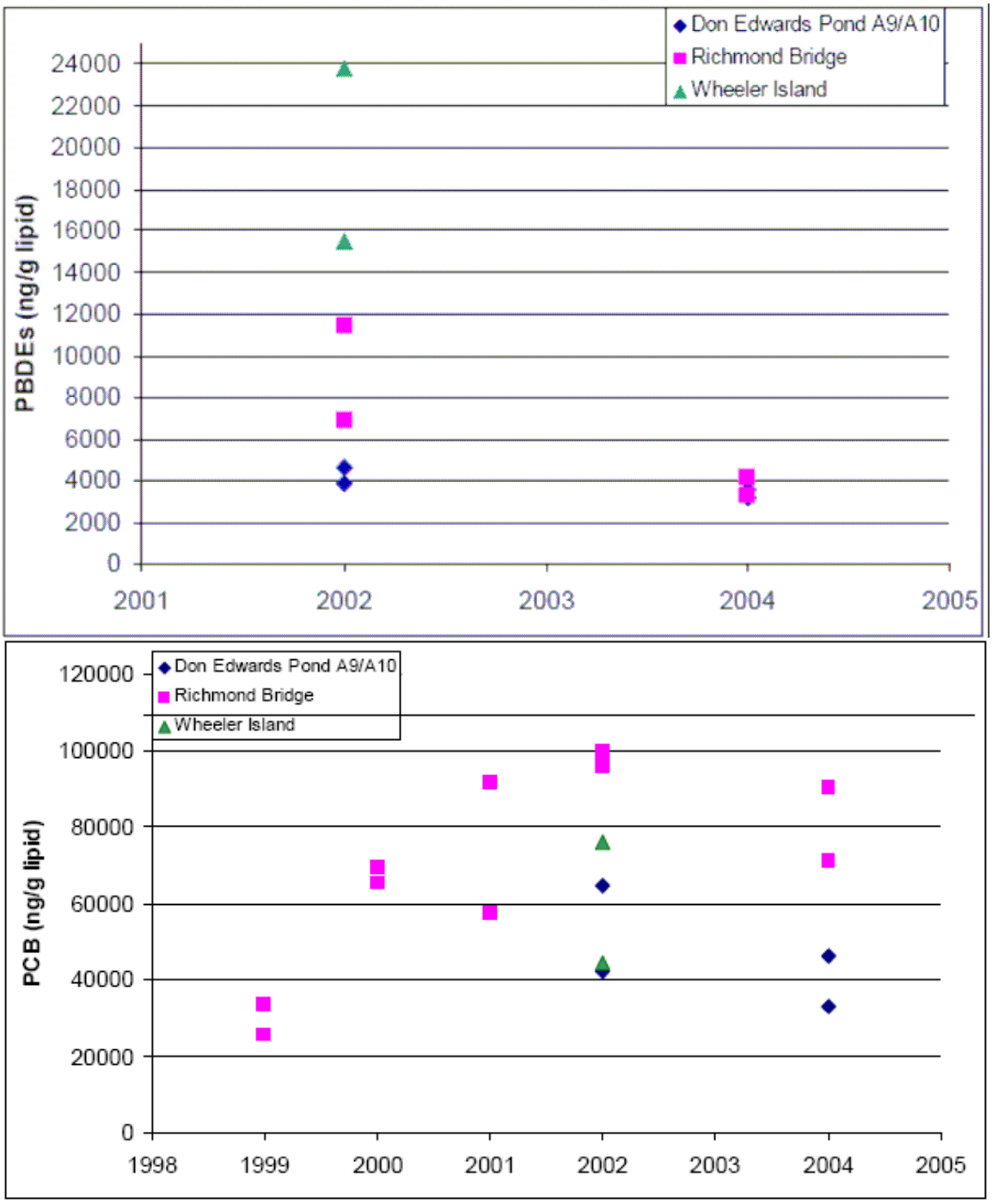

Figure 2-4. Concentrations of PBDEs (top) and PCBs (bottom) in cormorant eggs (RMP data. Note differences in scale.)

The concentrations of PBDEs is seal blubber were one of the most important factors in generating interest in PBDEs in San Francisco Bay. Seal blubber samples, which had been collected and archived from stranded, dead harbor seals over the period 1989 to 1998, were analyzed for PBDEs by She et al. (2002). Samples came from ten adults and one fetus. Total PBDEs ranged from 88 to 8,325 ng/g lipid, averaging 1,738 ng/g lipid, with the highest concentrations found in the seals with the lowest total fat content and from later years. These concentrations are among the highest reported for the species. Total PBDE concentrations in adult tissue samples, which were normalized for lipid content, showed increases with time (Figure 2-5), with concentrations doubling every 1.8 years.

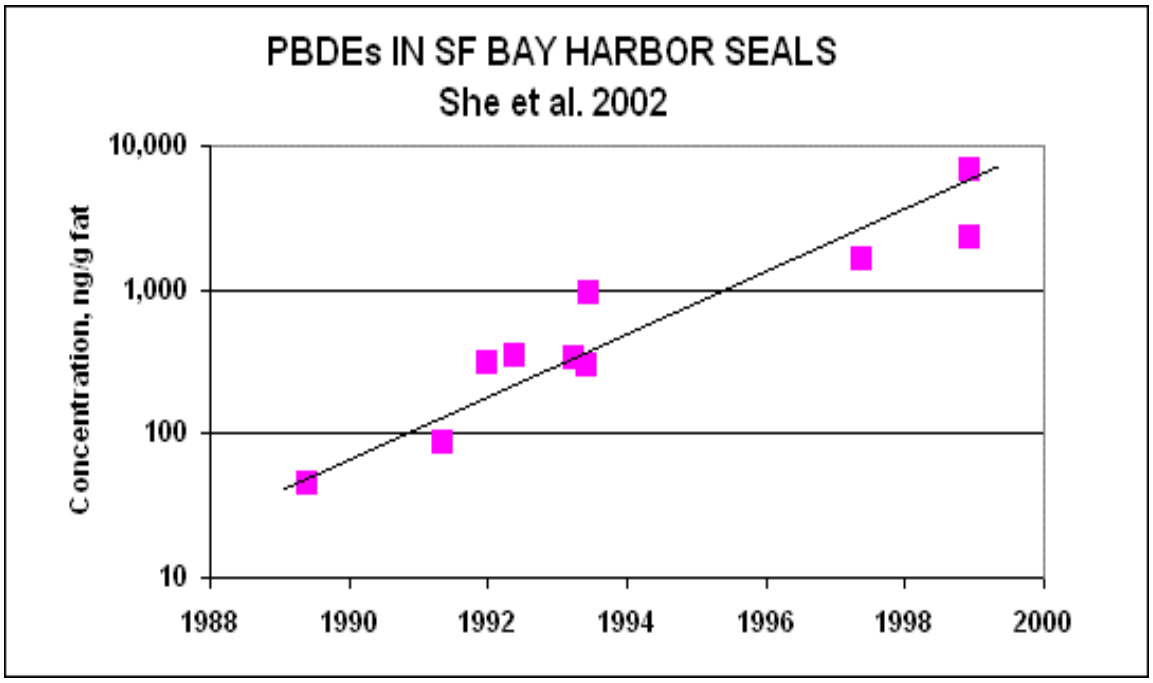

Figure 2-5. Concentrations of total PBDEs in San Francisco Bay harbor seals.

Although the elevated levels of PBDEs in wildlife species may be cause for concern, it is not possible to definitely state that the wildlife uses of the Bay have been impaired. To date, there is insufficient information on the levels of PBDEs in bird eggs or in marine mammals that cause effects.

2.3 Impairment Summary

Levels of PBDEs in sport fish and wildlife from San Francisco Bay are clearly elevated and suggest **possible impairment:** elevated levels of PBDEs suggest that there may be impairment, but the uncertainties preclude making a definitive judgment. Without defined standards, it is not possible to definitively state that beneficial uses of San Francisco, such as sport fishing (COMM) and wildlife uses (particularly RARE, WILD, or EST), are impaired by PBDEs.

European Union risk assessments (European Chemicals Bureau, 2000, 2002, 2003) used available data to develop predicted concentrations of PBDEs from water, sediments, air, and biota (Predicted Environmental Concentrations or PEC) and predicted concentrations at which no effect would be expected (Predicted No Effect Concentrations or PNEC). With similar or lower levels than have been observed in San Francisco Bay, the European Union risk assessments suggested that within their member nations, concentrations of PBDEs were high enough to pose possible local risks to aquatic life in the sediments and possible risk to top predators from PentaBDE, low risk from OctaBDE except when the hexabrominated component was considered, in which case there were possible risk to predators, and probably low risks from DecaBDE, except if it degraded to congeners with fewer bromine atoms.

Within the United States, EPA is enhancing its Integrated Risk Information System (IRIS) database on health risks from PBDEs and is working towards assessing risks. Risk assessment studies of individual penta-, hexa-, octa-, and decaBDEs (BDE-47, BDE-99, BDE-153, and BDE-209) have completed a peer-review process and are under continued agency review and revision. When completed, the assessments will assist in making a more definitive statement about impairment to San Francisco Bay.

3. Conceptual Model

This section presents the conceptual model for PBDEs in San Francisco Bay, including a description of **current conditions** within the Bay, recent information about some **sources**, a synthesis of what is known about **pathways** to the Bay, and an estimation of **loads**. A one-box fate model of PBDEs in water and sediment is developed to help synthesize the conceptual model and begin development of a **mass budget** of PBDEs in the Bay. The model is used to make an independent estimate of **loads** predict **pathways** and **rates of recovery** of the Bay under varied scenarios for continued loading.

3.1 Current Conditions

3.1.1 Water

The RMP has included PBDEs in its water monitoring program since 2002. Concentrations of total PBDEs in 2002 ranged from 3 to 513 pg/L (parts per quadrillion). The most recent data available are from 2004 and 2005 (Figure 3-1), during which dry-season samples were taken from 33 stations, 28 of which were randomly selected and located within the major hydrographic regions of the Bay. The remaining stations, designated "historic" stations, have been included in RMP status and trend monitoring to maintain time series for long-term trend analysis. Due to analytical complications, total PBDEs were not calculated from these data. Instead, two of the most abundant congeners, BDE-47 and BDE-209, were reported (for details, see Oros et al., 2005). The most commonly occurring congener was BDE-47, a major constituent of the PentaBDE formulation. Concentrations of BDE-47 in whole water samples ranged from 16.1 to 337 pg/L, with a spatially unbiased mean of 61 ± 5.6 pg/L, levels comparable to those reported from other waterbodies around the world (Oros et al., 2005). Concentrations of BDE-209, the major constituent of the DecaBDE formulation, ranged from 12.2 to 191 pg/L, with a spatially unbiased mean of 26 ± 3.6 pg/L. Most of the PBDEs detected were associated with suspended particulate matter rather than the dissolved portion of the samples. BDE-47 was consistently found throughout the Bay. No spatial pattern could be detected for BDE-209, a congener for which recoveries were poor and for which a large number of samples were near the detection limits.

Inventories of PBDEs in San Francisco Bay water, calculated from the concentration data, and an assumed total Bay water volume of 5.5×10^9 m^3 (Davis, 2004), totaled 0.33 kg BDE-47 and 0.14 kg BDE-209.

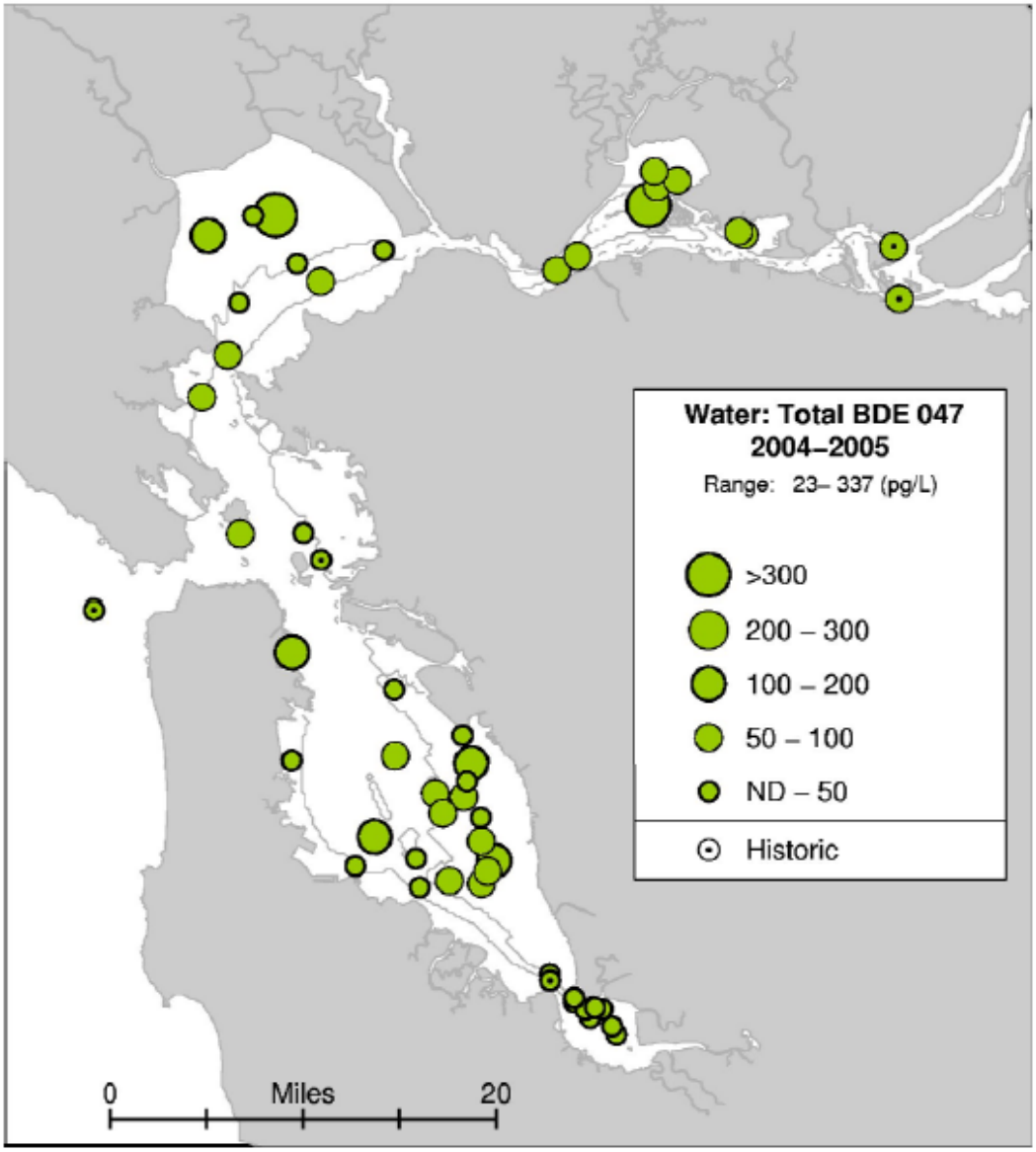

Figure 3-1. Concentrations of BDE-47 in water (RMP 2004 and 2005 data, "historic" refers to stations that have been included in RMP status and trends monitoring to maintain time series for long-term trend analyses.)

3.1.2 Sediments

The RMP also began monitoring PBDEs in surface sediments in 2002. The most recent available data are from 2004 and 2005 for BDE-47 (Figure 3-2) and from 2004 for BDE-209 (Figure 3-3). These data represent the first complete dataset for BDE-209, which is abundant but difficult to measure as the environmental concentrations are close to the detection limits. Samples were taken during the dry season from 47 stations. Similar to results in water, BDE-47 and BDE-209 account for most of the PBDEs found in Bay sediments. PBDE concentrations in sediments ranged from 0.5 to 3.84 µg/kg (equivalent to ng/g or parts per billion)

BDE-47 and 0.1 to 12.6 µg/kg BDE-209. Concentrations were generally uniform throughout the Bay and comparable or slightly higher than those found in other waterbodies of the world where PBDEs have been reported (Oros et al., 2005).

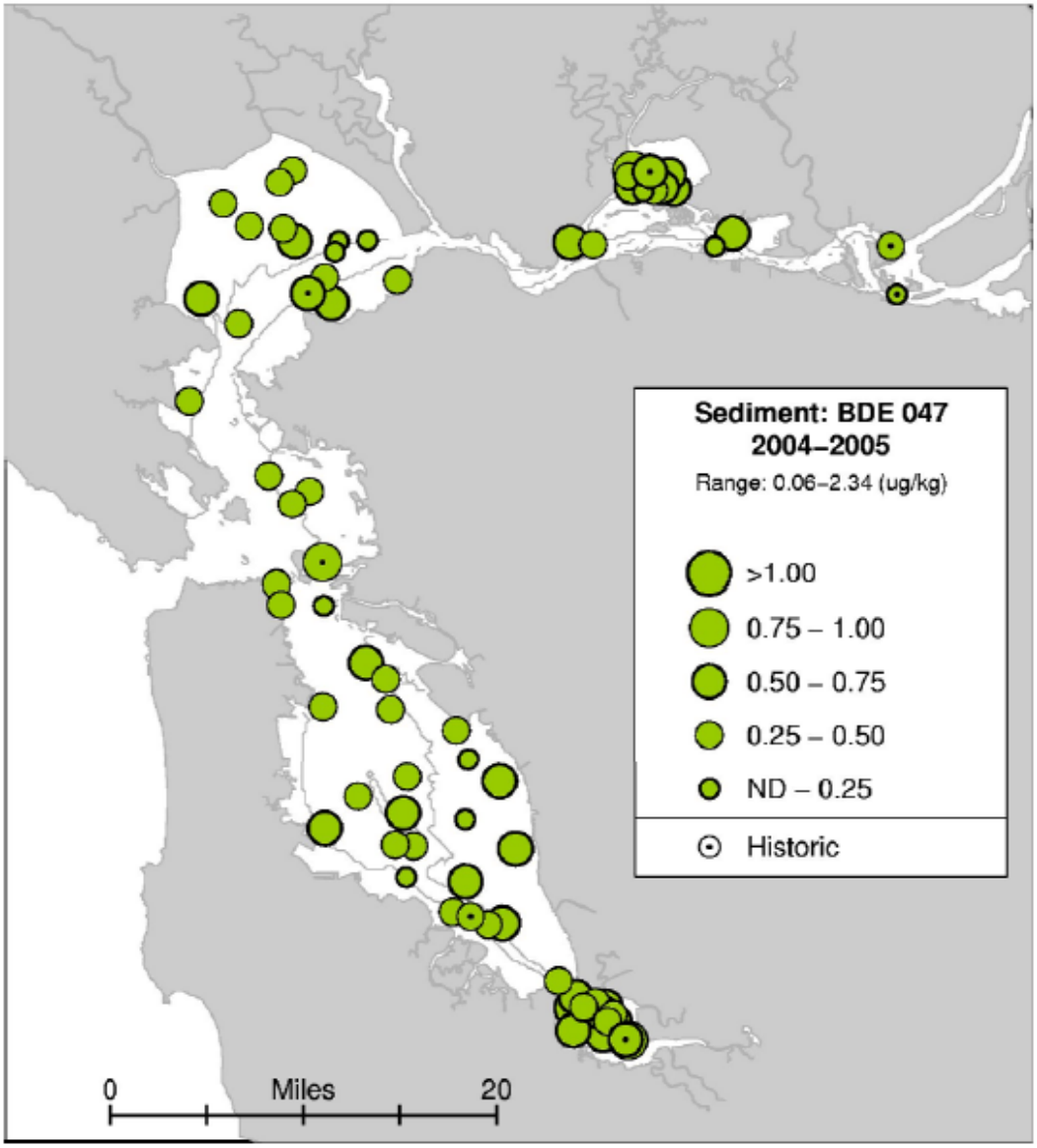

Figure 3-2. Concentrations of BDE-47 in surface sediments (RMP 2004 and 2005 data, "historic" refers to stations that have been included in RMP status and trends monitoring to maintain time series for long-term trend analyses.)

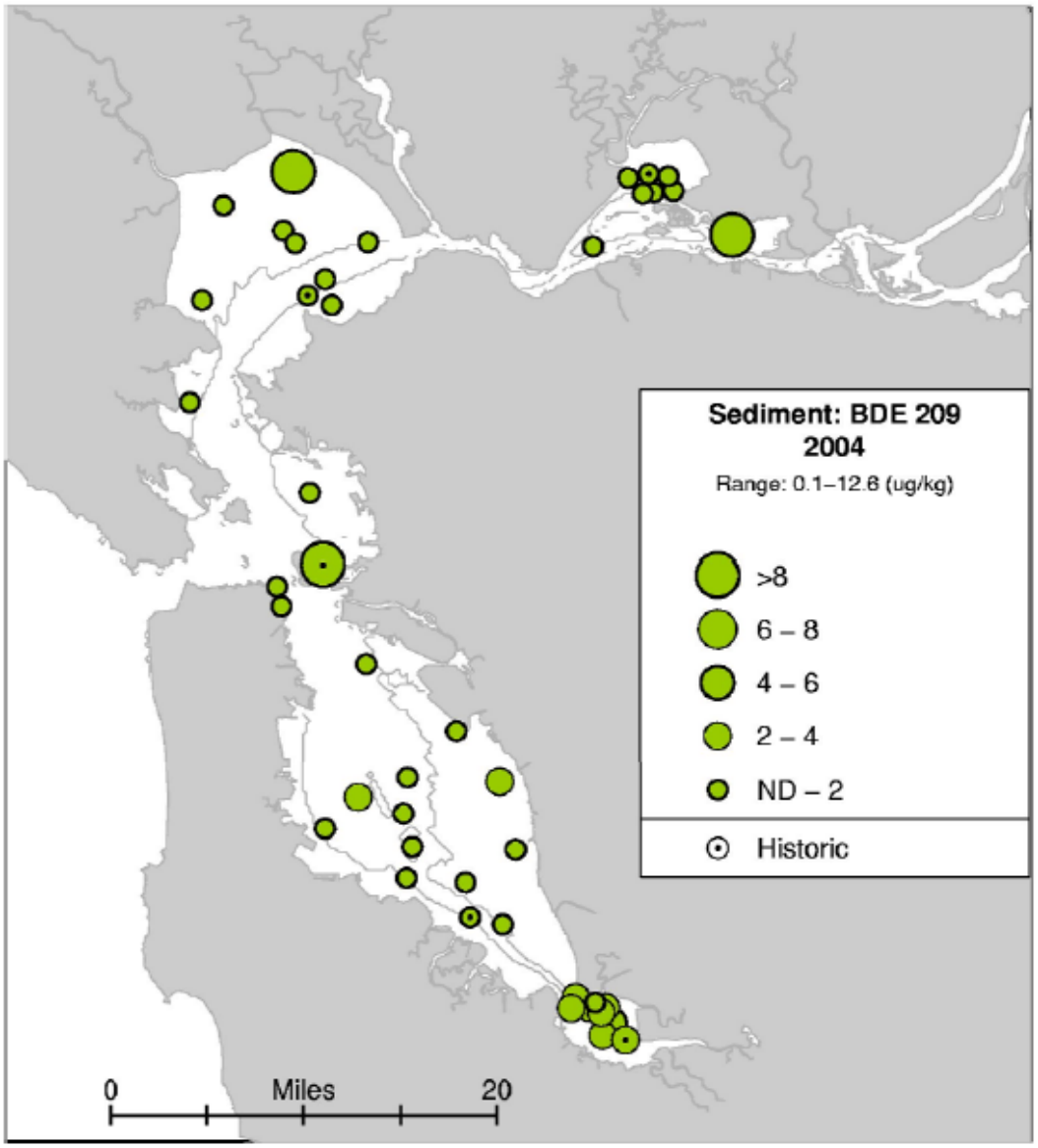

Figure 3-3. Concentrations of BDE-209 in surface sediments (RMP 2004 data, "historic" refers to stations that have been included in RMP status and trends monitoring to maintain time series for long-term trend analyses.)

Inventories of PBDEs in San Francisco Bay sediments, calculated from these concentration data, and assuming a surface-sediment volume of 1.6×10^8 m^3 and a concentration of 0.5 kg/L solids in sediment (Davis, 2004), totaled 31 kg BDE-47 and 98 kg BDE-209. (In contrast, inventories of PCBs in surface sediments of the Bay are estimated to be 2500 kg.)

No information is available on PBDE concentrations in the deep sediments. Sediment cores were collected in 2006, but analyses are not complete.

3.1.3 Environmental Trends

There are insufficient data to analyze temporal trends in PBDE concentrations in Bay water and sediments; however, there are recent data for clams and mussels, which have proven to be good indicators of environmental trends. The RMP has analyzed PBDEs in shellfish from the Bay, including resident clams (*Corbicula fluminea*) and transplanted oysters (*Crassostrea gigas*) and mussels (*Mytilus californianus* and *Mytilus edulis*). Oyster and mussel deployments are for 90 days at various stations around the Bay. Beginning in 2003, only mussels and resident clams have been collected and analyzed for contaminants. Concentrations of BDE-47, the most bioaccumulative common congener, ranged from 4 to 27 µg/kg in 2005 (Figure 3-4).

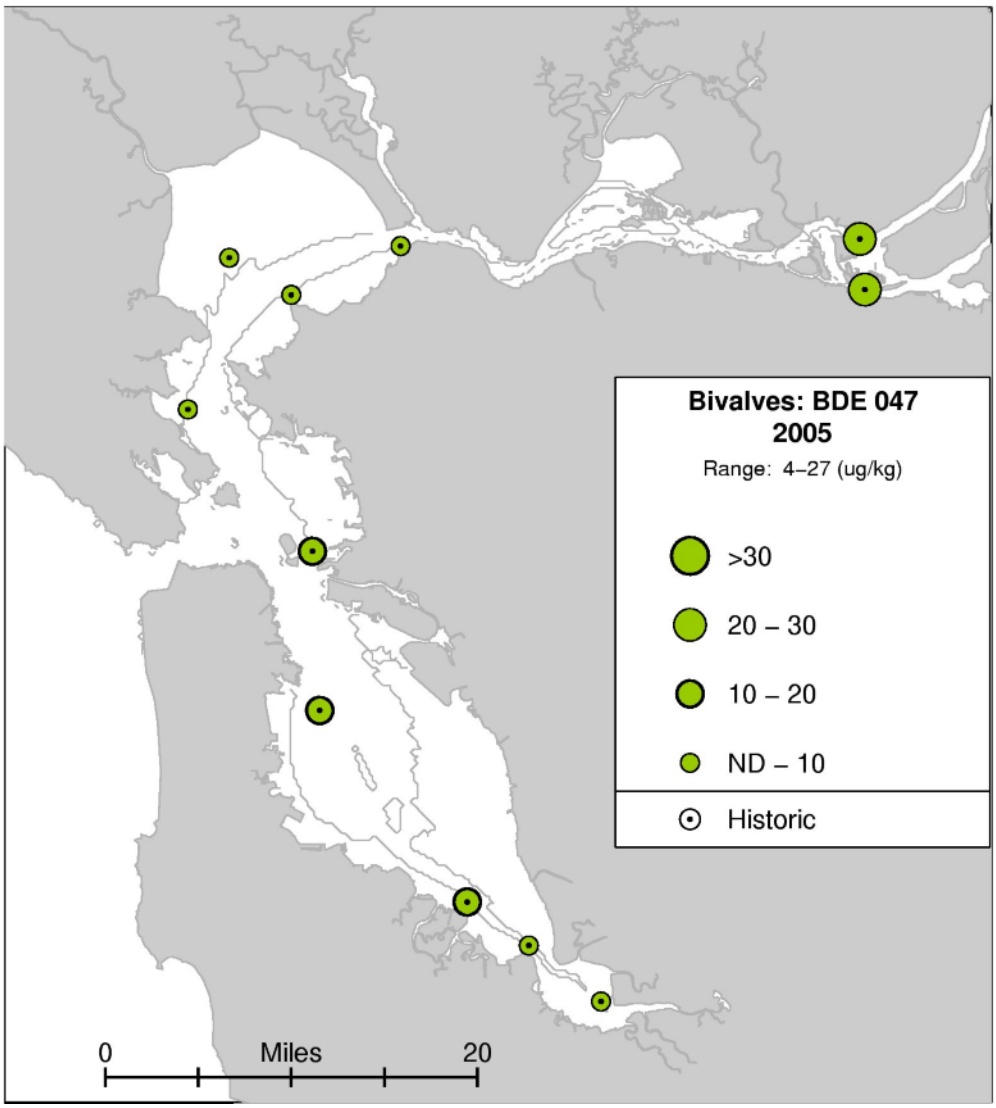

Figure 3-4. Concentrations of BDE-47 in resident clams and transplanted mussels (RMP 2005 data , "historic" refers to stations that have been included in RMP status and trends monitoring to maintain time series for long-term trend analyses.)

Over the 5-year period for which data are available, the total PBDE concentrations in clam and mussel tissue samples appeared to have reached a maximum level in 2003, decreasing in 2004 and 2005 (Figure 3-5). These data suggest that the apparent declines that were observed in PBDEs in cormorant eggs (see Section 2.2) may reflect a true decline of PBDEs in San Francisco Bay fauna.

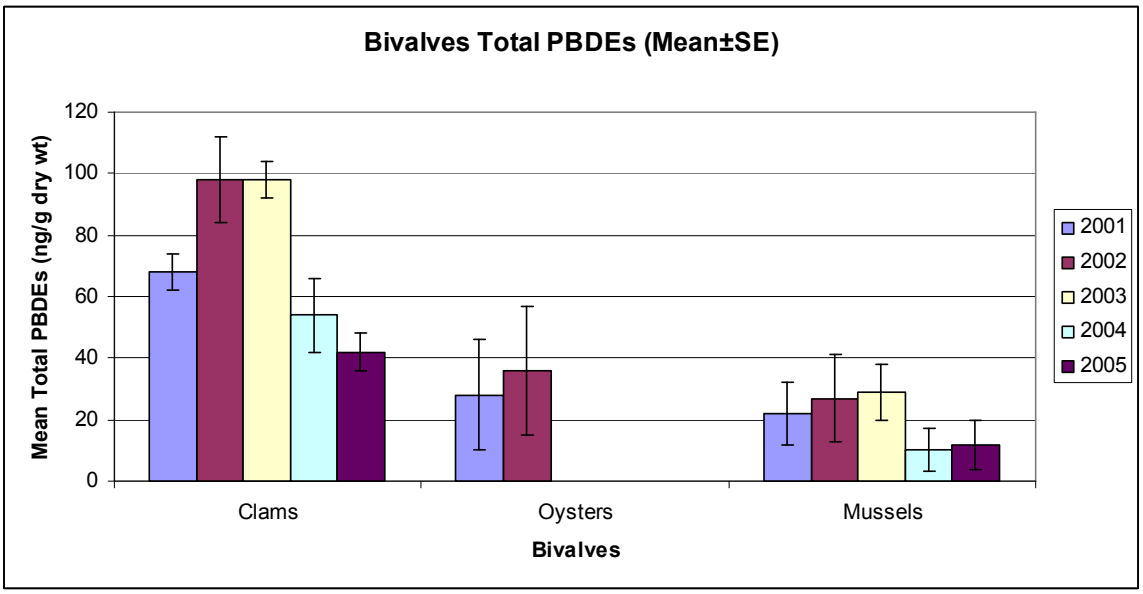

Figure 3-5. Concentrations of total PBDEs in San Francisco Bay shellfish (2001-2005 RMP data)

3.2 Sources

The ultimate source of PBDEs in the San Francisco Bay watershed is in the variety of materials to which they have been added. PBDEs are not manufactured in California (ASTDR, 2004), but PBDEs are added to products that are made within the state and are introduced in goods that are manufactured elsewhere. There is no historic or current inventory of sources within the Bay Area, such as:

- Manufacture of PBDE-containing materials, such as foams or plastics.
- Manufacture of goods containing those PBDE-containing materials.
- Use and cleaning of products containing PBDEs (resulting in indoor air emissions or cleaning water wastes).
- Management of PBDE-containing wastes.

The major sources of human exposure to PBDEs are currently thought to come from dust, respiration of indoor and outdoor air and foods (in contrast to PCBs in which the major source is food). The PentaBDE portion can comprise as much as 30% of polyurethane foam, so it is easy to envision that volatilization to indoor air could be a major source. How house dust could be a major source of PBDEs to

humans should be relatively easy to comprehend, but it has not been easy to explain the levels and congener patterns found in human studies.

Indoor air has been identified as a source of PBDEs to the outdoor regional environment. Butt et al. (2004) measured PBDEs in indoor and outdoor air in southern Ontario and found urban PBDE concentrations (~42 pg/m^3) were about ten times greater than rural concentrations (~4.5 pg/m^3), indicating an urban-rural gradient and greater PBDE sources in urban areas. Indoor PBDE levels were 1.5-20 times greater than outdoor levels, consistent with indoor sources of PBDEs and enhanced degradation outdoors (photolysis). Congener profiles were dominated by BDE-209 (51.1%), consistent with DecaBDE as the main source mixture, followed by congeners from the PentaBDE mixture (BDE-99: 13.6% and BDE-47: 9.4%) and some OctaBDE (BDE-183: 1.5%).

Locally, there have been two recent reports that provide information on sources of PBDEs in the Bay Area:

- A recent study analyzed PBDEs in known components of the California waste stream (Petras and Oros, 2006).
- The California Air Resources Board (ARB) measured indoor air at a computer training laboratory, outdoor and indoor air at an electronics recycling facility, and outdoor air at an automobile shredding/metal recycling facility in 2004 (Charles et al., 2005).

3.2.1 PBDEs in the Waste Stream

Petreas and Oros (2006) assumed that California uses 10% of the PBDE volume reported for North America and measured PBDEs in representative components, such as electronics equipment (known as e-waste once the equipment is discarded) and automobile shredder (autoshredder) waste. There is no estimate of the standing stock of PBDEs in electronic items, furniture, building materials, and other items that are not immediately entering the major waste streams.

Petreas and Oros (2006) estimated that e-waste dominates the PBDE waste stream in California, but that a sizable quantity of total PBDEs cannot be accounted for (Figure 3-6). The state has estimated that 530 million pounds of e-waste was in the California waste stream in 2001, with significant increases predicted by 2006 (Integrated Waste Management Board, 2001). Concentrations of total PBDEs in e-wastes ranged from low parts per million to percent levels (Figure 3-7). Concentrations varied by product, with VCRs having the highest concentrations. BDE-209, the major component of the DecaBDE formulation dominated the congener profile for electronic products.

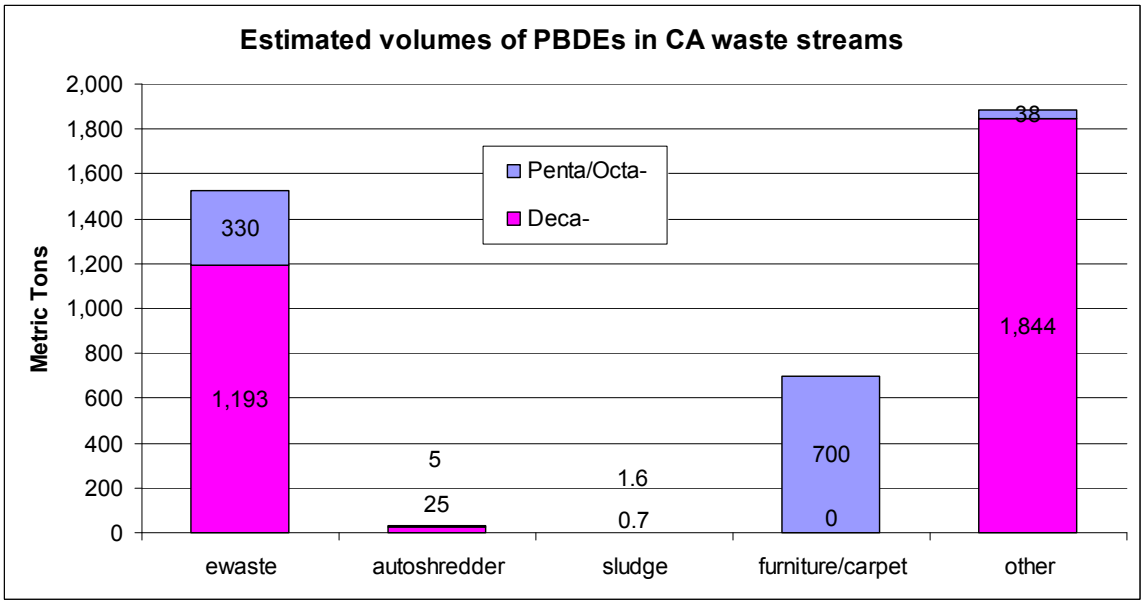

Figure 3-6. Estimated volumes of PBDE in California waste streams (Pyreas and Oros, 2006) ("Other" is calculated as the difference between estimated total PBDE use in California and that portion of the total that could be accounted for.)

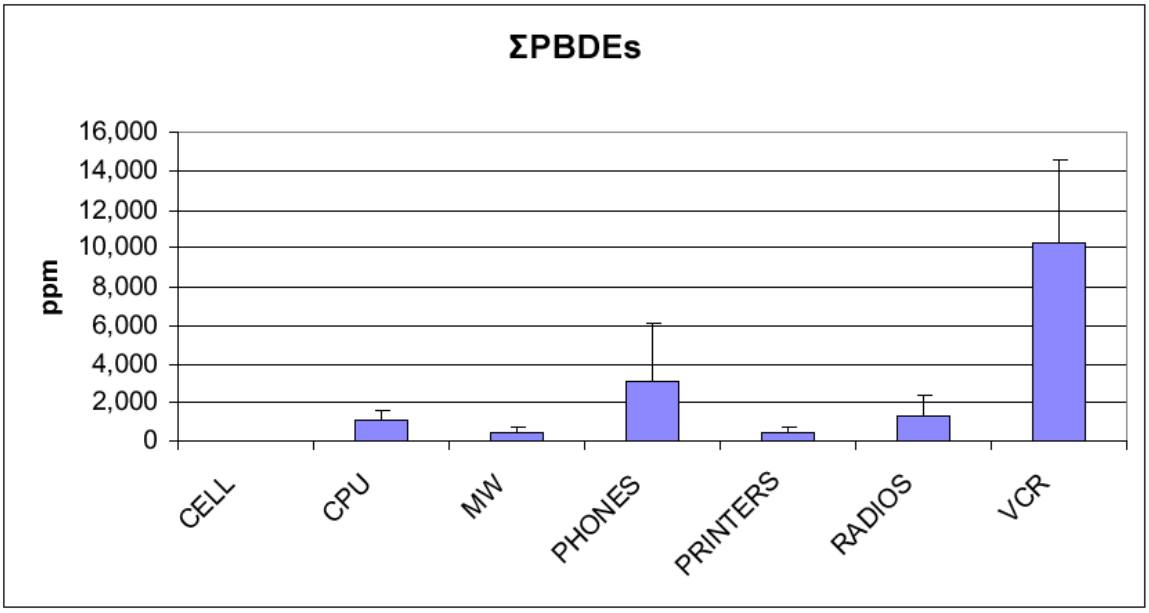

Figure 3-7. Total PBDE concentrations in discarded consumer electronics (Petreas and Oros, 2006) CELL=cell phones, CPU=computers, MW=microwaves (n=4 for each category)

Seven autoshredder facilities in California, three of which are in the Bay Area, generate an estimated 660 million pounds of waste (including millable components of automobiles, refrigerators, and ovens) each year (Department of Toxic Substances Control, 2002) to be used as alternative daily cover, material other than earth placed on the surface of municipal solid-waste landfills at the end of each operating day. Autoshredder waste was a relatively minor component of the waste stream but could be an important local source, if for example, the resulting "auto fluff" is blown into the Bay (Figure 3-8). Autoshredder waste contains approximately 100 parts per million total PBDEs, dominated by BDE-209 (Figure 3-9).

Figure 3-8. Auto fluff in Redwood City, in the South Bay (photo by Allison Luengen, UCSC)

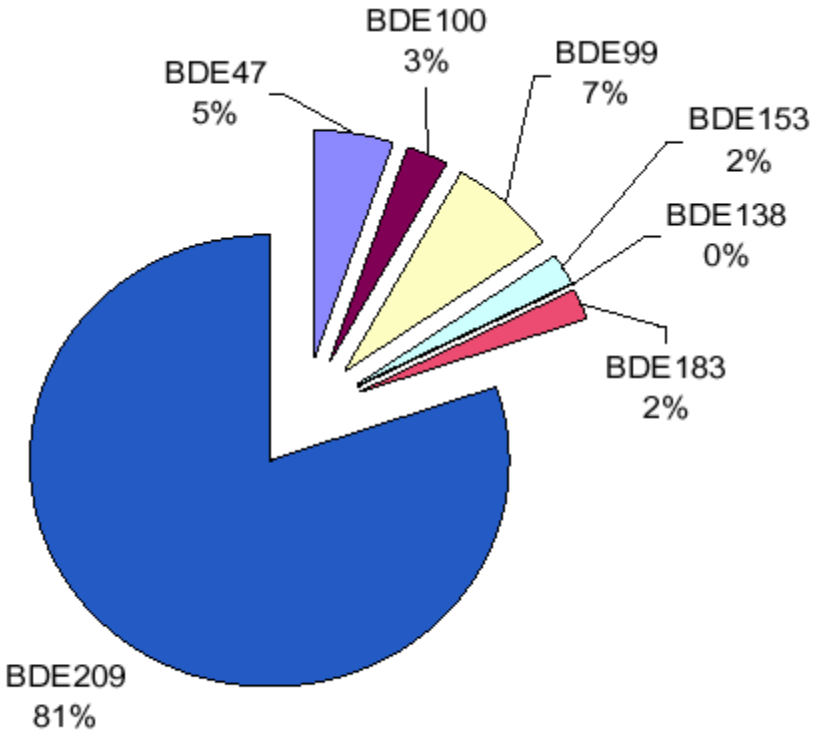

Figure 3-9. Congeners found in automobile shredder waste (Petreas and Oros, 2006)

3.2.2 PBDEs in Indoor Air

ARB measured indoor air at a computer training laboratory, outdoor and indoor air at an electronics recycling facility, and outdoor air at an automobile shredding/metal recycling facility (Charles et al., 2005). PBDEs are especially associated with older computers, and concentrations of PBDEs in air samples from the computer training facility were higher when the computers were turned on than when computers were turned off, with the congener mix suggesting volatilization of PentaBDE and DecaBDE commercial formulation congeners.

Total PBDE concentrations were not calculated for the study of the electronics recycling facility (Table 3-1). BDE-209 (the major congener in the DecaBDE formulation) was the most common congener, occurring at concentrations at least an order of magnitude higher than any other congener. Outdoor concentrations of BDE-209 ranged from 140 to 11,400 pg/m^3 in four samples collected on each of three days (total of 12 samples), as compared to 4.4 to 17 pg/m^3 in samples from a control site in Davis. Indoor concentrations were significantly higher.

Total PBDE concentrations were also not calculated at the automobile shredding facility. Concentrations of individual congeners were lowest when there was no shredding activity and were significantly higher downwind compared to upwind from the site, even when there was no shredding activity (Table 3-1). Even

upwind from the site, concentrations of PBDEs were higher than those observed at the Davis control site for most congeners.

Table 3-1. PBDE concentrations (pg/m^3) at an electronics recycling facility and an automobile shredding facility

Site	n	BDE-47	BDE-99	BDE-209
Davis (control site)	4	34.3 ± 11.9	11.8 ± 4.20	10.6 ± 6.57
Electronics recycling site, Near loading dock	6	58.6 ± 39.2	14.4 ± 6.97	301 ± 168
Electronics recycling site, far from loading dock	6	82.6 ± 32.0	38.6 ± 25.2	5230 ± 3840
Auto shredding facility, Upwind	3	30.1 ± 3.05	24.7 ± 3.23	152 ± 123
Auto shredding facility, Downwind	6	80.5 ± 6.82	84.7 ± 18.8	569 ± 678

3.3 Pathways and Loads

The pathways by which PBDEs get from a place of manufacture or use into the physical environment are not fully understood (Alcock et al., 2003), and the pathways to San Francisco Bay are even less known. Conceptually, release can occur during initial synthesis, during incorporation into commercial products, during wear or degradation of products, or during disposal and recycling, such as at the auto shredder facility discussed in Section 3.2.2 (Hale et al., 2003). PBDEs are manufactured in only a few locations, none of which are in the San Francisco Bay Area. Manufacturing of PBDE-containing products has occurred or occurs in many locations, and use of PBDE-containing products is widespread. How PBDEs get from computers, other electronics, sofas, carpeting, and cushions that are in use in homes and places of business into the San Francisco Bay is difficult to comprehend; there have been few studies of the magnitudes of released of in-use products (Palm et al., 2002; Alcock et al., 2003) and no comprehensive survey in California.

It is known that PBDEs enter the Bay from a variety of sources and follow several pathways:

- Direct input from activities in ports and other entities operating in close proximity to the estuary.
- Discharge of municipal and industrial wastewater.
- Atmospheric deposition.
- Runoff from local watersheds.
- Transport from the Sacramento and San Joaquin rivers.

Additional sources and pathways that have not been considered in this report may be determined in the future.

3.3.1 Direct Input into the Bay

Direct discharges into the Bay as a result of port activities or, for example, inputs from the autoshredder waste piles, either by air or by leaching, are not monitored, and inputs have not been quantified. Such inputs may be relatively uncommon, but may be locally significant. A proposed RMP special study would analyze PBDEs in the sediments, biota, and stormwater discharges adjacent to an autoshredder operation, but to date there is no available information.

3.3.2 Municipal and Industrial Wastewater (Effluents and Sludge)

PBDEs become part of the municipal waste stream when PBDE-containing products and dust from those products are washed into drains (Figure 3-10).

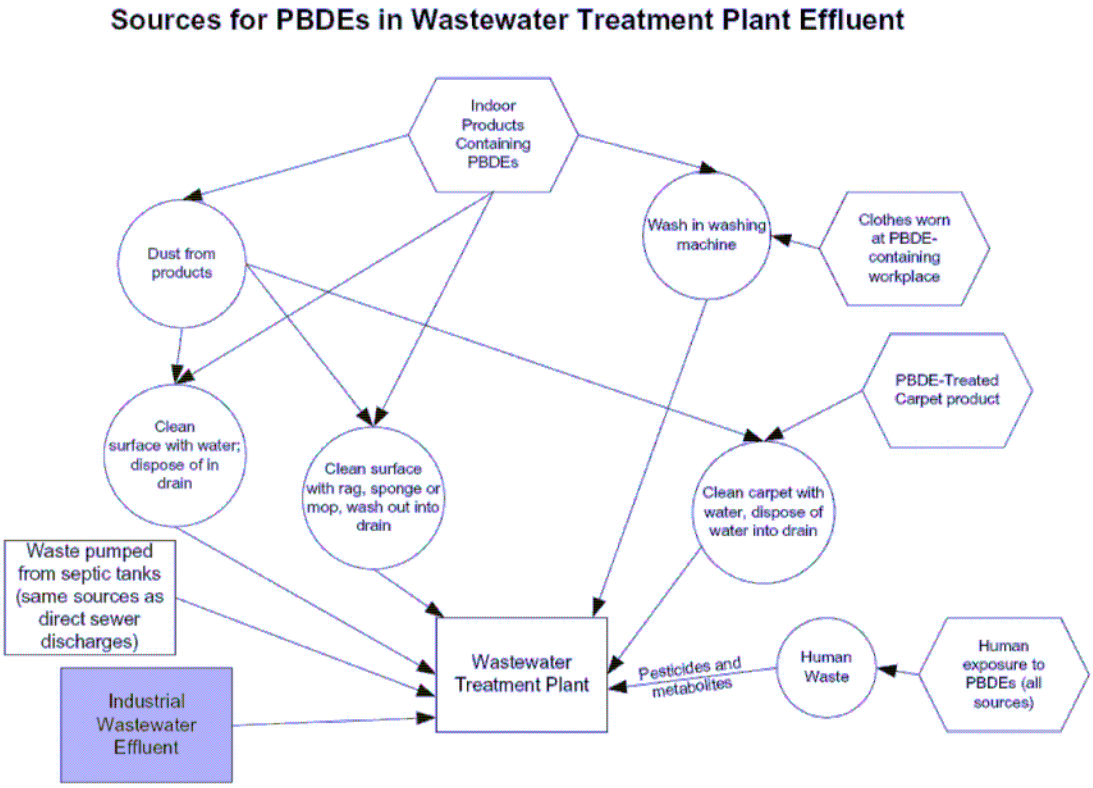

Figure 3-10. Pathways of PBDEs into municipal wastewater treatment plants (figure courtesy of Kelly D. Moran, TDC Environmental)

The RMP recently conducted a special study to measure PBDEs in the municipal effluents and sludges (or biosolids) from representative Bay Area municipal treatment plants. During one wet season and one dry season event in 2005, effluent and sludge samples were taken from each of three treatment plants, one of which discharges effluent into the Central Bay, one discharging into the North Bay, and one discharging into the South Bay. The plants represented a variety of

sizes of dischargers. Additional data are available from the Palo Alto Regional Water Quality Control Plant, which discharges effluent into the South Bay and where effluent and sludge samples were taken in August 2004 (North, 2004).

The municipal sludges in the region are incinerated, used as soil amendments, or applied as alternative daily cover at municipal landfills and do not directly enter the Bay. About 1.7 billion pounds (dry weight) of municipal sludge was generated in California in 2005, 550 million pounds of which was used as alternate daily cover (Petras and Oros, 2006).

Concentrations of PBDEs in treated effluents were higher in samples taken from the two treatment plants that discharge into the North Bay and Central Bay than the two that discharge into the South Bay. Mean concentrations ranged from 14,000 to 66,000 pg/L (14-66 ng/L, equivalent to parts per trillion). Percentage of the effluent made up of the fully brominated congener BDE-209 ranged from 6 to 28.

Due to the high affinity of PBDEs for suspended solids, most of the PBDEs entering the treatment plants were removed in the sludges and not discharged to the Bay. North (2004) estimated that 96 percent of the PBDEs entering the Palo Alto treatment plant were removed in the sludges, which were then incinerated in a multiple hearth incinerator equipped with emissions abatement equipment capable of destroying the PBDEs. Mean concentrations in the RMP municipal sludge samples ranged from 1,400 to 4,900 ng/g dry weight (1.4-4.9 µg/g or parts per million). About 30% of the PBDEs in the sludges were composed of BDE-209.

Using data from each of the treatment plants and extrapolating to all the municipal discharges in the Bay resulted in an estimated range of 12 to 58 kg of PBDEs entering the Bay through municipal discharges each year (Oros et al., 2005). Using the congener profiles reported by North (2004), annual loads of BDE-47 are 4.4 to 20.7 kg, and annual loads of BDE-209 are 0.7 to 3.4 kg. In comparison, the Water Board has estimated that only 2.3 kg PCBs enter the Bay in municipal discharges each year (San Francisco Bay Regional Water Quality Control Board, 2004). Thus, the level of PBDEs loading in effluents could range as much as six to 25 times greater than the PCB loading level, reflecting the ubiquitous and ongoing use of products containing PBDEs.

There are no data on PBDE loadings from the 27 industrial wastewater discharges to San Francisco Bay, but for this report, they are presumed to be very low. (The Water Board estimates that 0.0012 kg of PCBs enter the Bay in industrial discharges each year. PBDE loads are presumably higher.)

3.3.3 Atmospheric Deposition

In 2003 and 2004, the California Air Resource Board (ARB) measured concentrations of ambient air at six urban areas, including Oakland, Richmond, San Jose, Boyle Heights (Los Angeles County), Rubidoux (Riverside County), Wilmington (Los Angeles County), and San Francisco (data available at www.arb.ca.gov). The highest concentrations were found in San Jose where the average total PBDE concentration was 420 picograms per cubic meter (420,000 fg/m^3) in 2004 and the lowest in San Francisco where the average concentration was 35 pg/m^3 in 2004 (Figure 3-11). The especially high average concentration measured in San Jose in 2003 has not been explained.

Using these data, assuming that the PBDEs are half gaseous and half particulate (a reasonable assumption based on Henry's Law constants and findings from other regions), a deposition rate of 0.2 cm/second (the rate for 0.5 micron particles), and the area of the Bay surface (about 1,100 square kilometers), an estimated one to two kilograms of PBDEs enter the Bay through atmospheric deposition. A first order estimate of the diffusive flux of PBDEs across the air-water interface indicates no net diffusive exchange. Thus, total air-water exchange seems to be dominated by particle deposition on the order of 1 to 2 kg/year. (In contrast, there is a net loss of PCBs to the atmosphere via volatilization at the rate of 7 kg/year.)

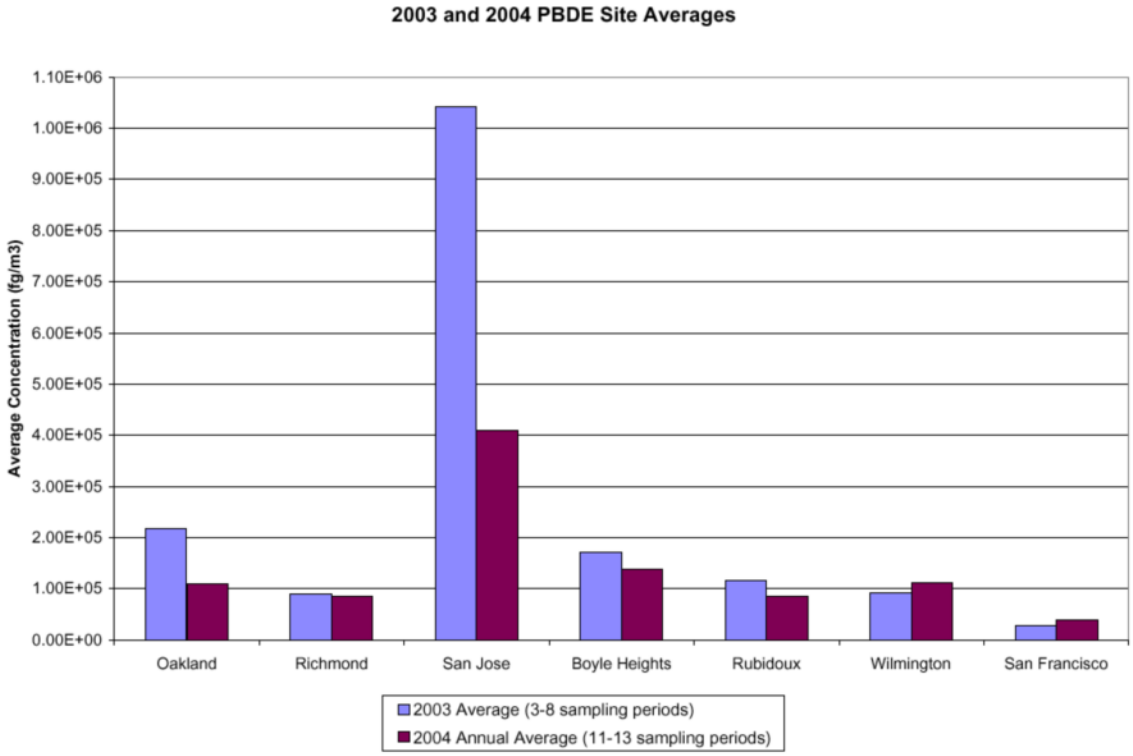

Figure 3-11. PBDEs in air samples from 6 months of 2003 and all of 2004 (California Air Resources Board data)

3.3.4 Runoff from Local Watersheds (Stormwater Runoff)

PBDEs from many sources enter the Bay through stormwater runoff (Figure 3-12). Approximately 10% of the water flow to the estuary flows from the local watersheds, with most flow entering through the Sacramento-San Joaquin Delta (see Section 3.3.5). Flows from the smaller watersheds may, however, result in significant inputs of PBDEs to the Bay. Flows into the South Bay may be particularly important, as that water residence times are longer than those for the North Bay into which the Delta flows.

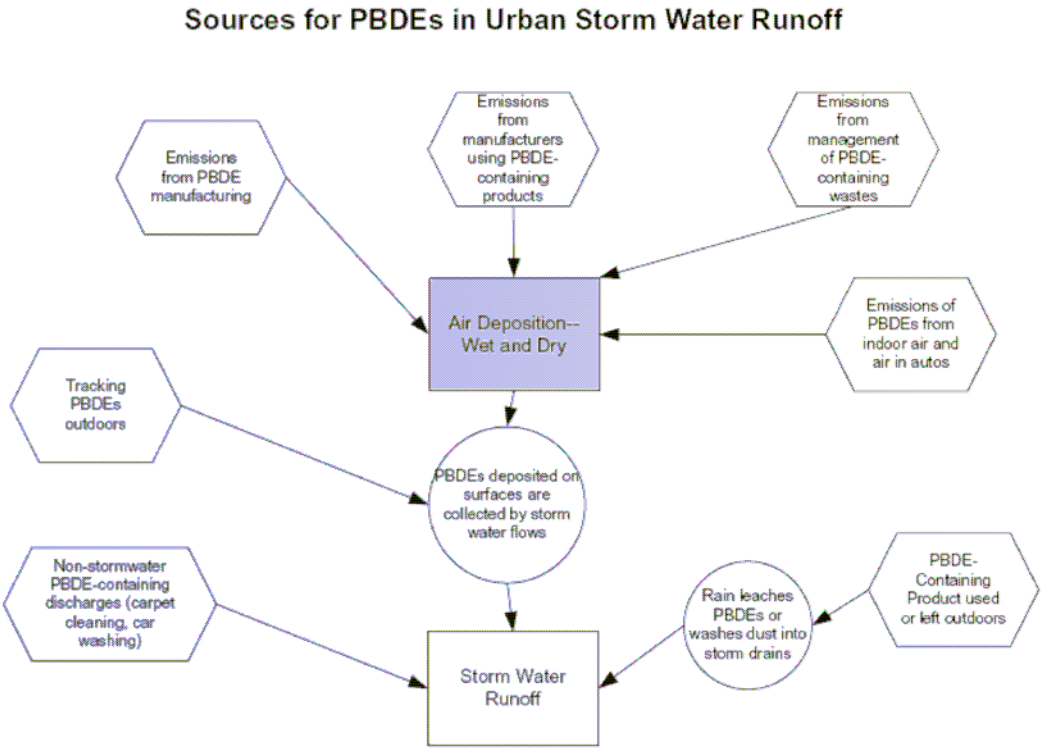

Figure 3-12. Sources and pathways of PBDEs that enter the Bay in stormwater runoff (figure courtesy of Kelly Moran, TCD Environmental)

Estimates of loading from the smaller watersheds were made using data from the Guadalupe River and Coyote Creek, both of which empty into the South Bay, and extrapolating to the other small watersheds that enter the Bay. This approach relies on an assumption that the Guadalupe River and Coyote Creek are representative of all the local watersheds, an assumption that is not true, as the smaller urban areas that drain the margins of the Bay are more heavily industrialized. A more urbanized area, known as Zone 4 Line A, has also been sampled, but results are not yet available.

Loads were calculated by relating measured concentrations of PBDEs to measurements of stream discharge and suspended solids concentrations. During Water Year (WY) 2005 (October 1, 2004 through September 30, 2005), seven samples for PBDE analysis were taken from Coyote Creek and twelve samples were taken from the Guadalupe River. Fourteen samples from the Guadalupe River were taken during WY 2006. Data on discharge and suspended solids concentrations were provided by the USGS.

Concentrations of total PBDEs in Guadalupe River water samples ranged from 16.8 to 370 ng/L (equivalent to 16,800 to 370,000 pg/L) in WY 2005 and 4.13 to 212 ng/L in WY 2006. BDE-47 accounted for 9% of the total PBDEs, and BDE-47 + BDE-209 accounted for an average of 63% of the total. Normalized to suspended solids concentrations, the concentrations of PBDEs in the Guadalupe River samples were among the highest reported in the world literature for estuarine and coastal sediments (Oram et al., in prep.). Concentrations in Coyote Creek samples were lower.

Instantaneous discharge in the Guadalupe River ranged from 0.4 to 112 m^3/s during WY 2005 and from 0.7 to 95 m^3/s during WY 2006. Annual discharge was 0.073 km^3 for WY 2005 and 0.127 km^3 for WY 2006. Suspended solids concentrations ranged from 0.2 to 1,160 mg/L n WY 2005 and from 4 to 779 mg/L in WY 2006. Instantaneous discharge at Coyote Creek ranged from 0.3 to 29.5 m^3/s and suspended solids concentrations ranged from 11 to 2,094 mg/L. Total annual discharge was 0.055 km^3.

As WY 2005 was the only year for which there were PBDE measurements in both the Guadalupe River and Coyote Creek, these data were used to estimate total annual loads. (Runoff during WY 2005 was considered near average for the Guadalupe River, although it was relatively low for Coyote Creek.) Extrapolation resulted in estimates of 2.9 kg BDE-47, 17.3 kg BDE-209, and 33.4 kg total PBDEs entering the Bay from all small tributaries.

3.3.5 Input from the Sacramento-San Joaquin River Delta

Loadings from the Sacramento-San Joaquin Delta, which drains the Central Valley and accounts for 90% of the water flow entering the Bay, were estimated from information on annual discharge, concentrations of suspended solids, and concentrations of PBDEs in water samples taken at Mallard Island, which is located just below the confluence of the two rivers. Estimates of discharge are available from the Interagency Ecological Program (IEP, 2006) for 1956 through WY 2005. Suspended sediment concentrations have been measured from February 1994 until the present (Buchanan and Schoellhamer, 1996, 1998, 1999; Buchanan and Ruhl, 2000, 2001; Buchanan and Ganju, 2002, 2003, 2004, 2005). The RMP collected water samples for analysis of PBDEs in WY 2005 and WY 2006; because concentrations were so close to detection limits, only data from WY 2005 were suitable for calculating loads.

Total PBDE concentrations in water samples from Mallard Island ranged from O.43 to 0.77 ng/L (equivalent to 430 to 770 pg/L), with a flow-weighted mean of 0.68 ng/L. BDE-47 made up 29% of the total, and BDE-47 + BDE-209 accounted for 58%.

Daily outflow ranged from 0.5 to 2550 m^3/s during WY 2005 and from 0 to 10,500 m^3/s during WY 2006. Total outflow from the Delta was 18.7 km^3 in WY 2005 and 51 km^3 in WY 2006. Instantaneous suspended solids concentrations ranged from 12.7 to 93.8 mg/L in WY 2005 and from 11.9 to 315 mg/L in WY 2006. Total annual suspended sediment loads were 0.42 million metric tons in WY 2005 and 1.99 million metric tons in WY 2006. The relationships between concentrations of PBDEs and suspended sediment showed considerable scatter, and were not significant in either water year. Flow-weighted mean concentrations were calculated and used to estimate annual loads of 3 kg BDE-47, 3 kg BDE-209, and 13 kg total entering San Francisco Bay from the Delta each year.

3.3.6 Summary of Estimated Loads

Table 3-2 summarizes estimates of current PBDE loads to the Bay, as calculated from information on pathways. (No estimate of direct inputs to the Bay could be made.) Considerable uncertainty is associated with the estimates. It is interesting to note that while PBDE loads are greater than PCB loads, the inventory of PCBs in the Bay (~2500 kg) is ten to 20 times greater than that of PBDEs (~136-250 kg). This finding suggests that either the PBDE inventory has not had the time to accumulate to the level of PCBs or that there are significant differences in the physical-chemical transport processes of PBDEs compared to PCBs.

Table 3-2. Summary of estimated total annual PBDE, BDE-47, and BDE-209 loads (kg) to the Bay. Total PCB loads are included for comparison. PBDE loads from local watersheds were calculated using only data from WY 2005 and therefore assume that it was representative of an average water year.

Source	Total PBDEs	BDE-47	BDE-209	PCBs
Municipal wastewater	12-58	4-21	1-3	2.5
Atmosphere	1-2	~1	~1	(-7)
Local watersheds	33	3	17	9-15
Delta	13	3	3	6-23
Total load	**59-106**	**11-28**	**22-24**	**10-34**

A modeling approach was also used to estimate loads from water and sediment levels. That approach is discussed in Section 3.4.2.

3.4 Mass Balance

Other Conceptual Model/Impact Assessment reports have successfully used a simple mass-balance model (Davis, 2004) to evaluate inputs and loss pathways of contaminants to and from the Bay and to estimate recovery rates under varied scenarios for continued loads. The same one-box fate model used by Davis (2004) to predict the long-term fate of PCBs in the Bay is used here to estimate the mass balance of PBDEs and predict future recovery.

BDE-47 and BDE-209 were selected for modeling, because they are the two most common congeners found in San Francisco Bay. The congeners were modeled separately from each other, and there was no attempt to account for debromination of higher weight to lower weight congeners.

3.4.1 Model Formulation

The one-box model of San Francisco Bay treats the Bay as a single well-mixed volume with two compartments representing the water column and the bed (surface) sediments. Conceptually, the model assumes that exchange between these two compartments is more important than exchange between the various geographic sub-regions of the Bay. The model includes the major processes governing fate and transport of organic contaminants in aquatic systems: external loads entering the water column, settling and resuspension of sediment particles, sediment-water diffusive exchange, atmospheric deposition, volatilization, degradation in water and sediment, tidal flushing, and outflow through the Golden Gate.

Bay-specific model parameters are listed in Table 3-3. They are identical to the values used by Davis (2004) in predicting the long-term fate of PCBs in the Bay. The only exception is the tidal flushing ratio (α), which was not included in Davis (2004).

Chemical-specific model parameters are listed in Table 3-4. The degradation rates listed are estimated values reported by Wania and Dugani (2003). Lacking any empirical quantitative information on the degradability of PBDEs, Wania and Dugani (2003) used an EPA approved software package (EPIWIN, http://esc.syrres.com/interkow/epi.htm) to estimate the degradation rates of PBDEs in air, water, soil, and sediment. All chemical-specific parameters listed in Table 3-4 are for BDE-47. Parameters for BDE-209 are generally of the same magnitude.

Table 3-3. San Francisco Bay specific model parameters

Parameter	Symbol	Value	Reference:
Surface area of water (m^2)	SAW	1.10E+09	Davis, 2004
Surface area of sediment (m^2)	SAS	1.10E+09	
Average depth of water (m)	DW	5.3	
Average depth of active sediment layer (m)	DS	0.15	
Water temperature (degrees C)	TW	15	
Delta outflow (m^3/s)	Qdelta	8.20E+02	
Concentration of particles in water (kg/L)	CPW	8.50E-05	
Concentration of particles in sediment (kg/L)	CSS	0.5	
Density of suspended sediments (kg/L)	dPW	1.1	
Density of sediment solids (kg/L)	dSS	2	
Organic carbon content of suspended sediment	OCPW	0.03	
Organic carbon content of bottom sediment	OCSS	0.01	
Density of organic carbon (kg/L)	dOC	1	
Solids settling rate (m/day)	Vs	1	
Sediment burial rate (m/day)	Vb	0	
pH of water	pH	7.8	
Average wind speed (mi/hr)	Ws	10.6	
Tidal flushing ratio	α	3.75	Davis and Oram, 2005

Table 3-4. Chemical specific model parameters

Parameter	Symbol	Value	Reference:
Degradation rate in water (1/day)	KWR	0.0046	Wania and Dugani, 2003
Degradation rate in sediment (1/day)	KSR	0.0012	
Water-side evaporation coefficient (m/day)	VEW	0.649	Based on PCB 118 from Davis, 2004
Air-side evaporation coefficient (m/day)	VEA	423	
Water-to-sediment diffusion coefficient (m/day)	Vd	0.0024	

Two key chemical specific model parameters not included in Table 3-4 are the air-water partitioning coefficient (Kaw) and the octanol-water partitioning coefficient (Kow). Values of these parameters were calculated using the following equations from Wania and Dugani (2003):

$$\text{Log Kaw} = -0.0036\ M_M - 1.617$$

$$\text{Log Kow} = 0.0051\ M_M + 3.8091,$$

where M_M is the molar mass (g/mol) of the individual PBDE congener (484 g/mol for BDE-47).

3.4.2 Estimation of Current Loads (Comparison of Conceptual and Numeric Models)

The model was first used to estimate current loads into the Bay. The analysis, known as "hindcast" modeling, was performed as an independent test of the load estimates discussed in Section 3.3.6. The model was initialized with zero PBDE mass in the Bay and allowed to run for 30 years under varied loading scenarios (Figure 3-13). Those results were then compared to the current estimate of PBDE mass in Bay water and sediment (described in Section 3.1).

For BDE-47, results indicated that under a continuous loading scenario of 20 kg/yr, there would be slightly less than 30 kg of BDE-47 in the Bay after 30 years. Running the model under conditions of 30 kg/yr suggested that there would be approximately 40 kg BDE-47 after 30 years. These loading estimates, 20 and 30 kg/yr, represent levels that are just below and just above the independent estimates of mass currently in the Bay, as derived from monitoring data. The results suggest annual loads of BDE-47 ranging between 20 and 30 kg/yr, a good agreement with the 11 to 28 kg/yr estimated from information on inputs.

For BDE-209, model results suggest that under a continuous loading scenario of 40 kg/yr, there would be slightly more than 50 kg of BDE-209 in the Bay after 30 years. Under continuous loading of 100 kg/yr, there would be approximately 140 kg of BDE-209 in the Bay after 30 years. These estimates closely approximate the 95 percent confidence limits around the mean estimate of mass inventory derived from field data. The confidence interval is large for BDE-209, at least partially because a large number of samples have concentrations of BDE-209 that are near or below detection limits. Focusing on the mean estimate, it is plausible that annual loads of BDE-209 to the Bay are 60 to 80 kg/yr. This estimate is significantly different from the 22 to 24 kg/yr estimated from data on pathways and suggests that loading of BDE-209 to the Bay is a subject warranting increased study.

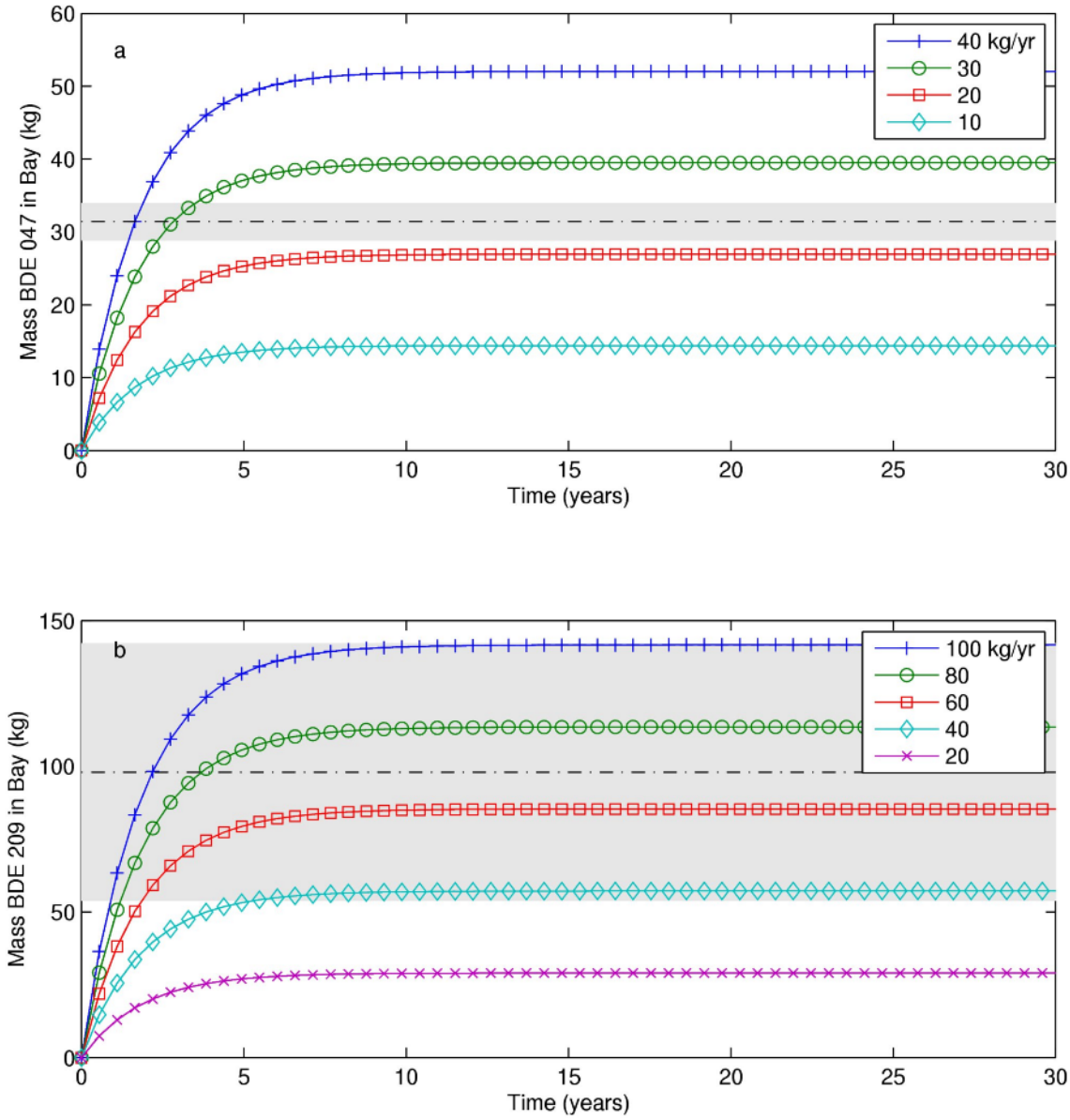

Figure 3-13. Model predictions for masses of BDE-47 (top) and BDE-209 (bottom) in the Bay under various loads and compared to estimates from field data. The dashed lines indicate the best current estimates of mass inventory in Bay water and sediment. The shaded regions indicate the 95 percent confidence limits around the means.

3.3.3 Predicted Loss Pathways and Bay Recovery

The model was used to determine the relative importance of loss pathways and to predict recovery of the Bay following declines in loads, what is known as "forecast" modeling. For this analysis the model was initialized with current average PBDE concentrations in water and sediment (Table 3-5). Lacking any empirical data on PBDE concentrations in the Pacific Ocean near the Golden Gate, a value of 15 pg/L was used, which is approximately one-quarter of the Bay average concentration (Cbay).

Table 3-5. Chemical concentrations used in one-box forecast model

Average BDE-47 Concentration	Symbol	Value	Reference:
Bay water (pg/L)	Cbay	59.6	RMP data, 2002-2005
Central Bay water (pg/L)	Ccb	51.5	
Bay sediment (ng/g)	Csed	0.47-1.9	
Pacific Ocean water (pg/L)	Cocean	15	Use 0.25xCbay as preliminary estimate
Bay water (pg/L)	Cbay	25.3	RMP data, 2002-2005
Central Bay water (pg/L)	Ccb	19.4	
Bay sediment (ng/g)	Csed	1.2	
Pacific Ocean water (pg/L)	Cocean	6.3	Use 0.25xCbay as preliminary estimate

Like other organic compounds, the major loss pathways for PBDEs from San Francisco Bay include degradation (primarily by photolysis and hydrolysis) and volatilization (Figure 3-14). Deep burial, a loss pathway in other estuaries, is not considered a factor in San Francisco Bay, which is a net erosional environment. Preliminary model results from the model suggest that outflow and degradation are the most important loss pathways and that loss by volatilization is minor, particularly for BDE-209.

Running the model using a continued loading scenario of 30 kg/yr BDE-47, a value at the upper end of the estimates of current loads, resulted in a predicted 20% increase in the total BDE-47 inventory in the Bay (Figure 3-15, top). However, a scenario of 10 kg/yr, a value at the low end of the current estimates of loads, suggested that a 55% decrease in the total inventory of BDE-47 would occur over 30 years. Recovery would be even greater and faster, reducing inventories to 10% of the current levels, if loading were completely ended. These recovery rates are considerably faster than those that have been predicted for PCBs (Davis, 2004). The difference in degradation rates is the likely driver for the different recovery rates; BDE-47 degrades more quickly than PCBs.

BDE-209 appears to be a critical juncture. Running the model with a continued load of 60 kg/yr, the lower value estimated by hindcast modeling, resulted in little change in current inventories (Figure 3-15, bottom). Greater loading would result in increased inventories, while decreases in loading would result in rapid improvements.

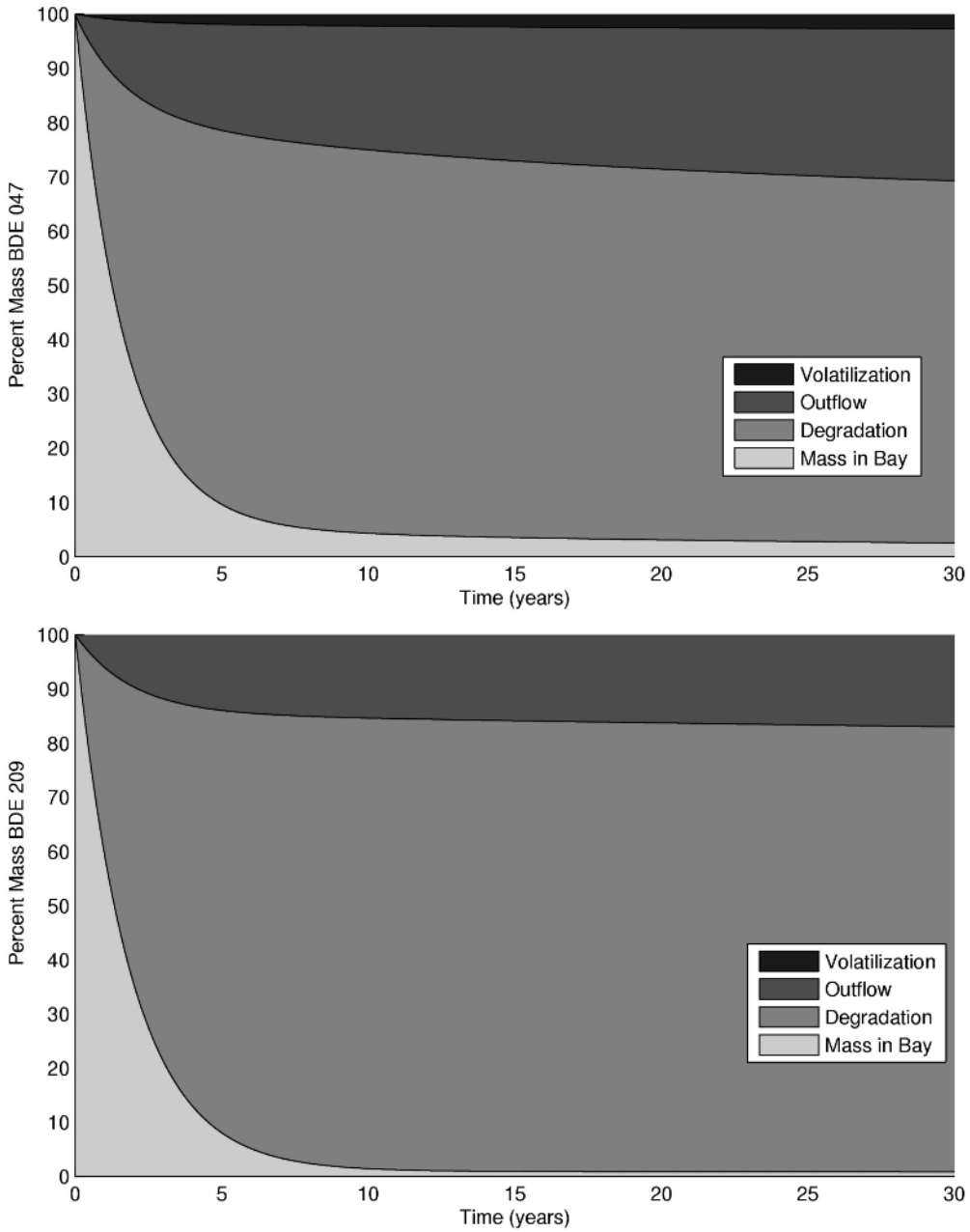

Figure 3-14. Predicted loss pathways estimated for BDE-47 (top) and BDE-209 (bottom) in San Francisco Bay

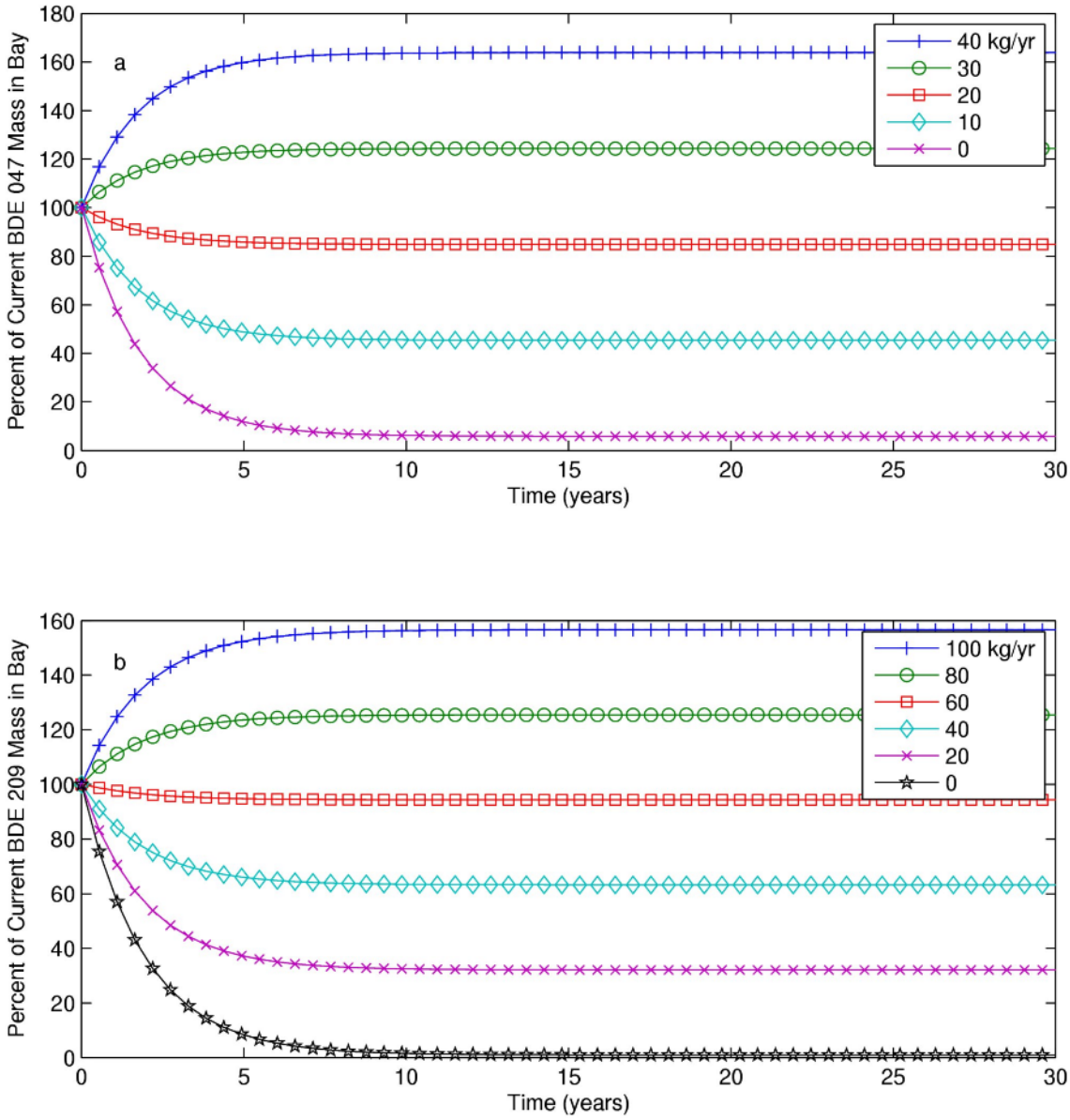

Figure 3-15. Predicted recovery of BDE-47 (top) and BDE-209 (bottom) under various loading scenarios (The mass in the Bay is normalized to the inventory estimated in Section 3.1).

3.4 Conceptual Model Summary

There are minimal data on PBDEs in San Francisco Bay, and many assumptions and estimates are necessary to assess the current status of the Bay and to predict the future. The emerging picture suggests that inventories of PBDEs in the San Francisco Bay water, sediments, and biota are about ten or more times lower than PCB inventories, although loadings of PBDEs are greater than loadings of PCBs. The probable reason for these differences is that PBDEs degrade more quickly than PCBs, and the result is that with the bans on the PentaBDE and OctaBDE formulations, some PBDEs, such as BDE-47, may decline more quickly than PCBs have declined since they were banned. Further, only small decreases in loads of BDE-209, the major constituent of the DecaBDE commercial formulation, could result in the beginning of recovery of the Bay.

This emerging model is cause for optimism. However, there remain large areas of uncertainty. One major discrepancy in the conceptual model is the difference in estimated BDE-209 loads based on information on pathways and loadings in comparison to those based on current inventories. Field data from the urbanized Zone 4 Line A monitoring study may help to refine loading estimates and reconcile the discrepancy.

Another concern is that DecaBDE can degrade to lower molecular weight congeners (e.g., de Wit, 2002). There will continue to be inputs of components of the DecaBDE formulation, which has not been banned. Recent research has indicated that soil microbes can transform congeners found in DecaBDE and OctaBDE mixtures to lower-brominated, more toxic congeners (He et al., 2006). Metabolism of DecaBDE congeners can also result in lower-brominated forms in fish (Stapleton et al., 2006).

One major unknown factor, beyond the information that was used to develop the conceptual model, is that risks to the biota are not understood. Consequently, appropriate goals declines in inventories have not been established.

4. Information Gaps

As described throughout this report, PBDEs are a relatively new concern for San Francisco Bay, and there is insufficient information to meet the general objectives for CM/IAs. With limited environmental data and in the absence of standards, it is impossible to state with certainty that the beneficial uses of the Bay are impaired. Development of those standards and continued monitoring will be necessary before a thorough impact assessment can be made.

The information on presence, inputs, and fate of PBDEs in San Francisco Bay and their potential effects on the environment and public health is extremely limited. There have been few years of monitoring data; for example, the 2005 data set is the only year for which there are data on concentrations of BDE-209 in the sediments. Monitoring data on total PBDEs in bird eggs and shellfish indicate that concentrations may be declining; additional data will be necessary to verify the declines.

Sources and pathways of PBDEs to the Bay are only beginning to be understood. There is no estimate of the standing stock of PBDEs in electronic items, furniture, building materials, and other items, nor is there a detailed understanding of the pathways that lead from these items to the atmosphere and rivers that will take PBDEs to the Bay. Direct discharges into the Bay through port activities have not been studied.

Preliminary estimates of loads from the local watersheds were made using monitoring data from two creeks entering the South Bay and extrapolating to all the local watersheds. This approach is not ideal, because the local watersheds of the Bay differ greatly in land-use patterns, hydrology, and other watershed characteristics. In particular, the sites that have been monitored, Coyote Creek and Guadalupe River, may contribute lower loads than some more urbanized areas. (A more urban area has been sampled, but results are not yet available.) Further, the estimates were made using data for only one year. The San Francisco Bay Area is subject to great year-to-year variability in storm patterns, so using data from one year ignores a significant issue. The lack of agreement in estimates of current loads of one congener, BDE-209, calculated from information on inputs and comparison of modeled results to data on current inventories in the water and sediments, further suggests that additional information on inputs is warranted.

Loss pathways were modeled rather than measured, and those estimates are subject to the uncertainties in model parameters. Uncertainties include PBDE-specific degradation rates, the rates at which more highly brominated compounds degrade to lower-brominated congeners, and the concentration of PBDEs outside the Golden Gate, which was assumed to be one quarter of the Bay average.

The critical needs are information to determine whether there are impacts and information to focus management strategies on potential problems. Possibly the most important ongoing study will be to continue to monitor PBDEs in the Bay to determine whether the declines that may have already begun are real and whether the prediction for relatively rapid declines following the bans of two of the formulations are correct. Other possible next steps for study include additional monitoring to understand inputs to the Bay; use of spatially resolved modeling to better understand loading, transport, and fate pathways; and a risk assessment study that goes beyond the framework of the Conceptual Model to assess the risks to critical species and humans.

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