

Polybrominated Diphenyl Ethers in San Francisco Estuary

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Abstract

The Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) monitors water, sediment, and biota on a routine basis to evaluate impacts of multiple discharges. In addition to trace metals, PCBs, pesticides, and PAHs, the RMP has recently begun monitoring polybrominated diphenyl ethers (PBDEs). PBDEs in sediment and water are dispersed and have relatively uniform concentrations, reflecting their ubiquitous use. In biota, the concentrations appear to be higher in the Delta tributaries, suggesting either a localized source or a significant loading from the Central Valley. Concentrations of PBDEs in biota in San Francisco Bay are some of the highest observed worldwide, suggesting the importance of continued monitoring, especially of biota. In addition, monitoring will be important for determining the efficacy of the recently implemented ban in California on penta-PBDE and octa-PBDEs (effective June 1, 2006).

Introduction

The largest estuary on the west coast, San Francisco Bay has a watershed that drains approximately 40 percent of the State of California (Conomos 1979) (*Figure 1*). The San Joaquin and Sacramento Rivers that enter the Estuary in the north contribute approximately 90 percent of the flow; the small tributaries primarily located in the South bay contribute the remaining 10 percent (Conomos 1979). In the summer months, no rainfall occurs and the discharges from wastewater treatment plants in the South Bay exceed tributary flows (Conomos 1979). The estuary is located in a largely urbanized area with approximately 10 million inhabitants.

The Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) monitors water, sediment, and biota on a routine basis to evaluate the cumulative impacts of multiple discharges to the Bay. This information is used to prepare National Pollution Discharge Elimination System permits, to develop Section 303 (d) listings of impaired segments of the Bay under the Clean Water Act, and to provide information for the development of Total Maximum Daily Loads. The RMP monitors trace elements, and organics including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and pesticides. In 2002, this list was expanded to include monitoring of polybrominated diphenyl ethers (PBDEs).

The results from the monitoring of water (2002 to 2005), sediment (2004), bivalves (2002 to 2005), cormorant eggs (2002 and 2004) and sport fish (2003) are presented below.

Methods

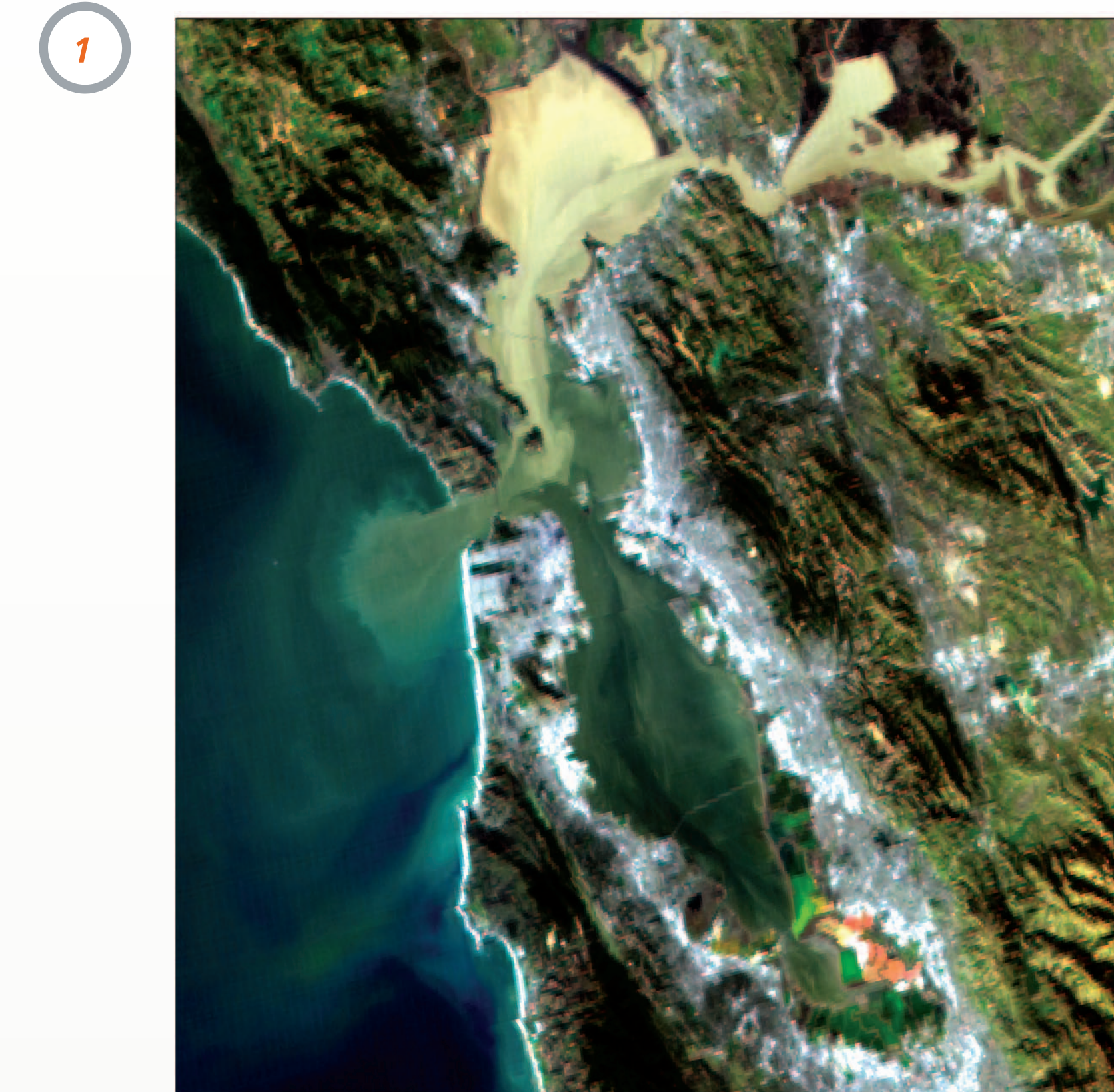
Samples were collected in accordance with *Field Sampling Manual for the Regional Monitoring Program for Trace Substances* (<http://www.sfei.org/rmp/documentation/fom/FOM2001.pdf>). *Quality Assurance Project Plan for the Regional Monitoring Program for Trace Substances* describes the quality assurance and quality control (QA/QC) protocols and requirements for RMP field sampling and laboratory analyses (http://www.sfei.org/rmp/reports/1999_QAPP/1999_QAPP.pdf).

Water

- Annual collection at 31 sites in dry season (July/August): 26 random and 5 fixed
- 100 L of water collected w/ AXYS Infiltrix system (1 µm glass fiber filter cartridge in series with XAD-2 resin filled Teflon® columns).
- Soxhlet extraction, gel permeation cleanup, Florisil and layered acid/base silica and alumina chromatographic fractionation.
- U.S. EPA Method 1668 Revision A analysis (HRGC/HRMS) on an HP 6890 gas chromatograph.

Sediment

- Annual collection at 47 sites in dry season (July/August): 40 random and 7 fixed.
- Surface sediment samples (top 5 cm) are collected with a Young-modified Van Veen grab and composited.
- Homogenized and dried with anhydrous granular Na₂SO₄, Dionex Accelerated Solvent Extraction, and cleaned up with an alumina/copper column.



- PBDE congeners were separated by the gas chromatograph and detected by HRMS with two exact m/z's monitored for each compound.
- Transplanted mussels (*Mytilus californianus*) collected from uncontaminated "background" site and deployed at 9 sites in the Bay for 90 days during the dry season (June to September) annually. Resident clams (*Corbicula fluminea*) collected from 2 Delta sites (Sacramento River and San Joaquin River).
- Homogenized and extracted by U.S. EPA Method 3545 (Pressurized Fluid Extraction). Dried and filtered extracts were cleaned through automated GPC (J2 Scientific AccuPrep 170) and fractionated on a Florisil column.
- Analysis on HP6890 high resolution dual column GC/ECD.

Cormorant Eggs

- Cormorant eggs collected from 3 locations (Wheeler Island, Richmond Bridge, and Don Edwards National Wildlife Refuge). Ten eggs composited and analyzed using a similar method as bivalves.

Sport Fish

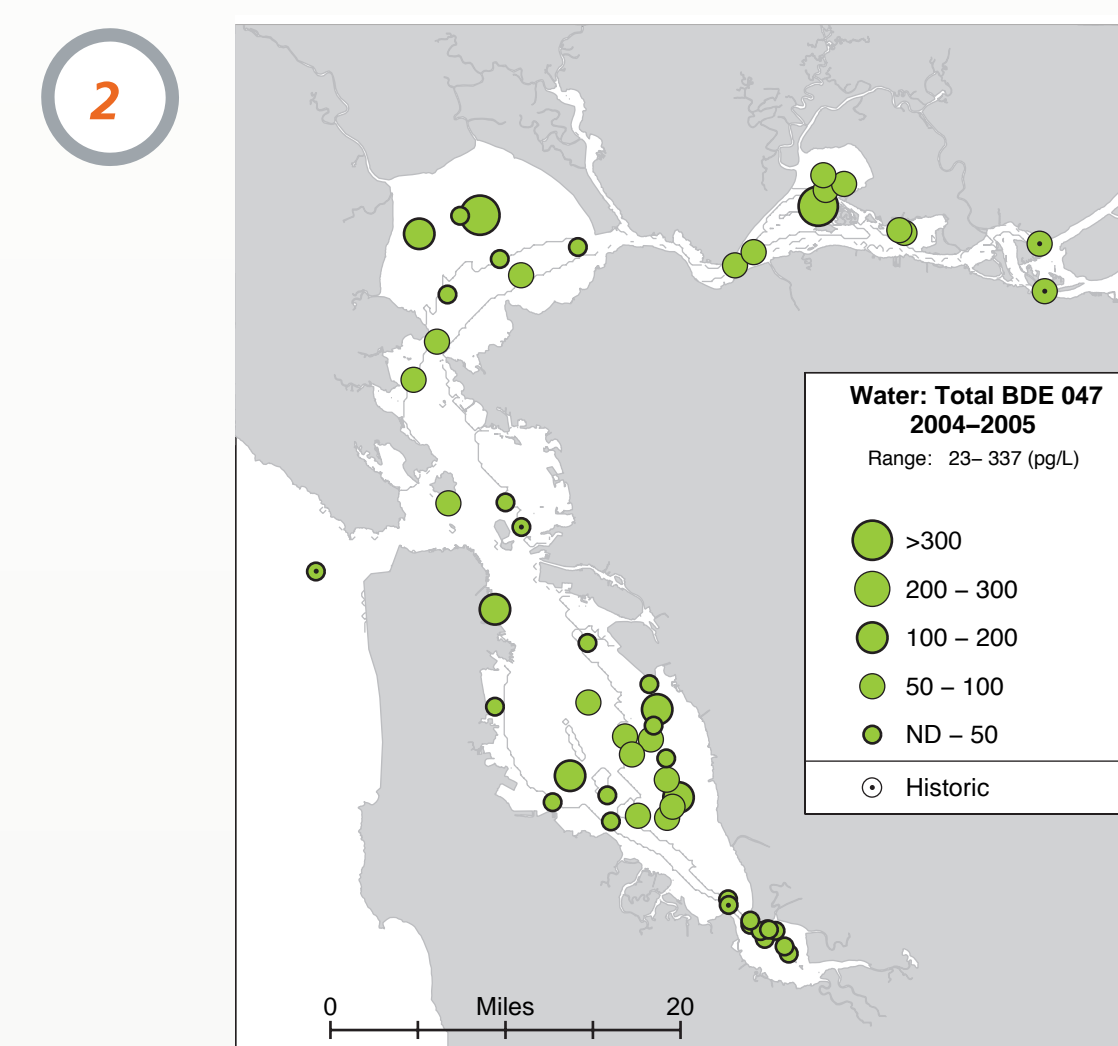
- Sport fish collected from 5 locations within the Bay triennially. Targeted species included California Halibut, jacksmelt, leopard shark, shiner surfperch, striped bass, white croaker and white sturgeon. Samples analyzed similar to bivalves.

Water

Table 1 shows PBDE concentrations for 2002 through 2005 water samples. Dominant congeners in water are PBDEs 17, 47, 99, 100, 153, 154, and 209. However, much of the 209 data was flagged as unreportable due to significant blank contamination (>30% of total concentration) and poor precision.

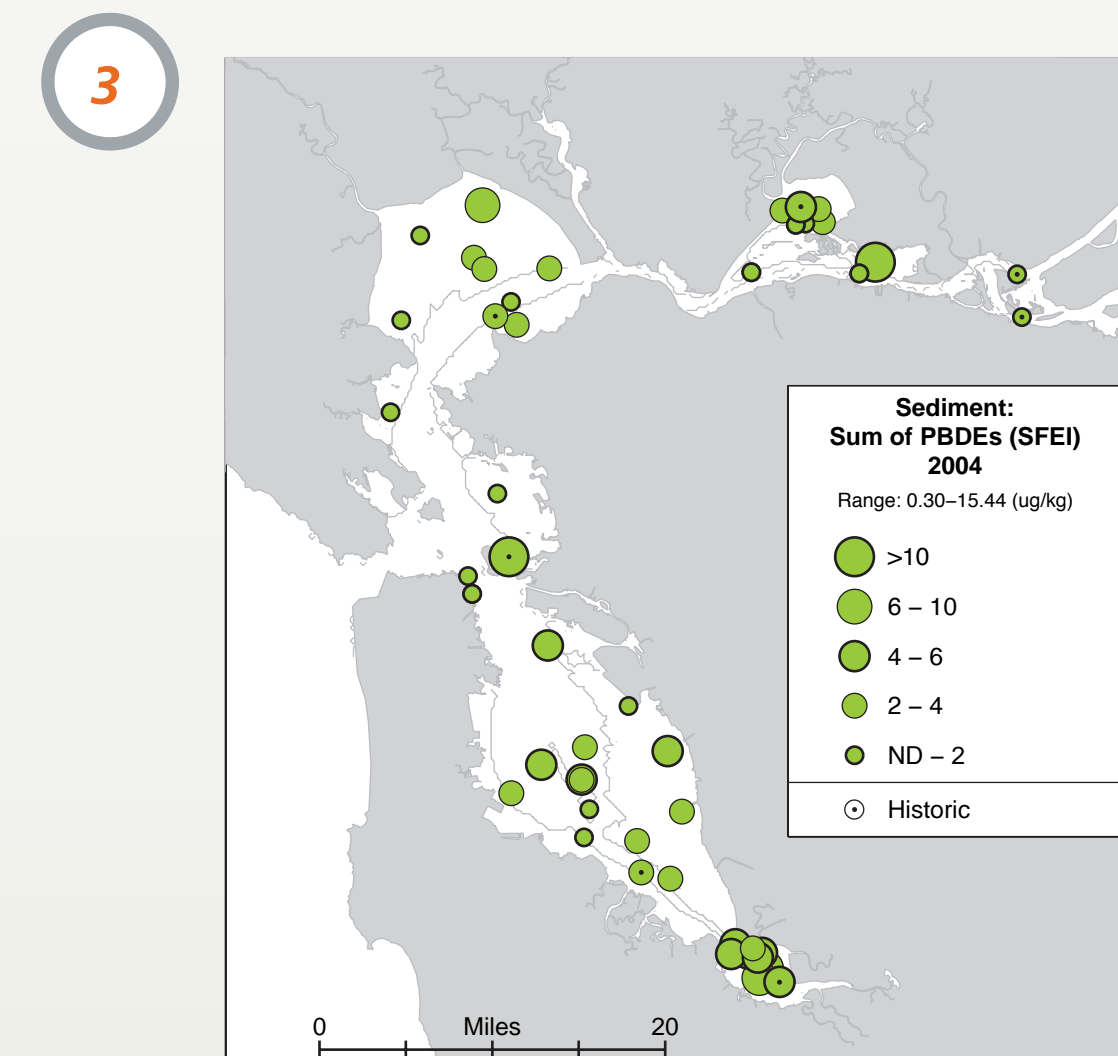
	17	47	99	100	153	154	209
Minimum	0.1	13.5	7.9	1.9	0.7	0.6	12.0
Maximum	50.3	337.0	189.0	73.3	19.9	20.5	1090.0
Average	8.9	63.7	39.0	12.6	4.3	3.5	309.0
Std dev	1.6	23.0	12.9	4.8	1.1	0.4	247.2

Concentrations of PBDE-47 are relatively uniform throughout the estuary, which may be a result of diffuse sources to the estuary or its solubility enhancing dissolved transport pathways. (*Figure 2*).



Sediment

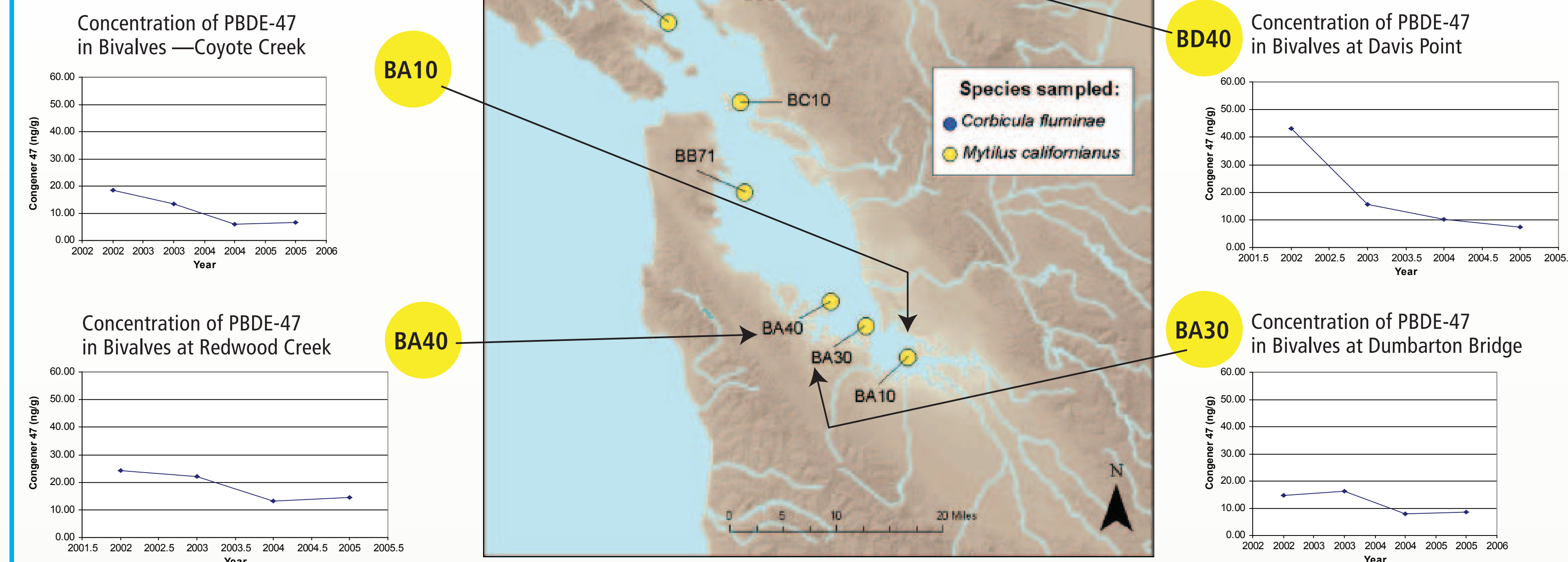
Total concentrations of PBDEs in sediment in 2004 ranged from 0.3 to 15.4 ug/kg with average(±stddev) of 3.4(± 2.9) ug/kg (*Figure 3*). Dominant congeners are (in order of decreasing concentration): PBDE-209; PBDE-47; PBDE-99; PBDE-204; and PBDE-17.



Results

Bivalves

Concentrations in bivalves ranged from 3.98 to 105.6 ug/kg with an average concentration of 29.5 ug/kg (± 25.9). Dominant congeners are 47 and 99. As shown on *Figure 4*, concentrations are highest in the bivalve samples from the Delta tributaries (resident clams) and lowest in the South Bay. Concentrations also decreased with time across all stations.



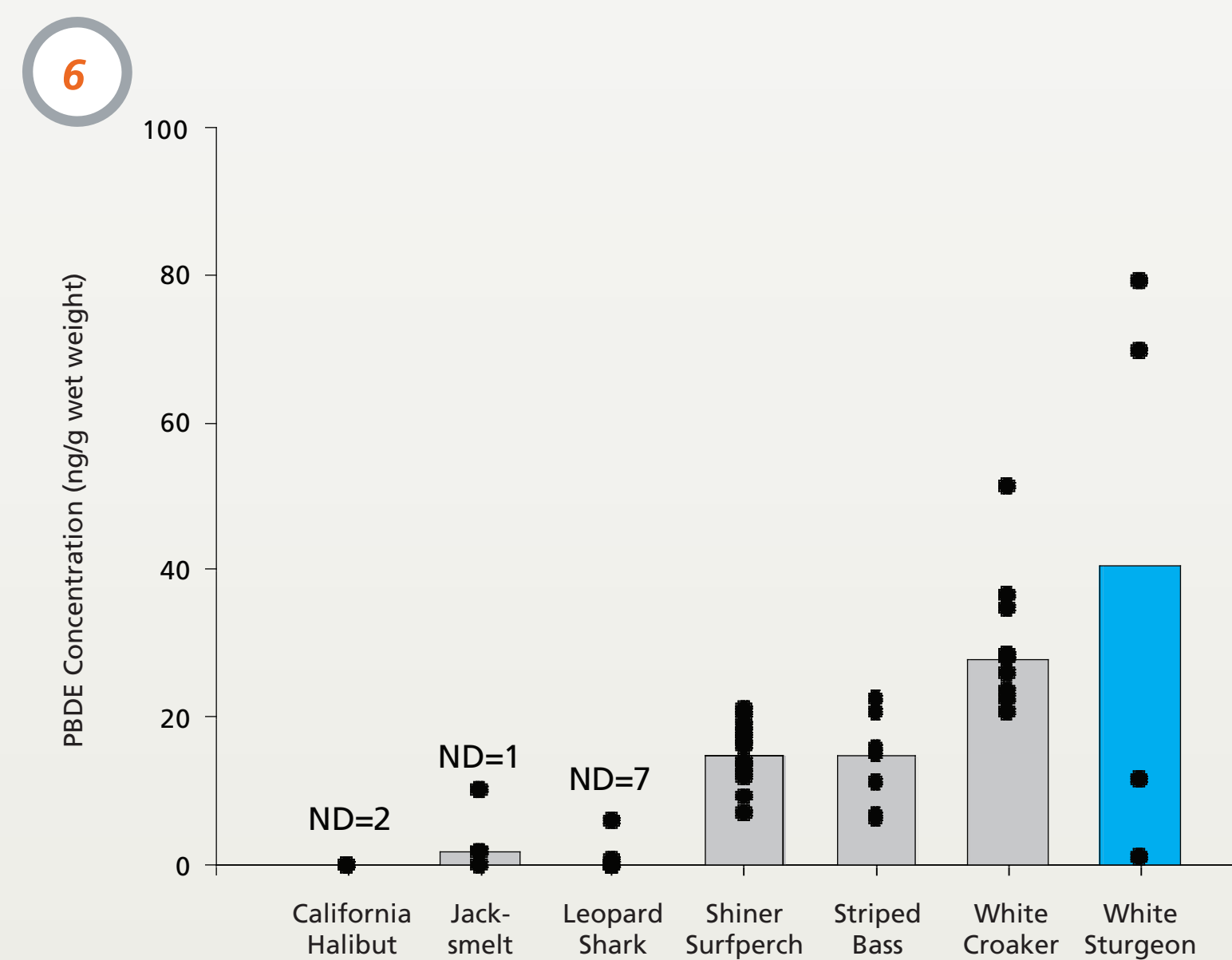
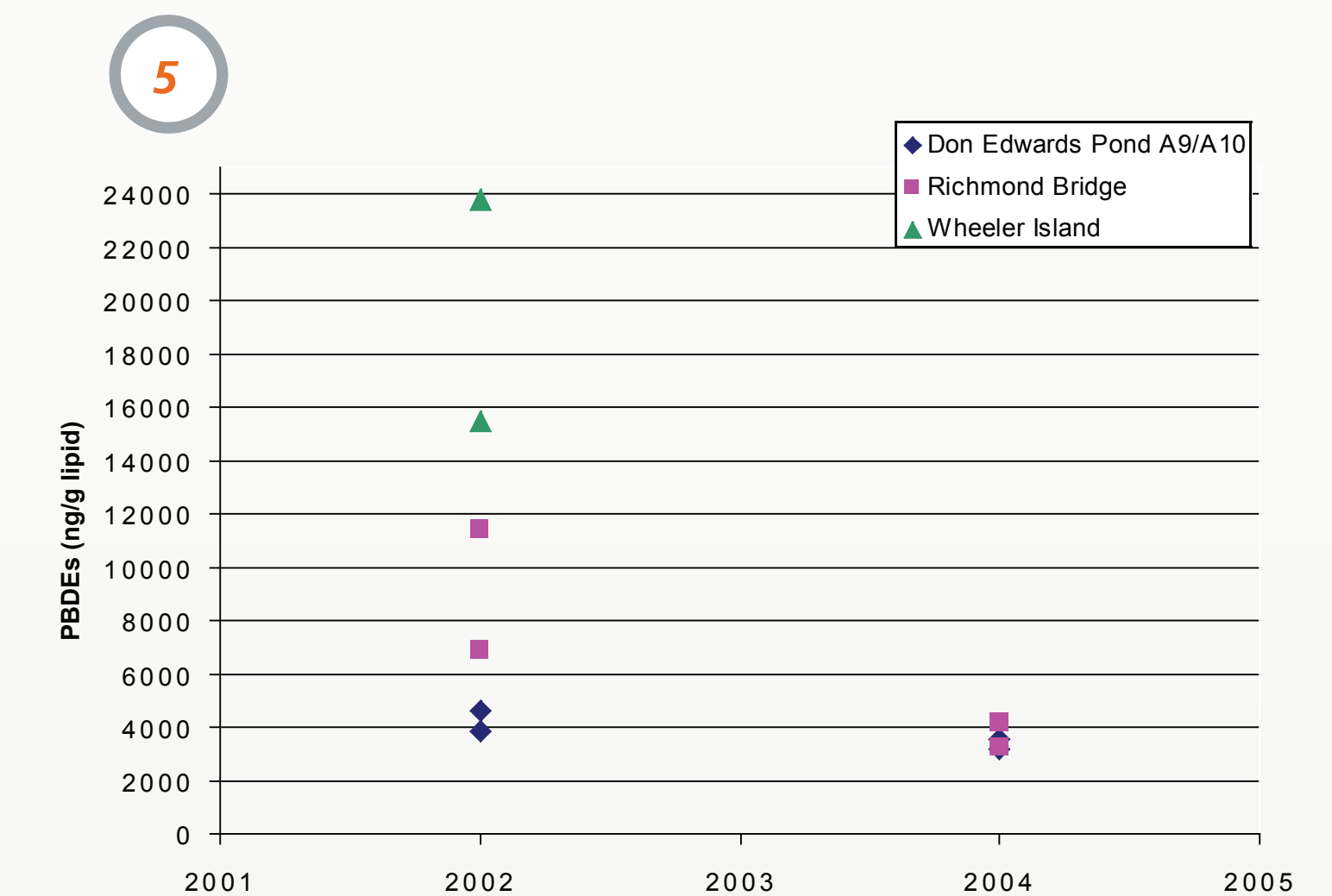
Cormorant Eggs

Map shows sampling locations of Cormorant eggs. *Figure 5* shows total PBDE concentrations in the composite samples. PBDE concentrations ranged from 3.2 ug/g (lipid weight – lw) at Don Edwards in 2004 to 24 ug/g lw at Wheeler Island in 2002. Dominant congeners were: 47, 100, and 99. Lower concentrations of 153/154 were also identified.



Sport Fish

Map shows the location of sportfish sampling and *Figure 6* shows PBDE concentrations in fish. Concentrations ranged from 79 ng/g to below detection. Highest concentrations of PBDEs were observed in white sturgeon and white croaker (i.e., median concentrations of 40 ng/g and 28 ng/g, respectively). Dominant congeners in order of decreasing concentration are: PBDE-47, PBDE-100, and PBDE-154



Discussion and Recommendations

Water and Sediment

- Very few studies have characterized concentrations of PBDEs in water; however of those studies, values for the San Francisco Bay are within the reported range. PBDEs in Lake Ontario ranged from 4 to 13 pg/L, with PBDE-47 and PBDE-99 representing 90 percent of the total PBDEs (Luckey et al. 2001). Sediment concentrations are in the range of values reported in the literature with PBDE-209 typically being the dominant congener (Law et al. 2006). Reflecting the diverse uses of PBDEs, concentrations in water and sediment are relatively uniform.
- Concentrations in the South and Central Bays were on average higher than those in the North Bays (i.e., 4.0 ug/kg vs. 2.4 ug/kg) reflecting the lower flow, increased urbanization, greater influence of POTWs, and the higher percentage of finely grained sediments in the South Bay.

Biota

- Concentrations observed in bird eggs in the San Francisco Bay area (e.g., 24,000 ng/g lw) are among the highest observed worldwide. Hites (2004) reported gull eggs concentrations in 2000 to be on the order of 7,500 ng/g lw. Similar to other studies (Hites 2004), congener 47 is the dominant congener in piscivorous bird eggs.
- Bivalve concentrations in the Bay (i.e., on average 29.5 ng/g) are higher than those reported in the literature, 1.7 ng/g (dry) to 13.5 ng/g (lipid) (Hites 2004; Law et al. 2006). Fish concentrations corrected for lipid content (average 1089 ng/g lw) are on the order of those reported by Hites (2004) for North American fish (average 1050 ng/g lw).
- San Francisco Bay area has relatively high concentrations of PBDEs in biota in comparison to other study sites; however, recent bird egg and bivalve results suggest that concentrations of PBDEs may be decreasing.

Recommendations

- Continued monitoring of PBDEs is important to determine the efficacy of the ban of penta and octa mixes.
- Continued monitoring of biota is important to determine whether there is a significant long-term decreasing trend in biota.

Acknowledgements

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