PBDES IN THE SAN FRANCISCO BAY FOOD WEB

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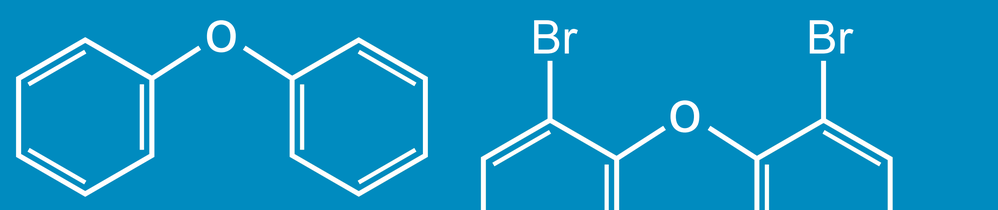


Introduction

Some of the highest concentrations of polybrominated diphenyl ethers (PBDEs) in the world have been observed in San Francisco Bay wildlife and humans (She et al. 2002, 2008). These results and the pervasive use of these compounds prompted the Regional Monitoring Program for Water Quality in the San Francisco Bay (RMP) to focus significant resources in understanding the occurrence of PBDEs in Bay biota, sediment and water beginning in 2002. The RMP has ten years' worth of occurrence data for a variety of biota that reside in San Francisco Bay, including deployed and resident bivalves, sport fish, and tern and cormorant eggs.

In part as a result of the widely detected presence of PBDEs in the environment, the major manufacturer, Great Lakes Chemical Corporation (now Chemtura Corporation) of two of the three PBDE formulations (Penta and Octa) ceased production of these compounds at the end of 2004. The California Legislature banned Penta and Octa in 2006. Also in 2006, the USEPA issued a significant new use rule on these compounds, requiring that any use proposed in the future be reviewed for safety.

The Deca formulation is scheduled to be phased out in 2013. The long-term and ongoing monitoring of PBDEs undertaken by the RMP allows us to observe whether these actions have resulted in reduced contamination of the Bay.

Materials and Methods

The RMP has monitored the following matrices:

- Sediment and water (2002 – 2012)
- Transplanted and resident bivalves (2002, 2003, 2005, 2006, 2008, 2010, 2012)
- Sport fish (2000 (semi-quantitative), 2003, 2006, 2009)
- Cormorant and tern eggs (2002, 2004, 2006, 2009)

Sediment and water samples are spatially distributed throughout the Bay using a Generalized Random Tessellation-Stratified (GRTS) statistical design. Sediment was sampled at 40 random sites and 7 historical sites in the summer; biennial winter sampling commenced in 2010 using at least 20 random and 7 historical sites. Surface sediment samples were collected at a depth of 0 to 5 cm using a Van Veen grab. Sediment from two or more grabs taken at each site was composited, homogenized by hand mixing, and shipped to AXYS Analytical (Sidney, Canada) for extraction and analysis.

Water samples were collected annually in the summer at 17 random locations and 5 historical sites. Solid phase extracted water samples were collected one meter below the surface using the AXYS Infiltrex 300 system pumping 100L through a 1 µm glass fiber cartridge particulate filter and columns filled with XAD-2 resin. Samples were analyzed by AXYS Analytical.

Transplanted bivalves (*Mytilus californianus*) were deployed at nine stations in the Bay for 90 days during the summer. At two river sites, resident bivalves (*Corbiculva fluminea*) were collected. Bivalves were retrieved, processed using clean techniques, and aliquoted for analysis. Generally, 30-40 bivalves were composited from each site. Samples were homogenized, extracted, and analyzed by California Department of Fish and Game (CA-DFG) in 2005 and prior, and AXYS Analytical since 2006.

Cormorant eggs were collected at three fixed locations within the Bay: Richmond Bridge (Central Bay); Wheeler Island in Suisun Bay (North Bay), and Don Edwards Wildlife refuge (South Bay). At each site, two composites were formed from seven to ten eggs. Tern eggs were collected from established colonies at variable locations within the Bay (most in South Bay). Eggs were composited, homogenized, and analyzed by CA-DFG.

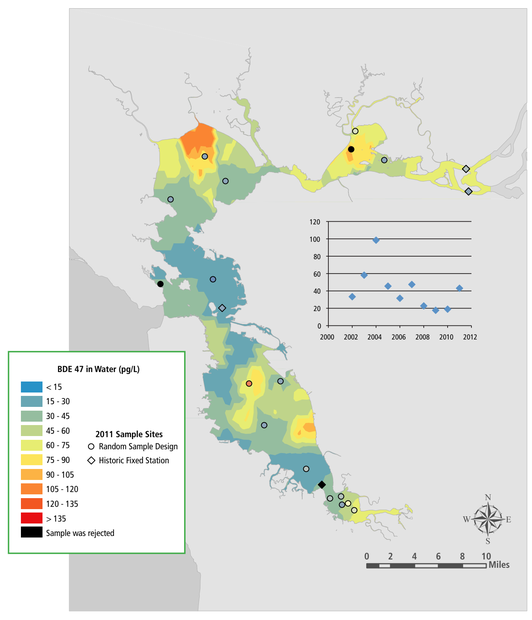
Eight species of sport fish were collected at five popular recreational fishing areas within the Bay every three years. Most sites were located in the Central Bay. Fish were typically dissected skin-off, and only the fillet muscle tissue was analyzed. Some species (e.g., shiner surfperch) too small to be filleted were processed whole but with head, tail, and viscera removed. Samples, typically composites of three or more fish, were analyzed by CA-DFG.

PBDEs were analyzed in all matrices using lab-modified implementations of EPA Method 1614. Results were generally good for QC samples, aside from sporadic contamination found in blank samples, with results censored if the signal found in the blank was one-third or more of a sample result.

Results and Discussion

Concentrations in water (**Figure 1**) and sediment (**Figures 2** and **3**) have remained largely constant over the last ten years with an interdecile range of total PBDEs (the sum of measurable congeners) from 65 to 603 pg/L (median 154 pg/L) in water and 1 to 9 (median 3.0) ng/g dw in sediments. This apparent lack of trend may be due to several factors. In sediments, this may be an artifact of compositing the top 5 cm of sediment; the sediment accretion rate in most areas of the Bay is <0.5 cm/year, and surface sediments are mixed by bioturbation and wind wave resuspension, so any recent trends could be easily obscured by compositing and/or mixing. In water samples, the low ambient concentrations combined with laboratory blank contamination makes detection of any real trends difficult. In marked contrast, concentrations of total PBDEs in several biological matrices have shown a dramatic decline.

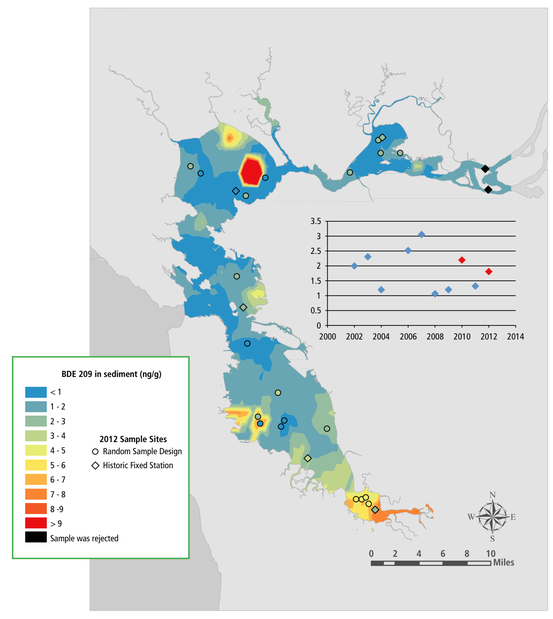
Figure 1*
Concentrations of BDE-47 in water in San Francisco Bay (pg/L)



BDE-47, the dominant congener in water, shown as an index of total PBDEs. Map plot based on 206 RMP data points from 2002-2011. Trend plot shows annual Bay-wide averages.

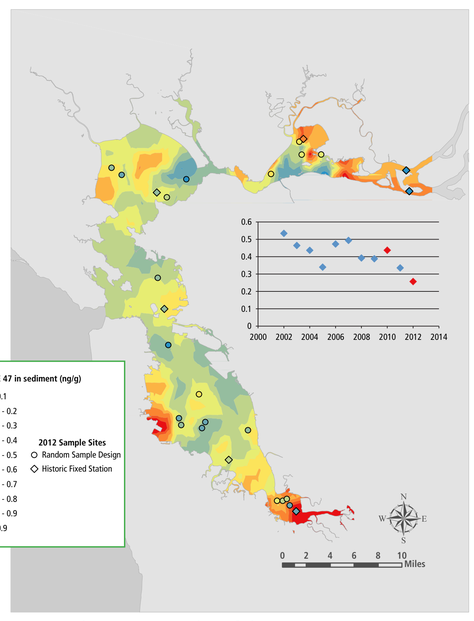
*Colored symbols on map show results for samples collected in 2011. Circles represent random sites. Diamonds represent historic fixed stations.

Figure 2**
Concentrations of BDE-209 in sediment in San Francisco Bay (ng/g dry weight)



BDE-209, the dominant congener in sediment, shown as an index of total PBDEs. Contour plot based on 293 RMP data points from 2002, 2003, 2004, 2006, 2007, 2008, 2009, 2011. Trend plot shows annual Bay-wide averages.

Figure 3**
Concentrations of BDE-47 in sediment in San Francisco Bay (ng/g dry weight)



BDE-47 shown as an index of the PentaBDE mixture. Contour plot based on 338 RMP data points from 2002–2009 and 2011. Trend plot shows annual Bay-wide averages.

**Colored symbols on map show results for samples collected during the wet season (April) in 2012. Diamonds represent random sites. Diamonds represent historic fixed stations. Red circle on trend plot indicates a wet season sample; other samples were dry season.

Bivalves

Concentrations of total PBDEs were mostly between 6.2 and 62 ng/g dw (interdecile range) with a median across the monitored period of 20 ng/g dw. Resident bivalves located in the river stations had higher concentrations (median 61 ng/g dw when considered separately), perhaps as a result of a longer exposure period, interspecies differences, or localized PBDE sources. In general, the more highly brominated congeners that comprise the Deca formulation were not detected in bivalves. The most abundant congener was BDE-47, a major ingredient in the Penta formulation. Concentrations in bivalves did not exhibit a high degree of spatial variation. Concentrations of this congener have declined dramatically at all sites across the Bay in both transplanted and resident bivalves (**Figure 4**).

Bird Eggs

Concentrations of PBDEs in cormorant eggs have also decreased over the ten-year period (**Figure 5**). Major congeners observed were BDE-47, -99, and -100. The highest concentrations observed were at Wheeler Island in Suisun Bay, an area that is relatively undeveloped but may be influenced by activities nearby and upstream in the Delta.

She et al. (2008) reported the world's highest concentrations of PBDEs in biota: 63,000 ng/g lipid in Forster's tern eggs from the South Bay. Samples of tern eggs collected in 2009 in the same region suggest a dramatic decline, with concentrations ranging from 670 to 2,400 ng/g lipid. In addition, recent work sponsored by the RMP suggests that these concentrations are well below thresholds that may cause effects to pipping and hatching success (Rattner et al. 2011).

Sport Fish

Although PBDEs have been monitored in a variety of fish over the last decade, including white croaker, anchovy, sturgeon, and jacksmelt, the RMP has focused its long-term trend comparisons on shiner surfperch (*Cymatogaster aggregata*). Annual average concentrations of PBDEs in this species ranged from 15 to 8 ppb (wet weight), with a nearly two-fold decline between earlier measurements (2003, 2006) and those made in 2009 (**Figure 6**; Davis et al. 2011). None of the concentrations of any species of sport fish monitored exceeded the recently developed human health fish advisory tissue level of 100 ppb for the consumption of fish twice a week (Klasing and Brodberg 2011).

Figure 4
Concentrations of BDE-47 in Bivalves (ng/g dw)

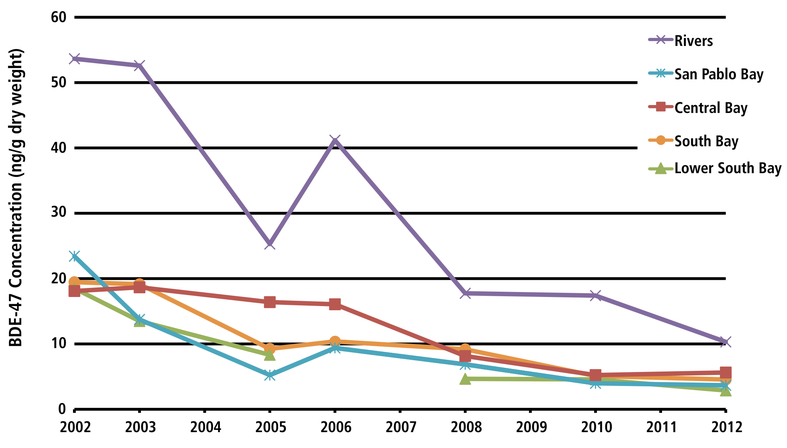


Figure 5
Concentrations of Total PBDEs in Cormorant Eggs (ng/g lipid)

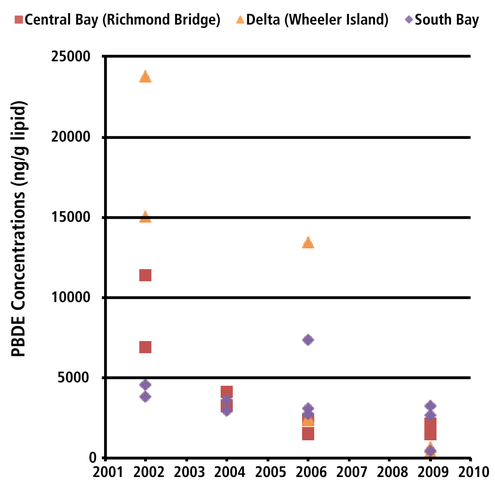
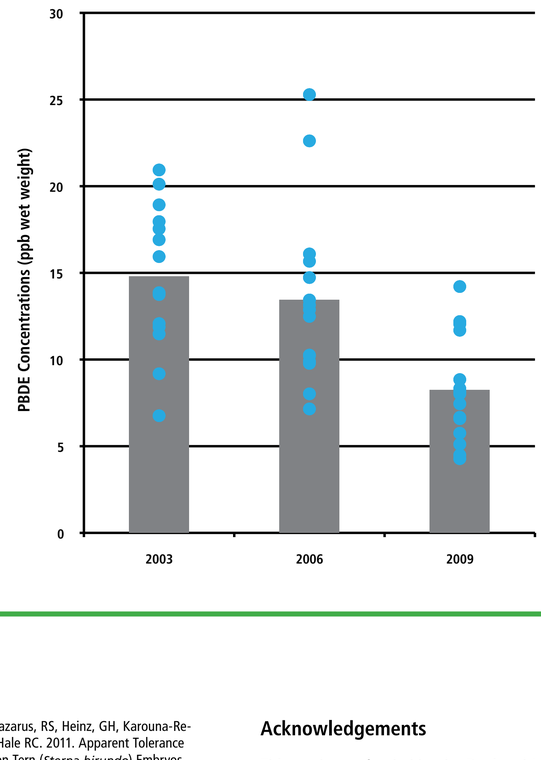


Figure 6
PBDE concentrations (ppb wet weight) in shiner surfperch in San Francisco Bay, 2003-2009. Bars indicate averages. Points represent composite samples.



Conclusions

Although concentrations in abiotic Bay media such as sediment and water have shown few noticeable temporal trends over the ten-year monitoring period, concentrations in biota have declined dramatically, suggesting that management actions have been very successful in reducing pollutant concentrations in the food web. Investigation of potential contamination "hot spots" in the margins surrounding the Bay may prove useful in understanding the specific exposure pathways leading to PBDE declines in wildlife.

References

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Acknowledgements

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