

PBDES IN THE BAY:

Sacramento/San Joaquin River

Wastewater Treatment Plants

Local Tributaries

RAPID RISE, RAPID FALL?

By JOHN ORAM (joram@sfei.org) and JEN HUNT (jhunt@sfei.org)

THE RAPID RISE

Polybrominated diphenyl ethers (PBDEs), due to their use as flame retardants in plastics, electronics, and furniture, are now observed in virtually every part of the biosphere and are correctly described as ubiquitous environmental pollutants. Beginning in the 1980s, reports of PBDEs in environmental samples emerged from North America, Scandinavia, Europe, and Japan. Following on this early work, a growing number of recent studies have confirmed that PBDEs are present in urban and rural soils, river and urban stormwater, sediments of lakes, bays, and oceans, air, sewage sludge, treated wastewater effluent, shellfish, fish, birds, mammals, and humans.

THE SAN FRANCISCO BAY AREA IS A KNOWN GLOBAL PBDE HOT SPOT. STUDIES HAVE FOUND ELEVATED CONCENTRATIONS OF PBDES IN BAY AREA WILDLIFE AND HUMANS THAT ARE AMONG THE HIGHEST REPORTED IN THE WORLD.

The San Francisco Bay Area is a known global PBDE hot spot. Studies have found elevated concentrations of PBDEs in Bay Area wildlife and humans that are among the highest reported in the world. A recent local study showed that concentrations of PBDEs in Bay seals had doubled every 1.8 years throughout the 1990s, with concentrations at the end of the decade among the highest ever reported. There have also been reports of PBDE concentrations in human breast tissue, where concentrations are the highest ever reported in human tissues and are at or near levels thought to be of concern for human health.

PBDE concentrations in San Francisco Bay bivalves are also among the highest reported worldwide, while concentrations



CONTAMINANTS IN YOUR COUCH:

INVESTIGATION OF ALTERNATIVE FLAME RETARDANT CHEMICALS IN SAN FRANCISCO BAY

After five years of studying polybrominated diphenyl ether (PBDE) flame retardants and their bioaccumulation in Chesapeake Bay food webs, last year I drove to the West Coast to start my scientific career at SFEI. I found a place to live and moved in, but needed furniture. As I was buying my couch, I did think about flame retardants and what chemicals might be used in place of the recently banned PBDEs. But I needed something to sit on, so I went ahead with the purchase and thoughts of flame retardants ended up on the back burner. Then I met Arlene Blum. Arlene is a local scientist who began working on the flame retardant issue back in the 1970s. She is still at it and subsequently offered to test my recently purchased couch to find out if it contained brominated chemicals. I showed up at Arlene's door with couch cushion in hand and she zapped the foam with a portable X-ray fluorescence analyzer. The result: the couch material contained 4% bromine, telling me that brominated flame retardants had been added—but which ones? That got me thinking and I set out on a quest to discover what chemicals were in my new couch.

Worldwide restrictions on the use of PBDEs, which are suspected neurotoxins and endocrine disruptors, have led to the use of alternative flame retardant chemicals in order to meet California's furniture flammability standards. Many chemicals can potentially serve as replacements for PBDEs, though information on which chemicals are currently in use and their specific applications is not readily available. This lack of information impedes determining whether these chemicals are accumulating in the environment. Assessment of some of the chemicals currently used to replace the banned Penta-BDE has thus far not been possible because their chemical identities are considered confidential business information. As a result, little information on the toxicity and fate of these chemicals is available, though it is greatly needed to assess the risk they may pose to wildlife and people.

I called the chemical company that produces the flame retardant mixture reportedly used in the highest volume to meet the California furniture flammability standard. Even though the chemicals in the mixture are considered confidential business information, I requested that they send me a sample. I also couldn't help but wonder, is this stuff in my couch?

Using the sample donated by the chemical company, Alex Konstantinov at Wellington Laboratories identified the two brominated chemicals (a tetrabrominated benzoate (TBB) and a tetrabrominated phthalate (TBPH)) in this commercial



BY SUSAN KLOSTERHAUS (susan@sfei.org)

AS I WAS BUYING MY COUCH, I DID THINK ABOUT FLAME RETARDANTS AND WHAT CHEMICALS MIGHT BE USED IN PLACE OF THE RECENTLY BANNED PBDES. BUT I NEEDED SOMETHING TO SIT ON, SO I WENT AHEAD WITH THE PURCHASE AND THOUGHTS OF FLAME RETARDANTS ENDED UP ON THE BACK BURNER.

mixture. TBPH is analogous to the commonly used plasticizer DEHP, a chemical of concern due to its potential reproductive toxicity (see http://www.sfei.org/rmp/rmp_news/RMPNews_Vol10_issue1.pdf for more information on DEHP). I was surprised to find that despite the high volume use of TBPH in this mixture and its similar structure to DEHP, information is not available in the public domain regarding the toxicity and fate of TBPH in the environment. However, now that the identity of the replacement flame retardant is known, we can begin to fill the large data gaps needed to assess the risk of exposure to these chemicals in the environment.

As a first step to determine if these chemicals are migrating out of consumer products and thus potentially accumulating in San Francisco Bay sediments and wildlife, I sent samples of biosolids (sludge) collected from two municipal wastewater treatment plants (WWTPs) that discharge effluent to the Bay to Heather Stapleton at Duke University for analysis of TBB and TBPH. TBB and TBPH were detected in biosolids from both WWTPs, marking the first time these chemicals have been detected in environmental samples. At one WWTP, concentrations were within range of BDE 209 (the PBDE congener frequently detected at the highest concentrations in aquatic sediments and the primary chemical in Deca-BDE, the only PBDE mixture not banned in the state of California). Detection in biosolids at concentrations comparable to BDE 209 suggests that TBB and TBPH also have the potential to accumulate to significant concentrations in aquatic environments.

But what about my couch? Along with the biosolids, I also sent a chunk of foam from my couch seat cushion to Duke University for chemical analysis. TBB and TBPH were indeed the brominated chemicals added to make the foam flame resistant. I was somewhat relieved to find out that my couch foam didn't contain PBDEs—but are TBB and TBPH any safer? Without toxicity and fate studies we will unfortunately have to wait for the answer to this question.

In the summer of 2008, the RMP will measure TBB, TBPH, and several other chemicals that could potentially be used as PBDE replacements in San Francisco Bay biota and sediments. Results from this study will provide much-needed information on the bioaccumulation potential of these chemicals and whether further evaluation of exposure and risk in San Francisco Bay wildlife is warranted.



PBDEs IN THE BAY

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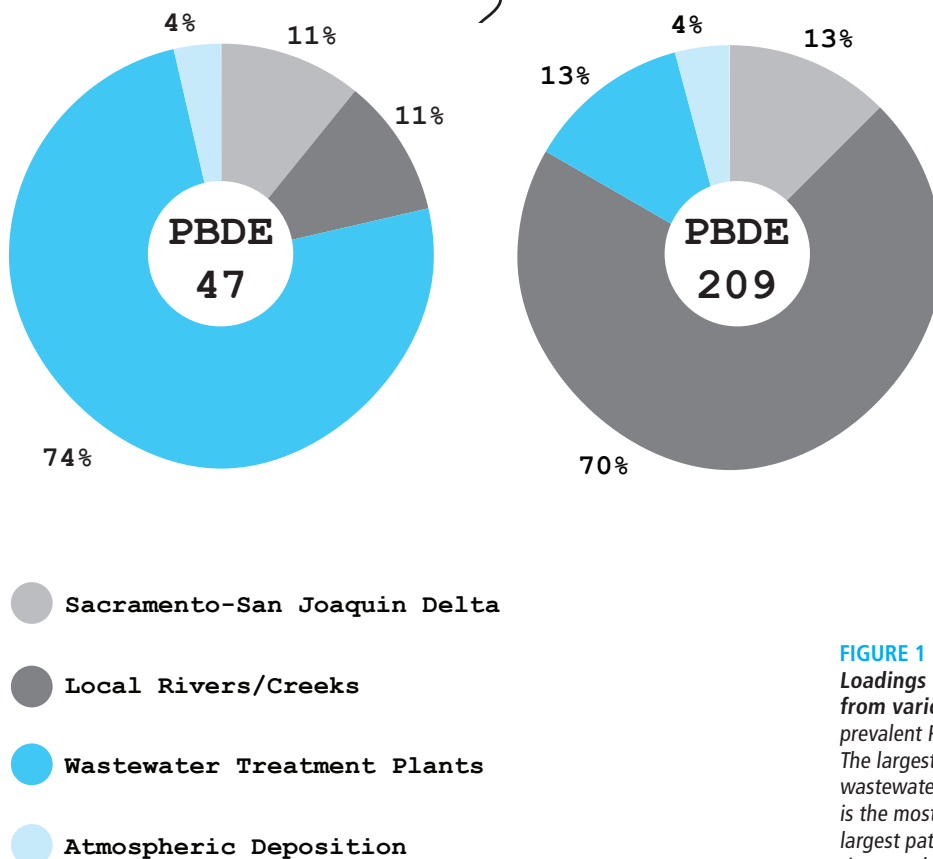


FIGURE 1

Loadings of PBDEs to San Francisco Bay from various pathways. PBDE 47 is the most prevalent PBDE found in Bay fish and wildlife. The largest pathway of PBDE 47 to the Bay is wastewater treatment plant outflow. PBDE 209 is the most prevalent PBDE in Bay sediment. The largest pathway of PBDE 209 is runoff from local rivers and creeks.

PBDES IN THE BAY: RAPID RISE, RAPID FALL?



ONE OF THE MORE INTERESTING FINDINGS IN THIS STUDY WAS THAT LOCAL TRIBUTARIES, SUCH AS THE GUADALUPE RIVER IN THE SOUTH BAY, CONTRIBUTE HIGHER AMOUNTS OF PBDES TO THE BAY THAN THE MUCH LARGER SACRAMENTO/SAN JOAQUIN RIVER SYSTEM.

in San Francisco Bay fish are 10 to 100 times higher than fish concentrations in Japan or Europe. PBDEs in Forster's tern from the Bay hold the world record for the highest concentrations measured in any living thing.

Clearly understanding sources (where PBDEs come from in the watershed), pathways (how these contaminants get into the Bay and the Bay food web), fate (movement within the Bay), and the toxicity of PBDEs is of paramount importance. The RMP recently completed a first-of-its-kind study to determine the quantity of PBDEs in the waters and sediments of San Francisco Bay and surrounding watersheds, to identify the pathways by which PBDEs are transported to the Bay, and to improve understanding of the processes controlling the ultimate fate of PBDEs in the ecosystem. The study provides a framework into which future monitoring and modeling efforts can be incorporated and by which potential management actions can be evaluated.

HOW DO PBDES ENTER THE BAY FROM THE WATERSHED?

Small Tributaries Carry Large Loads

San Francisco Bay is the largest estuary on the West Coast of the US, with a watershed consisting of about 40% of California's land area. Therefore, a high percentage of runoff from California's cities, towns, and open space drains into the Bay. There are many different pathways that bring PBDEs into San Francisco Bay, including rivers and creeks, storm water runoff, wastewater effluents, and deposition from air. Results from a recent RMP study indicate that wastewater effluent

and local urban rivers are the largest contributors of PBDEs to the Bay (**FIGURE 1**).

One of the more interesting findings in this study was that local tributaries, such as the Guadalupe River in the South Bay, contribute higher amounts of PBDEs to the Bay than the much larger Sacramento/San Joaquin River system. The Sacramento/San Joaquin River contributes an estimated 6 kg/year to the Bay while local tributaries contribute an estimated 20 kg/year. Local tributaries and their watersheds in the immediate Bay Area are highly urbanized: the Guadalupe River watershed is approximately 84% urbanized while the Sacramento/San Joaquin River watershed is about 2% urbanized. The data suggest that the urban landscape is a much larger source of PBDEs than more rural areas of the state.

There are also different PBDE loading signals within a watershed that lend support to the notion that this contaminant comes largely from the urban landscape. Rains from winter storms flow off the landscape and mobilize contaminants in the watershed into rivers and eventually into the Bay. Runoff from the lower watershed - in the case of the Guadalupe, the more urban part of the watershed - reaches the river first and leads to a rise in river height, while runoff from the upper watershed reaches the river later as the water height begins to fall. PBDE concentrations were measured at both the rising and falling heights of river flooding and showed that concentrations were higher in the rising stage (urban signal) than the falling stage (rural signal). This finding indicates the urban source of PBDEs and suggests that efforts to reduce urban PBDE loading could have a large impact on in-Bay concentrations.

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Avian Cholera in San Francisco Bay: A New Occurrence?

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On February 9, 2008, an already-skittish public woke up to read in the San Francisco Chronicle that an unusual number of dead birds were washing up on the shores of Richardson Bay.

Richardson Bay had received light oiling in the wake of the November 7, 2007 Cosco Busan oil spill. Then, in January and February, there were spills of treated and raw sewage. It was hard for the public not to think that these bird deaths were related to the spills.

The continuing bad news was difficult to accept. Richardson Bay is one of the most charming parts of San Francisco Bay. It is a popular recreation spot for kayakers and swimmers, and it provides significant habitat for birds and harbor seals. Historically, Richardson Bay supported diverse shellfish resources, and it remains an important spawning ground for the Pacific herring.

One week after the news broke, the California

Department of Fish and Game reported that at least some of the bird deaths may have been due to avian cholera. (The final report found that three of ten birds tested positive for avian cholera; for the others, the cause of death remained undetermined.)

Was news of avian cholera cause for relief? Or was it a new concern?

Avian cholera is an infectious disease, caused by the bacterium *Pasteurella multocida*. It is not related to human cholera. Avian cholera infections are common, and infected birds tend to die quickly, sometimes within hours of being infected. The disease is thought to have first been detected in the United States in the 1880s, and it was first reported in the San Francisco Bay region during the winter of 1943-44 (Rosen and Bischoff, 1949). It has been detected throughout the U.S. and in many countries.

Richardson Bay was not the only place in the

Bay Area to suffer from avian cholera this year. A much bigger outbreak occurred at the South Bay's Hayward Regional Shoreline, where about 700 birds died. While it was the first outbreak at the Hayward Regional Shoreline in several years, avian cholera occurs on almost an annual basis in California. This past winter, the USGS Wildlife Health Center reported deaths from avian cholera in many parts of the state: Siskiyou County in the north, Imperial and San Diego counties in the south, the Central Valley, and the Bay Area (www.nwhc.usgs.gov). Outbreaks are particularly common in the Central Valley.

Nationally, avian cholera occurs from coast to coast but is most common in the western and central states. Last fall, a particularly large outbreak in Utah's Great Salt Lake made national news when approximately 15,000 out of a population of 1.5 million eared grebes succumbed to the illness. Most outbreaks occur during the winter, when there are cold temperatures and dense

congregations of birds in wintering sites.

The tendency for avian cholera outbreaks to occur year-after-year in the same areas has prompted research into the possibility that wetlands might be reservoirs for the disease (e.g., Friend, 1999). That theory has not panned out (Samuel et al., 2004; Lehr et al., 2005; Blanchong et al., 2006). The *Pasteurella multocida* bacterium does not persist over time in the water or sediments. Rather, the disease is spread from bird to bird. Birds that survive an outbreak may become carriers, bringing the disease to new geographic areas or reintroducing it in the same location in subsequent years.

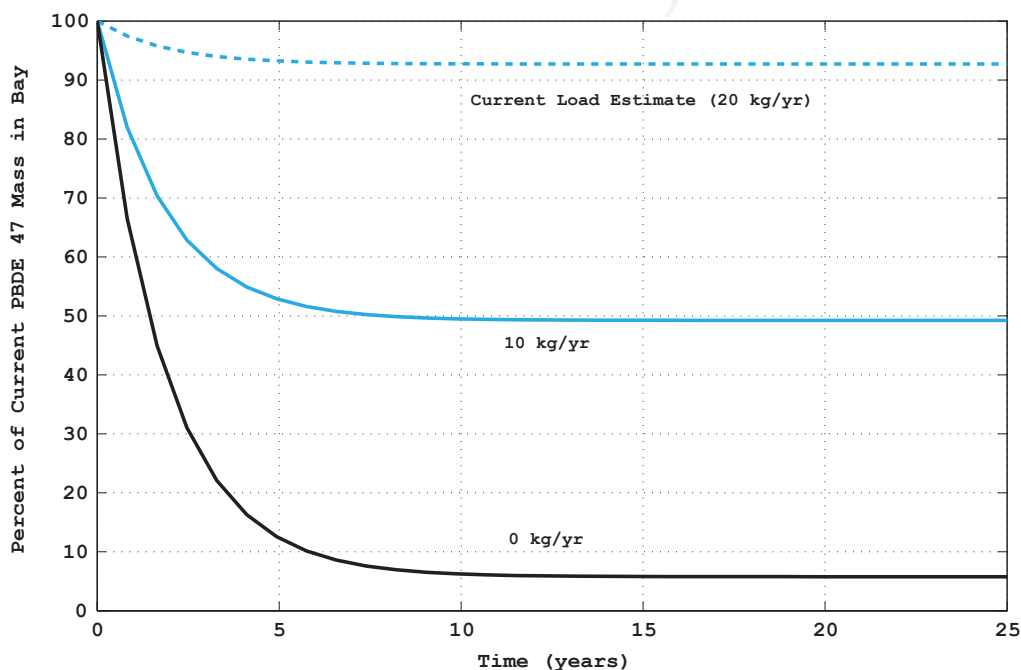
Susceptibility to the disease may depend on many factors, such as sex, age, genetic variation, previous exposure, other infections, nutritional status, or virulence of the strain (Friend, 1999). When the dead birds were recovered from Richardson Bay, some environmentalists and scientists questioned wheth-

er the recent insults of the oil and sewage spills could have increased susceptibility of the birds to disease. That question cannot be easily answered. Most of the birds recovered from Richardson Bay were emaciated, but a general lack of food this year could explain their condition. The presence of avian cholera in San Francisco Bay was not unusual or a cause of new alarm, and future outbreaks can be expected.



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**FIGURE 2**

PBDE concentrations in the Bay are expected to fall rapidly when inputs are reduced. This figure shows projected recovery curves for the Bay based on three PBDE loading scenarios. Scenario 1 (dashed, 20 kg/year): in-Bay PBDE levels are predicted to decrease slightly but level off at about 92% of what is currently in the Bay. Scenario 2 (blue, 10 kg/year): reducing current loads to 10 kg/year is predicted to result in a 50% reduction of PBDE levels in about 6 years. Scenario 3 (black, 0 kg/year): completely eliminating PBDE loads, if that was possible, would be predicted to result in a 95% reduction of PBDE levels in about 10 years.

FORECASTING THE FUTURE OF PBDES IN SAN FRANCISCO BAY

A Rapid Fall Expected

Results of RMP monitoring of PBDEs in the Bay and its watersheds were incorporated into a computer model to provide insight into where PBDEs end up in the Bay and how long they might persist. The model suggests that the Bay is highly sensitive to changes in PBDE loads. It is plausible that reductions in PBDE loads to the Bay will result in measurable decreases in concentrations in Bay water and sediment. Additionally, the decreases in in-Bay PBDE concentrations are estimated to occur quite rapidly (FIGURE 2). Much of the decrease of in-Bay PBDE concentrations is predicted to occur within 10 years following load reductions. This is in sharp contrast to PCBs, a legacy contaminant that remains problematic 30 years after its use was banned. The difference in response times of PBDEs and PCBs is attributed to the increased susceptibility of PBDEs to chemical and biological degradation.

Toward Better Predictions

Forecast models are valuable tools that can aid Bay managers in understanding the processes controlling the fate of pollutants in the Bay. However, these models are only as accurate as the information put into them. The largest uncertainties in this model of PBDEs are the estimate on Bay-wide PBDE loadings and the estimates of in-Bay degradation. The PBDE model represents a first step in improving our knowledge of PBDEs in the San Francisco Bay and gives water quality managers a framework through which potential management actions can be assessed. The RMP will continue to monitor and model PBDEs in the Bay and its watersheds to meet the needs of water quality managers.



FACES OF THE RMP

A PARTICIPATING SCIENTIST MAKES IMPORTANT CONNECTIONS ACROSS THE AMERICAS

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What do pesticide policies in Central and South America have to do with birds in the U.S.? Quite a bit, according to the Exposure and Effects Workgroup science advisor, Dr. Michael Fry. The RMP is fortunate to have nationally known scientists like Dr. Fry overseeing the work conducted in the RMP. The panel members assure that the Program is using the best science possible. The RMP newsletter is starting a profile series on our science advisors. This month we are highlighting Dr. Fry, a Ph.D. toxicologist who has spent many years studying the effects of chemical contaminants on birds. Dr. Fry has investigated causes of reproductive failure in California condors and has been particularly active in the effort to ban lead based ammunition in condor habitat. Dr. Fry is also an expert on the endocrine disrupting effects of contaminants on birds.

Dr. Fry is director of Conservation Advocacy at the American Bird Conservancy (ABC) in Washington D.C. Previous to ABC, Dr. Fry was a researcher at UC Davis studying the effects of chemical pollutants on birds. Dr. Fry has studied the exposure and effects of many pesticides including DDT on California gulls and burrowing owls. His expertise on contaminant exposure and effects has made important contributions to the development of exposure and effects studies in the RMP.

ABC is an organization that works to 'conserve native wild birds and their habitats throughout the Americas.' Because many birds overwinter in countries that are thousands of miles away from their summer nesting sites, ABC serves an important function by comprehensively addressing use of pesticides and land use throughout the Americas, a crucial step in conserving species and habitat along important bird migratory pathways. ABC has also created the National Pesticide Reform Coalition (NPRC). This consortium of environmental organizations works to evaluate the EPA's pesticide registration process. Dr. Fry and the NPRC have been very active in the EPA's current process to review the pesticide carbofuran, a pesticide that has been associated with bird kills in California and Oklahoma near pesticide application sites. Based on the findings presented during the re-registration process of carbofuran, the EPA has issued a Notice of Intent to Cancel (NOIC) this pesticide.

The advocacy and collaborative work of ABC is crucial in protecting important migratory bird species through the creation and conservation of habitat. Dr. Fry's pesticide work also creates an important linkage between science and policy. Ongoing identification of pesticides of concern and communicating these concerns to the EPA is an effective way of removing toxic pesticides from commercial use. For more information on Dr Fry and ABC's work please go to www.abcbirds.org.



REDUCING POLLUTANTS IN OUR RIVERS, CREEKS, AND BAY

WHAT YOU CAN DO

We are all contributors when it comes to pollutants in our waterways - but we can also be part of the solution. There are many web sites that provide strategies on how you can reduce your impact on our waterways and wild places. You can help reduce pollution by taking these small steps:

- Consider the use of a nontoxic alternative in place of toxic household cleaners (<http://tinyurl.com/4tb68u>)
- Buy rechargeable batteries. Nickel-cadmium batteries are more expensive than alkaline, but can be recharged up to 100 times which saves money in the long run and keeps toxic metals out of the local landfill or incinerator
- Do not use wood preservatives containing creosote, pentachlorophenol, or arsenic
- Never pour or flush oil, antifreeze, or other automotive chemicals down a storm drain or discard them in a careless manner
- Use non-phosphate or very low-phosphate, biodegradable, mild soaps or detergents
- Use low-toxicity pest controls on your gardens and lawns and use chemical pesticides only as a last resort
- Reduce pollutants released from automobiles: carpool, bike, or take public transit to work and for errands
- Never pour fats, oil, or grease down drains, even if you have a garbage disposal. Pour cooking oil and grease into a sealable container with an absorbent such as paper garbage and discard with your other garbage.
- Spread the word about these tips to others.

Read more tips here:

Baywise.ORG - <http://www.baywise.org/>
Our Water Our World - <http://www.ourwaterourworld.org/>





SAVE THE DATE the

**RMP 2008
Annual Meeting**

OCTOBER 7, 2008

**Tuesday, October 7
Oakland Museum
Oakland, CA**



REGIONAL MONITORING PROGRAM
FOR WATER QUALITY IN THE SAN FRANCISCO ESTUARY

*A Cooperative Program Managed and Administered
by the San Francisco Estuary Institute*

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