

2013

A Report of the Regional Monitoring Program for Water Quality in San Francisco Bay

THE PULSE

CONTAMINANTS OF EMERGING CONCERN

OF THE BAY



2013

A Report of the Regional Monitoring Program for Water Quality in San Francisco Bay

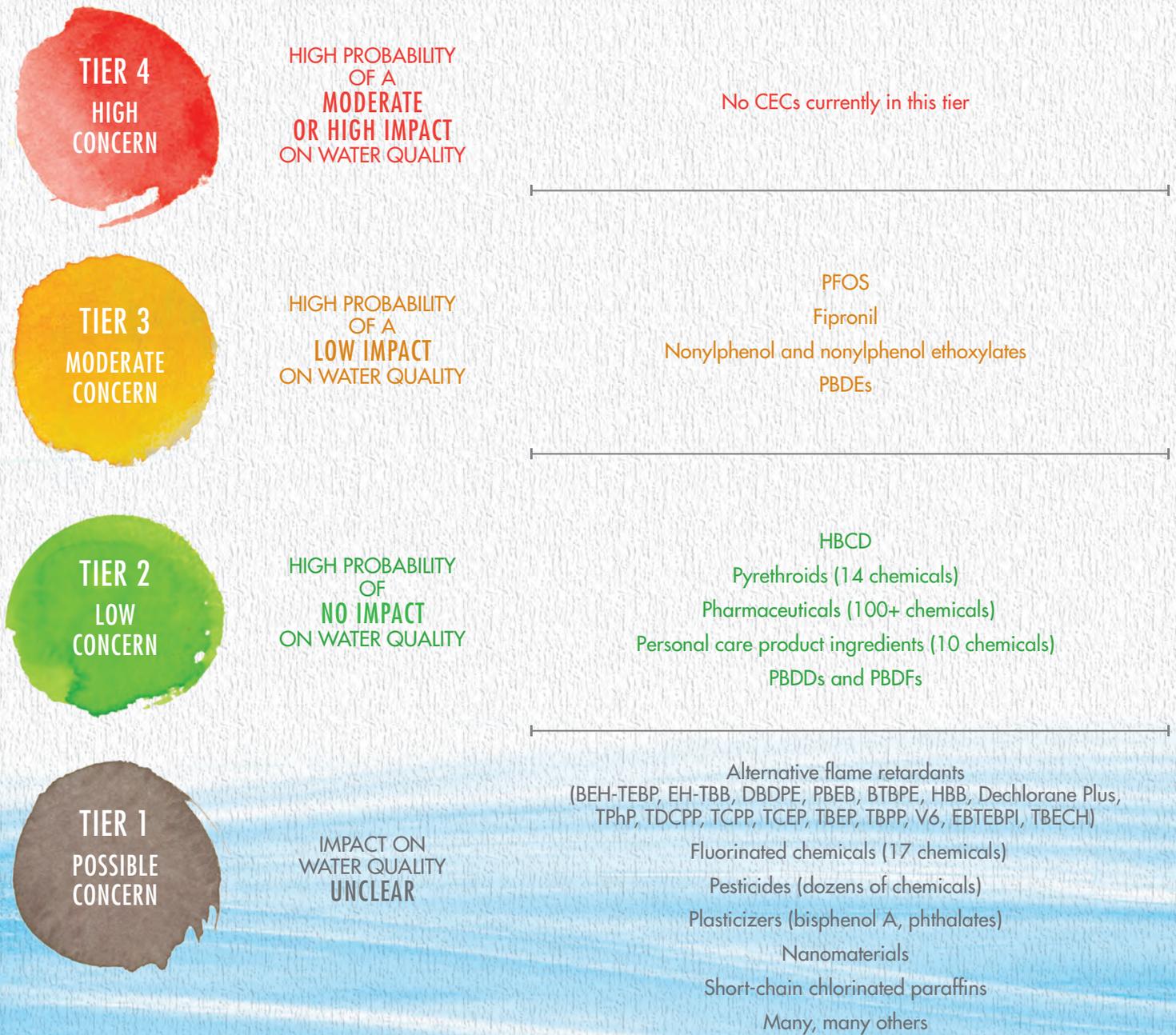
THE PULSE
CONTAMINANTS OF EMERGING CONCERN
OF THE BAY

OVERVIEW

CONTAMINANTS OF EMERGING CONCERN IN SAN FRANCISCO BAY

Society enjoys many benefits from our ingenuity in synthesizing chemicals that enhance our health, food, homes, and the products we use. These chemicals are pervasive in our lives and our economy. An estimated \$700 billion worth of chemistry products flow through the US economy each year (US Department of Commerce 2013). More than 100,000 chemicals have been registered or approved for commercial use in the US, including more than 84,000 industrial chemicals, 9,000 food additives, 3,000 cosmetics ingredients, 1,000 pesticide active ingredients, and 3,000 pharmaceuticals (Muir and Howard 2006, Benotti et al. 2009, USEPA 2013). Global chemical production is projected to continue growing by about 3% per year, and double every 24 years (Wilson and Schwarzman 2009).

Prioritization Scheme for CECs in San Francisco Bay



Although these chemicals generally enhance our lives in many ways, they can sometimes have undesired side effects. Some chemicals escape and persist beyond their intended uses and enter aquatic ecosystems where they pose health threats to aquatic life and to people who consume fish and shellfish. Aquatic organisms in urban water bodies like San Francisco Bay are exposed to a dilute soup of antibiotics, beta blockers, stimulants, pain relievers, lipid reducers, antidepressants, anxiety reducers, hypertension relievers, insect repellents, stain repellents, detergents, flame retardants, insecticides, herbicides, fungicides, rodenticides, lubricants, polymers, plasticizers, nanomaterials, and many other chemicals, not to mention byproducts and degradation products.

Assessing the environmental hazard posed by these thousands of chemicals is a daunting task. It requires information on how they move and persist after they are released to the environment, how potent they are as toxicants, and measurements of their occurrence in ecosystems of interest. For many of these chemicals, assessment of their potential impacts on Bay water quality is severely hampered by the lack of information on the chemicals present in commercial products, their movement in the environment, and their toxicity. Screening of chemical properties and toxicity is currently required for some chemicals, but could be improved and expanded. Many chemicals enter the market despite little to no data on toxicity or environmental impacts. Furthermore, much of the information that does exist is not made available to the public. Measuring chemicals in Bay samples at the low concentrations that can cause toxicity is challenging and often requires customized and expensive analytical chemistry methods. When the identities of the potentially problematic chemicals are not known, it is exceptionally challenging.

When we do have sufficient information on occurrence and toxicity, some of these chemicals can be identified as contaminants of emerging concern, or CECs. A CEC can be defined as any chemical that is not regulated or commonly monitored but that has the potential to enter the environment and cause adverse ecological or human health impacts.

Fortunately, many of the more than 100,000 chemicals in commerce do not pose threats to water quality. Only a small percentage of this universe of chemicals fits the description of a CEC. Furthermore, only a handful of CECs rise to a level of concern corresponding to a real or suspected impact on the quality of the Bay as habitat for aquatic species or as a source of fish and shellfish for human consumption. Early identification of these problem CECs and quick action to nip them in the bud is an optimal and cost-effective strategy for protecting water quality. This is especially true in an ecosystem like the Bay, which is a long-term trap for persistent contaminants, with recovery taking decades or even centuries when the contamination is extensive.

For the past decade the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has been making a concerted effort to identify problem CECs. Bay water quality managers and RMP scientists have developed a tiered scheme for prioritizing CECs that is used to guide decisions on monitoring (PAGE 48) and management (PAGE 3) (PAGE 8). The good news is that, in spite of diligent surveillance, no CECs are presently classified as a high concern, where a severe or moderate impairment of water quality is considered highly probable. A few CECs have risen to a level of moderate concern - including the stain repellent PFOS (PAGE 55), the insecticide fipronil (PAGE 83), the detergent ingredients nonylphenols and nonylphenol ethoxylates (PAGE 59), and the flame retardants known as PBDEs (PAGE 63) - where there is a high probability of a low degree of impairment of water quality. On the other hand, many CECs have been monitored in the Bay and found to be of low concern, where concentrations are well below known thresholds for adverse effects. A multitude of CECs fall into a final category of possible concern, where knowledge of occurrence in the Bay or of effect thresholds are not sufficient to allow assignment into the low, moderate, or high concern tiers.

CEC studies performed by the RMP have been guided by some of the world's leading experts on this subject (PAGE 51), and are chiefly responsible for making the Bay one of the most thoroughly-monitored aquatic ecosystems in the world with respect to CECs. For some chemicals, such as PFOS (PAGE 55) and PBDEs (PAGE 63), Bay monitoring by the RMP and others has revealed contamination that rivals the highest concentrations observed in the world.

Bay monitoring is also providing documentation of what appears to be a prime example of effective CEC management. PBDEs are bromine-containing flame retardants that were practically unheard of in the early 1990s, but increased rapidly in Bay fish and wildlife over the next 10 years to become pollutants of concern. The high and rapidly increasing levels of PBDEs in marine mammals and humans from the Bay Area were particularly alarming, and it seemed that PBDEs could become the next persistent legacy contamination problem for the Bay. In 2004, two of three popular commercial PBDE mixtures, PentaBDE and OctaBDE, were voluntarily phased out by the manufacturer, slightly preceding a California ban that was to take effect in 2006. RMP monitoring over the past 10 years has documented the success of this management action - dramatic reductions have been observed in PBDE concentrations in bivalves, fish, and bird eggs (PAGE 65). In addition, understanding of the toxicity of PBDEs to humans and wildlife has improved, and Bay concentrations are well below the effect thresholds that are now more firmly established for birds and for humans; concern remains, however, for some other Bay species. Through management, monitoring, and improved understanding, PBDEs have shifted from being a contaminant of emerging concern 10 years ago to a contaminant of diminishing concern today.

Preventing water quality impairment from happening, rather than waiting to react once environmental degradation has occurred, is the ideal way to protect the health of the Bay and other aquatic ecosystems. The California Department of Toxic Substance Control's Safer Consumer Products Regulations (PAGE 13) are poised to become an excellent example of this type of management approach.

This edition of the Pulse provides a summary of the current state of knowledge of CECs in the Bay. Profiles of the CECs of greatest concern summarize information on their use, properties, recent findings from monitoring in the Bay and elsewhere, and developments in management.

CEC monitoring is one of the top priorities of the RMP. The RMP and its partners will continue to strive to protect Bay water quality through vigilant surveillance and management of CECs in the years to come. ●

2 OVERVIEW

6 MANAGEMENT UPDATE

8 MANAGEMENT OF CECs IN SAN FRANCISCO BAY

- 13 California Safer Consumer Products Regulations
- 14 Treating CECs in Municipal Wastewater
- 15 Pesticide Management
- 16 Target Organisms and Application Sites of Pesticides with Pathways to San Francisco Bay
- 18 Cradle to Cradle Certified^{CM} Products
- 19 REACH for Safer Chemicals in Europe
- 20 Biomonitoring California Measures Contaminants in Californians
- 22 The Turning Tide
- 23 The 303(d) List and Regulatory Status of Pollutants of Concern

24 STATUS AND TRENDS UPDATE

8 LATEST MONITORING RESULTS

- 26 Nutrients 28 Mercury 31 Selenium
- 32 PCBs 34 PAHs 36 PBDEs

38 WATER QUALITY TRENDS AT A GLANCE

- 38 Toxics and Bacteria 39 Chlorophyll and Dissolved Oxygen
- 40 Nutrients and Sediment 41 Flows and Loads
- 42 Human Presence 43 Climate and Habitat
- 44 Populations 45 Graph Details

46 CEC MONITORING

48 MONITORING CONTAMINANTS OF EMERGING CONCERN IN SAN FRANCISCO BAY

- 51 The RMP Emerging Contaminants Workgroup

54 A GUIDE TO CECs IN THE BAY

- 54 Introduction 55 Perfluorooctane Sulfonate
- 59 Alkylphenols and Alkylphenol Ethoxylates
- 63 Polybrominated Diphenyl Ethers
- 67 Alternative Flame Retardants
- 71 Pharmaceuticals and Personal Care Products
- 75 Triclosan 79 Pyrethroids 83 Fipronil
- 87 Currently Used Pesticides
- 91 Nanoparticles or Nanomaterials
- 92 Chlorinated Paraffins
- 93 Polybrominated Dioxins and Furans
- 94 On the Lookout for New CECs

TIER 4

TIER 3

TIER 2

TIER 1

95 REFERENCES

97 RMP COMMITTEE MEMBERS AND PARTICIPANTS

98 CREDITS AND ACKNOWLEDGEMENTS

Comments or questions regarding *The Pulse* or the RMP can be addressed to Dr. Jay Davis, RMP Lead Scientist, (510) 746-7368, jay@sfei.org

MANAGEMENT UPDATE

8 MANAGEMENT OF CECs IN SAN FRANCISCO BAY

13 California Safer Consumer Products Regulations

14 Treating CECs in Municipal Wastewater

15 Pesticide Management

16 Target Organisms and Application Sites of Pesticides
with Pathways to San Francisco Bay

18 Cradle to Cradle Certified^{CM} Products

19 REACH for Safer Chemicals in Europe

20 Biomonitoring California Measures Contaminants in Californians

22 The Turning Tide

MANAGEMENT OF CECs IN SAN FRANCISCO BAY

TOM MUMLEY and NAOMI FEGER,
San Francisco Bay Regional Water Board
Thomas.Mumley@waterboards.ca.gov

KARIN NORTH,
City of Palo Alto

LORIEN FONO,
Patricia McGovern Engineers

KELLY MORAN,
TDC Environmental

HIGHLIGHTS

The Bay Area regulatory, scientific, and stakeholder community has been proactive in putting together a framework to guide management and monitoring of contaminants of emerging concern (CECs) in San Francisco Bay

The framework is tiered with levels of management and monitoring that correlate with the estimated environmental risk posed by a CEC

Bay Area agencies have been implementing management actions locally and pursuing actions at the federal and state level that are consistent with the framework for more than ten years, including public education and outreach, local ordinances, regulations, and legislation

Polybrominated diphenyl ether (PBDE) flame retardants are one success story, where a phase-out in 2004 and a state ban in 2006 appear to have caused a marked decline in concentrations in the Bay food web

As CEC science continues to advance, we will refine our efforts and improve our strategy for managing CECs, building upon implementation successes and lessons learned

An Ounce of Prevention

Scientific knowledge about contaminants of emerging concern (CECs) in the environment has been accumulating at a rapid rate since the late 1990s. The concern is no longer “can we find them?” since they’ve been shown to be ubiquitous in the aquatic environment; now managers, scientists, and stakeholders are asking “what should we do about them?” There are tens of thousands of potential emerging contaminants, with more continually being introduced, and toxicological research and water quality standards development do not keep up with the rate at which we are finding them in the environment. Additionally, regulatory constraints and barriers pose challenges for management and control of CECs.

The Bay Area regulatory, scientific, and stakeholder community has been proactive in putting together a framework to guide management and monitoring of CECs in San Francisco Bay. This approach, which is the focus of this article, provides a risk-based screening of CECs to identify possible bad actors, and then applies an appropriate management response. The goal is to prevent water quality impairment rather than waiting to react once adverse effects are observed.

A Tiered Framework for Management and Monitoring

The San Francisco Bay Regional Water Board and local agencies (e.g., the Bay Area Pollution Prevention Group), are using information generated by the Regional Monitoring Program (RMP) to inform CEC management strategies, and to adapt our CEC monitoring strategy. Our approach is based on a tiered risk framework (TABLE 1), wherein the type and level of management and monitoring effort correlate with the latest understanding of environmental risk posed by a CEC. The RMP’s Emerging Contaminants Workgroup (PAGE 51) has been a focal point for developing and adapting this approach.

The goal is to prevent CECs from reaching the high-risk tier by implementing the most feasible, cost-effective actions. This prevention-based strategy encompasses the following components to be considered and implemented within the tiered framework.

- Track consumer product and use trends, including new products and new uses for existing products. Rank CECs on the basis of their chemical properties, effects thresholds, and likely or known occurrence in the Bay.
- Track state, national, and international CEC monitoring and management efforts. Identify potential CECs and management strategies to support or preclude local or regional efforts.
- Track trends in occurrence of CECs in the Bay through the RMP.
- Track the loading of CECs through different pathways, such as discharge of municipal wastewater or urban runoff.
- Reduce loading from controllable sources through cost-effective pollution prevention, source control, and treatment strategies.

Overview of the Risk Tiers

The environmental risk tiers and associated monitoring strategies and management actions are described below. Although the tiers are presented as a risk-based hierarchy, the listed monitoring strategies and management actions are not intended to be unique to each tier. Strategies and actions in higher or lower tiers may be implemented depending on the state of knowledge of specific contaminants or categories of contaminants and the cost and feasibility of candidate strategies and actions.

TIER 1 ● POSSIBLE CONCERN

The Tier 1, Possible Concern Risk Level includes contaminants where knowledge is sufficient to merit concern, but significant uncertainties about Bay impacts still exist. Those uncertainties include information about their occurrence in the Bay or uncertainty about the concentration at which they cause adverse impacts. The potential for concern is based on information in the literature, expert knowledge, or data from other geographic locations. The RMP’s Emerging Contaminants Workgroup (PAGE 51) provides an ongoing forum to identify and prioritize CECs of potential concern by tracking national and international efforts and consumer product and product use trends. The Workgroup also develops and oversees studies to determine the presence of

The goal is to prevent water quality impairment rather than waiting to react once adverse effects are observed

CECs in the Bay and potential sources. Key management actions include: 1) development of improved analytical methods and bioanalytical screening methods; 2) identification of potential sources to the Bay; 3) determining potential exposure pathways and toxicity; and 4) identification of easy and low-cost pollution prevention actions for contaminants with product use or market trends that suggest possible increasing occurrence in the Bay.

TIER 2 ● LOW CONCERN

The Tier 2, Low Concern Risk Level includes contaminants where Bay occurrence data are available and indicate that the contaminant is present below effect thresholds. Management actions for Tier 2 chemicals may include no action and no further monitoring for contaminants that we have reasonable confidence will have no increasing trend in Bay occurrence. Alternatively, they may include easy and low-cost source identification and pollution prevention actions for contaminants with use trends that suggest possible increases in the Bay. Use trends would also affect the frequency of further monitoring for occurrence in the Bay or decisions to track trends in wastewater or runoff.

TIER 3 ● MODERATE CONCERN

The Tier 3, Moderate Concern Risk Level includes contaminants that are frequently found at concentrations that are equal to or slightly higher than an effect threshold. A monitoring and management strategy will be developed for each Tier 3 CEC, including consideration of non-regulatory and regulatory actions. The Emerging Contaminants Workgroup will develop and oversee pilot and special studies to evaluate fate, effects, and loadings to inform management decisions. All Tier 3 contaminants will be evaluated to determine whether they become part of routine monitoring in the RMP.

Specific management actions could include aggressive pollution prevention measures or low-cost wastewater or runoff treatment controls. Regulatory actions may include permit requirements and development of water quality objectives. The California Department of Toxic Substance Control's Safer Consumer Products regulatory program (PAGE 13) is poised to become a viable action mechanism for source control. Pesticides will be referred to the US Environmental Protection Agency (USEPA) or the California Department of Pesticide Regulation for action (PAGE 15).

TIER 4 ● HIGH CONCERN

The Tier 4, High Concern Risk Level includes contaminants that occur frequently in the Bay at levels that indicate a high probability of a moderate or high level effect on aquatic life, wildlife, or people. This would likely result in placing the entire Bay, or any affected Bay segments, on the state 303(d) List of impaired waters for these contaminants. Listing would include the development of a Total Maximum Daily Load (TMDL) and implementation plan for the contaminant, or an alternative management plan in lieu of a TMDL that would resolve the impairment. Implementation actions would include aggressive pollution prevention and treatment control actions for all controllable sources including wastewater and runoff to the Bay.

Technical Challenges

The biggest challenges in monitoring and managing CECs are: 1) the ever-increasing number of new chemicals in commerce that have the potential to cause adverse environmental impacts, 2) the lack of water quality standards or adverse effects thresholds to allow for interpretation of exposure levels, and 3) the absence of practical analytical methods to measure many CECs. Thus far, no CECs have been classified in the high concern tier. However, this may be partially explained by the lack of water quality criteria or thresholds for specific chemicals, and a lack of tools to evaluate the potential additive or synergistic effects of multiple contaminants. Consequently, many CECs fall into the possible concern tier, corresponding to an unknown level of risk for the Bay.

	TIER ASSIGNMENTS	MANAGEMENT	MONITORING	
	TIER 4 HIGH CONCERN	No CECs currently in this tier	303(d) listing TMDL or alternative management plan. Aggressive control actions for all controllable sources	Studies to support TMDL or an alternative management plan
	TIER 3 MODERATE CONCERN	PFOS Fipronil Nonylphenol and nonylphenol ethoxylates PBDEs	Action plan or strategy Aggressive pollution prevention Low-cost control actions	Consider including in Status and Trends Monitoring Special studies of fate, effects, and sources, pathways, and loadings
	TIER 2 LOW CONCERN	HBCD Pyrethroids Pharmaceuticals and personal care products PBDDs and PBDFs	Low-cost source identification and control Low-level pollution prevention Track product use and market trends	Discontinue screening, or periodically screen in water, sediment, or biota Periodic screening in wastewater effluent or urban runoff to track trends
	TIER 1 POSSIBLE CONCERN	Alternative flame retardants Pesticides Plasticizers Many, many others	Identify and prioritize contaminants of potential concern, track international efforts Develop targeted and non-targeted analytical methods	Screening in water, sediment, biota, wastewater effluent, urban runoff

TABLE 1
Tiered framework for management and monitoring CECs in San Francisco Bay.

In response to the lack of effects thresholds for the vast majority of CECs, we are participating in an evolving effort to identify chemicals or chemical classes with similar modes or mechanisms of adverse action by developing and testing “bioanalytical” methods. These methods integrate the activity of multiple chemicals into a response based on a single biological mode-of-action, such as endocrine disruption or mutagenicity. These methods may be used in combination with conventional toxicity bioassays based on test organism survival, inhibited reproduction, or inhibited growth that are used extensively. These bioanalytical tools do not supersede the need for chemical-specific thresholds and water quality standards. Rather, if successful, they provide a means of prioritizing chemicals or classes of chemicals for further evaluation.

Taking Action

We have been implementing management actions within the Bay Area and pursuing actions at the federal and state level that are consistent with the tiered framework for more than ten years. The actions include multiple institutional tools that have been successfully used to curb or minimize discharges of CECs to the aquatic environment.

- Public Education and Outreach – Government agencies, non-governmental organizations, and local agency pollution prevention programs can provide information to the public that influences voluntary actions among individuals and groups to curtail the use of products that may pose a risk to the environment.
- Local Ordinances – Municipalities and local agencies can set their own guidelines for which products can be used by their organizations and how they can be used by their workers. They can also control product use by private individuals under some circumstances.
- Regulations – State agencies that oversee classes of products such as pesticides can set regulations that affect which chemicals are available for sale and how they are used. They can also establish a process or requirements for identifying alternatives to chemicals or products that pose risks to consumers and the environment.
- Legislation – State or federal government may ban a chemical or a way of using a chemical.

Examples of some of these actions at the local and state level are described in the following sections.

Wastewater Agency Pollution Prevention Efforts

Bay Area wastewater agencies have teamed up to prevent CEC pollution at the source. Wastewater treatment plants are designed to remove conventional pollutants such as suspended solids, biodegradable organic material, and some toxic pollutants, but they are not designed to remove low concentrations of synthetic organic compounds, which includes most CECs. Fortunately, there are pollution prevention tools that have been successfully used to keep some CECs out of sewer systems, and therefore out of the aquatic environment, avoiding potentially costly end-of-pipe treatment (PAGE 14). The Bay Area Pollution Prevention Group (BAPPG – bacwa.org/committees/bay-area-pollution-prevention-group), a consortium of 43 wastewater agencies, crafts regional outreach messages to reduce the amount of CECs that enter the Bay. As CECs emerge, BAPPG modifies its outreach messages to include new pollutants of concern. Some examples of BAPPG’s efforts on individual CECs are described below.

- Triclosan (PAGE 75) is an antibacterial agent, disinfectant, and fungicide found in certain types of liquid hand soap, toothpaste, cosmetics, and deodorants. The uses of triclosan have increased substantially over the past decade. Triclosan, as well as other antibacterial agents and their degradation byproducts, are now found ubiquitously in the environment, including surface waters, soil, and fish tissue. The BAPPG reviewed scientific literature on the efficacy of triclosan, determined that triclosan was not effective in reducing bacteria during hand washing, and began to deliver that message to the public through agency newsletters and community events. Many BAPPG agencies also led by example and stopped purchasing antibacterial hand soaps that contain triclosan. Since triclosan is a registered pesticide, BAPPG members have also provided comments during the ongoing triclosan registration review process urging the US Environmental Protection Agency (USEPA) to limit the use of triclosan-containing products.
- Nanosilver is currently incorporated into a variety of products that prevent bacterial growth, and its use is on the rise. It is often embedded in sports clothing to

prevent odors and stains, which provides a pathway to the sewer when these articles are washed. Nanosilver has not yet been fully studied to determine its impact on human health or the environment. It is being considered a CEC, even though overall silver concentrations in the Bay are already regulated. The BAPPG collaborated with the Bay Area Water Supply and Conservation Agency to remove the rebate incentive for the Samsung silver ion washing machine to discourage its sale in the Bay Area. Since nanosilver is a pesticide, the BAPPG has also submitted letters to the USEPA and the California Department of Pesticide Regulation (DPR) encouraging them to consider pathways to the aquatic environment in their regulation of nanosilver. BAPPG members are tracking the continuing emergence of these nanoparticles, helping to ensure that any products marketed locally fully comply with federal and state requirements for antibacterial pesticides.

- Pharmaceuticals (PAGE 71) enter the sewer system from excretion of partially-metabolized medications by the human patients who take them and through flushing of unused or expired medications. The BAPPG has been supporting national and statewide groups, specifically the Product Stewardship Institute and the California Product Stewardship Council, that are pursuing producer-responsibility laws that require manufacturers to pay for the disposal of unwanted medications. Since the two largest sources of unused pharmaceuticals entering the sewer system are hospitals and residents, the BAPPG has worked on educating both hospital staff and residents on the proper disposal of pharmaceuticals.
 - o Hospital Outreach - The BAPPG created a California-specific update to the Hospitals for a Healthy Environment’s *Managing Pharmaceutical Waste*, which guides hospitals and clinics on best management practices (BMPs) to handle pharmaceutical waste. The BAPPG hired a national pharmaceutical disposal expert to provide a training class to hospital staff around the Bay Area on the BMPs for proper pharmaceutical disposal.
 - o Residential Outreach - Since 2005, the BAPPG has been actively promoting the need for col-

lection events and permanent pharmaceutical disposal locations for unwanted medications from residents. As a result of BAPPG's 2006 Safe Medicine Disposal Days campaign, more than 100 permanent collection locations have been established in the Bay Area. The BAPPG also supported the successful passage in 2012 of Alameda County's Safe Drug Disposal Ordinance, which requires manufacturers to develop and fund the collection of unwanted medications from residents.

State Regulatory and Legislative Actions

A key component of the regional CEC management strategy is to support state and federal CEC initiatives. Management of CECs is complicated by federal and state rules and regulations that govern production, sales, and use of products. This can result in water quality initiatives being stymied by rules set by other agencies. For example, locally initiated drug take-back programs have been hampered by Federal Drug Enforcement Agency regulations related to the handling of controlled substances. There are also European Union and Canadian initiatives that address emerging contaminants in products that would have a positive benefit if applied here. For example, the European Union requires the submission of environmental risk assessments of the fate and effects of compounds to gain market approval for new pharmaceuticals (PAGE 19). A similar requirement is under development in Canada. In the United States, these types of initiatives have been difficult to implement at the federal and state levels.

There are, however, two notable State initiatives, by the DPR and the Department of Toxic Substances Control (DTSC), that have key roles in governing use and disposal of products.

- DPR promulgated regulations in 2012 to prevent surface water contamination by pesticides used in outdoor non-agricultural (e.g., urban) settings. This is part of an evolving effort to manage urban pesticides that can adversely affect water quality (PAGE 15).

- DTSC is developing Safer Consumer Products Regulations that will require manufacturers to consider alternatives to a subset of specifically identified toxic chemicals contained in products (PAGE 13). However, these regulations exclude products already regulated by other entities, such as prescription medications and pesticides.

Legislation can be an effective means to target CECs when the weight of evidence suggests that a particular chemical is harmful. However, legislation is challenging, and even if successful, can take years to enact and additional years to go into effect. One success story is that of polybrominated diphenyl ether (PBDE) flame retardants, a class of compounds that bioaccumulate in the food web (PAGE 63). Many forms of PBDEs are considered potential endocrine disruptors and are found throughout San Francisco Bay. Two commercial PBDE mixtures, PentaBDE and OctaBDE, were banned by the California legislature in 2003. The ban was to take effect in 2006, but manufacturers voluntarily phased these mixtures out by 2004, and we have since observed decreasing concentrations in the Bay. However, this good news is tempered by observations of replacement flame retardants in the Bay (PAGE 67), and legislative efforts to address them have not been successful.

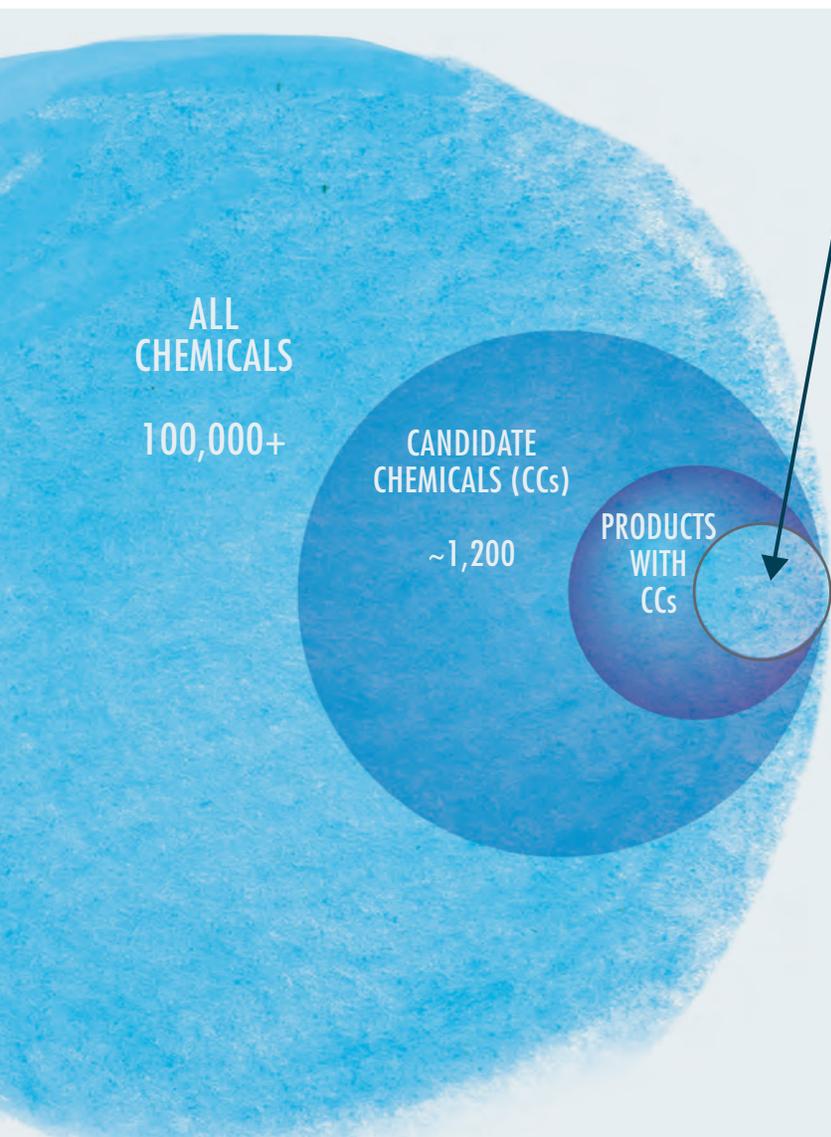
A major shortcoming of chemical by chemical legislative bans is that a ban on one chemical can lead to the use of a potentially harmful replacement chemical. This underscores the purpose of green chemistry initiatives, like the DTSC Safer Consumer Products Regulations, to address this issue by requiring an alternatives assessment as a necessary component of phasing out a chemical's usage. Also, when regulations drive the use of toxic chemicals, as in the case of the flammability standards for household furnishing (PAGE 66), there is also the opportunity to review those regulations and assess whether they can be revised. California is doing just that. The California Bureau of Home Furnishings has been directed to revise existing flammability standards and recommend changes to reduce the use of toxic flame retardants while maintaining the fire safety of products.

The Future

As emphasized throughout this article, the goal is to prevent CECs from reaching levels that can cause adverse impacts in San Francisco Bay. As CEC science continues to advance, we will refine our efforts and improve our strategy for managing CECs, building upon implementation successes and lessons learned. At a minimum, our actions will include the following elements.

- Continuing to implement and improve the San Francisco Bay CEC management strategy and working proactively to reduce the likelihood that any CEC presents a high risk.
- Continuing to proactively identify and investigate possible CECs and collect the necessary information to make informed management decisions about CECs of moderate risk.
- Beginning to test and implement bioanalytical tools to advance understanding of effects due to CECs and legacy contaminants in San Francisco Bay.
- Working with state and federal agencies to prevent or limit the use of CECs that could cause harm to the aquatic environment.

California Safer Consumer Products Regulations



PRIORITY PRODUCTS AND THEIR COCs

- Alternatives Analyses
- Regulatory Response(s) for selected Alternative and/or Priority Product

A Candidate Chemical (CC) is a chemical that is a candidate for designation as a Chemical of Concern.

Each Candidate Chemical exhibits one or more hazard traits and/or environmental or toxicological endpoints.

The Candidate Chemicals that will be evaluated for development of the first Priority Products List will be ~230 chemicals that have both listed hazard traits and listed exposure concerns.

A Chemical of Concern (COC) is a Candidate Chemical that is the basis for a product-chemical combination being listed as a Priority Product.

The California Safer Consumer Products Regulations (www.dtsc.ca.gov/SCPRegulations.cfm) should help reduce CECs in the Bay. These regulations will establish a process to evaluate whether there are safer alternatives to a chemical of concern in a product, and to allow the Department of Toxic Substance Control (DTSC) to implement appropriate controls. In simple terms, the regulations require a manufacturer whose consumer product contains a chemical of concern to ask: Is this ingredient necessary? Is there a safer alternative? Is that alternative ingredient feasible? In addition, by listing the chemicals that the State will be examining in consumer products, manufacturers will have the opportunity to eliminate the use of those chemicals ahead of a regulatory action.

The regulations establish a list of Candidate Chemicals (approximately 1,200) and specify a process for the California DTSC to identify additional Candidate Chemicals that exhibit one or more hazard traits. They require DTSC to evaluate and prioritize product/Candidate Chemical combinations to develop a list of "Priority Products" for which alternatives analyses must be conducted. The first Priority Products List will be developed using approximately 230 Candidate Chemicals that have a combination of listed hazard traits and exposure concerns. Manufacturers (or other responsible entities) of a product listed as a Priority Product must perform an alternatives analysis for the product and the chemical(s) of concern in the product to determine how best to limit exposures to, or the level of adverse public health and environmental impacts posed by, the chemical or chemicals of concern in the product.

Ultimately, the regulations require DTSC to identify and require implementation of regulatory responses (e.g., product information for consumers, use restrictions, or product sales prohibitions) designed to protect public health and the environment, and to maximize the use of acceptable and feasible alternatives of least concern. DTSC may require regulatory responses for a Priority Product (if the manufacturer decides to continue using the chemical of concern in its product).

Source: Department of Toxic Substances Control, January 2013

Treating CECs in Municipal Wastewater

Many CECs, including pharmaceuticals and personal care products, have been detected at low levels in treated municipal wastewater.

Traditional wastewater treatment processes remove CECs to some degree, depending on their chemical properties (e.g., affinity for particles) and biodegradability. These properties influence whether a CEC will remain in water (like many pharmaceuticals) or be removed with wastewater solids and sludge (e.g., certain antibiotics). Wastewater disinfection processes using chlorine can reduce concentrations of certain CECs. Treatment targeted at nutrient removal (e.g., nitrification) has

been shown to enhance the removal of some CECs. Additional removal can be obtained via chemical oxidation (e.g., effluent ozonation), which is a means of enhancing breakdown of the organic matter in wastewater. Engineered treatment wetlands can also remove CECs from wastewater through processes such as microbial degradation and degradation caused by exposure to sunlight. Efforts to implement wastewater treatment improvements to remove CECs must consider various challenges. Obviously, capital and operating costs increase with the level of treatment provided, but there are other consequences of enhanced levels of treatment. For example, advanced treatment approaches can be very energy-intensive and increase carbon dioxide emissions, resulting in carbon footprint and climate change implications. In addition, some treatment processes convert CECs to degradation products whose toxicological properties and environmental persistence are not well known. These ramifications need to be weighed with the desired benefit of keeping CECs out of the Bay. The optimum treatment improvements will be those that remove multiple CECs or remove CECs along with other pollutants. More treatment process research, advances in treatment technology, and improvements in our knowledge of CECs in the Bay and wastewater as a source of CECs are needed to better inform decisions on wastewater treatment of CECs.



Pesticide Management

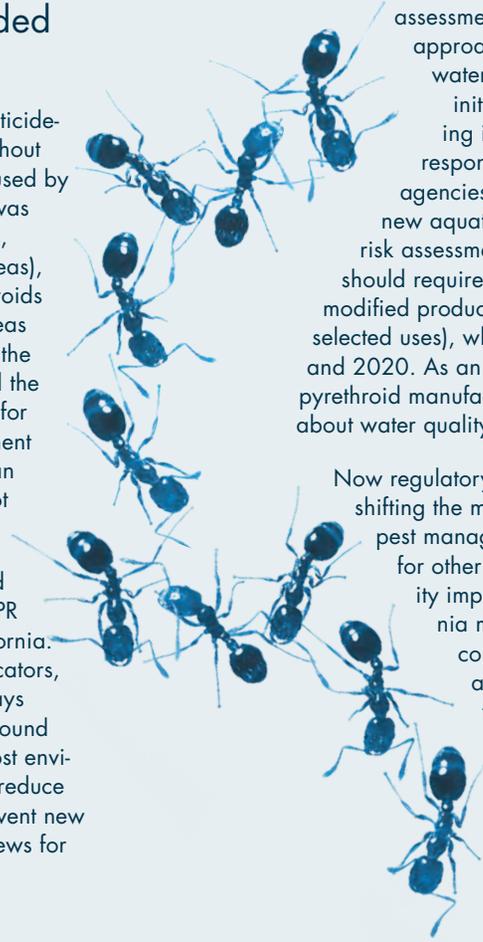
California water quality monitoring data have revealed previously unrecognized gaps in pesticide regulatory review procedures intended to prevent water pollution.

In recent years, numerous studies have documented the presence of pesticide-caused toxicity in both water and sediment in rivers and streams throughout California, particularly in urban watersheds, and almost exclusively caused by currently used pesticides (PAGE 79-90). In many locations toxicity that was caused by organophosphate pesticides (e.g., diazinon and chlorpyrifos, formerly the most commonly applied insecticides in California urban areas), has been replaced by toxicity caused by pyrethroids (PAGE 79). Pyrethroids became the most commonly applied insecticides in California urban areas after most urban uses of diazinon and chlorpyrifos were phased out by the US Environmental Protection Agency (USEPA) in 2004. Both USEPA and the California Department of Pesticide Regulation (DPR) have responsibility for regulating pesticides and must consider adverse effects on the environment in their review of pesticides. However, the procedures used to identify an adverse effect under pesticide law allow acceptance of risks that are not consistent with the Clean Water Act and the California Water Code.

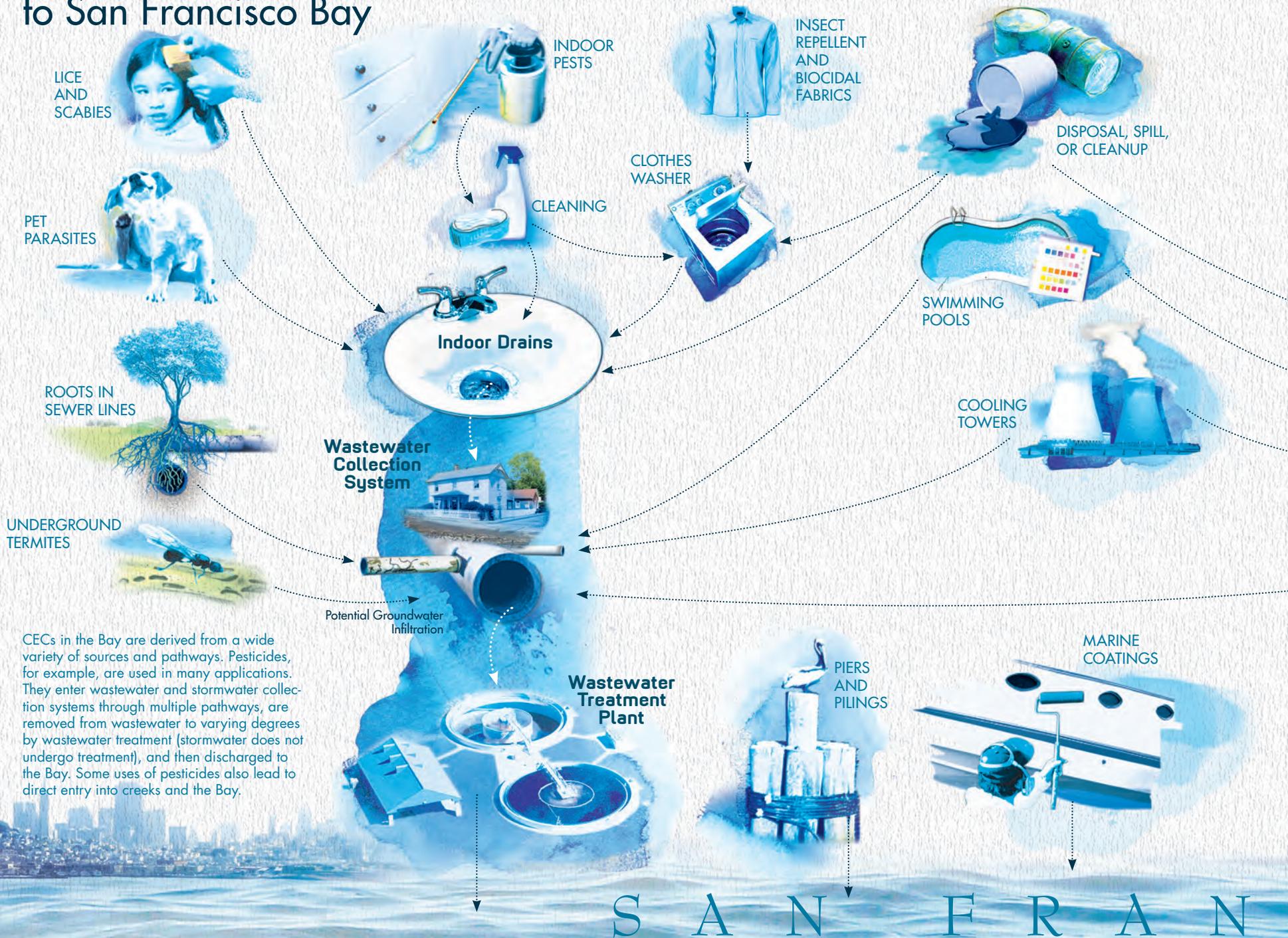
In response, Bay Area municipal stormwater management agencies and wastewater treatment plants joined together to work with USEPA and DPR toward the goal of eliminating pesticide-related water pollution in California. This multi-agency collaboration, which also included professional applicators, led to landmark regulations enacted by DPR in 2012 that restrict the ways professional applicators are allowed to apply pyrethroid insecticides around buildings. Together with special restrictions placed on bifenthrin (the most environmentally persistent pyrethroid), the new regulations are expected to reduce pyrethroid-caused toxicity by 80-90%. In 2012, DPR also moved to prevent new water pollution by eliminating procedural gaps in its surface water reviews for new pesticides.

There are also improvements at the federal level. Recognizing that a key regulatory gap stemmed from programmatic differences between its separate Pesticides and Water Offices, in 2009, USEPA began developing a common "effects assessment methodology" to establish a consistent approach for defining when pesticides are causing water pollution. From 2009 to 2012, USEPA initiated reviews of all pyrethroids, advancing its regularly scheduled periodic reviews in response to input from California water quality agencies. The reviews now involve generation of new aquatic toxicity data, preparation of detailed risk assessments, and decisions as to whether USEPA should require nationwide risk mitigation actions (e.g., modified product application instructions, discontinuing selected uses), which would be implemented between 2016 and 2020. As an interim measure, in 2009, USEPA asked pyrethroid manufacturers to voluntarily place user instructions about water quality protection on product labels.

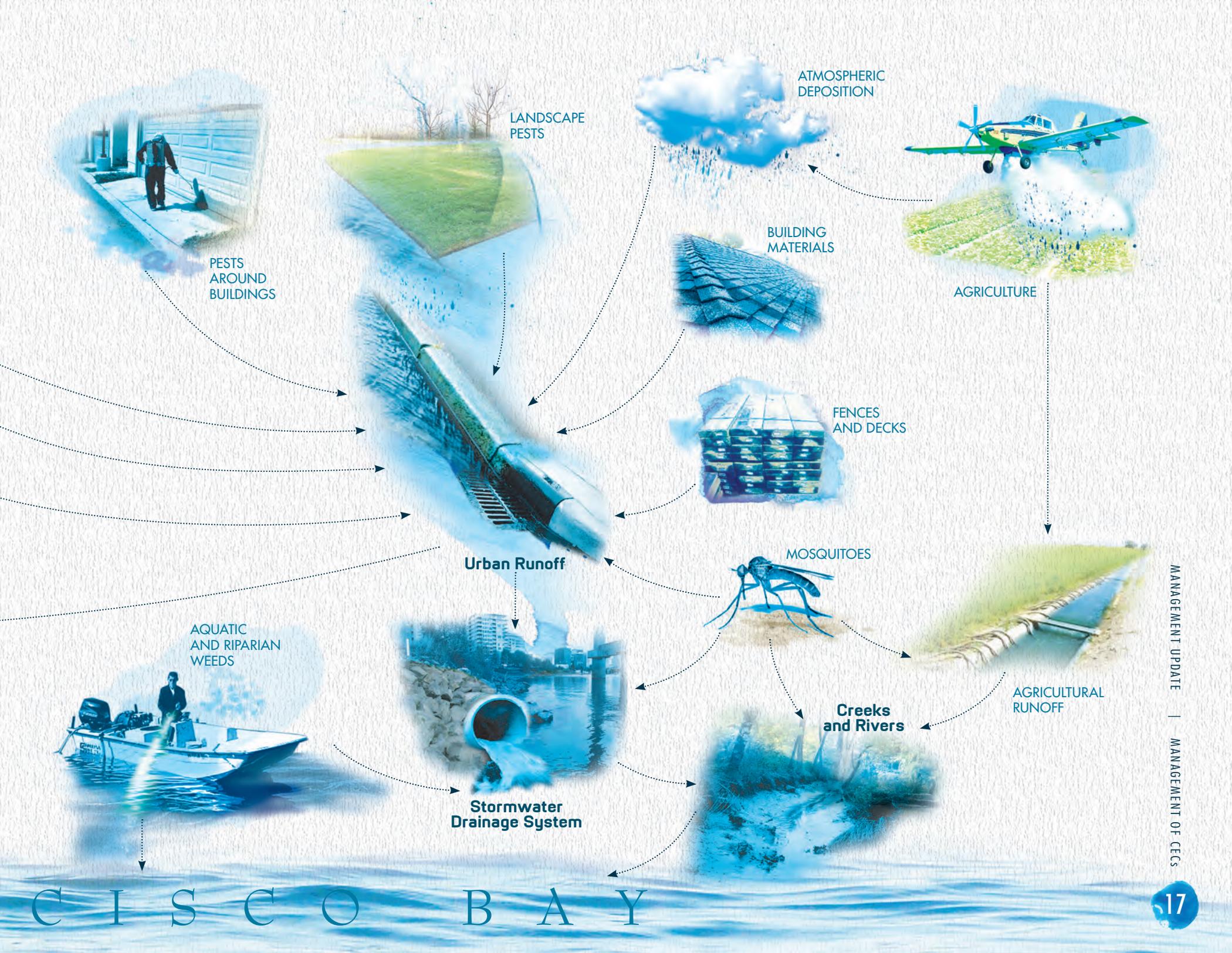
Now regulatory actions addressing pyrethroids are again shifting the market, creating opportunities for less toxic pest management, but also creating a growing market for other insecticides associated with water quality impacts, such as fipronil (PAGE 83). California monitoring data show rapidly increasing concentrations of fipronil, a reminder that additional work will be needed to end pesticide-related toxicity in urban watersheds, to prevent a transition to other harmful products, and to achieve the ultimate goal of ensuring that pesticides do not harm San Francisco Bay and aquatic ecosystems in the Bay watershed.



Target Organisms and Application Sites of Pesticides with Pathways to San Francisco Bay



CECs in the Bay are derived from a wide variety of sources and pathways. Pesticides, for example, are used in many applications. They enter wastewater and stormwater collection systems through multiple pathways, are removed from wastewater to varying degrees by wastewater treatment (stormwater does not undergo treatment), and then discharged to the Bay. Some uses of pesticides also lead to direct entry into creeks and the Bay.



Cradle To Cradle Certified^{CM} Products

SUSAN KLOSTERHAUS, susan@c2ccertified.org, Cradle to Cradle Products Innovation Institute

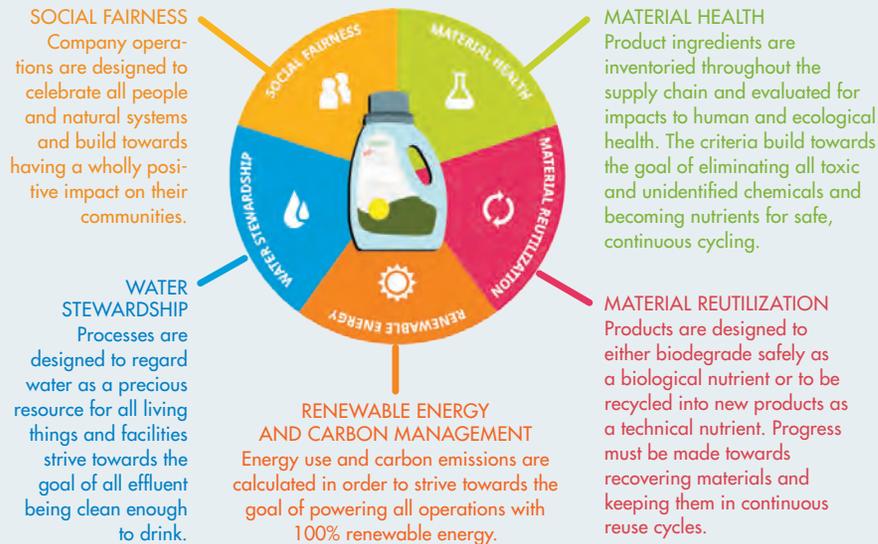


Cradle to Cradle Certified^{CM} is a certification mark licensed exclusively for the Cradle to Cradle Products Innovation Institute.

One solution for the continued accumulation of hazardous chemicals in the environment and people is adoption of the Cradle To Cradle Certified^{CM} Product Standard, a systematic approach to product innovation that is spurring a global paradigm shift in the way products are made. By committing to meet the requirements for certification, designers and manufacturers are making products that not only contain chemicals that are safer for people and the environment, but products that can also be recycled for future uses and are manufactured using responsible practices.

The product certification standard is based on the design principles outlined in the 2002 book, 'Cradle to Cradle: Remaking the Way We Make Things' by William McDonough and Michael Braungart: eliminate the concept of waste, use renewable energy, and celebrate diversity.

The materials and manufacturing practices of each product are assessed in five categories



The Cradle to Cradle^{CM} Products Program rates products across five critical quality categories and recognizes achievement and a commitment to continual improvement with five award levels.

Product certification is awarded at five levels in version 3.0 of the standard (Basic, Bronze, Silver, Gold, Platinum), with each higher level addressing a more rigorous set of requirements. Continued participation in the program requires that manufacturers commit to meeting higher and higher levels of certification over time, thus committing to continuous improvement of their products and manufacturing processes. By providing this pathway for improvement, the certification standard encourages innovation and the design of products that effectively and positively impact people and the environment.

Products that meet the requirements of the standard are awarded use of the Cradle to Cradle certification mark, indicating their commitment to sustainability.

The Cradle to Cradle design framework was originally created by McDonough Braungart Design Chemistry, LLC (MBDC) in cooperation with EPEA Internationale Umweltforschung GmbH, and has been developed and practiced over the past 20 years. Since product certification began in 2005, more than 125 companies have adopted the Cradle to Cradle approach. Over 400 product certifications (both individual products and product lines representing several products) have been issued in product categories including building materials, interior design, textiles and fabrics, paper and packaging, and personal and homecare. Participating companies include Puma, Steelcase, Herman Miller, Shaw Industries, Aveda, Method, and a government leader, the United States Postal Service.

The Cradle to Cradle Products Innovation Institute, an international non-profit organization co-founded by William McDonough and Michael Braungart in San Francisco, is working to scale up the adoption of the Cradle to Cradle Certified Product Standard by manufacturers and designers. For more information, please visit <http://www.c2ccertified.org/>

REACH for Safer Chemicals in Europe

NICOLE DAVID, San Francisco Estuary Institute (nicole@sfei.org)

In 2006, the European Union adopted a regulation to improve the protection of human health and the environment from the risk that can be posed by chemicals. REACH stands for registration, evaluation, authorization, and restriction of chemicals and provides the legislative framework for the disclosure of detailed information on the safe handling and use of chemicals. With chemical sales in the European Union amounting to nearly \$460 billion in 2007 (about 30% of global chemical sales) this change in regulation was extremely important. It gave rise to one of the most intense lobbying battles in the history of the European Union, pitting green campaign managers against the powerful chemical industry. But the benefits of REACH are gradually being realized as more and more chemicals are being regulated and chemicals are being effectively assessed and controlled, resulting in a safer environment. The European Commission already considers chemicals significantly safer for workers, consumers, and the environment due to new information on uses and properties of the chemical substances that are placed on the market. Despite the costs associated with the implementation of REACH, a positive economic effect has been reported due to innovation and enhanced competition in the chemical industry.

REACH places the burden of proof on manufacturers and importers. These companies are required to submit information on the properties of each chemical and chemical mixture they produce. The information is stored in a central database run by the European Chemicals Agency (ECHA) in Helsinki, Finland. ECHA coordinates in-depth evaluations of the chemical data and maintains a public database with hazard information. The first goal was to evaluate a smaller number of 'substances of very high concern' that are suspected of causing cancer or disturbing the human reproductive system. A progressive substitution of dangerous chemicals is enforced, and risk management measures for the safe use of chemicals are communicated. Until 2018, when the regulatory phase-in of substances (registration windows for chemicals according to their production volume) is expected to be completed, REACH seeks to improve the early identification of harmful chemicals and the integration with international efforts. In 2010, the ministry of environmental protection in China brought into force a very similar regulation, also known as 'China REACH', that will facilitate import and export agreements between the EU and China.

As a result of REACH, the European Commission proposed to add 15 chemicals to the Watch List of 33 chemicals that are monitored and controlled in European surface waters. Chemicals on this priority substances list are regularly monitored to assure concentrations stay below standards (effect levels for aquatic life) and emissions into water will be phased out over the next 20 years. For the first time, three pharmaceuticals were included on the priority substances list. The popular pain-killer diclofenac is one of them. Additionally, six chemicals have been banned, and unless a specific exemption is obtained, companies are not able to sell items containing banned chemicals. This approach is an important advance in improving water quality in rivers, lakes, and coastal waters in the European Union.

WATER WATCH LIST (2009)

Alachlor
Anthracene
Atrazine
Benzene
Brominated diphenyl ether: Pentabromodiphenyl ether (congener numbers 28, 47, 99, 100, 153, and 154)
Cadmium and its compounds
Chloroalkanes, C10-13
Chlorfenvinphos
Chlorpyrifos
1,2-Dichloroethane
Dichloromethane
Bis(2-ethylhexyl)phthalate (DEHP)
Diuron
Endosulfan
Fluoranthene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclohexane
Isoproturon
Lead and its compounds
Mercury and its compounds
Naphthalene
Nickel and its compounds
Nonylphenols (4-nonylphenol)
Octylphenols: (4-(1,1',3,3'-tetramethylbutyl)-phenol)
Pentachlorobenzene
Pentachlorophenol
Polycyclic aromatic hydrocarbons: Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene
Simazine
Tributyltin compounds (Tributyltin-cation)
Trichlorobenzenes
Trichloromethane (Chloroform)
Trifluralin

Link for REACH introduction: http://ec.europa.eu/environment/chemicals/reach/reach_en.htm

Link for priority substances in the field of water policy: http://ec.europa.eu/environment/water/water-framework/priority_substances.htm

ADDED (2012)

Aclonifen
Bifenox
Cypermethrin
Dicofol
Heptachlor
Quinoxifen
Cybutryne
Dichlorvos
Terbutryn
Perfluorooctane sulfonate (PFOS)
Hexabromocyclododecane (HBCDD)
Dioxin and Dioxin-Like PCBs
17 alpha-ethinylestradiol (EE2)
17 beta-estradiol (E2)
Diclofenac

BANNED

DEHP (phthalates)
BBP (phthalates)
DBP (phthalates)
musk xylene (fragrance)
HBCD (flame retardant)
MDA (epoxy resin-hardener)

TO BE BANNED BY 2017

DIBP (phthalates)
Diarsenic trioxide (decolorizing agent)
Diarsenic pentoxide (dye)
Lead chromate molybdate sulfate red (paint additive)
Lead sulfochromate yellow (paint additive)
Lead chromate molybdate sulfate red (paint additive)
TCEP (flame retardant)
2,4-DNT (plasticizer)
Ammonium dichromate (dye)
Potassium chromate (dye)
Acids generated from chromium trioxide and their oligomers
Chromium trioxide (electroplating)
Potassium dichromate (dye)
Sodium chromate (corrosion inhibitor)
Sodium dichromate (dye)
Trichloroethylene (solvent)

Biomonitoring California Measures Contaminants in Californians

By measuring chemicals in body fluids, such as blood or urine, scientists can determine the levels of contaminants that get into people from all sources (e.g., air, soil, water, dust, and food) combined. These “biomonitoring” investigations can provide useful information on exposure to toxic chemicals.

The California Environmental Contaminant Biomonitoring Program (also known as Biomonitoring California) was established in 2006 by Senate Bill 1379 (Perata and Ortiz). The legislation set forth three main goals: a) determine levels of environmental chemicals in a representative sample of Californians; b) establish trends in the levels of these chemicals over time; and c) help assess the effectiveness of public health efforts and regulatory programs to decrease exposures to specific chemicals.

The Program is a collaboration among three state departments: The California Department of Public Health (CDPH), the Office of Environmental Health Hazard Assessment (OEHHA) and the Department of Toxic Substances Control (DTSC). CDPH is the lead department for the Program.

A panel of experts, the Scientific Guidance Panel (SGP), helps guide the Program's design and implementation. The SGP recommends which chemicals to prioritize for biomonitoring in California, based on concerns for potential human exposure and adverse health effects.

Biomonitoring California's priority chemicals list, updated in May 2013, includes a number of Bay CECs:

- PFOS and other perfluorochemicals (PAGE 55);
- PBDE flame retardants (PAGE 63) and their metabolites;
- many alternative flame retardants (PAGE 67);

- some chemicals found in personal care products (PAGE 71), including phthalates, parabens, and cyclosiloxanes;
- some chemicals in other consumer products, such as bisphenol A (PAGE 71) and related compounds
- the antibacterial chemical triclosan (PAGE 75), and
- pyrethroids (PAGE 79) and many other pesticides (PAGE 87).

Other priority chemicals include:

- diglycidyl ethers of bisphenols (used to line food cans);
- polychlorinated biphenyls (PCBs; legacy contaminants once widely used in the electrical industry and banned in 1979) (PAGE 32);
- polycyclic aromatic hydrocarbons (PAHs; air pollutants typically produced by burning fossil fuels) (PAGE 34);
- perchlorate (rocket fuel component and drinking water contaminant);
- diesel exhaust;
- tobacco smoke; and
- metals like arsenic, cadmium, lead, and mercury (PAGE 28).

While California's budget woes have prevented full implementation of Biomonitoring California's goal of analyzing contaminant levels in a representative sample of Californians, the Program's scientists have developed analytical methods for detecting a large number of environmental contaminants in blood and urine. Biomonitoring California has undertaken several collaborative biomonitoring projects.

- The Maternal Infant Environmental Exposure Project (MIEEP) – This project is measuring environmental chemical exposures in 65 maternal-infant pairs and an additional 27 pregnant women, recruited from San Francisco General Hospital. The study is being conducted in collaboration with the University of California (UC)

REBECCA SUTTON, San Francisco Estuary Institute, (rebeccas@sfei.org)

San Francisco's Program on Reproductive Health and the Environment and the UC Berkeley School of Public Health. The goals of the project include identifying sources of toxic exposures and developing methods for communicating biomonitoring results to participants.

- Firefighter Occupational Exposures (FOX) – This study is measuring environmental chemical exposures in 101 Orange County firefighters. It is being conducted in collaboration with UC Irvine's Center for Occupational and Environmental Health and the Orange County Fire Authority.
- The Biomonitoring Exposures Study (BEST) – This is a pilot study of 112 adults in the Central Valley, conducted in collaboration with Kaiser Permanente Northern California. This is the first Biomonitoring California study to collect samples from participants randomly selected across gender, age, race/ethnicity, and location.

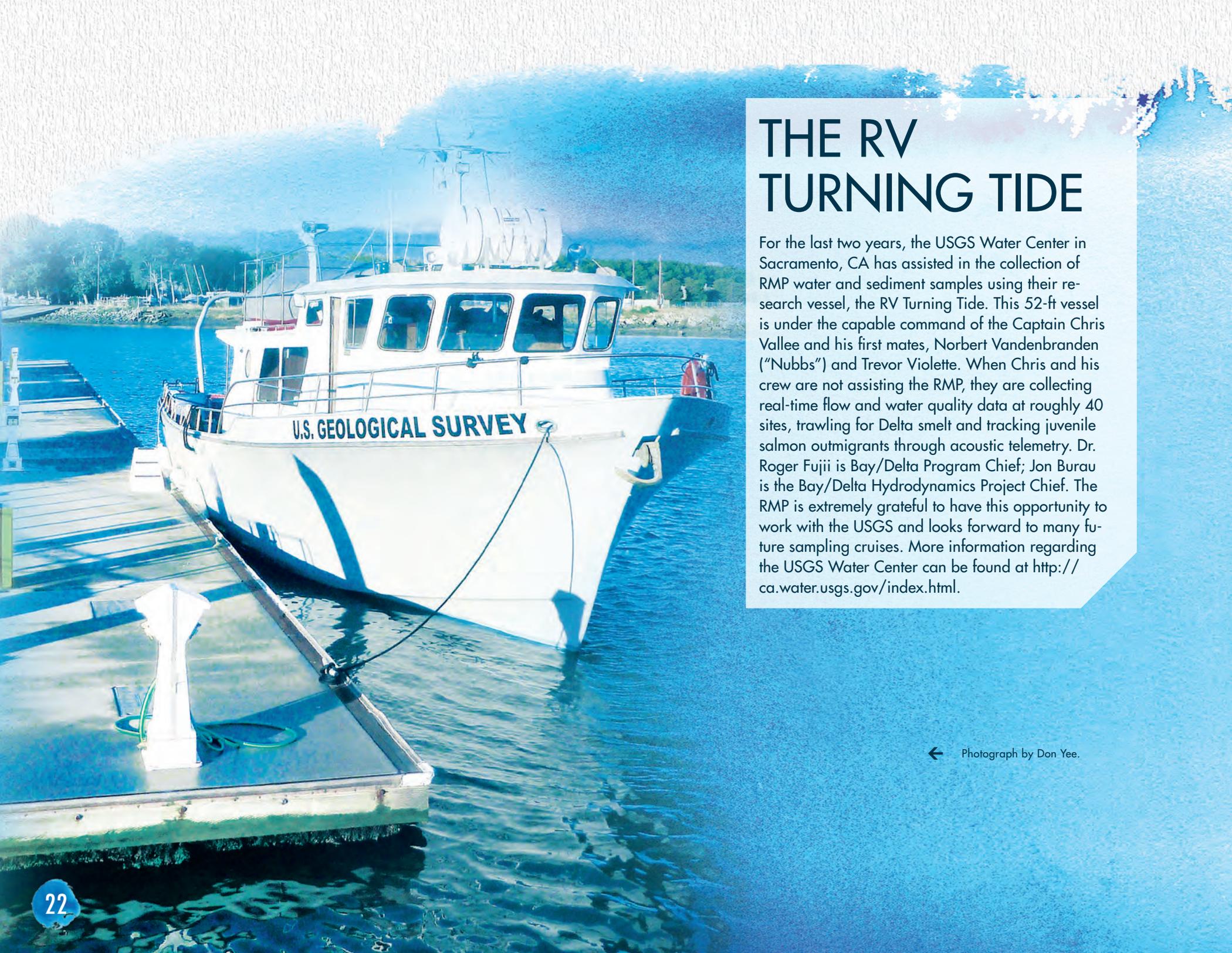
Even with the currently limited funding, these Biomonitoring California projects are already helping scientists and policymakers answer such questions as:

- Which chemicals are in people's bodies and how high are the levels?
- Are the levels of chemicals changing over time?
- Are there groups or populations in California that have higher exposures to certain chemicals?
- Do regulatory efforts, including bans or phase-outs of chemicals, actually reduce exposures among Californians?

For more information about Biomonitoring California, visit www.biomonitoring.ca.gov



Photograph courtesy of Biomonitoring California. →



THE RV TURNING TIDE

For the last two years, the USGS Water Center in Sacramento, CA has assisted in the collection of RMP water and sediment samples using their research vessel, the RV Turning Tide. This 52-ft vessel is under the capable command of the Captain Chris Vallee and his first mates, Norbert Vandenbranden (“Nubbs”) and Trevor Violette. When Chris and his crew are not assisting the RMP, they are collecting real-time flow and water quality data at roughly 40 sites, trawling for Delta smelt and tracking juvenile salmon outmigrants through acoustic telemetry. Dr. Roger Fujii is Bay/Delta Program Chief; Jon Burau is the Bay/Delta Hydrodynamics Project Chief. The RMP is extremely grateful to have this opportunity to work with the USGS and looks forward to many future sampling cruises. More information regarding the USGS Water Center can be found at <http://ca.water.usgs.gov/index.html>.

← Photograph by Don Yee.

THE 303(D) LIST

Section 303(d) of the 1972 Federal Clean Water Act requires that states develop a list of water bodies that do not meet water quality standards, establish priority rankings for waters on the List, and develop action plans, called Total Maximum Daily Loads (TMDLs), to improve water quality.

The list of impaired water bodies is revised periodically (typically every two years). The RMP is one of many entities that provide data to the State Water Board to compile the 303(d) List and to develop TMDLs.

The primary pollutants/stressors for the Estuary and its major tributaries on the current 303(d) List include:

Trace Elements

Mercury and Selenium

Pesticides

Dieldrin, Chlordane, and DDT

Other Chlorinated Compounds

PCBs, Dioxin and Furan Compounds

Others

Exotic Species, Trash, and Polycyclic Aromatic Hydrocarbons (PAHs)

REGULATORY STATUS OF POLLUTANTS OF CONCERN

POLLUTANT	STATUS
Copper	Site-specific objectives approved for entire Bay San Francisco Bay removed from 303(d) List in 2002
Dioxins / Furans	TMDL in early development stage
Legacy Pesticides (Chlordane, Dieldrin, and DDT)	Under consideration for delisting
Mercury	Bay TMDL and site-specific objectives approved in 2008 Guadalupe River Watershed TMDL approved in 2010
Pathogens	Richardson Bay TMDL adopted in 2008 Bay beaches (multiple listings); TMDL in early development stage
PCBs	TMDL approved in 2009
Selenium	TMDL in development – completion projected for 2014/2015
Trash	Central and South Bay shorelines added to the 2010 303(d) List

Approved: State Water Board and USEPA approval

← Photograph by Elaine Bond.

STATUS AND TRENDS UPDATE

8 LATEST MONITORING RESULTS

26 Nutrients 28 Mercury 31 Selenium

32 PCBs 34 PAHs 36 PBDEs

38 WATER QUALITY TRENDS AT A GLANCE

38 Toxics and Bacteria 39 Chlorophyll and Dissolved Oxygen

40 Nutrients and Sediment 41 Flows and Loads

42 Human Presence 43 Climate and Habitat

44 Populations 45 Graph Details

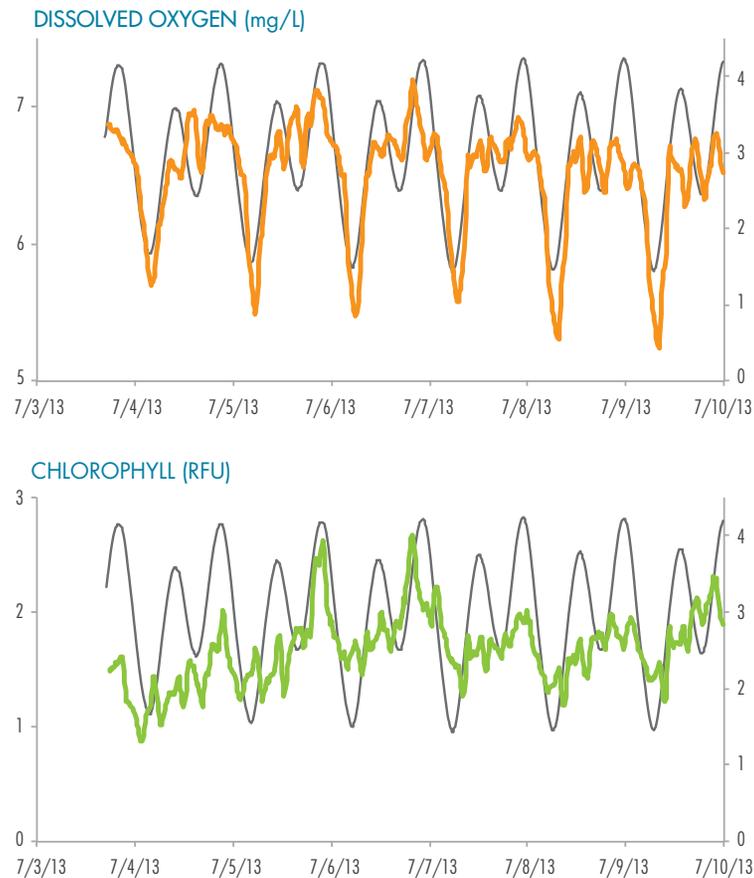
LATEST MONITORING RESULTS

Nutrients

There is a growing body of evidence, including increases in phytoplankton biomass and declines in dissolved oxygen, that suggests the historic resilience of the Bay to the harmful effects of nutrient enrichment is weakening. The complexity of the ecosystem, uncertainty about future conditions, and the potentially great cost of reducing nutrient inputs underlie the importance of nutrient and phytoplankton monitoring, research, and modeling.

A New Chapter in RMP Water Monitoring

Concerns about high nutrient loads to San Francisco Bay, and recent observations of the Bay's changing response to nutrients (see PAGE 48 of the 2011 PULSE), have led regulators and stakeholders to collaboratively develop a Nutrient Strategy (<http://bayareanutrients.aquaticscience.org/>) for San Francisco Bay to inform important and potentially costly management decisions related to prevention of problematic levels of phytoplankton growth. As an early step in implementation of the Nutrient Strategy, the RMP funded a nutrient conceptual model report (Senn et al. 2013) that described the current state of the science and identified priority science needs. One of



Dissolved oxygen reaches a daily minimum at lowest tide

Chlorophyll fluctuates with the tides due to the movement of different water masses past the sensor

the report's recommendations was to develop a network of continuous monitoring stations at key locations in the Bay to complement the current ship-based monitoring program. These stations can provide high temporal resolution water quality data to: 1) identify the onset of events (e.g., large phytoplankton blooms); 2) improve understanding about the processes that influence phytoplankton blooms and other nutrient-related responses; 3) assess oxygen budgets; and 4) provide high temporal resolution data to calibrate water quality models.

San Francisco Estuary Institute staff collaborated with USGS staff from Menlo Park and Sacramento to install a RMP-funded continuous monitoring station at the Dumbarton Bridge on July 3, 2013. Water quality sensors at the Dumbarton station measure multiple parameters:

temperature, salinity, dissolved oxygen, pH, turbidity, fluorescent dissolved organic matter (a surrogate for chlorophyll, and therefore phytoplankton, abundance), and nitrate. Real-time data are transmitted via cell phone, and a public website is being developed for viewing and downloading data. While these sensors are providing valuable new information, the approach is not without its problems - biofouling is a major issue that needs to be managed at the Dumbarton site (photo PAGE 45). Two more continuous monitoring stations will be added in South Bay and Lower South Bay in 2014. Prior to that, effort will be directed toward field studies for calibration and testing of sensor accuracy and precision, developing protocols for sensor maintenance and minimizing biofouling, pilot field deployments to inform future site selection, and data analysis.

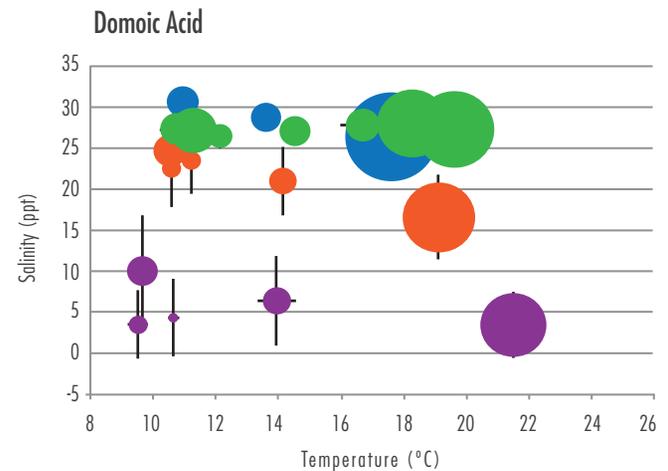
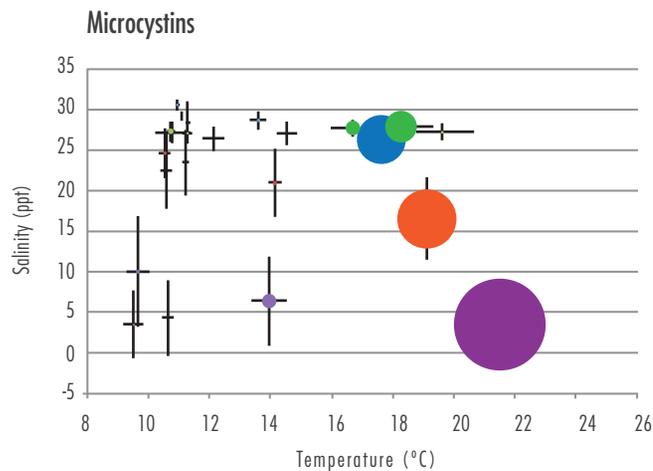
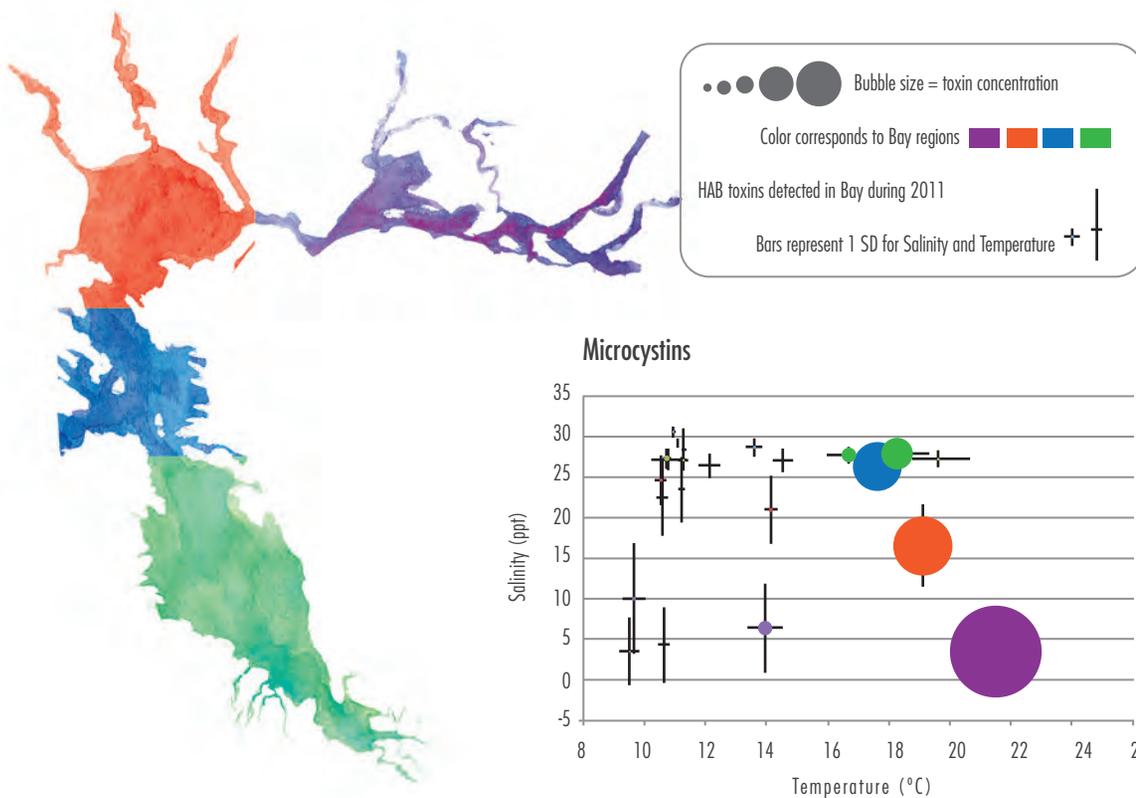
Nutrients *(cont)*

Algal Toxins Ubiquitous in the Bay

Some phytoplankton (or algae) species produce toxic compounds that can bioaccumulate in food webs, harm aquatic biota, and cause severe illness or death in humans or domestic animals who consume tainted seafood or swim in contaminated water. Algal toxin concentrations are typically highest during so-called harmful algal blooms (HABs). HABs and associated toxin production are a growing problem globally in coastal waters, and are the focus of numerous research efforts. However, until recently, algal toxin concentrations had not been monitored in San Francisco Bay.

In 2011, researchers from UC Santa Cruz collaborated with the USGS and the RMP to measure algal toxins in the Bay. The approach involved deploying a small packet of toxin-binding resin – SPATT (solid phase adsorption toxin tracking) – in a stream of Bay water continuously pumped from 1 meter below the surface and into the ship’s lab as it travelled Bay transects during monthly sampling cruises. The SPATT chemically adsorbs algal toxins as Bay water flows past it. Back at UC Santa Cruz, the algal toxins were extracted from the resin and analyzed. One SPATT packet was used for each subembayment, providing a relatively inexpensive, spatially-integrated measure of toxin abundance.

The graphs show results for two algal toxins, microcystin and domoic acid, measured during monthly cruises during 2011. Both of these toxins are likely derived from algae outside of the Bay proper, with microcystin originating from the Delta and domoic acid coming from the ocean. Toxin concentration varied over a wide range; however, both toxins were detected during all cruises, in all subembayments, and across a wide range of temperature and salinity. While detection of the toxins was noteworthy, the ecological significance of these concentrations is not yet known. To inform future monitoring efforts, the RMP funded a special study in 2013, both to measure algal toxins during monthly cruises and to attempt to establish a way of estimating water concentrations from SPATT results.



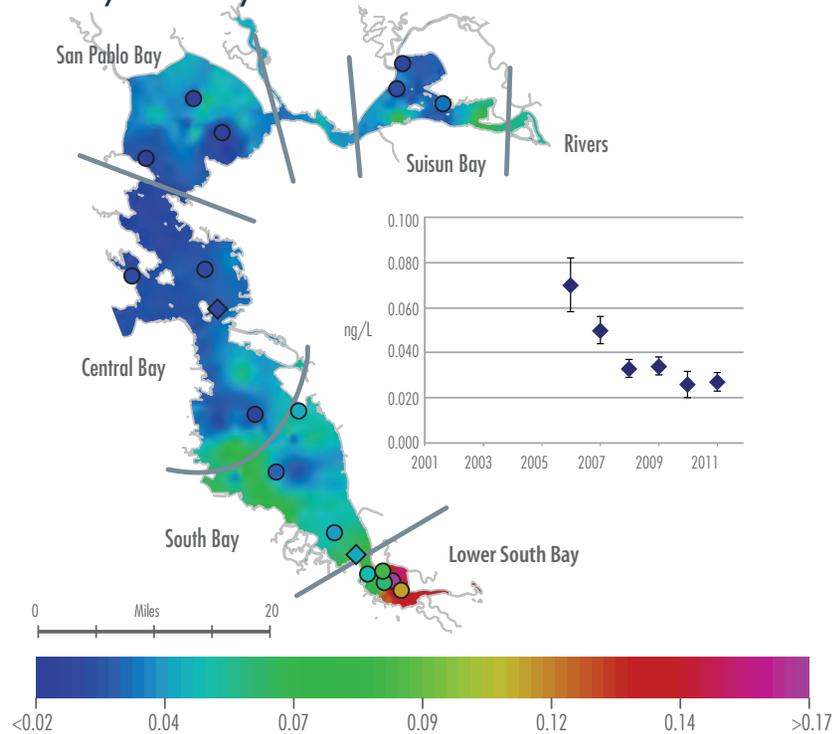
Source: R Kudela, UCSC

Footnote: Circle size denotes toxin relative concentration, and color represents the subembayment (see map).

Mercury

Mercury contamination is one of the top water quality concerns in the Bay and mercury clean-up is a high priority for the Water Board. Mercury is a problem because it accumulates in the form of methylmercury to high concentrations and poses risks to some fish and wildlife species. Humans and wildlife that consume fish face the greatest health risks from mercury.

Methylmercury in Water



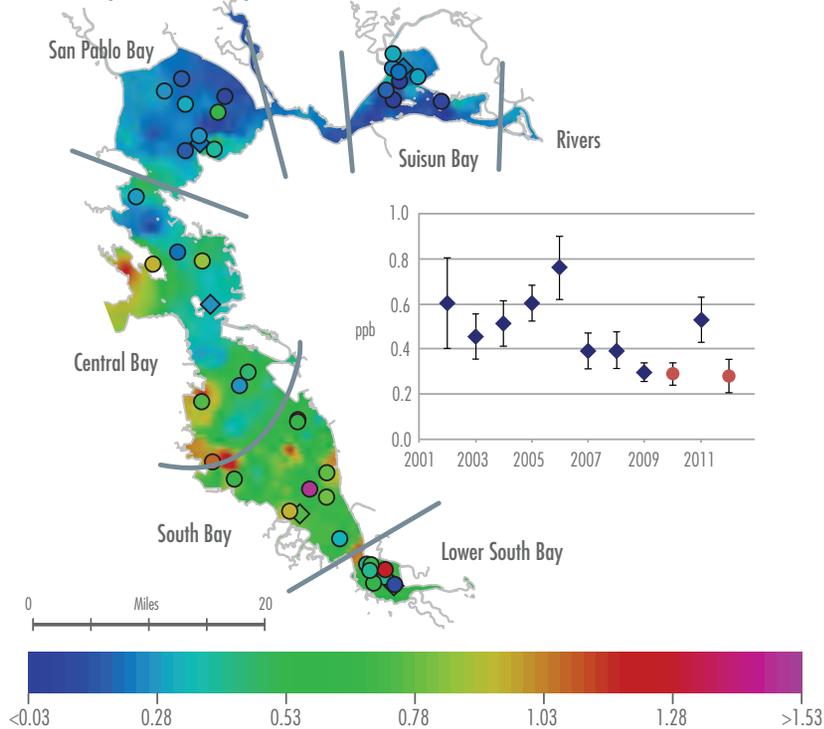
Water from Lower South Bay had the highest average concentration of methylmercury by far (0.11 ng/L) of any segment from 2006 to 2011. South Bay had the next highest average (0.07 ng/L). Methylmercury typically represents only about 1% of the total of all forms of mercury in water or sediment, but is the form that is readily accumulated in the food web and poses a toxicological threat to highly exposed species. Methylmercury has a complex cycle in the Bay, influenced by many processes that vary in space and time. No regulatory guideline exists for methylmercury in Bay water. The Bay-wide average in 2011 was 0.03 ng/L. The Bay-wide average for the six-year period was 0.04 ng/L. The Bay-wide averages for 2008-2011 were lower than those observed in 2006 and 2007.

Footnote: Water is sampled only in the dry season, and was not sampled in 2012. Colored symbols on map show results for samples collected in 2011: circles represent random sites; diamonds represent historic fixed stations. Contour plot based on 111 RMP random station data points from 2006-2011. Trend plot shows annual Bay-wide random station means with error bars indicating the 95% confidence intervals of the means. Earlier years not included because a less sensitive method was employed. The maximum concentration was 0.28 ng/L at a site in Lower South Bay in 2011. Data are for total methylmercury (dissolved plus particulate).

← Photograph by Meg Sedlak.

Mercury (cont)

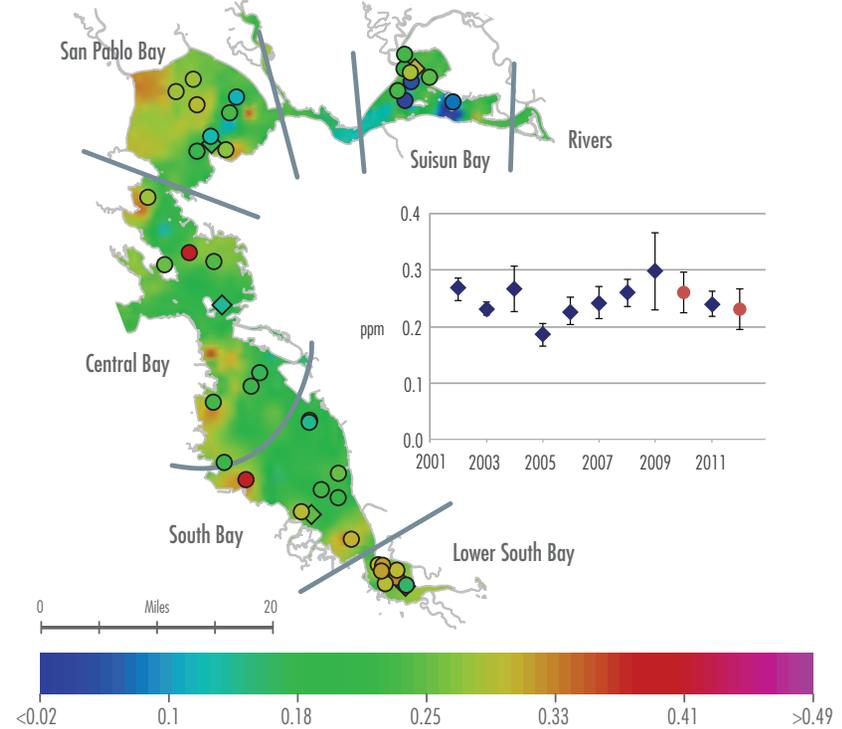
Methylmercury in Sediment



Concentrations of methylmercury in sediment south of the Bay Bridge have been consistently higher than those in the northern Estuary. Methylmercury production can vary tremendously over small distances and over short time periods, so the colored contours shown should be viewed as the result of several “snapshots” of Bay conditions at the time of the surveys. Samples were collected in the dry season in 2002-2009 and 2011, and in the wet season in 2010 and 2012 (wet season data are excluded from the contours on the map and the averages that follow). Long-term (2002-2011) average dry season concentrations have been highest in South Bay and Lower South Bay (0.72 and 0.68 ppb, respectively), and lowest in Suisun Bay (0.20 ppb) and San Pablo Bay (0.27 ppb). The Bay-wide average concentration for the wet season in 2012 (0.28 ppb) was the lowest annual average over the 11-year period. The annual Bay-wide averages for the two rounds of wet season sampling were relatively low compared to the averages for the dry season. No regulatory guideline exists for methylmercury in Bay sediment.

Footnote: Colored symbols on map show results for wet season samples collected in 2012: circles represent random sites; diamonds represent historic fixed stations. Contour plot based on 360 RMP data points from random stations over nine rounds of dry season sampling from 2002-2009 and 2011 (data from wet season sampling in 2010 and 2012 are excluded). Trend plot shows annual Bay-wide random station means with error bars indicating 95% confidence intervals of the means. Red circles on trend plot indicate wet season samples; blue diamonds indicate dry season samples. The maximum dry season concentration at a random station was 2.4 ppb at a site in Central Bay in 2002. Concentrations presented on a dry weight basis.

Mercury in Sediment



In contrast to methylmercury, long-term average total mercury concentrations in sediment during the dry season have been highest in San Pablo Bay (0.27 ppm). Average concentrations have been slightly lower in Lower South Bay and Central Bay (both 0.26 ppm) and South Bay (0.22 ppm), and lowest in Suisun Bay (0.17 ppm). The Bay-wide average for the nine rounds of dry season sampling was 0.25 ppm. Also in contrast to methylmercury, Bay-wide average concentrations of total mercury in sediment have shown relatively little variability over this period, ranging from a low of 0.19 ppm in 2005 to a high of 0.30 ppm in 2009. The annual Bay-wide averages for the two rounds of wet season sampling were similar to the averages for the dry season. No regulatory guideline exists for total mercury in sediment.

Footnote: Colored symbols on map show results for wet season samples collected in 2012: circles represent random sites; diamonds represent historic fixed stations. Contour plot based on 360 RMP data points from random stations collected over nine rounds of dry season sampling from 2002-2009 and 2011 (data from wet season sampling in 2010 and 2012 are excluded). Trend plot shows annual Bay-wide random station means with error bars indicating 95% confidence intervals of the means. Red circles on trend plot indicate wet season samples; blue diamonds indicate dry season samples. The maximum dry season concentration was 0.94 ppm in Central Bay in 2009. Concentrations presented on a dry weight basis.

Mercury (cont)

Statewide Survey Underscores High Mercury in Bay Food Web

In 2012 the State Water Resources Control Board's Surface Water Ambient Monitoring Program (SWAMP) published results from a 2009-2010 survey of contaminants in fish on the California coast. The survey was performed in close collaboration with the RMP and the Southern California Bight Regional Monitoring Program. The survey was the largest of its kind ever conducted, analyzing 3,483 fish from 46 species at 68 coastal locations.

The survey summary included a comparison of Bay striped bass mercury concentrations with those in other US estuaries. Striped bass are a relevant and useful indicator species for comparing mercury contamination across US estuaries due to several factors: their popularity for consumption; their dependence on estuaries; their broad spatial integration across the estuaries in which they reside due to their variable use of fresh, brackish, and saline habitat; and their wide distribution on the east, west, and Gulf coasts. Striped bass from San Francisco Bay had the highest average mercury concentration (0.44 ppm, estimated for a 60 cm fish) among the six estuaries with data. The New Jersey coast had the second highest average concentration (0.39 ppm, but based primarily on fish greater than 84 cm). Average mercury concentrations in striped bass from other US coastal areas were much lower, ranging from 0.12 to 0.23 ppm.

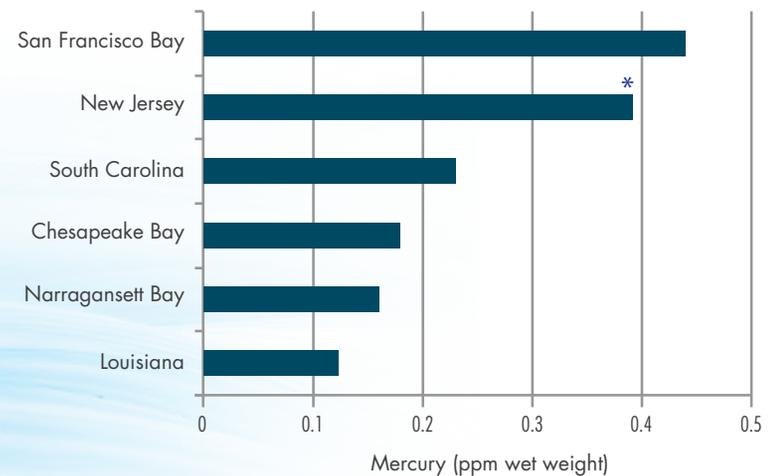


The San Francisco Estuary is the only coastal ecosystem in California where striped bass occur. Results for shiner surfperch, a species with a more widespread distribution along the coast and that is a valuable indicator of spatial patterns, also documented elevated mercury concentrations in the Bay food web (data not shown). The five locations sampled in the Bay (out of 17 total across the state) accounted for the five highest concentrations for this species statewide.

While the mercury concentrations in the Bay food web stood out when comparisons could be made within single species, the survey also showed that mercury accumulation in fish is of high concern along much of the California coast. Long-lived predator species that are common along the coast, such as various rockfish and shark species, generally had high concentrations.

The public can access results for individual fishing locations from the Coast Survey and other statewide SWAMP fish surveys through the California Water Quality Monitoring Council's "My Water Quality" web portal at: www.CaWaterQuality.net

The Coast Survey Report ("Contaminants in Fish from the California Coast, 2009-2010") is available on the SWAMP website at: www.waterboards.ca.gov/water_issues/programs/swamp/coast_study.shtml

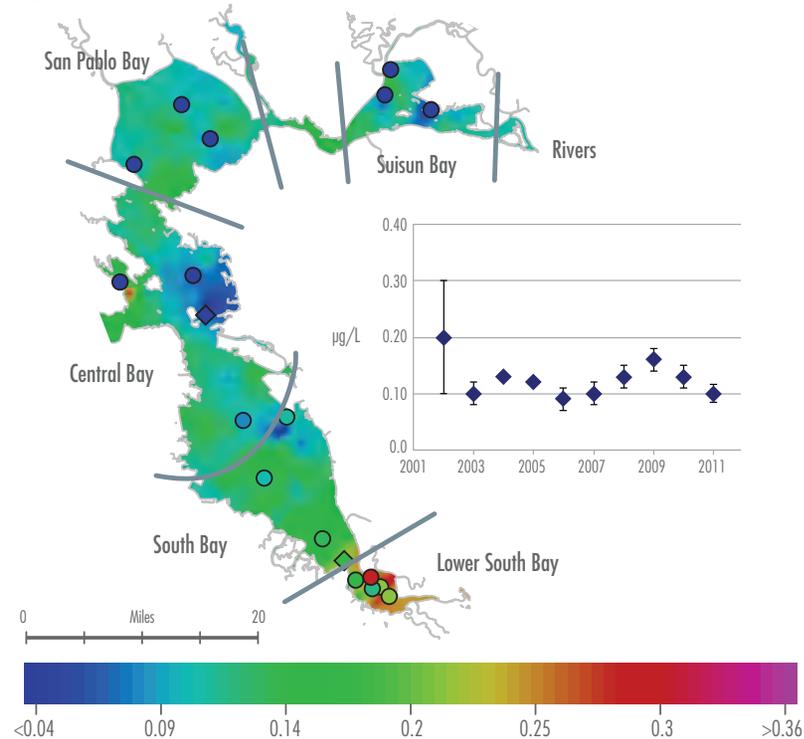


* The median size of striped bass sampled in New Jersey was 84 cm, substantially larger than the Bay average for a 60 cm fish. The larger size of the New Jersey fish would inflate the mercury concentrations measured.

Selenium

Selenium contamination is a continuing concern in the Bay. Selenium accumulates in diving ducks to concentrations that pose a potential health risk to human consumers. Selenium concentrations also pose a threat to wildlife. Recent studies suggest that selenium concentrations may be high enough to cause deformities, growth impairment, and mortality in early life-stages of Sacramento splittail and white sturgeon.

Selenium in Water



Selenium concentrations in water are well below the water quality objective established by the California Toxics Rule (CTR), but concerns still exist for wildlife exposure as indicated by studies on early life-stages of fish. The highest concentration observed in water at random stations from 2002 to 2011 was 0.63 $\mu\text{g/L}$, much lower than the CTR objective (5 $\mu\text{g/L}$). The Lower South Bay had a higher average concentration over this period (0.25 $\mu\text{g/L}$) than the other Bay segments, which had very consistent average concentrations (all other averages were between 0.12 and 0.14 $\mu\text{g/L}$). The Bay-wide average concentration in 2011 (0.10 $\mu\text{g/L}$) was slightly lower than the long-term Bay-wide average (0.13 $\mu\text{g/L}$).

Footnote: Water is sampled only in the dry season, and was not sampled in 2012. Colored symbols on map show results for samples collected in 2011: circles represent random sites; diamonds represent historic fixed stations. Contour plot based on 210 RMP random station data points from 2002-2011. Trend plot shows annual Bay-wide random station means with error bars indicating the 95% confidence intervals of the means. The maximum concentration was 1.15 $\mu\text{g/L}$ at a historical fixed station in the Southern Sloughs in 2002. Data are for total selenium (dissolved plus particulate).

← Photograph by Meg Sedlak.

PCBs

PCB contamination remains one of the greatest water quality concerns in the Bay, and PCB cleanup is a primary focus of the Water Board. PCBs are a problem because they accumulate to high concentrations in some Bay fish and pose health risks to consumers of those fish.

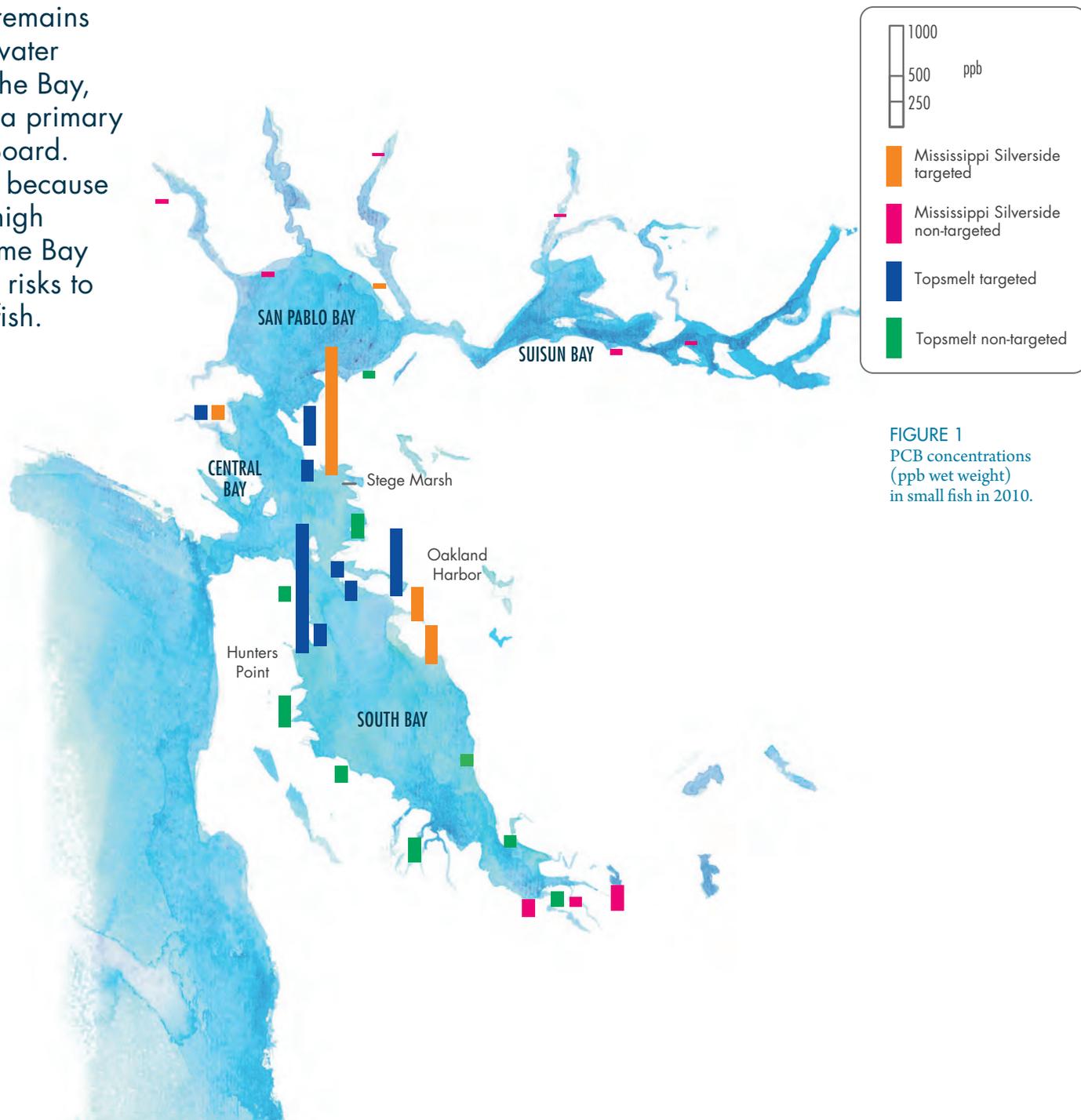


FIGURE 1
PCB concentrations
(ppb wet weight)
in small fish in 2010.

PCBs (cont)

Little Fish, Big PCBs

New information obtained from RMP monitoring of small fish has fundamentally altered our understanding of PCB contamination of the Bay food web and potential pathways of exposure of sensitive piscivores such as birds and seals. The RMP conducted pilot monitoring of PCBs in small fish in 2007 and 2010 (Greenfield and Allen 2013), piggybacking on a more extensive multi-year RMP study of methylmercury in small fish.

Confirming earlier pilot studies, concentrations in the small fish were surprisingly high. The average concentration in small fish in 2010 was 216 ppb, much higher than the average for the most contaminated sport fish species sampled in 2009 (shiner surfperch – 121 ppb). Concentrations reached a maximum of 1100 ppb at Hunters Point (FIGURE 1).

These high concentrations in small fish were unexpected because PCBs are among the contaminants that biomagnify: concentrations increase with each step up the food chain. Therefore, for species belonging to the same food web, small species such as silverside, topsmelt, and anchovy that eat plankton should have lower concentrations than species such as white croaker, white sturgeon, and striped bass that eat fish and larger invertebrates.

These comparisons apply to concentrations expressed per gram of lipid (or fat) because PCBs accumulate in lipid, and lipid content varies among species and tissues. When expressed on a lipid weight basis, topsmelt, silverside, and anchovy all had concentrations that were greater than species higher in the food chain such as white sturgeon and striped bass (FIGURE 2). The consistently high concentrations in anchovy are noteworthy, as this is the most abundant fish species in the Bay and an important wildlife prey item.

A hypothesis to explain these patterns is that the PCBs accumulated by small fish species are derived from a “bathtub ring” of sediment contamination at legacy hotspots along the margins of the Bay, while the PCBs accumulated by sport fish species higher in the food chain are derived primarily from less-contaminated sediment in open Bay habitat. Concentrations of PCBs and other legacy contaminants remain elevated in the margin hotspots due to reduced transport and long residence times in these low energy environments. PCB concentrations in the small fish in this survey were found to correlate well with concentrations in nearby sediment, supporting this hypothesis.

The high PCB uptake observed in small fish is an important element of the linkage between PCB sources and accumulation in the Bay food web. PCB concentrations in small fish are an important indicator of food web contamination and exposure and risk to piscivores in the Bay, with great utility for identifying margin areas of concern and for tracking recovery.

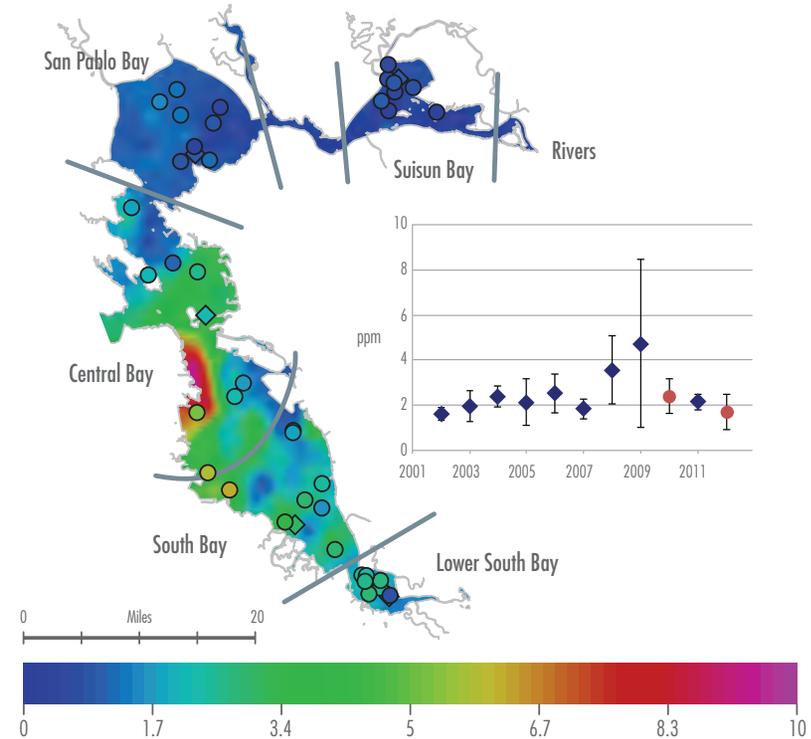


FIGURE 2
PCB concentrations in small fish (even when expressed on a lipid weight basis) are comparable and often greater than concentrations in large sport fish species.

PAHs

PAHs (polycyclic aromatic hydrocarbons) are included on the 303(d) List for several Bay locations. Concentrations tend to be higher near the Bay margins, due to proximity to anthropogenic sources. Increasing population and motor vehicle use in the Bay Area suggest that PAH concentrations could increase due to deposition from the air directly into the Bay and from the air to urban runoff and into the Bay via stormwater.

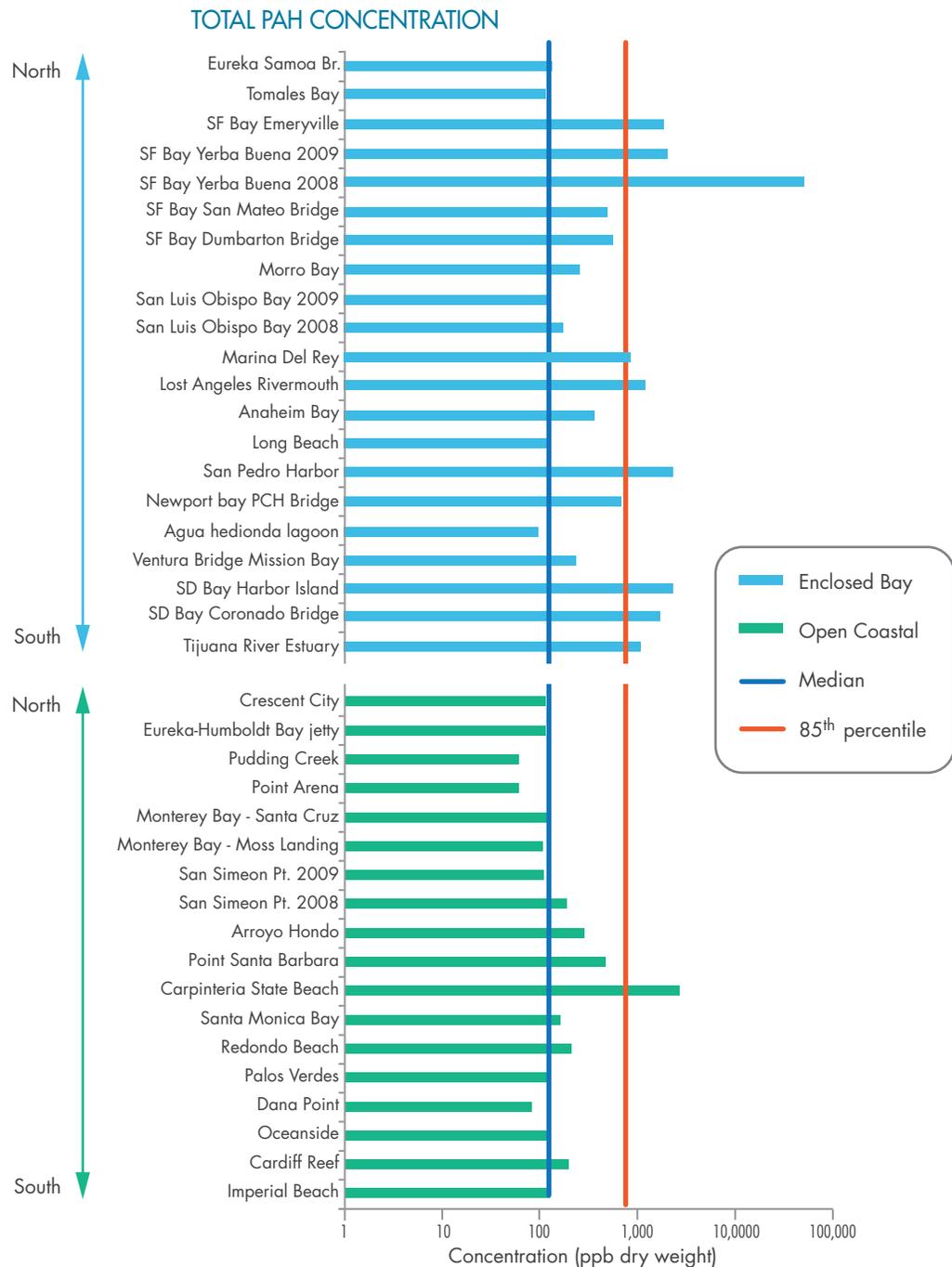
PAHs in Sediment



Average dry season PAH concentrations in sediment have been highest along the southwestern shoreline of Central Bay. Central Bay has had the highest average dry season concentration (4.0 ppm) of any Bay segment. South Bay had the next highest average concentration (2.4 ppm), followed by Lower South Bay (1.9 ppm), San Pablo Bay (1.0 ppm), and Suisun Bay (0.5 ppm). The Bay-wide average in 2012 (wet season) was 1.7 ppm - the lowest annual average observed over the 11 years of sampling. The high annual average dry season concentrations observed in 2008 and 2009 were largely driven by a few unusually contaminated sites sampled in those years, including the maximum concentration of 43 ppm at a site on the southwestern Central Bay shoreline in 2009. Seven of the 10 highest samples in the 11 year period were from Central Bay.

Footnote: Colored symbols on map show results for wet season samples collected in 2012: circles represent random sites; diamonds represent historic fixed stations. Contour plot based on 360 RMP data points from random stations collected over nine rounds of dry season sampling from 2002-2009 and 2011 (data from wet season sampling in 2010 and 2012 are excluded). Trend plot shows annual Bay-wide random station means with error bars indicating 95% confidence intervals of the means. Red circles on trend plot indicate wet season samples; blue diamonds indicate dry season samples. Concentrations presented on a dry weight basis.

PAHs (cont)



Large But Fleeting Impact of the Cosco Busan Oil Spill on PAHs in Mussels

In November 2007, the Cosco Busan oil tanker gouged its hull on a Bay Bridge support tower, releasing 54,000 gallons of bunker fuel oil into the Bay. This resulted in a brief period in which PAH concentrations were extremely high in the parts of the Bay affected by the spill. Fortunately, a study of contaminant accumulation in mussels, including sampling at Yerba Buena Island shortly after the spill, was underway at that time. The mussel monitoring was part of a collaboration between the State Water Board and the National Oceanic and Atmospheric Administration (NOAA) that measured PAHs and other contaminants in mussels along the California coast.

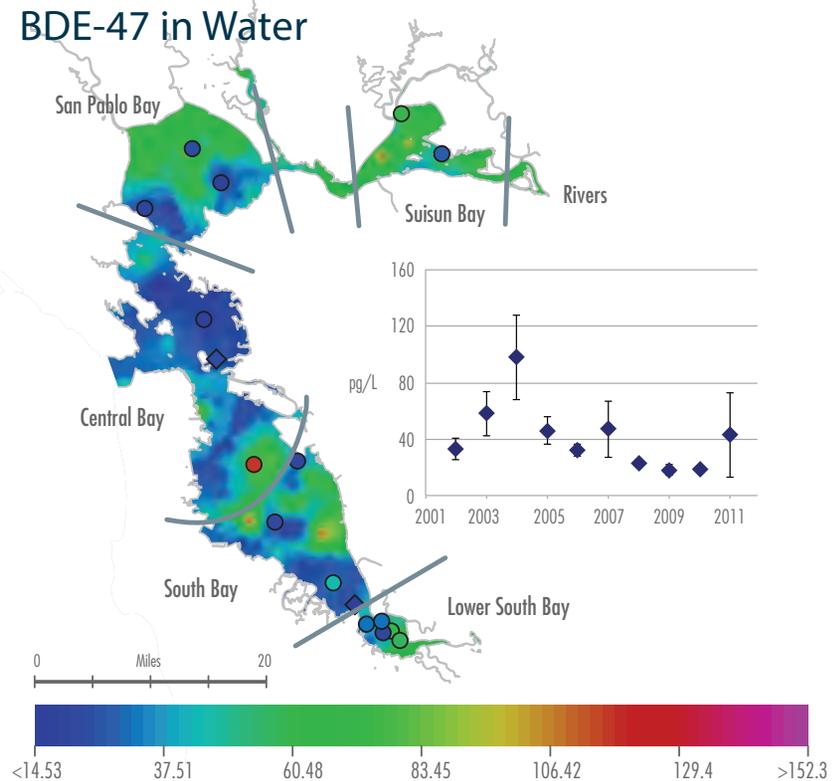
The PAH concentrations observed in mussels at Yerba Buena Island, a sampling station very close to the spill site, in early 2008 after the spill (48,000 ppb dry weight) were far higher than any others measured in the state from 2007-2009. The concentration at Yerba Buena Island in December 2007 was 18 times higher than the next highest measurement (2,700 ppb at Carpinteria State Beach). Yerba Buena Island was sampled again in December 2008. By that time, the PAH concentration fell down to 1,900 ppb, a concentration more typical for San Francisco Bay and other enclosed bays in California. Consistent with these observations, the spill resulted in a temporary advisory recommending no consumption of mussels from two nearby areas (Berkeley Marina and Rodeo Beach) impacted by the spill (Brodberg et al. 2007).

PAH concentrations observed at Yerba Buena Island in 2009 and at the other Bay locations were at the higher end of the range for enclosed bays in California, and about 10 times higher than concentrations typical for other open coast locations.

References: Brodberg et al. 2007. Report on the safety of consuming fish and shellfish from areas impacted by the M/V Cosco Busan oil spill in San Francisco Bay, California. California Office of Environmental Health Hazard Assessment, Sacramento, CA. <http://oehha.ca.gov/fish/pdf/SF%20BayFishShell112907.pdf>

PBDEs

Polybrominated diphenyl ethers (PBDEs), bromine-containing flame retardants that were practically unknown to water quality managers in the early 1990s, increased rapidly in the Bay through the 1990s to become pollutants of concern. The California Legislature banned the use of two PBDE mixtures in 2006; the third will be phased out in 2013. Declining trends in these chemicals indicate that the bans have been effective in reducing accumulation in the Bay.

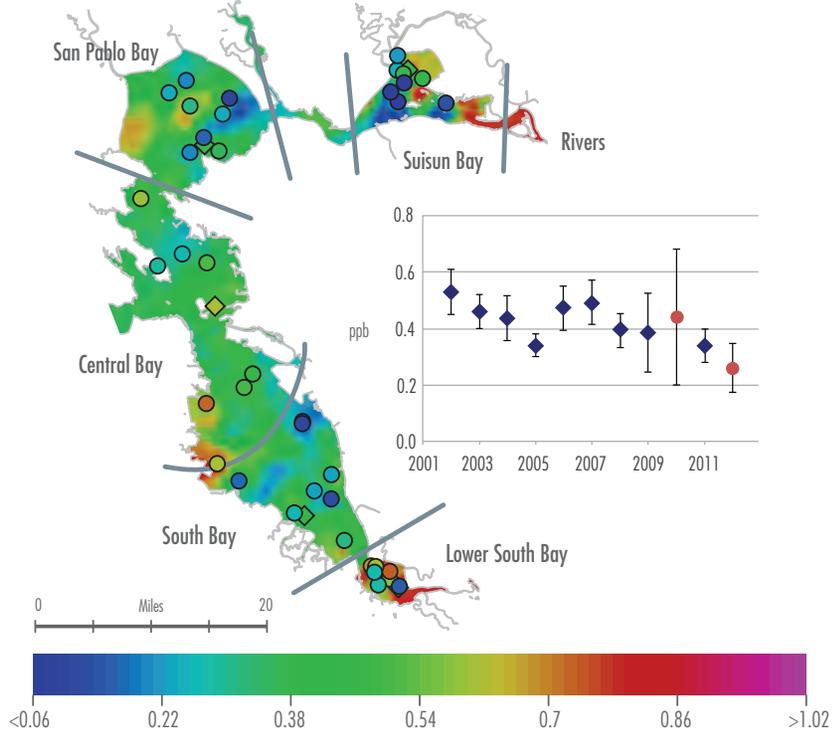


Concentrations of BDE-47 in water (one of the most abundant PBDEs and an index of the banned PentaBDE mixture) appear to be on the decline, though this trend was obscured by one outlier value in 2011. The average BDE-47 concentration in Bay water in 2011 (43 pg/L) was higher than the averages for 2008-2010 (ranging from 18 to 23 pg/L), but this was largely due to one high value measured in Central Bay (117 pg/L). The Bay-wide average concentration for the 10 year period was 45 pg/L. The three lowest annual average concentrations were measured in 2008-2010. Suisun Bay had the highest long-term average concentration of BDE-47 from 2002-2011 (65 pg/L), suggesting the presence of PBDE inputs into the northern Estuary. The maximum concentrations, two samples greater than 300 pg/L, were observed at locations in Suisun Bay and San Pablo Bay, both in 2004.

Footnote: Water is sampled only in the dry season, and was not sampled in 2012. Colored symbols on map show results for samples collected in 2011: circles represent random sites; diamonds represent historic fixed stations. Contour plot based on 201 RMP random station data points from 2002-2011. Trend plot shows annual Bay-wide random station means with error bars indicating the 95% confidence intervals of the means. The maximum concentration was 337 pg/L at a site in Suisun Bay in 2004. Data are for total BDE-47 (dissolved plus particulate).

PBDEs (cont)

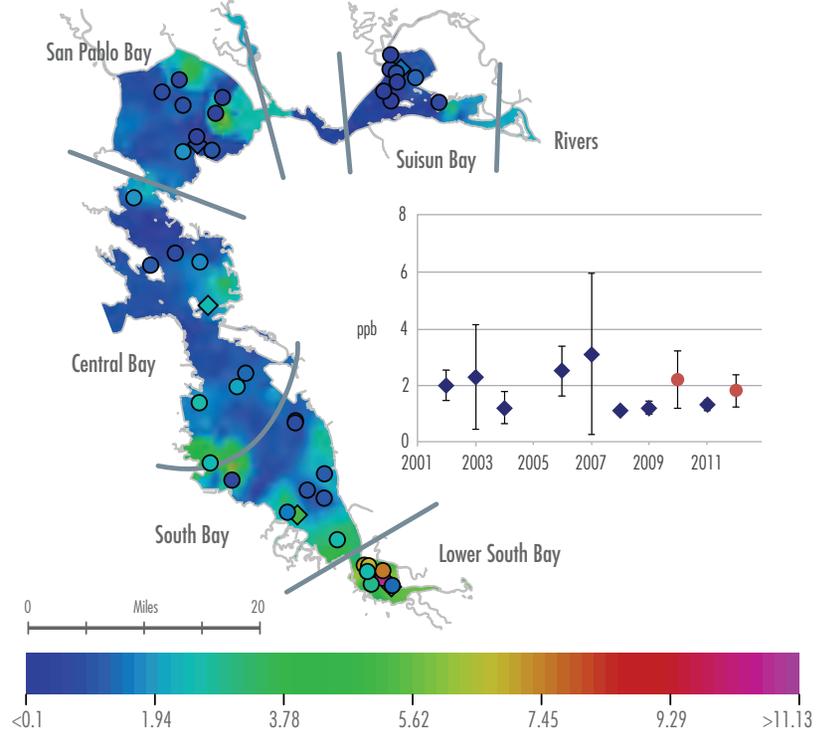
BDE-47 in Sediment



Concentrations of BDE-47 in sediment, consistent with the data for water and biota (PAGE 63), appear to be on the decline. The Bay-wide average for 2012 (0.26 ppb, a wet season value) was the lowest observed in the 11 years of sampling, and 50% lower than the average observed in 2002. In contrast to the results obtained from water monitoring, long-term average dry season concentrations of BDE-47 in sediment have been highest, by far, in Lower South Bay (0.71 ppb). Average concentrations in the other segments ranged from 0.36 ppb in South Bay to 0.46 ppb in Central Bay.

Footnote: BDE-47 is one of the most abundant PBDEs and was consistently quantified by the lab. Colored symbols on map show results for wet season samples collected in 2012: circles represent random sites; diamonds represent historic fixed stations. Contour plot based on 357 RMP data points from random stations collected over nine rounds of dry season sampling from 2002-2009 and 2011 (data from wet season sampling in 2010 and 2012 are excluded). Trend plot shows annual Bay-wide random station means with error bars indicating 95% confidence intervals of the means. Red circles on trend plot indicate wet season samples; blue diamonds indicate dry season samples. The maximum concentration, by far, was 3.8 ppb in Lower South Bay in 2005. Concentrations presented on a dry weight basis.

BDE-209 in Sediment



BDE-209 (also known as decabromodiphenyl ether) represents the one remaining PBDE mixture (“DecaBDE”) that is still being used in California. In contrast to BDE-47, Bay-wide average concentrations of BDE-209 in sediment do not appear to be declining. The average concentration in the wet season sampling of 2012 (1.8 ppb) was slightly below the long-term dry season average of 1.9 ppb. Similar to BDE-47 in sediment, long-term average dry season concentrations of BDE-209 from 2004-2009 were highest in Lower South Bay (5.4 ppb), followed by South Bay and San Pablo Bay (2.0 ppb), Central Bay (1.8 ppb), and Suisun Bay (0.8 ppb).

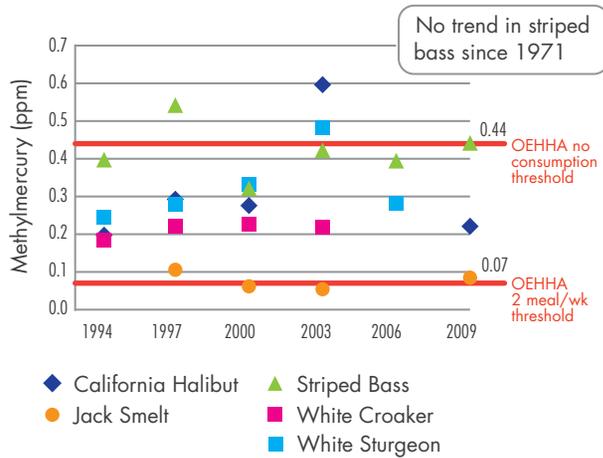
Footnote: BDE-209 shown as an index of the DecaBDE mixture. Colored symbols on map show results for wet season samples collected in 2012: circles represent random sites; diamonds represent historic fixed stations. Contour plot based on 310 RMP data points from random stations collected over eight rounds of dry season sampling from 2002-2004, 2006-2009, and 2011 (data from wet season sampling in 2010 and 2012 are excluded). Data from 2005 are not available. Trend plot shows annual Bay-wide random station means with error bars indicating 95% confidence intervals of the means. Red circles on trend plot indicate wet season samples; blue diamonds indicate dry season samples. The maximum concentration by far was 52 ppb in San Pablo Bay in 2007 (the next highest concentration was 19 ppb in South Bay in 2006). Concentrations presented on a dry weight basis.

WATER QUALITY TRENDS AT A GLANCE

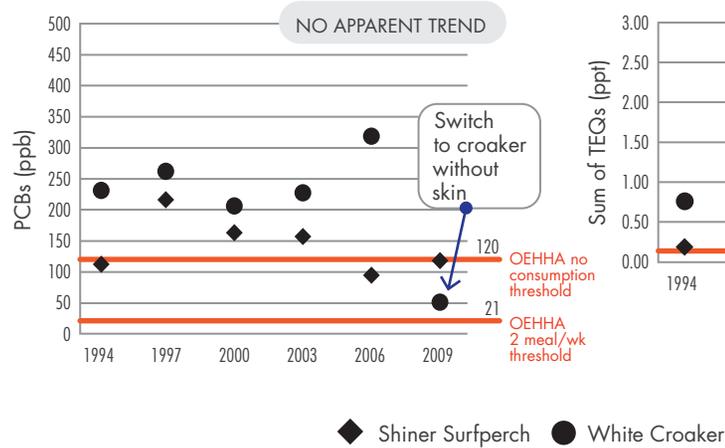
Toxics and Bacteria

SEE PAGE 45
FOR GRAPH DETAILS 

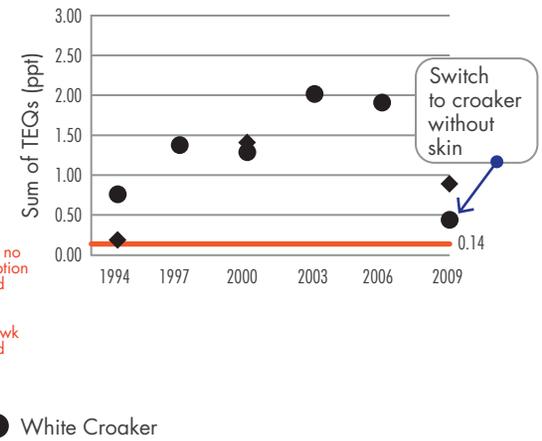
1. Methylmercury in Sport Fish



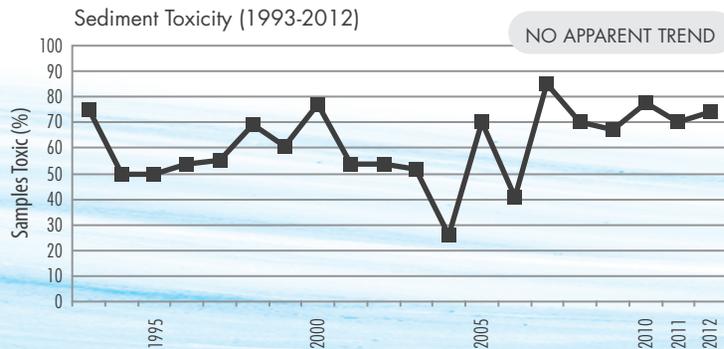
2. PCBs in Sport Fish



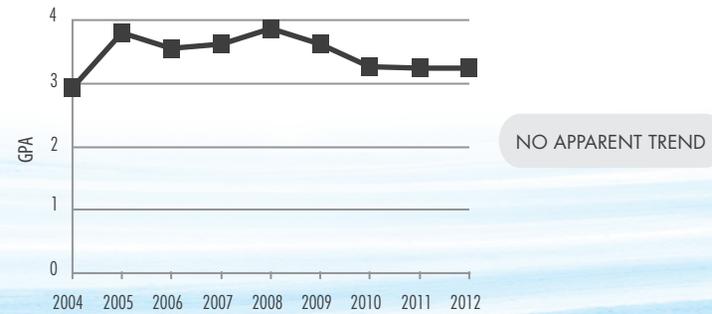
3. Dioxins in Sport Fish



4. Percent Toxic Sediment Samples



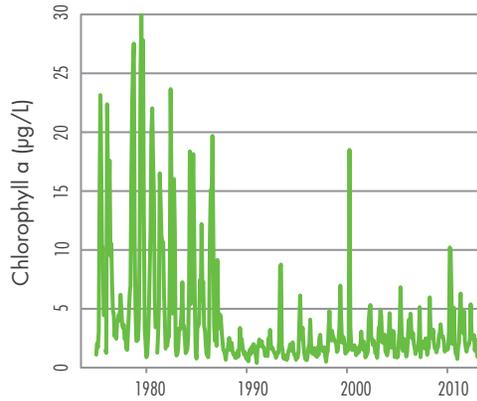
5. Beach Report Card Grades



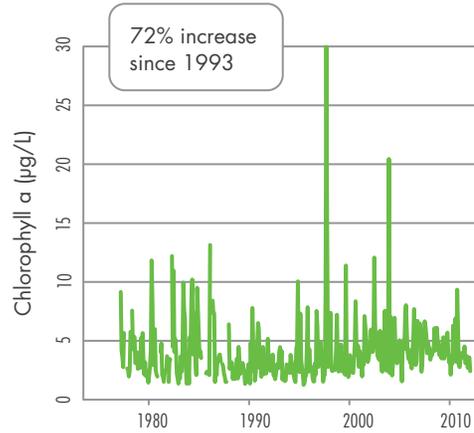
Chlorophyll and Dissolved Oxygen

SEE PAGE 45
FOR GRAPH DETAILS 

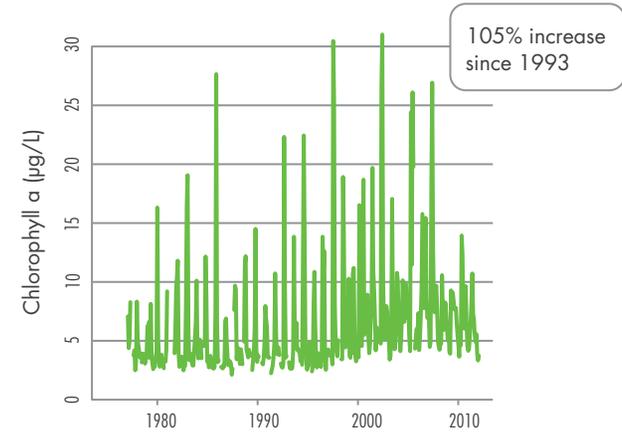
1. Chlorophyll in Suisun Bay



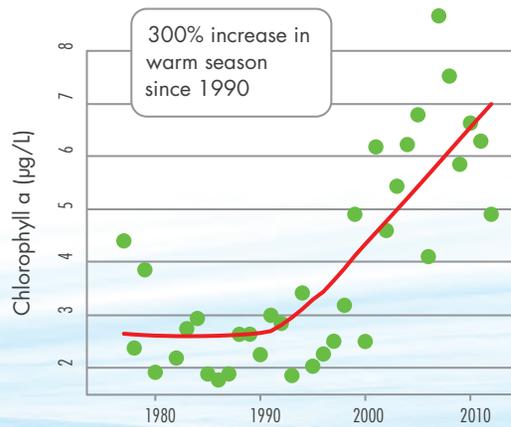
2. Chlorophyll in San Pablo Bay



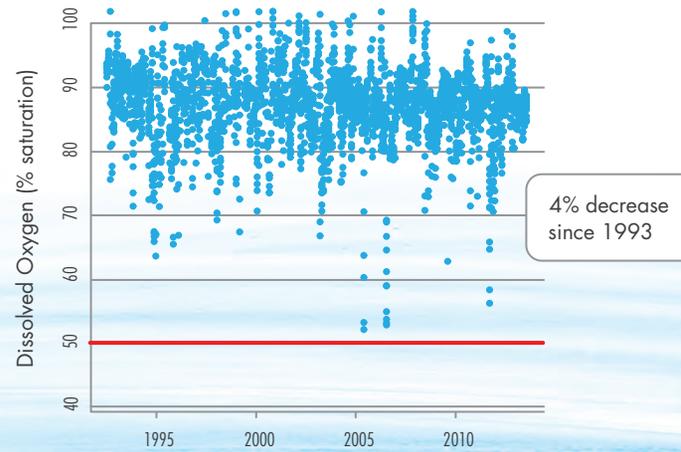
3. Chlorophyll in South Bay



4. Summer Chlorophyll in South Bay

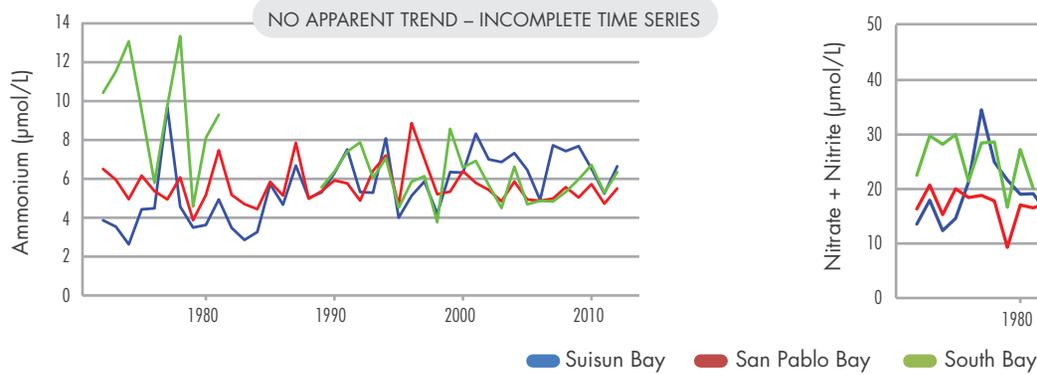


5. Bottom Dissolved Oxygen in South Bay

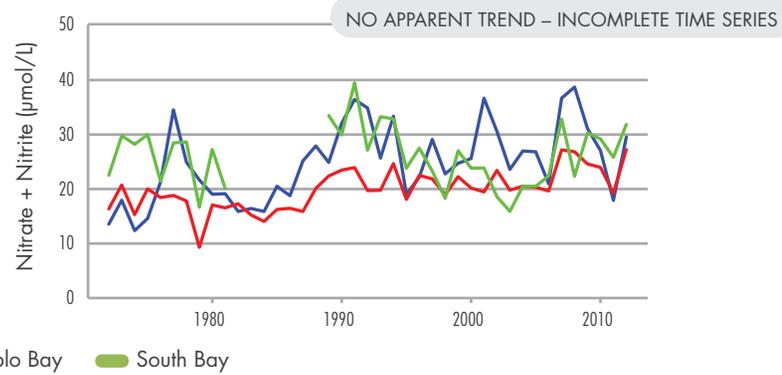


Nutrients and Sediments

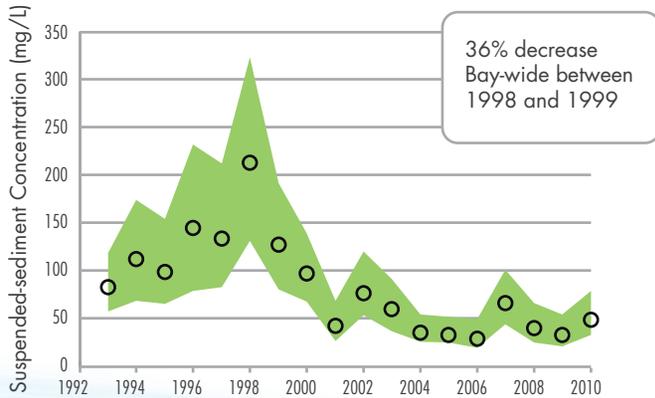
1. Ammonium



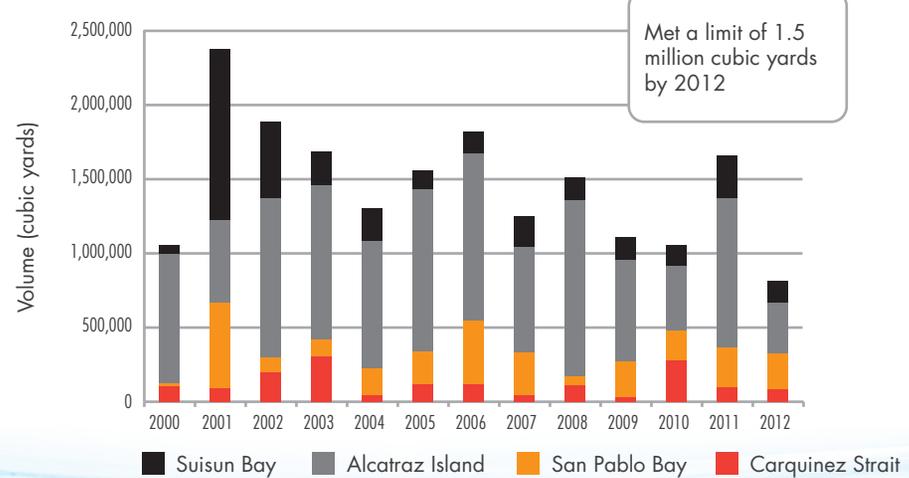
2. Nitrate and Nitrite



3. Suspended Sediment



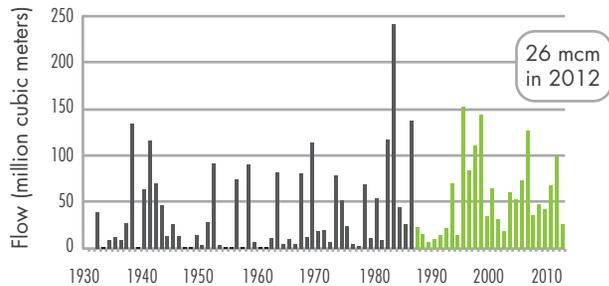
4. In-Bay Disposal of Dredged Material



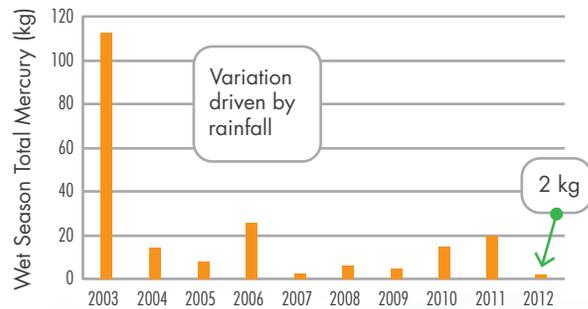
Flows and Loads

SEE PAGE 45
FOR GRAPH DETAILS 

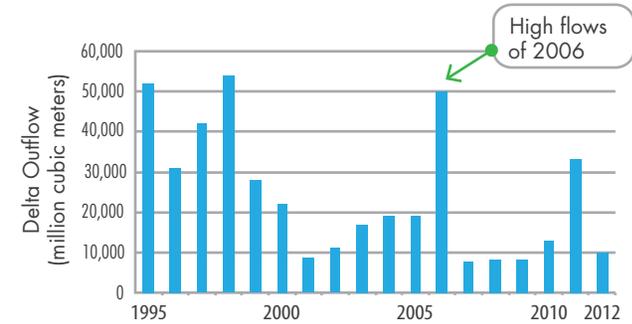
1. Guadalupe River Flow



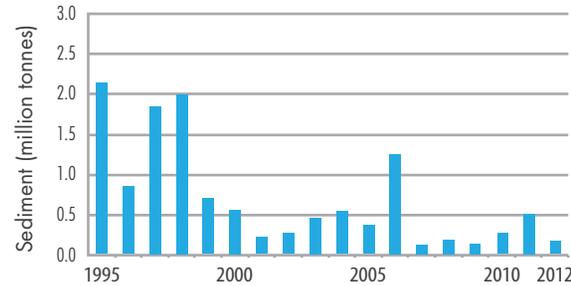
2. Guadalupe River Mercury Load



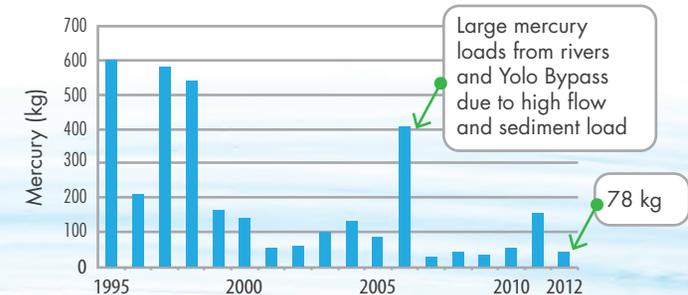
3. Delta Outflow



4. Delta Sediment Load



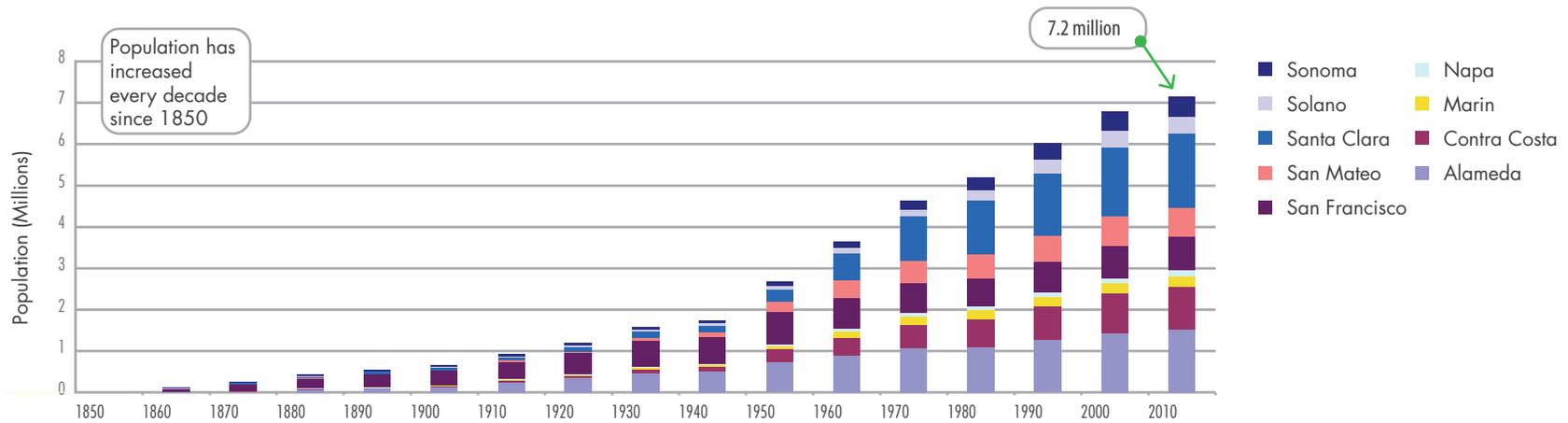
5. Delta Mercury Load



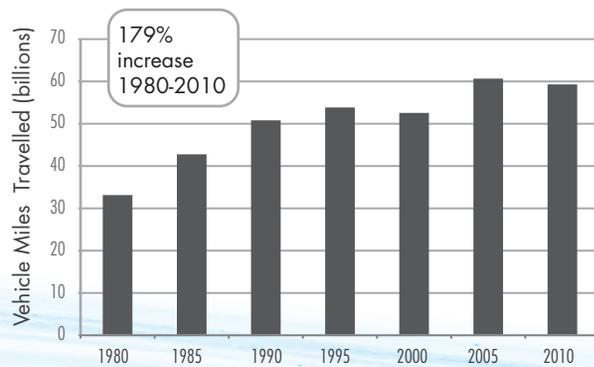
Human Presence

SEE PAGE 45
FOR GRAPH DETAILS 

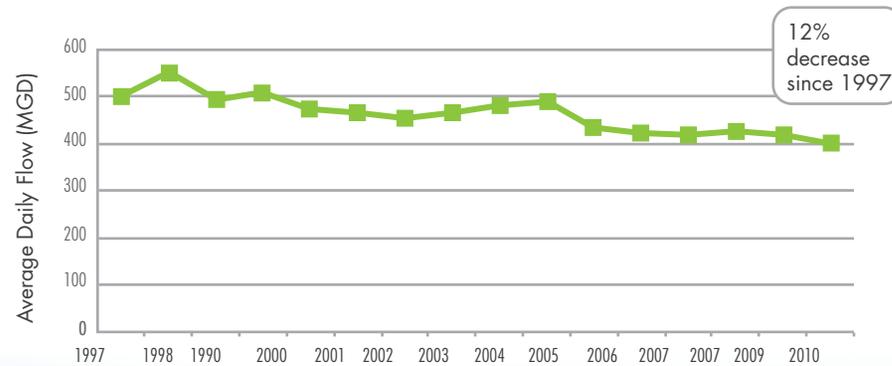
1. Bay Area Population



2. Bay Area Vehicles Miles Traveled



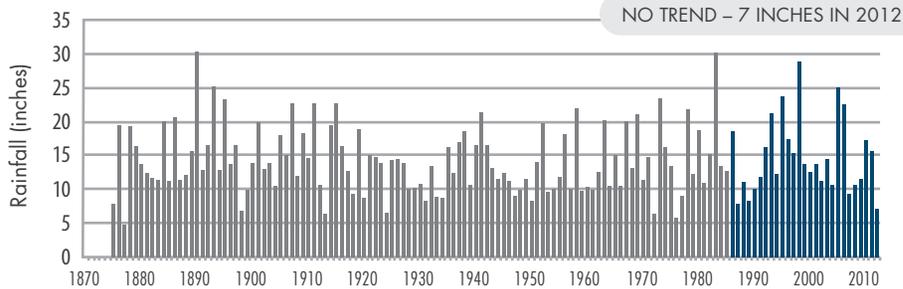
3. Flows from Top Ten Wastewater Treatment Plants



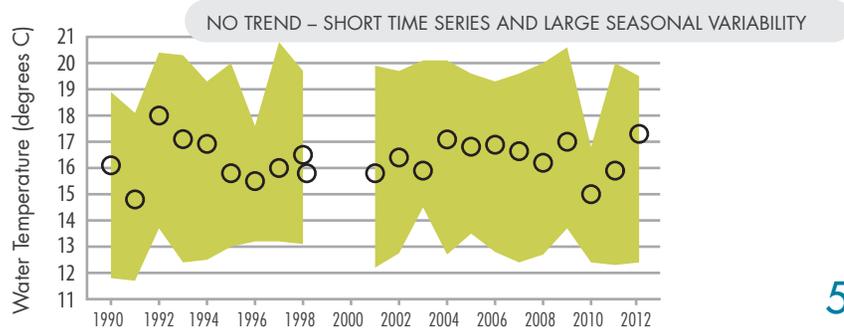
Climate and Habitat

SEE PAGE 45
FOR GRAPH DETAILS 

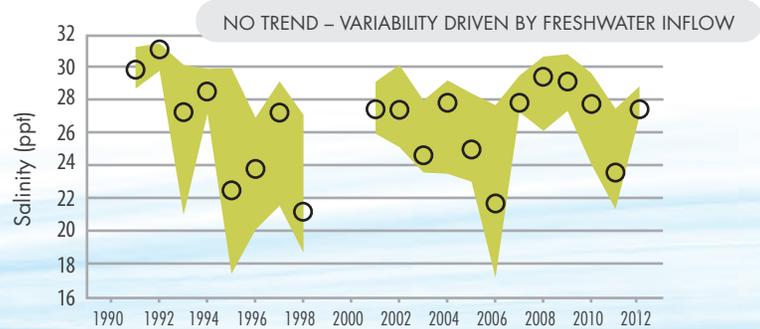
1. Rainfall in the Bay Area



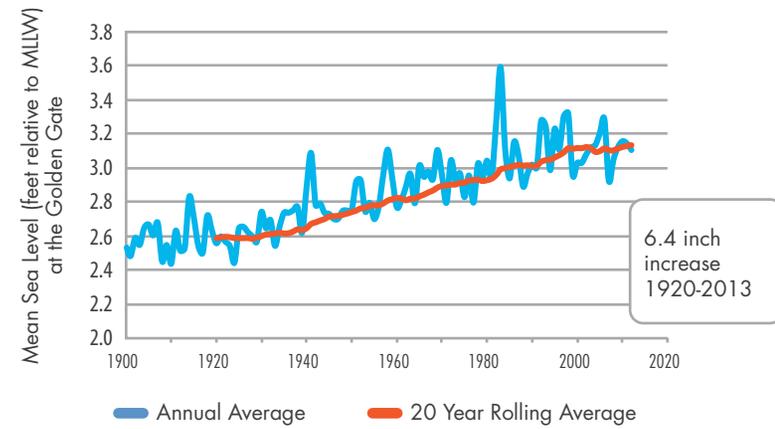
3. Water Temperature



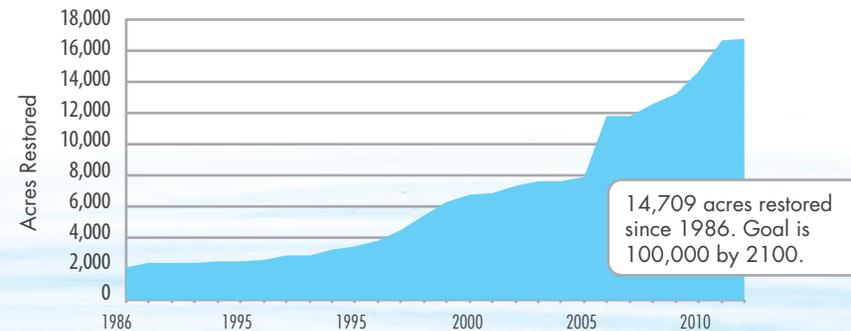
4. Salinity



2. Sea Level at Golden Gate

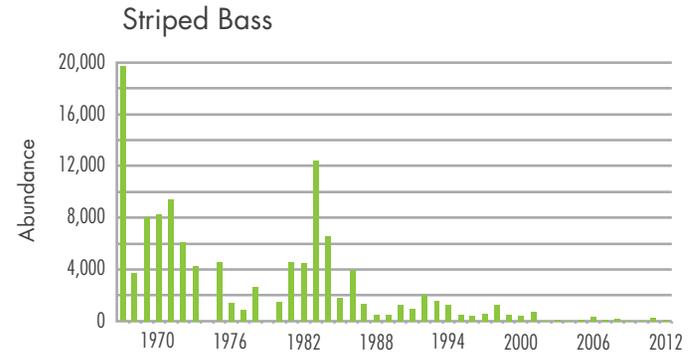
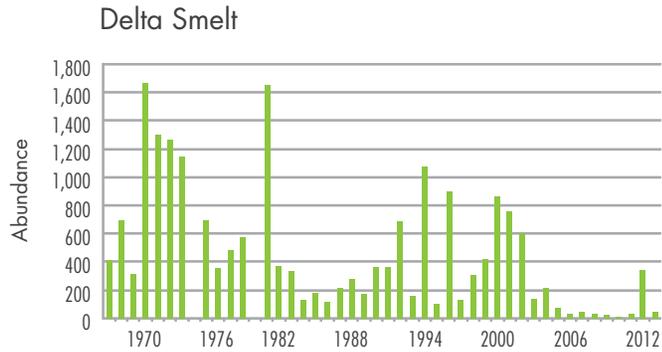


5. Restored Wetland Opened to Tidal Action

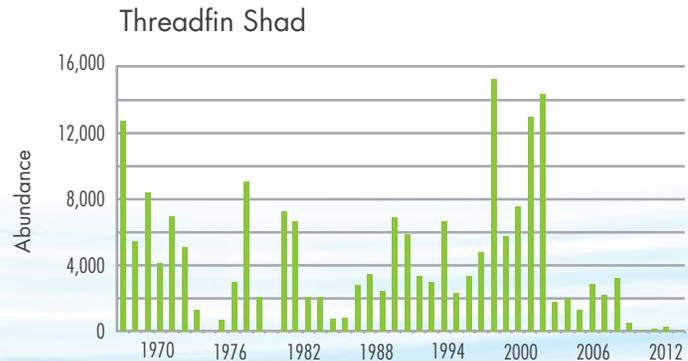
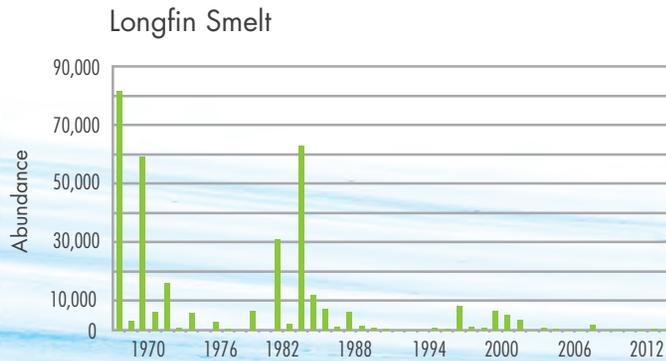


Populations

Pelagic Organism Decline



◆ ◆
All species have been near
record lows since 2002
◆ ◆



Graph Details

PAGE 38

1) Bay-wide average methylmercury concentrations. Averages for striped bass based on concentrations for individual fish normalized to 60 cm. The no consumption advisory tissue level for mercury is 440 ppb, and the two serving advisory tissue level is 70 ppb.

2) Bay-wide average PCB concentrations. The no consumption advisory tissue level for PCBs is 120 ppb, and the two serving advisory tissue level is 21 ppb. White croaker were analyzed without skin in 2009, and with skin in previous years.

3) Bay-wide average dioxin TEQ concentrations. The San Francisco Bay Water Quality Control Board has developed a screening value for dioxin TEQs of 0.14 parts per trillion (ppt). White croaker were analyzed with skin from 1994-2006, and without skin in 2009.

4) Sediment samples are tested using amphipods and mussel larvae.

5) Average of Bay Area summer beach season (April-October) grades from Heal the Bay's annual beach report card.

PAGE 39

Data from USGS: sfbay.wr.usgs.gov/access/wqdata. Data from prior to 1969 from USGS. Data collected monthly at fixed stations along the spine of the Bay. Data for stations D10, D8, D7, D6, and D41 from IEP: <http://www.water.ca.gov/bdma/meta/Discrete/data.cfm>.

1) Chlorophyll a, averaged over top 3 meters and all stations, in Suisun Bay (stations D10, D8, D7, D6, s4, s5, s6, and s7).

2) Chlorophyll a, averaged over top 3 meters and all stations, in San Pablo Bay (stations D41, s11, s12, s13, s14, and s15).

3) Chlorophyll a, averaged over top 3 meters and all stations, in South Bay (stations s21, s22, s23, s24, s25, s26, s27, s28, s29, s30, s31, s32, and s33).

4) Chlorophyll a in South Bay, averaged over top 3 meters, all stations, and June-October season for each year. Trend line is a smoothed fit.

5) Minimum dissolved oxygen percent saturation from each South Bay station, averaged over all stations. Minimum dissolved oxygen values typically occur at or near the bottom. Horizontal line indicates 50% saturation.

PAGE 40

1 and 2) Data from USGS: sfbay.wr.usgs.gov/access/wqdata

3) Water year median and interquartile range suspended-sediment concentration, Dumbarton Bridge, 20 feet below mean lower low water. Based on 15-minute data collected by the U.S. Geological Survey (Buchanan and Morgan 2010). Water years 2008-2010 are provisional data.

4) Data from the U.S. Army Corps of Engineers.

PAGE 41

1) Data from the U.S. Geological Survey. Data for all of these graphs are for water years (Oct 1 to Sep 30).

2) Total loads for each water year. Additional matching funds for this study provided by the CEP, USACE, SCVWD, and SCVURPPP.

3) Daily average Delta outflow from DAYFLOW. DAYFLOW data are available from the California Department of Water Resources (www.water.ca.gov/dayflow/).

4) Total sediment loads for each water year. Loads based on continuous measurements taken at Mallard Island by USGS (http://sfbay.wr.usgs.gov/sediment/cont_monitoring/).

5) Total loads for each water year. Loads from 2002-2006 are based on field data. Loads for earlier and later years are estimated from relationships observed between suspended sediment and mercury in 2002-2006.

PAGE 42

1) Data from the Association of Bay Area Governments and U.S. Census Bureau. <http://census.abag.ca.gov/counties/counties.htm>

2) Data from Caltrans: <http://traffic-counts.dot.ca.gov/>

3) Data provided by the ten largest municipal wastewater dischargers to the Bay: San Jose, East Bay Dischargers, East Bay MUD, San Francisco, Central Contra Costa, Palo Alto, Fairfield-Suisun, South Bayside System Authority, San Mateo, Vallejo.

PAGE 43

1) Annual rainfall measured at San Jose shown as index for Bay Area rainfall. These data are for climatic years (July 1 to June 30 with the year corresponding to the end date). Source: Jan Null, Golden Gate Weather Services

2) Data from National Oceanic and Atmospheric Administration: http://iidesandcurrents.noaa.gov/data_menu.shtml?bdate=19000520&edate=20110521&wl_sensor_hist=W5&relative=&datum=6&unit=1&shift=g&stn=9414290+San+Francisco%2C+CA&type=Historic+Tide+Data&format=View+Data

3) Water year median water temperature and interquartile range, San Mateo Bridge, 4 feet below mean lower low water. From 15-minute data collected by the U.S. Geological Survey (Buchanan 2009). 1999-2000 not shown because data were temporarily not collected during bridge construction. Some variation is caused by different periods of missing data.

4) Same information as 3). Salinity reflects freshwater inflow to the Bay with lower values for higher inflows. Ocean water has a salinity of 35 ppt.

5) Data from the California Wetlands Portal (www.californiawetlands.net/tracker/).

PAGE 44

All data from: Baxter, R. et al. 2010. Interagency Ecological Program 2010 Pelagic Organism Decline Work Plan and Synthesis of Results. <http://www.water.ca.gov/iep/docs/FinalPOD2010Workplan12610.pdf>

Biofouling of water quality sensors. Photograph by Emily Novick. →



CEC MONITORING

48 MONITORING CONTAMINANTS OF EMERGING CONCERN IN SAN FRANCISCO BAY

51 The RMP Emerging Contaminants Workgroup

54 A GUIDE TO CECs IN THE BAY

- 54 Introduction
- 55 Perfluorooctane Sulfonate
- 59 Alkylphenols and Alkylphenol Ethoxylates
- 63 Polybrominated Diphenyl Ethers
- 67 Alternative Flame Retardants
- 71 Pharmaceuticals and Personal Care Products
- 75 Triclosan
- 79 Pyrethroids
- 83 Fipronil
- 87 Currently Used Pesticides
- 91 Nanoparticles or Nanomaterials
- 92 Chlorinated Paraffins
- 93 Polybrominated Dioxins and Furans
- 94 On the Lookout for New CECs

TIER 4

TIER 3

TIER 2

TIER 1

MONITORING CONTAMINANTS OF EMERGING CONCERN IN SAN FRANCISCO BAY

JAY DAVIS, MEG SEDLAK, and REBECCA SUTTON
San Francisco Estuary Institute

HIGHLIGHTS

Contaminants of emerging concern (CECs) are synthetic or naturally occurring chemicals that are not regulated or commonly monitored but have the potential to adversely impact water quality

Determining which of the thousands of chemicals in commerce are CECs and whether or not they may be a problem is a formidable challenge due to a lack of knowledge of what chemicals are in use, analytical methods, and information on toxicity to aquatic species

San Francisco Bay is one of the most thoroughly-monitored aquatic ecosystems in the world with respect to CECs

The RMP is employing a three-pronged approach to identify and monitor CECs in the Bay, including targeted monitoring using a risk-based, tiered prioritization scheme; keeping an eye on chemicals under evaluation by other programs and investigators; and applying open-ended, "non-targeted" monitoring tools that can screen for broad classes of compounds

Surveillance of CECs using this three-pronged approach is going to remain a high priority for the RMP in years to come

The CEC Challenge

More than 100,000 chemicals have been registered or approved for commercial use in the US, including more than 84,000 industrial chemicals, 9,000 food additives, 3,000 cosmetics ingredients, 1,000 pesticide active ingredients, and 3,000 pharmaceutical drugs (Muir and Howard 2006; Benotti et al. 2009, USEPA 2013) (FIGURE 1). Global chemical production is projected to continue growing by about 3% per year, and double every 24 years (Wilson and Schwarzman 2009).

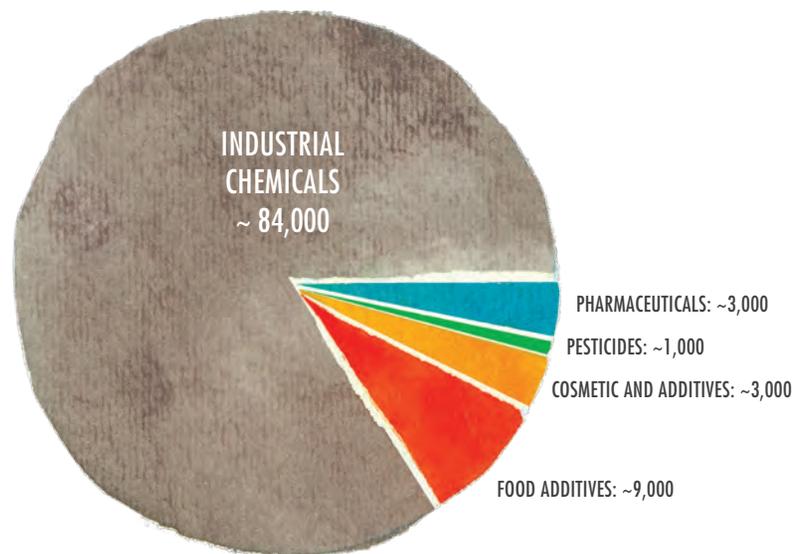
However, for the vast majority of chemicals currently in use, major information gaps limit the ability of scientists to assess their potential risks, and monitoring of these chemicals does not routinely occur. Efforts to monitor the environmental impacts of these chemicals are severely hampered by the lack of information on their presence in commercial products, their movement in the environment, and their toxicity. As a result, many chemicals that have not been adequately tested for their potential impacts to humans and wildlife are continuously released into the environment, ultimately washing into aquatic ecosystems such as San Francisco Bay.

Over the last decade, researchers and government agencies have begun to collect occurrence, fate, and toxicity data for a variety of chemicals that have not yet been regulated for environmental impacts. Analytical methods have continually improved, which has led to frequent detection of a variety of previously unmonitored chemicals in the environment. Some of these chemicals have been classified as contaminants of emerging concern (CECs). CECs can be broadly defined as any synthetic or naturally occurring chemical that is not regulated or commonly monitored in the environment but has the potential to enter the environment and cause adverse ecological or human health impacts. Characteristics used to identify CECs include high volume use, potential for toxicity in aquatic species, and occurrence in the environment.

Determining which of the thousands of chemicals in commerce are CECs and whether or not they may be a problem is a formidable challenge. For most chemicals in use, a number of limitations prevent researchers from assessing their potential risks.

FIGURE 1
Approximately 100,000 chemicals were registered for commercial use in the US from 1975-2005. Identifying which of these chemicals pose the greatest risks to water quality is a formidable challenge.

Footnote: From Muir and Howard (2006).



- The identities of many chemicals used in commercial formulations, their applications, and product-specific uses are characterized as confidential business information or are not readily available due to other reasons.
- Analytical methods to measure many CECs in the environment (sediment, water, and aquatic organisms) do not exist, and development of new analytical methods for chemicals is expensive.
- Little to no information exists on toxicity for many chemicals, especially for sublethal effects from realistic longer-term exposures, toxicity in aquatic species, or sensitive toxicological endpoints such as endocrine disruption. Knowledge of toxic modes of action for most CECs is minimal, and details of toxicity studies conducted by chemical manufacturers are typically not available for public review.

These obstacles make it very challenging for environmental researchers and regulators to pre-emptively target CECs for monitoring and control. For the vast majority of chemicals in use today, the occurrence, persistence, and toxicity data needed to protect the beneficial uses of aquatic ecosystems are in short supply.

A Bright Spot in CEC Monitoring

Thanks largely to the Regional Monitoring Program (RMP), San Francisco Bay is one of the most thoroughly monitored aquatic ecosystems in the world with respect to CECs. The RMP's stable funding base has allowed the Program to continually adapt to meet the needs of water quality managers, including addressing the challenge of CECs. RMP studies of legacy problems such as mercury and PCBs have shown how the Bay can be a long-term trap for persistent contaminants, with recovery taking decades or even centuries when the contamination is extensive. Preventing the entry of problematic contaminants into this vulnerable ecosystem is therefore the ideal way to protect Bay water quality. With these lessons in mind, the RMP has made a concerted effort in recent years to identify and monitor CECs. CEC studies by the RMP and others have revealed the Bay to be a hotspot for contamination by certain substances, such as PFOS (PAGE 55) and PBDEs (PAGE 63). These studies also appear to be providing evidence that actions to reduce the uses of CECs and their input to the Bay can be effective in lowering concentrations in the Bay, as seen for PBDEs (PAGE 63).

Keys to the Success of RMP CEC Monitoring

Three ingredients have been key to the success of RMP monitoring for CECs. The first, already mentioned above, is a stable base of funding that has been allocated to investigating CECs over the past 10 years. Current plans for the RMP (SFEI 2012) call for continuing the flow of funding for this high priority topic over the next several years.

Another essential ingredient of RMP CEC monitoring has been guidance from leading CEC scientists. In 2006 the RMP formed the Emerging Contaminants Workgroup (ECWG). RMP workgroups consist of regional scientists and regulators and invited scientists recognized as authorities in their field. The workgroups guide the planning and implementation of RMP studies. The RMP has had the extremely good fortune of having some of the world's experts on CECs serve as advisors on the ECWG (PAGE 51). The guidance of these outstanding scientists has helped the RMP focus on the CECs of greatest concern for the Bay and on using monitoring techniques with the greatest likelihood of yielding valuable information. In addition, many of these scientists have conducted pro bono work for the RMP, including monitoring the Bay for perfluorinated compounds (PAGE 55), nanoparticles (PAGE 91), and chlorinated paraffins (PAGE 92). The ECWG has become an important forum where the cutting edge of CEC science is applied to answering questions regarding Bay water quality.

A third important ingredient in RMP CEC monitoring has been collaboration. Pro bono work, matching funds, and partnerships with many organizations have substantially augmented RMP studies (TABLE 1). AXYS Analytical (www.axysanalytical.com), for example, is a laboratory that performs chemical analysis of organic contaminants for the RMP. AXYS is a world leader in development of analytical techniques for CECs, and has performed a considerable amount of pro bono work for the RMP on a diverse array of CECs, including pharmaceuticals, personal care products, alkylphenols, perfluorinated compounds, and brominated dioxins (Klosterhaus et al. 2013). Another significant example of collaborative CEC monitoring was a survey of

Stable funding, guidance from leading scientists, and collaboration have been key to the success of RMP CEC monitoring

a wide variety of CECs in mussels on the California coast, including the Bay. This major collaboration with the National Oceanic and Atmospheric Administration, Southern California Coastal Water Research Project, State Water Resources Control Board, and others culminated in a series of papers published in a special issue of *Marine Pollution Bulletin* in 2013.

RMP CEC Studies to Date

The sustained focus of the RMP on CECs over the past 10 years, aided by guidance from the science advisors and stakeholders and extensive collaboration, has allowed the Program to perform a substantial body of work (TABLE 2). These studies have yielded a wealth of information on CECs in the Bay that has supported policy decisions, and they have made the Bay a primary proving ground for testing advanced approaches for CEC monitoring.

A RMP-funded summary of CEC monitoring in the Bay to date was recently completed (Klosterhaus et al. 2013). This review set the stage for development of a CEC monitoring strategy (Sutton et al. 2013) to guide RMP studies over the next several years. The review also served as a source of much of the information presented in this edition of *The Pulse*.

A Three-Pronged Approach

The RMP CEC Strategy calls for a three-pronged approach to identifying and monitoring CECs in the Bay. The first element of the Strategy applies to chemicals where occurrence data for the Bay are available. For these chemicals, relative risk is evaluated using a tiered framework (FIGURE 2). With regard to monitoring, the framework guides decisions on “targeted” investigation of CEC sources, occurrence, and impacts on Bay water quality. Targeted monitoring is possible when methods for chemical analysis

of specific CECs are available and affordable. The framework provides guidance on inclusion of each chemical in RMP “status and trends” monitoring (routine monitoring of water, sediment, mussels, sport fish, and bird eggs) and on the need for special studies on sources, fate, or effects. The results of the monitoring and special studies help to refine the placement of chemicals within the framework. With regard to management, the framework also guides decisions on actions needed to reduce impacts on Bay water quality (PAGE 8).

CEC science is a rapidly growing and evolving field, with a vast amount of work occurring beyond the boundaries of the RMP. The second element of the RMP CEC Strategy is to learn as much as possible from work being done by others. This entails thoroughly reviewing the scientific literature, staying apprised of other CEC aquatic monitoring efforts, and maintaining a dialogue with leading CEC scientists as a means of identifying new CECs to target and new approaches for monitoring. Candidate chemicals for monitoring are evaluated by the ECWG, and the chemicals with the greatest potential to impact Bay water quality are selected for preliminary studies to determine whether they are present in the Bay.

A major challenge in monitoring CECs is the absence of analytical methods to perform targeted monitoring of many of the thousands of chemicals that occur in the environment. The third element of the Strategy circumvents this problem by employing open-ended, “non-targeted” monitoring tools that can screen for broad classes of compounds. One non-targeted approach is based on the use of an analytical instrument called a mass spectrometer, which can allow identification of unknown compounds by breaking the contaminant molecules into fragments and then examining the atomic masses of the fragments (“mass spectra”). Sometimes, but not all the time, the analytical chemist can deduce the identity of a contaminant based on comparison to libraries of mass spectra or through an

The RMP Emerging Contaminants Workgroup

understanding of general fragmentation patterns. The RMP, in collaboration with the National Institute of Standards and Technology, recently completed a two-year study screening for CECs in Bay biota using a sophisticated mass spectrometry method (Kucklick et al. in prep).

The RMP is also evaluating another non-targeted approach that aims to screen for classes of compounds with a similar mode of toxic action. For example, many environmental contaminants act as “endocrine disruptors,” chemicals that interfere with hormonal physiological controls, often by mimicking endogenous hormones like estrogen, testosterone, cortisol, or thyroxine. A RMP study initiated in 2013 is developing a tool for evaluating the presence of estrogenic compounds in samples from the Bay. Many CECs and other contaminants are estrogen mimics. If this work is successful, it will be possible to measure the overall estrogenic potency of the combination of contaminants present in Bay samples. This type of technique is referred to as a “bioanalytical tool” because it uses a biological response to measure the CECs in a sample.

Surveillance of CECs using this three-pronged approach is going to remain a high priority for the RMP in years to come. This monitoring is one critical component of a strategy to prevent the occurrence of new contamination problems that threaten the health of present and future generations of Bay wildlife and Bay Area residents. Ultimately, “green chemistry” (PAGE 13) and reduced use of toxic chemicals in products is the ideal way to protect the Bay from the emergence of new chemicals of concern.

An essential key to the success of RMP CEC monitoring has been guidance from leading CEC scientists and stakeholders. In 2006 the RMP formed the Emerging Contaminants Workgroup (ECWG). RMP workgroups consist of regional scientists and regulators and invited scientists recognized as authorities in their field. The workgroups guide the planning and implementation of RMP studies. The RMP has had the extremely good fortune of having some of the world’s experts on CECs serve as advisors on the ECWG. The guidance of these outstanding scientists has helped the RMP focus on the CECs of greatest concern for the Bay and monitoring techniques with the greatest likelihood of yielding valuable information. In addition, many of these scientists have conducted pro bono work for the RMP. The ECWG has become an important forum where the cutting edge of CEC science is applied to answering questions regarding Bay water quality.

Stakeholders

EVA AGUS, EBMUD
 MIKE CONNOR, East Bay Dischargers Authority
 ERIC DUNLAVEY, City of San Jose
 AMY CHASTAIN, San Francisco Public Utilities Commission
 NAOMI FEGER, San Francisco Bay Regional Water Board

KELLY MORAN, TDC Environmental
 TOM MUMLEY, San Francisco Bay Regional Water Board
 KARIN NORTH, City of Palo Alto
 LUISA VALIELA, USEPA
 IAN WREN, San Francisco Baykeeper
 SIMRET YIGZAW, City of San Jose

Regional Scientists

JONATHAN BENSKIN, AXYS Analytical
 JAY DAVIS, San Francisco Estuary Institute
 NATE DODDER, Southern California Coastal Water Research Project
 RICHARD GRACE, AXYS Analytical
 DENISE GREIG, California Academy of Sciences
 KEITH MARUYA, Southern California Coastal Water Research Project
 MEG SEDLAK, San Francisco Estuary Institute
 JUNE SOO PARK, California Department of Toxic Substances Control
 REBECCA SUTTON, San Francisco Estuary Institute
 DON YEE, San Francisco Estuary Institute

Science Advisors



LEE FERGUSON, Duke University



JENNIFER FIELD, Oregon State University



PHIL GSCHWEND, Massachusetts Institute of Technology



DAVID SEDLAK, University of California – Berkeley



DEREK MUIR, Environment Canada



TIER ASSIGNMENTS

MANAGEMENT

MONITORING



No CECs currently in this tier

303(d) listing
TMDL or alternative management plan.
Aggressive control actions for all controllable sources

Studies to support TMDL or an alternative management plan



PFOS
Fipronil
Nonylphenol and nonylphenol ethoxylates
PBDEs

Action plan or strategy
Aggressive pollution prevention
Low-cost control actions

Consider including in Status and Trends Monitoring
Special studies of fate, effects, and sources, pathways, and loadings



HBCD
Pyrethroids
Pharmaceuticals and personal care products
PBDDs and PBDFs

Low-cost source identification and control
Low-level pollution prevention
Track product use and market trends

Discontinue screening, or periodically screen in water, sediment, or biota
Periodic screening in wastewater effluent or urban runoff to track trends



Alternative flame retardants
Pesticides
Plasticizers
Many, many others

Identify and prioritize contaminants of potential concern, track international efforts
Develop targeted and non-targeted analytical methods

Screening in water, sediment, biota, wastewater effluent, urban runoff

FIGURE 2

The first element of the RMP's three-pronged approach to CEC monitoring applies to chemicals where occurrence data for the Bay are available. For these chemicals, management and monitoring are guided by a tiered framework based on the degree of risk associated with each chemical. With regard to monitoring, the framework guides decisions on "targeted" investigation of their sources, occurrence, and impacts on Bay water quality. The framework provides guidance on inclusion of each chemical in RMP "status and trends" monitoring (routine monitoring of water, sediment, mussels, sport fish, and bird eggs) and on the need for special studies on sources, fate, or effects. The results of the monitoring and special studies help to refine the placement of chemicals within the framework. With regard to management, the framework also guides decisions on actions needed to reduce impacts on Bay water quality (PAGE 8).

TABLE 1
Pro bono work, matching funds,
and partnerships with many organizations
have substantially augmented RMP studies.

Applied Marine Sciences
AXYS Analytical
California Department of Fish and Wildlife
Cal Poly San Luis Obispo
Canada Department of Fisheries and Oceans
City of Palo Alto
Duke University
Environment Canada
The Marine Mammal Center
National Institute of Standards and Technology
National Oceanic and Atmospheric Administration
San Diego State University
Southern California Coastal Water Research Project
Southern Illinois University
State Water Board
University of California – Berkeley
University of Florida
University of Minnesota
US Environmental Protection Agency
US Geological Survey

TABLE 2
RMP CEC Studies to Date.

TOPIC	COLLABORATORS	PUBLICATIONS/STATUS
CECs in Bay Water		Oros et al. 2003
PBDEs in Bay Fish	Environmental Working Group	Lunder and Sharp 2003
Pharmaceuticals and Personal Care Products in Effluent and Bay Water		Harrold et al. 2009
Perfluorinated Compounds	University of California at Berkeley; The Marine Mammal Center; CDFW	Sedlak et al. 2012, work ongoing; Houtz and Sedlak 2012
Alternative Flame Retardants	Duke University; Southern Illinois University; The Marine Mammal Center	Klosterhaus et al. 2009 (SETAC Poster), 2012a; work ongoing
Chlorinated Paraffins in Biota	Canada Department of Fisheries and Oceans; The Marine Mammal Center	Completed small pilot study
Triclosan in Sediment	USEPA	Completed small pilot study
Profiles on CECs in Wastewater: Triclosan and Triclocarban, Alkylphenol Ethoxylates, Carbamazepine		Klosterhaus et al. 2011, 2012b
Nonylphenol in Small Fish	California Polytechnic, San Luis Obispo	Diehl et al. 2012
AXYS Brominated Dioxins in Sediments and Biota	AXYS Analytical; University of MN; The Marine Mammal Center	Completed small pilot study; potential UM article forthcoming
PBDE Effects on Terns	USGS	Rattner et al. 2011; Rattner et al. 2013
Broadscan Screening of Biota for CECs	National Institute of Standards and Technology; Southern California Coastal Water Research Project; The Marine Mammal Center, San Diego State University	Kucklick et al. 2013
AXYS Mussel Study	AXYS Analytical	Klosterhaus et al. 2013
NOAA Mussel Pilot Study	National Oceanic and Atmospheric Administration; Southern California Coastal Water Research Project; State Water Resources Control Board	Maruya et al. 2013a,b; Dodder et al. 2013; Alvarez et al. 2013
CEC Synthesis		Klosterhaus et al. 2013
CEC Strategy		Sutton et al. 2013a
Bioanalytical Tools	University of Florida; SCCWRP	Work ongoing
PBDE Synthesis		Sutton et al. 2013b
Nanoparticles	USGS; Duke University	Klosterhaus et al. 2012
Siloxanes in Bivalves	Environment Canada	Sedlak, Muir, Sverko, Yee – unpublished data

A GUIDE TO CECs IN THE BAY

A bewildering array of chemicals is swirling around in the Bay. As part of the RMP, water quality scientists and managers are rising to the challenge of identifying the subset of these chemicals that poses the greatest and clearest threats to Bay health.

FOR MORE INFORMATION

RMP Web Page on CECs: www.sfei.org/content/RMPCEC

CEC Synthesis Report: Klosterhaus et al. 2013. Contaminants of Emerging Concern in San Francisco Bay: A Summary of Occurrence Data and Identification of Data Gaps. RMP Contribution #698. San Francisco Estuary Institute, Richmond, CA.

CEC Strategy Document: Sutton et al. 2013. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. RMP Contribution #700. San Francisco Estuary Institute, Richmond, CA.

This section of *The Pulse* provides a guide to the chemicals that are brightest on the CEC surveillance radar screen. For each chemical or class of chemicals, a synopsis is provided that describes the properties, uses, sources, environmental fate, occurrence, trends, risks, information gaps, and milestones in management. These concise summaries are based on thorough reviews and more extensive documents that are listed on the RMP web page on CECs (link provided on this page).

CEC science is a rapidly evolving field. New information is continually being generated, including quite a bit by the RMP, that is causing shifts in the levels of concern associated with individual CECs. This guide represents a series of snapshots based on what we know now (August 2013).

The RMP will continue to track advances in CEC science, evaluate their relevance for the Bay, and provide this information to managers, scientists, and the public in a manner that supports protection of Bay water quality.

Perfluorooctane Sulfonate (PFOS)

**TIER 3
MODERATE
CONCERN**

MEG SEDLAK,
San Francisco Estuary Institute
(meg@sfei.org)

Quick Summary

Since the late 1940s, PFOS has been widely used as a stain repellent for textiles, furniture, and carpets; as a surfactant in fire-fighting foams and metal finishing processes; as an ingredient in the production of fluoropolymers; and as an insecticide. PFOS repels both water and oil and is highly stable. Consequently, it has been used extensively and has been widely detected in the global environment, including in San Francisco Bay birds and seals and to a lesser extent in fish and bivalves. Bird eggs collected in the southern portion of the Bay in 2006 and 2009 contained levels of PFOS above a threshold for impacts on offspring survival in birds. Fortunately, the most recent PFOS egg results in South Bay (2012) were 70% lower than prior levels and well below this threshold. However, PFOS concentrations in seals do not show similar declines. The pathways by which these compounds enter the Bay are not fully understood.

What Is It?

- PFOS is a fluorine-containing surfactant (chemical that is soluble in both water and oil) that is a very persistent environmental contaminant.
- PFOS is a type of perfluorinated chemical (PFC) – a diverse class of fluorine-containing compounds that are extremely stable in the environment, excellent surfactants, and used in a wide range of applications.
- PFOS accumulates in biota.

What Is It Used For?

- For the last 50 years, PFCs have been used extensively in industrial, commercial, and consumer applications. PFOS has been used as a stain repellent for carpets, textiles, and paper products (“grease-proof” paper); in aqueous film-forming foams (AFFF) used at refineries, airports, and military or industrial facilities to suppress fires; in electronics and metal-finishing; and as a pesticide.
- PFOS was first widely detected in wildlife throughout the world in 2000 (Giesy and Kannan 2001). At the same time, it was also found to be a pervasive contaminant in human blood in the US (Hansen et al. 2001). As a result, the major US manufacturer of PFCs voluntarily withdrew PFOS and other structurally similar compounds, and its use in North America and Europe was restricted. Despite use reductions, PFOS continues to be detected in the environment as a result of the continued use of PFOS precursors that degrade to PFOS, historic reservoirs of these chemicals in products and the environment, PFOS impurities in other PFCs, and the continued production of PFOS and PFC precursors in other parts of the world, such as China.

Perfluorooctane Sulfonate (PFOS)

How Is It Getting Into the Bay?

- The sources and pathways of PFOS to the Bay are not fully understood.
- Research in the Great Lakes and elsewhere suggests that wastewater effluent and urban tributaries are important pathways. Also potentially significant are point sources such as contaminated sites where PFOS has been directly released to the environment (e.g., as a result of the use of AFFF to fight fires, spills from production sites, and the land application of biosolids).
- Municipal wastewater treatment plant (WWTP) effluent is a major pathway. Uses in consumer, commercial, and industrial products result in transport to WWTPs. WWTPs are not effective at removing PFCs and in some instances promote the formation of PFOS from precursors (Schultz et al. 2006, Becker et al. 2008).
- In a recent RMP study, the average concentration in effluent from six Bay Area WWTPs was 24 nanograms per liter (ng/L) (Sedlak and Allen in prep). This value is on the low end of the range of concentrations commonly seen in effluent nationally (Plumlee et al. 2008). Concentrations from WWTPs receiving industrial wastewater are typically higher.
- Urban stormwater, which flows directly into the Bay untreated, is another potential source of PFOS to the Bay.
 - In a survey of three Bay Area tributaries, PFOS concentrations ranged from below detection to 14 ng/L (Sedlak and Allen in prep). These values are in the range observed in other Bay Area studies and nationally (Plumlee et al. 2008, Houtz and Sedlak 2012).
 - Unknown precursors in tributaries may be converted to PFOS (Houtz and Sedlak 2012).
- Rain can be a pathway for PFOS. Concentrations of PFOS in Bay Area rainwater have not been measured.
- Other possible point sources are facilities that may use AFFF such as refineries and airports, or facilities where these materials are discarded such as landfills. PFC concentrations at such point sources have not been monitored in the Bay Area.

- Shorter-chained fluorinated compounds are being substituted for PFOS. Perfluorobutanesulfonate (PFBS), one of the substitutes, has been detected in Bay effluents and tributaries at relatively low concentrations (10 ng/L). Shorter-chained compounds such as PFBS are believed to be less toxic and less bioaccumulative.
- Precursors that degrade to PFOS may be another source (Higgins et al. 2005).

What Happens to It in the Bay?

General Properties

- Longer-chained PFCs (with eight carbons or more) can degrade to PFOS, which is not known to undergo further degradation in the environment.
- Unlike legacy contaminants such as PCBs and DDT that accumulate in fatty tissues, PFOS binds to proteins and is most frequently detected in blood and liver.

Patterns of Occurrence in the Bay and in Other Aquatic Ecosystems

- Bay sediment concentrations ranged from 0.4 to 3.2 parts per billion (ppb) (Sedlak and Allen in prep). The highest concentrations were observed in the South Bay.
 - These values are consistent with prior studies of San Francisco Bay and are within the range of concentrations observed nationally in estuaries and lakes. For example, concentrations from Lake Ontario were higher on average (26 ppb) (Myers et al. 2012).
- Average PFOS concentrations in Bay surface water in 2009 were 7 ng/L. These were generally lower than other urban water bodies such as Tokyo Bay (0.3-58 ng/L) and Lake Ontario (3.6-38 ng/L), but exceed concentrations measured in more pristine environments.
- PFOS accumulates in Bay birds and seals to levels that may be of concern (FIGURES 1 AND 2). Bay seal and bird egg concentrations have been some of the highest observed worldwide.

- Cormorant eggs have been collected from three Bay sites on three occasions: 2006, 2009 and 2012. Average PFOS concentrations in eggs from the South Bay in 2006 (1,300 ppb) and 2009 (1,200 ppb) exceeded a threshold of 1,000 ppb, above which adverse outcomes have been observed for survival. In 2012, PFOS in South Bay bird eggs was substantially lower (385 ppb).
- Concentrations of PFOS in seal blood have remained relatively constant over time. Similar to birds, the highest concentrations were observed in the South Bay (1,000 ng/mL, parts per billion (ppb) followed by Central Bay (80 ppb)). Background concentrations observed in seals from Tomales Bay in the Point Reyes National Seashore were much lower (12 ppb).
- PFOS was infrequently detected in sport fish tissues. Of the 21 fish analyzed in 2009, PFOS was detected in four samples (leopard shark, anchovies, and white sturgeon) with a maximum concentration of 18 ppb. There are no California thresholds for evaluating risks to humans from PFOS concentrations in Bay sport fish. The State of Minnesota has established a sport fish threshold of 40 ppb for one serving of fish per week.
- PFCs do not appreciably bioaccumulate in mussels. As part of a larger California survey and a RMP special study, PFOS was monitored in mussels at 13 Bay sites in 2010. PFOS was detected in two samples from the South Bay at concentrations of 35 ng/g dw and 76 ng/g ww.

Trends in the Bay and Nationally

- No trend data for Bay sediment and water are available.
- PFOS was lower in the most recent sampling of Bay bird eggs, but no sign of a trend has been observed in Bay seals (FIGURES 1 AND 2).

Is There a Risk of Harm in the Bay?

- In mammals, PFOS exposure has been associated with compromised immune systems, reproductive and developmental defects, neurotoxicity, and cancer (DeWitt et al. 2012).

Perfluorooctane Sulfonate (PFOS)

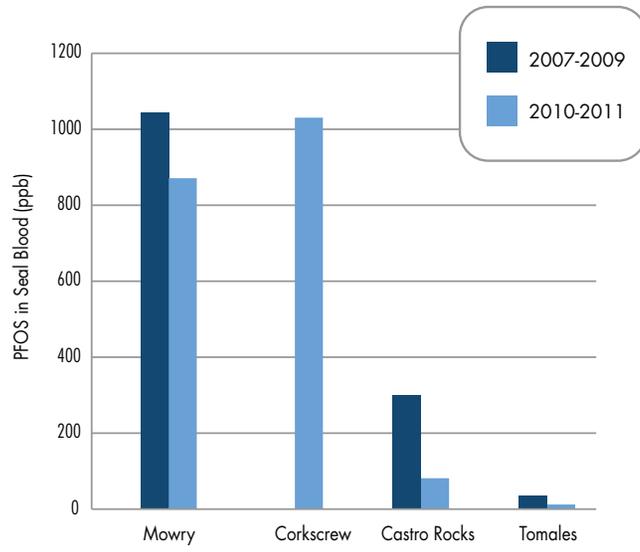
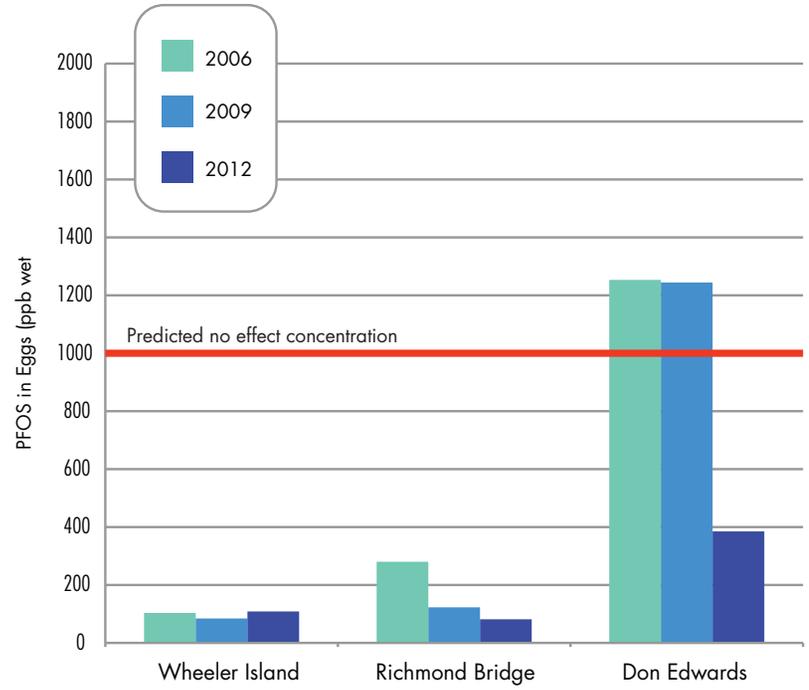


FIGURE 1
PFOS accumulates in Bay seals and birds to levels that may be of concern and are among the highest observed worldwide. Concentrations of PFOS in seal blood have remained relatively constant over time. The highest concentrations were observed in the South Bay (1,000 ng/mL, parts per billion (ppb)) followed by Central Bay (80 ppb). Background concentrations observed in seals from Tomales Bay in the Point Reyes National Seashore were much lower (12 ppb).

FIGURE 2
Average PFOS concentrations in cormorant eggs from the South Bay in 2006 (1,250 ppb) and 2009 (1,240 ppb) exceeded a threshold of 1,000 ppb, above which adverse outcomes have been observed for embryo survival. In 2012, PFOS concentrations in South Bay eggs were substantially lower (385 ppb).

Footnote: Each bar represents the average of three composite samples, with seven eggs in each composite.



Perfluorooctane Sulfonate (PFOS)

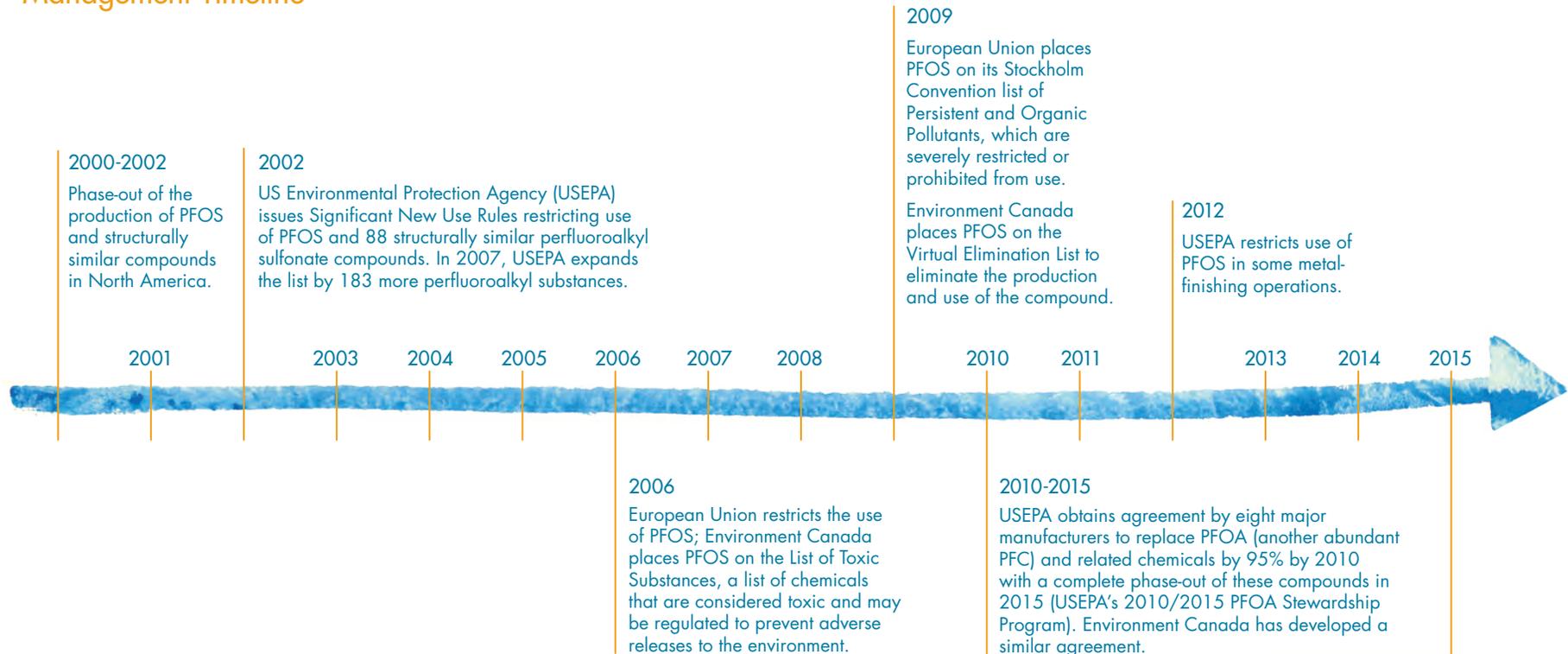
- A predicted no effect concentration for PFOS has been developed for bird eggs of 1,000 ppb (Newsted et al. 2005). Concentrations in Bay cormorant eggs have exceeded this threshold, but the most recent data from 2012 were substantially below this threshold.
- In a study of California sea otters (Kannan et al. 2006), PFOS concentrations similar to those observed in Bay harbor seals were associated with a higher incidence of disease and mortality.

Key Information Gaps

- Few studies have evaluated the effects of PFOS exposure in seals.
- The sources of PFCs to Bay biota are not well understood.
- Little is known regarding the presence and pathways by which precursors form PFOS in the Bay.

- Manufacturers are shifting to fluorinated compounds that are expected to be less toxic and less likely to accumulate in biota. It will be important to monitor to ensure that these are not accumulating in the Bay or in Bay biota.

Management Timeline



Alkylphenols and Alkylphenol Ethoxylates

**TIER 3
MODERATE
CONCERN**

CHRISTINE WERME,
Independent Consultant
(werme@sbcglobal.net)

Quick Summary

Alkylphenols, including nonylphenol and octylphenol, are key breakdown products of alkylphenol ethoxylate (APE) surfactants, once common in household detergents and other cleaning products and also used in a number of industrial applications. Alkylphenols and APEs have been detected in water, sediment, mussel, small fish, and cormorant egg samples from the Bay, sometimes at relatively high concentrations. Alkylphenols and some APEs are known endocrine disruptors. While concentrations measured in the Bay have mostly been below those known to cause chronic toxicity in marine organisms, there is new evidence that the existing levels of alkylphenols and APEs, in combination with pyrethroid pesticides, may be affecting Bay fish populations through endocrine disruption. A recent RMP report on APEs (Klosterhaus et al. 2012) presents additional information on use and production, fate in wastewater treatment plants and the environment, potential impacts, and information gaps.

What Are They?

- Alkylphenols are a family of synthetic organic compounds consisting of chains of carbon atoms, typically branched and consisting of eight or nine carbon atoms, attached to a six-carbon phenol ring.
- Alkylphenols are used to make APE surfactants, detergent-like compounds that have been widely used since the 1940s.
- Eighty to eighty-five percent of the APEs in use in the US are nonylphenol ethoxylates (USEPA 2010); octylphenol ethoxylates are the next most common APE (Chiu et al. 2010).
- Once released into the environment, APEs often break down into alkylphenols like nonylphenols and octylphenols
- The US Environmental Protection Agency (USEPA) has identified nonylphenol ethoxylates as priorities for voluntary phase-out.

What Are They Used For?

- APEs are commonly used as surfactants in detergents and cleaning products for industrial and institutional settings. They are now less common in products for the home.
- APEs have been added to pesticide formulations as “inert ingredients” to enhance performance.
- They are also used in paper production, leather and textile processing, metalworking, as oilfield chemicals and for dispersal of petroleum spills, and as ingredients in paints, adhesives, personal care products, and spermicidal lubricants.

How Are They Getting Into the Bay?

- Municipal wastewater treatment plant effluent is likely the major pathway to aquatic environments, although more information is needed on other potential pathways.
 - Long-chain APEs biodegrade during wastewater treatment to form nonylphenol and other compounds like short-chain APEs and oxidized APEs. Most studies have focused on nonylphenol and nonylphenol ethoxylates like nonylphenol monoethoxylates or diethoxylates.
 - Removal efficiencies in wastewater treatment through sorption to sludge are high, but APEs and their breakdown products are nevertheless commonly detected in wastewater effluent as a result of the high volume of use.
- Urban stormwater, septic system seepage, atmospheric deposition, and direct discharge, including application of pesticides to aquatic vegetation, are other important pathways.



Alkylphenols and Alkylphenol Ethoxylates

What Happens to Them in the Bay?

General Properties

- Alkylphenols and APEs entering the water column have a strong tendency to bind to sediment particles.
- APEs can be broken down by microbes or sunlight into alkylphenols and other compounds in the Bay, depending on environmental conditions. The environmental fate of these breakdown products is not well understood.
- Nonylphenol itself does not break down easily and is considered a persistent pollutant in aquatic environments.
- Alkylphenols and APEs are somewhat volatile, so a portion of these chemicals may be removed from the Bay by transfer into the air.
- Alkylphenols and APEs are known to accumulate in wildlife, especially invertebrates and fish. Most studies have focused on nonylphenol and octylphenol, as they are readily accumulated and stored in fat tissues and there is concern for toxicity, particularly endocrine disruption.

Patterns of Occurrence in the Bay and in Other Aquatic Ecosystems

- There are RMP occurrence data for nonylphenol, octylphenol, and nonylphenol ethoxylates in the Bay (Klosterhaus et al. 2013a).
 - Only nonylphenol has been detected in Bay water samples, with concentrations less than 100 nanograms per liter (ng/L), compared to a USEPA saltwater chronic water criterion of 1,700 ng/L.
 - Nonylphenol, nonylphenol monoethoxylates, and nonylphenol diethoxylates were consistently detected at moderately high concentrations in RMP sediment samples, with a median of 35 ppb for nonylphenol.
- Detection was sporadic in RMP mussel samples, but concentrations were sometimes high, with maximum measurements of nonylphenol, nonylphenol monoethoxylates, and nonylphenol diethoxylates of 1,290, 300, and 1,420 ppb, respectively.
- High concentrations of nonylphenol (maximum 123 ppb) and nonylphenol ethoxylates (maximum 228 ppb) have also been found in Bay cormorant eggs.
- Octylphenol was not detected in water, sediment, or mussel samples.
- The NOAA Mussel Watch California CEC Pilot Study (Mussel Watch) 2010 found lower concentrations in some cases than had been measured in RMP samples, but still higher concentrations than many other contaminants found in Bay mussels.
 - Concentrations of some compounds in Mussel Watch samples, for example 4-nonylphenol monoethoxylate, were high, at levels comparable to sites in Southern California (FIGURE 1). The maximum level of 4-nonylphenol monoethoxylate measured in the Bay was 300 ppb.
 - Bay mussel concentrations for other compounds, for example nonylphenol, were low in comparison to samples from Southern California (FIGURE 2).
- Overall, levels found in Bay samples were typically lower than those found in effluent-dominated systems, and similar to or lower than other marine and estuarine areas of the US.
- Diehl et al. (2012) found that concentrations of nonylphenol in mussels and small fish (gobies) from San Francisco Bay were lower than in Morro Bay and Tomales Bay, two undeveloped coastal areas. The maximum concentration of nonylphenol in Bay small fish was 420 ppb. Seepage from septic systems appeared to be one major pathway for nonylphenol to enter Morro Bay, with toilet paper a likely source (Diehl et al. 2012).

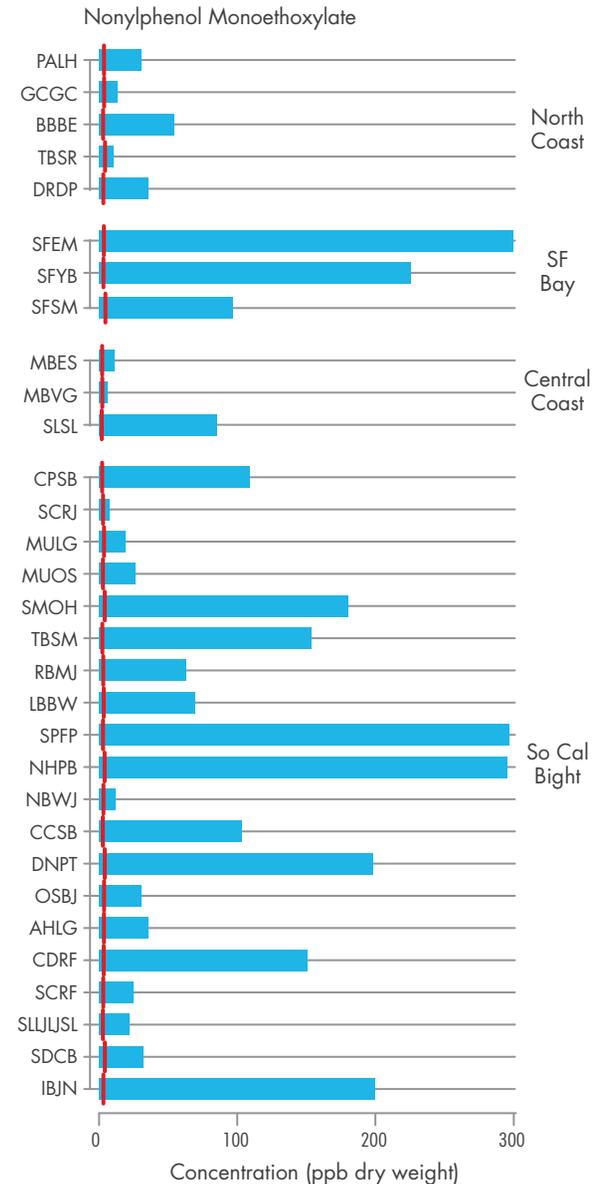


FIGURE 1

Of the three alkylphenol compounds that are detected frequently in the environment, 4-nonylphenol monoethoxylate is relatively abundant in San Francisco Bay as well as at stations in Southern California. It was detected in all 32 of the NOAA Mussel Watch stations sampled. Red lines indicate limit of detection.

Footnote: SFEM-San Francisco Bay, Emeryville; SFYB-San Francisco Bay, Yerba Buena; SFSM-San Francisco Bay, San Mateo Bridge

Alkylphenols and Alkylphenol Ethoxylates

Endocrine disruption caused by mixtures of pyrethroid insecticides, alkylphenols, and alkylphenol ethoxylates could be contributing to the pelagic organism decline (POD)

Trends in the Bay and Nationally

- No trend data are available.

Is There a Risk of Harm in the Bay?

- Alkylphenols and some APEs are known endocrine disruptors.
- Concentrations of nonylphenol and nonylphenol ethoxylates in the Bay are generally well below concentrations shown to be toxic to aquatic organisms, such as the USEPA saltwater chronic water criterion of 1,700 ng/L.
- An exception is a study suggesting the potential for impacts on barnacle settlement due to exposure to nonylphenol concentrations of 60 ng/L in water (Billinghurst et al. 1998).
- Sites near wastewater or stormwater outfalls may have higher concentrations of these contaminants and be at greater risk.
- Schlenk et al. (2012) found estrogenic activity in laboratory fish exposed to mixtures of pyrethroid pesticides, alkylphenols, and APEs. Pesticides alone did not cause estrogenic activity. Their results suggested that endocrine disruption, caused by these mixtures, could be partially responsible for the observed declines of pelagic fish populations in the San Francisco Bay-Delta.

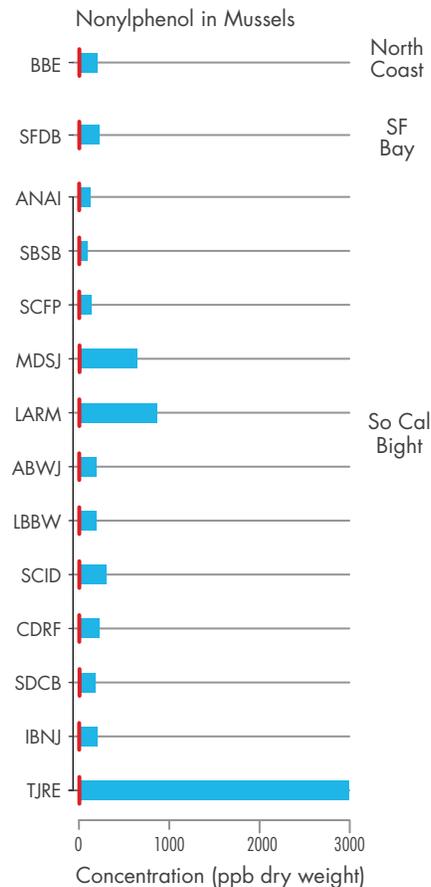


FIGURE 2
4-Nonylphenol was found at the highest concentration, 3,000 ppb, in a NOAA Mussel Watch sample from the Tijuana River in Southern California. The concentration in the Bay sample from near the Dumbarton Bridge (SFDB) was not high relative to other stations. Red lines indicate limit of detection.

Alkylphenols and Alkylphenol Ethoxylates

Key Information Gaps

- Although APEs and alkylphenols are widely used and ubiquitous in the environment, even in remote areas, there is a need for basic information.
- More complete characterization of concentrations of alkylphenols and APEs throughout the Bay and particularly near outfalls, including monitoring

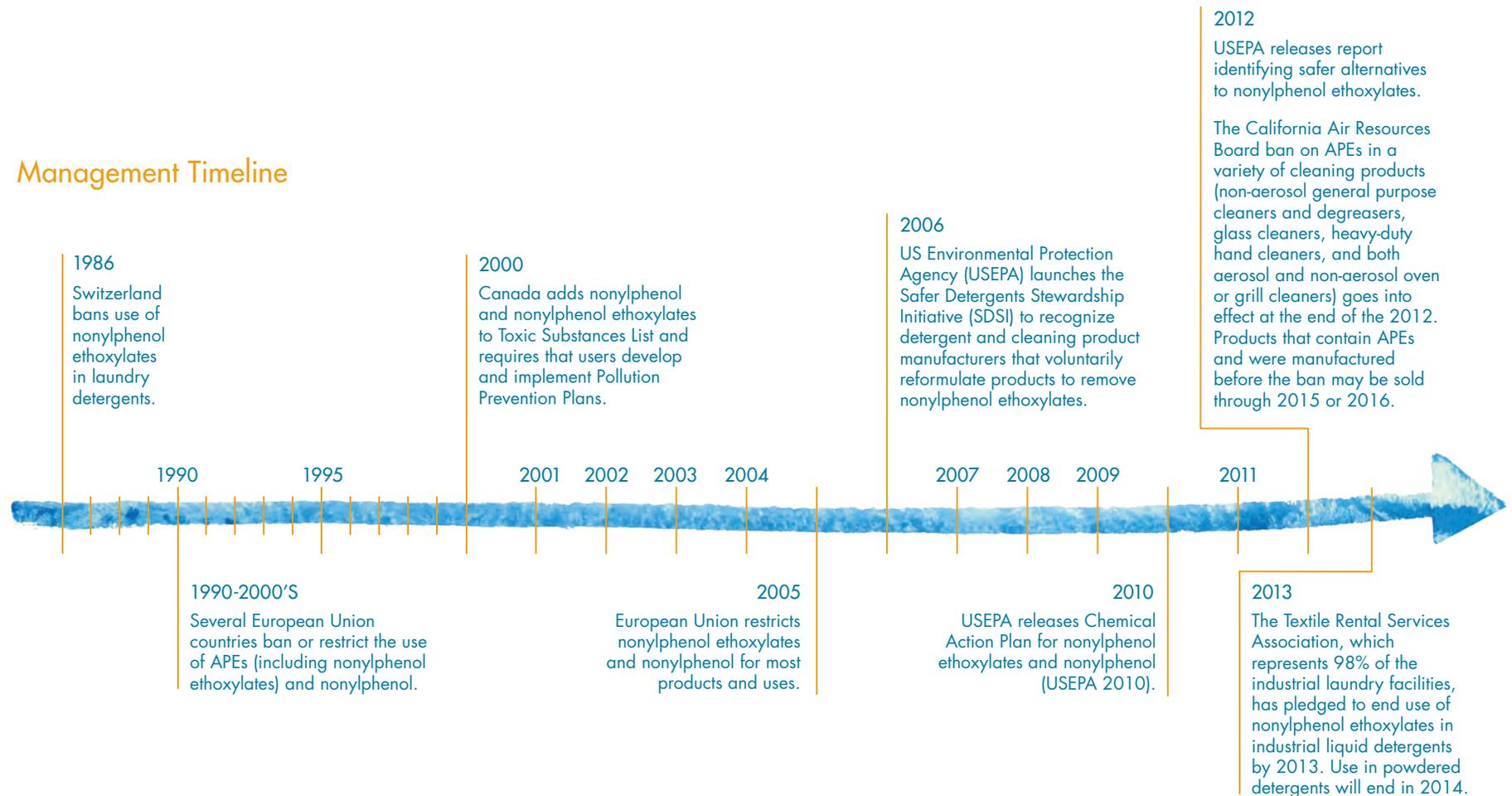
for a full range of long-chain APEs and a greater variety of important degradation products.

- Information on potential long-term effects on Bay wildlife.
- Information on combined effects of multiple endocrine disruptors in mixture exposures.
- Information on combined biological effects of

APEs and alkylphenols with pesticides like pyrethroids.

- Better sampling and analytical methods for alkylphenols and APEs.

Management Timeline



Polybrominated Diphenyl Ethers (PBDEs)

**TIER 3
MODERATE
CONCERN**

REBECCA SUTTON,
San Francisco Estuary Institute
(rebeccas@sfei.org)

Quick Summary

PBDEs are flame retardants once common in foam furniture, electronics, and many other products. Bans and phase-outs are eliminating these chemicals from new goods, but they remain present in products in use today and in the wastestream. PBDEs have been extensively monitored in San Francisco Bay water, sediment, and wildlife. In wildlife, levels appear to be declining over time, likely a response to the chemical bans. Preliminary research indicates concentrations in Bay harbor seals may be present at harmful levels, but those found in bird eggs do not appear to be problematic. Levels of PBDE contamination in sport fish do not pose risks to people who eat them. However, there is little information about the effects of contamination on the health of the fish themselves. California's unusually strict flammability standards have resulted in widespread use of chemical flame retardants in products. An effort is underway to revise these standards to provide fire safety while reducing the need for added flame retardants.

What Are They?

- A class of synthetic bromine-containing chemicals.
- Used as flame retardants in polyurethane foam, plastics, and textiles.
- Produced in three commercial mixtures named for the average number of bromines in each: PentaBDE, OctaBDE, and DecaBDE.
- Structurally similar to PCBs, a class of legacy pollutants that are persistent, bioaccumulative, highly toxic, and commonly found in the Bay.

What Are They Used For?

- Chemical flame retardants like PBDEs are often added to products to meet the unusually strict flammability standards set by the state of California. Most furniture sold in the US meets California flammability standards.
- PentaBDE, composed primarily of PBDEs containing four and five bromines (e.g., BDE-47 and BDE-99), was commonly used as a flame retardant in polyurethane foam in furniture cushions, car seats, and mattresses. It was also used in foam-based packaging and carpet padding.
- OctaBDE, composed primarily of PBDEs containing six, seven, and eight bromines (e.g., BDE-183, BDE-197, and BDE-203), was used as a flame retardant in plastic housings for electrical and electronic equipment.
- PentaBDE and OctaBDE are no longer manufactured or added to new products in the US. They were banned in California in 2006. However, they are still found in many consumer goods made before the ban went into effect.
- DecaBDE, composed primarily of BDE-209, is a flame retardant used with virtually any type of polymer, including plastics, textiles, and back-coatings of consumer electronics.

- By the end of 2013, DecaBDE will no longer be manufactured in the US. Because this phase-out is voluntary, DecaBDE may still be present in imported products.
- If California's existing flammability standards are not revised, manufacturers of consumer goods will likely simply substitute new chemical flame retardants for PBDEs. Some of these alternative flame retardants are potentially harmful to human health or wildlife and have already been detected in the Bay (PAGE 67).
- The California bureau charged with consumer product fire safety has proposed revised flammability standards that will provide fire protection without requiring the use of added chemical flame retardants in many consumer goods.

How Are They Getting into the Bay?

- PBDEs are not chemically bound to the polymers or products that contain them, so they can escape via volatilization to the air or on loose particles. They are a major contaminant of indoor dust.
- Discharges of treated wastewater from municipal wastewater treatment facilities are considered the major pathway for BDE-47 (one of the most abundant PBDEs) to enter the Bay.
- On the other hand, urban stormwater is considered the major pathway for BDE-209 (another abundant PBDE, and the primary component of DecaBDE) to enter the Bay.
- Flows from the Delta and direct atmospheric deposition are minor PBDE pathways to the Bay.

Polybrominated Diphenyl Ethers (PBDEs)

What Happens to Them in the Bay?

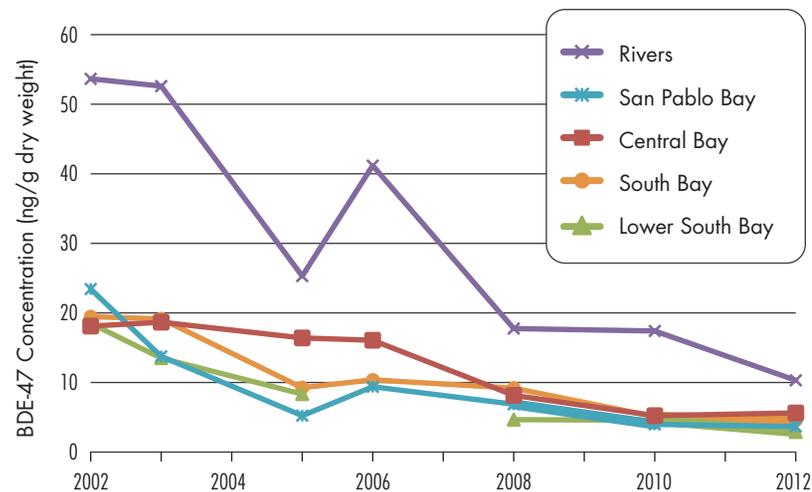
General Properties

- Individual PBDEs have different chemical properties depending on the number of bromine atoms they contain. This range of chemical properties affects how individual PBDEs behave in the environment.
- PBDEs tend to associate with sediment particles, and those with more bromine atoms show a stronger particle affinity. Bay sediment tends to contain a large proportion of all PBDEs, especially BDE-209, which has ten bromine atoms. BDE-47, with four bromine atoms, is the dominant PBDE found in Bay water, though it is still mainly found in sediment.
- PBDEs are generally lipophilic (“fat-loving”), and many accumulate in organisms. However, the most lipophilic, BDE-209, is not often detected in Bay wildlife. It may be too strongly bound to sediments to be transferred to organisms. It may also be too large to pass readily through an organism’s cell membranes.
- PBDEs are generally persistent chemicals in the environment. However, PBDEs with larger numbers of bromine atoms can be debrominated via microbial and metabolic processes or exposure to sunlight, forming PBDEs with fewer bromines.
- Debromination of BDE-209 can result in formation of less-brominated PBDEs with higher toxicity and greater tendency to bioaccumulate.

Patterns of Occurrence in the Bay and in Other Aquatic Ecosystems

- PBDEs are common in Bay sediment (PAGE 37). The dominant PBDE found in sediment is BDE-209 (PAGE 37), the major component of the DecaBDE commercial mixture.
- In 2011 and 2012, most sediment samples contained PBDE levels totaling 52 parts per billion (ppb) or less. Levels are similar to those found in other areas, such as the coastal regions of Southern California and Canada (Grant et al. 2011, Dodder et al. 2012).

PBDEs in Bay Bivalves



Footnote: River bivalves are resident clams, while Bay bivalves are primarily mussels deployed for 90 days and then collected for monitoring. The higher levels present in river bivalves are likely due to their longer exposure time.

FIGURE 1

PBDE levels in Bay bivalves have declined over the last decade, likely a result of both the nationwide phase-out and state ban of PentaBDE and OctaBDE. BDE-47 is the dominant form of PBDEs in wildlife and is graphed here as an indication of overall PBDE levels. BDE-47 is a major component of the PentaBDE mixture.

- However, sediment from two contamination “hotspot” sites located in the margins of the Bay (San Leandro Bay and Mission Creek), contained more than four times the maximum amount reported for more typical Bay locations (220 and 240 ppb, respectively).
- In Bay water samples, BDE-47 is the dominant PBDE detected. The Baywide average level of BDE-47 was 43 picograms per liter (pg/L) in 2011 (PAGE 36).
- PBDEs are detected in all Bay wildlife monitored by the RMP. The dominant PBDE in wildlife samples is BDE-47. BDE-209 is rarely detected.
- Bay mussels are widely contaminated with PBDEs. The National Oceanic and Atmospheric Association considers Bay mussels highly contaminated relative to other parts of the US (Kimbrough et al. 2009). However, RMP measurements from 2002 to 2012 show levels have begun to decline (FIGURE 1).
- Bay sport fish also contain PBDEs, with concentrations that vary widely by species. Levels in shiner surfperch,

a fish that tends to feed over a relatively small territory, indicate regional variation in contamination, along with an overall decline in PBDEs from 2003 to 2009 (FIGURE 2).

- A tern egg collected from the Bay in 2002 contained the highest level of PBDEs ever measured in an organism at that time, 63,300 ppb lipid weight (nanograms of PBDE per gram of lipid [or fat] in the sample) (She et al. 2008).
- The RMP analyzed tern eggs in 2009 and found a maximum value of 2,400 ppb lipid weight (lw); the eggs averaged 1,400 ppb lw.
- Cormorant eggs collected by the RMP from three different locations also generally show declining levels of PBDE contamination from 2002 to 2009 (FIGURE 3).
- A decade ago, a California Environmental Protection Agency study showed PBDE levels in Bay harbor seal blubber samples were as high as 8,300 ppb lw and were doubling every 1.8 years (She et al. 2002). Recent results suggest that contamination in adult harbor seals may have stabilized or begun to decline.

Polybrominated Diphenyl Ethers (PBDEs)

Trends in the Bay and Nationally

- PBDE levels are generally declining in Bay wildlife. Over the last ten years, RMP monitoring of bivalves, fish, and bird eggs consistently indicates falling levels of pollution (FIGURES 1, 2, and 3).
- Other studies have identified potential PBDE declines, including osprey eggs in the Pacific Northwest (Henny et al. 2009), sockeye salmon from the northeast Pacific Ocean (Ikonomou et al. 2011), and trout in the Great Lakes (Crimmins et al. 2012).
- BDE-47 levels in sediment also appear to have declined over the past 10 years (PAGE 37).
- Concern remains despite evident declines, as PBDEs present in existing products can be sources of continuing contamination of the environment over time.

Is There a Risk of Harm in the Bay?

- Bay sport fish do not contain PBDE levels that would make them unfit for human consumption based on comparison to thresholds developed by the California Office of Environmental Health Hazard Assessment (Klasing and Brodberg 2011).
- PBDEs also appear unlikely to affect the reproduction and development of Bay birds, according to a recent study of the toxicity of PentaBDE to tern embryos (Ratner et al. 2011).
- Current levels of PBDE contamination may be harmful to Bay harbor seals (Neale et al. 2005), though further research is needed to investigate these potential health impacts.
- There are few studies on the effects of PBDEs on fish. One study (Arkoosh et al. 2010) documented increased susceptibility to pathogenic microorganisms in young Chinook salmon at a PBDE concentration that has been exceeded in some Bay fish samples. Bay fish samples from 2009 had lower levels of PBDEs than in prior years.
- PBDE levels are declining, so any risk of harm should decline as well.

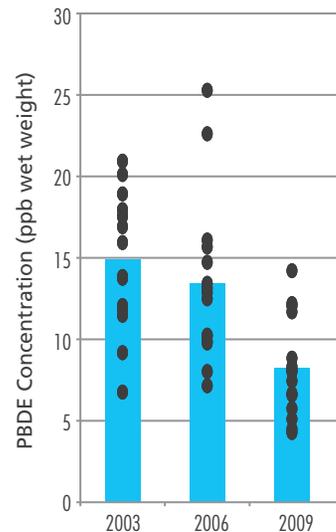


FIGURE 2 PBDE concentrations in shiner surfperch, a popular Bay sport fish, were significantly lower in 2009 as compared to previous years. This decline is likely due to the nationwide phase-out and state ban of PentaBDE and OctaBDE. All sport fish examined in the Bay contained PBDE levels below 100 ppb, meaning an adult person can safely eat up to three servings per week according to the California Office of Environmental Health Hazard Assessment (Klasing and Brodberg 2011).

Footnote: Bars indicate average concentrations. Points represent composite samples. The RMP examined eight sport fish species in 2009; shiner surfperch had the highest levels of contamination, and therefore represent the worst-case exposure.

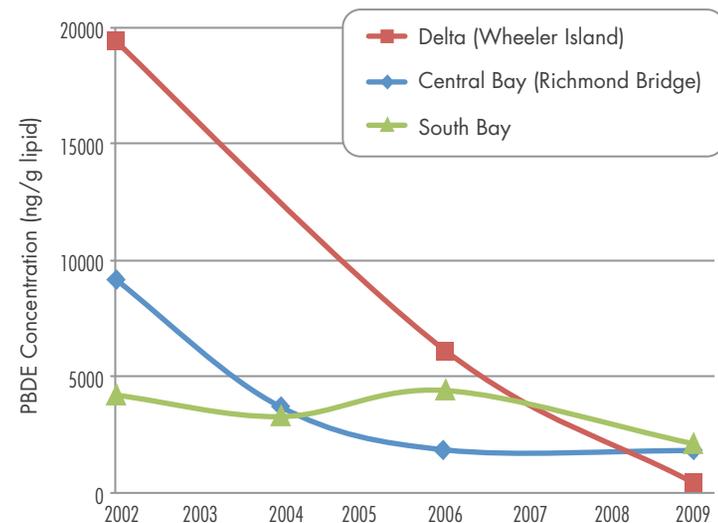


FIGURE 3 PBDE levels in cormorant eggs show general declines from 2002 to 2009, likely a result of both the nationwide phase-out and state ban of PentaBDE and OctaBDE. Cormorants are piscivores and prefer to forage in open Bay waters.

Footnote: Each value is an average of two or three composite samples. Each composite sample is made up of the contents of seven to ten eggs.

Polybrominated Diphenyl Ethers (PBDEs)

Key Information Gaps

- The impact of current levels of contamination on Bay harbor seals and fish.
- Characterization of PBDE levels in Bay water, sediment, and biota in the margins of the Bay, where localized “hotspots” of contamination are likely.
- Degradation and debromination rates for BDE-209, the primary component of DecaBDE.
- Toxicity assessment of lower-brominated congeners created through environmental debromination processes and not found in commercial mixtures.

Management Timeline

2004

In response to pressure from the US Environmental Protection Agency (USEPA), the major manufacturer of PentaBDE and OctaBDE agrees to stop producing the compounds in 2004.

2006

The state of California bans production, use, and sale of products containing PentaBDE and OctaBDE. USEPA issues a Significant New Use Rule for PentaBDE and OctaBDE, allowing the agency to review and regulate any new uses for these compounds.

2013

In response to pressure from USEPA, the major manufacturers of DecaBDE agree to stop producing this mixture by the end of 2013.

The California state agency responsible for flammability standards (www.bearhfti.ca.gov) proposes new standards that will eliminate the need for added chemical flame retardants in many consumer goods (www.bhfti.ca.gov/about/laws/propregs.shtml).

2005

2007

2008

2009

2010

2011

2012



Alternative Flame Retardants

TIER 1
POSSIBLE
CONCERN
Most
Compounds

TIER 2
LOW
CONCERN
HBCD

CHRISTINE WERME,
Independent Consultant
(werme@sbcglobal.net)

Quick Summary

After two classes of polybrominated diphenyl ether (PBDE) flame retardants were banned, manufacturers began to substitute other flame retardant chemicals in consumer products. Some of these chemicals have been in use for decades, while others are new. The phase-out of the third and final class of PBDEs will be complete by the end of 2013. Little is known about many of the diverse array of bromine-, chlorine-, and phosphate-containing compounds that have replaced PBDEs. Recent studies have detected some of these alternative flame retardants in Bay samples. Typically, they are found in lower concentrations than PBDEs. The concentrations observed have been far below the effects thresholds that exist for a few of these compounds, but for most of these chemicals the potential risks are unknown. Proposed changes to California's strict flammability standards may lessen the use of chemical flame retardants in consumer products and therefore lessen the potential risks in the Bay.

What Are They?

- Synthetic organic chemicals typically containing bromine, chlorine, or phosphate.
- These compounds have a wide variety of chemical structures. Some undergo chemical reactions to bind to the products they treat ("reactive" flame retardants), while others do not ("additive" flame retardants).

What Are They Used For?

- Used as flame retardants and for some other purposes, such as plasticizers. Increased use of these compounds as flame retardants occurred following bans of two classes of PBDEs.
- Uses of the alternative flame retardants detected in the Bay are varied.
 - Hexabromocyclododecane (HBCD): primarily used in polystyrene insulation panels or boards in buildings (e.g., thermal insulation); also used in foams for furniture, and in the automotive and electronics industries.
 - Pentabromoethylbenzene (PBEB): used in circuit boards, cables, and other electronics; and in textiles, adhesives, and polyurethane.
 - 1,2-Bis (2,4,6, tribromophenoxy) ethane (BT-BPE): used in plastics that require high temperatures during manufacture, such as polystyrene, and in resins.
 - Bis (hexachlorocyclopentadieno) cyclooctane (DP or Dechlorane Plus): used in coatings for wires and cables and in plastic roofing materials for commercial buildings. DP has also been used as a pesticide.

- Tris (1,3-dichloro-2-propyl) phosphate (TDCPP or "chlorinated tris"): briefly used in children's pajamas in the 1970s. Now widely used in polyurethane foam and found in a range of household items, including baby strollers and other baby products, pillows, foam mattress pads, and foam furniture.
- Tris (1-chloro-2-propyl) phosphate (TCPP): used in rigid polyurethane foams and in flexible polyurethane foams for furniture and upholstery.
- Tris (2-chloroethyl) phosphate (TCEP): used in polyurethane foams.
- Triphenyl phosphate (TPhP): used as a flame retardant and a plasticizer in the automotive industry, in roofing paper, and in other applications. Also a component of Firemaster 550, a flame retardant mixture widely used in polyurethane foam.
- Tris (2-butoxyethyl) phosphate (TBEP): used as a flame retardant and as a plasticizer in floor polishes, plastics, and acrylic paints.
- Tributyl phosphate (TBP): used in aircraft hydraulic fluid.

How Are They Getting into the Bay?

- Municipal wastewater treatment plant effluent is probably the major pathway to the Bay, although there is little information on other potential pathways.
- Urban stormwater, which flows directly into the Bay untreated, is another potential pathway. Stormwater is a known pathway for PBDEs, the compounds the alternatives are replacing, to enter the Bay.
- Other potential sources include atmospheric deposition and inputs from the Delta.

Alternative Flame Retardants

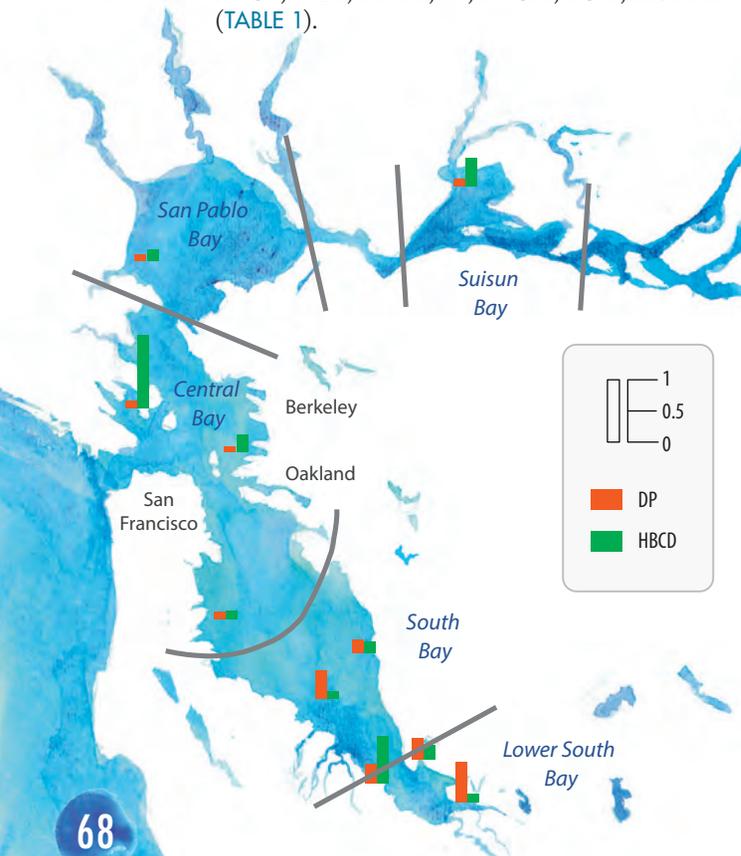
What Happens to Them in the Bay?

General Properties

- Depending upon their individual physical and chemical traits, the alternative flame retardants may adsorb to sediment particles; degrade by chemical processes, sunlight, or metabolic activity; volatilize into the atmosphere; or accumulate in Bay biota.

Patterns of Occurrence in the Bay and in Other Aquatic Ecosystems

- Five water soluble alternative flame retardants were present in Bay waters analyzed using passive samplers: TDCPP, TCPP, TPhP, TCEP, and TBP (TABLE 1).
- Compounds detected in sediment samples include HBCD, PBEB, BTBPE, DP, TDCPP, TCPP, and TPhP (TABLE 1).



- Concentrations of HBCD and DP, two of the alternative flame retardants most frequently detected in sediment samples, tended to be highest in the Central and Lower South Bay (FIGURE 1).
- Phosphate flame retardants TDCPP, TCPP, and TPhP are relatively abundant in Bay sediment, with concentrations comparable to those of PBDEs and polychlorinated biphenyls (PCBs) in the same samples.
- Alternative flame retardants detected in Bay wildlife include HBCD, PBEB, DP, TCPP, TCEP, TBEP, and TPhP (TABLE 1).
 - In general, concentrations of alternative flame retardants in Bay wildlife are low compared to concentrations of PBDEs (Klosterhaus et al. 2012, 2013).
 - In Bay wildlife samples, HBCD was detected at levels that were one-tenth to one-thousandth of PBDE concentrations in the same samples.
 - PBEB was detected in all adult and most harbor seal pups sampled.
 - Despite its occurrence in sediment samples, BTBPE was not detected in Bay wildlife.
 - DP was detected in most wildlife samples but in concentrations lower than HBCD in the same samples.
 - TCPP, TCEP, and TBEP were detected in all bird egg samples.
 - TPhP was detected in mussel samples.

FIGURE 1

Concentrations of DP and HBCD (ng/g dry weight), two alternative flame retardants most frequently detected in sediment samples, tended to be highest in the Central and Lower South Bay (Klosterhaus et al. 2012).

- Concentrations of alternative flame retardants in the Bay are similar to or lower than concentrations in other locations (Klosterhaus et al. 2012).
- Four other bromine-containing and six phosphate-containing chemicals have been targeted for analysis but have not been detected in Bay samples (TABLE 2).

Trends in the Bay and Nationally

- Very little trend information is available for many alternative flame retardants.
- Measurements of HBCD in California sea lions indicate levels of contamination increased from 1993 to 2003 (Stapleton et al. 2006). Increasing HBCD contamination has also been observed in marine mammals and fish elsewhere in the US (Chen et al. 2011; Hoguet et al. 2013).
- Analysis of sediment cores from the Great Lakes indicates DBDPE and BTBPE contamination is increasing exponentially. DBDPE levels doubled every 3-5 years from 1950 to present in Lake Michigan and every 7 years from 1950 to present in Lake Ontario. BTBPE levels doubled every 7 years from 1950 to present in Lake Michigan and every 5 years from 1950 to 2000 in Lake Ontario, though recent Lake Ontario measurements suggest contamination may be leveling or declining (Yang et al. 2012).
- DBDPE, BTBPE, and HBB were commonly detected in eggs collected from colonies of Great Lakes herring gulls. The measurements suggest a possible increase in these compounds during the most recent years of sampling (2004-2006). Trends were not obvious for the other flame retardants examined (Gauthier et al. 2009).
- DP levels in Great Lakes herring gull eggs show greater contamination starting in the mid-1990s (Gauthier and Letcher 2009). In contrast, measurements of DP and related compounds in Niagara River suspended sediment as well as Lake Ontario sediment cores and lake trout suggest peak contamination in the 1980s followed by declines (Shen et al. 2011).

Alternative Flame Retardants

TIER 1

TIER 2

Is There a Risk of Harm in the Bay?

- Risks are largely unknown due to a lack of information for the wide variety of chemical compounds.
 - HBCD is considered to be a neurotoxin and endocrine disruptor. It may also cause neurodevelopmental harm and decrease fertility. Levels detected in the Bay are lower than toxicity thresholds for algae (Birnbaum and Staskal 2012), and use is likely to decline following a recent global agreement to phase out this flame retardant.

- There are no toxicity data for PBEB.
- BTBPE is structurally similar to known endocrine disruptors.
- DP is toxic to insects and used as an insecticide.
- Chlorinated tris or TDCPP is a mutagen and carcinogen. It was added to the Proposition 65 list of chemicals known to the state of California to cause cancer in 2011. TDCPP also has the potential to act as a neurotoxin and endocrine disruptor (Meeker and Stapleton 2010, Dishaw et al. 2011).
- TCPP is structurally similar to known carcinogens.
- TCEP has been shown to cause tumors and reduce fertility in laboratory animals and has been identified by the European Chemicals Agency as a Substance of Very High Concern. TCEP was added to the Proposition 65 list of chemicals known to the state of California to cause cancer in 1992.
- TPhP is a known neurotoxin and has been linked to lowered sperm production. The European Chemicals Agency considers TPhP very toxic to aquatic life, and capable of producing long lasting effects.
- TBEP may affect liver function; its long-term toxicity is unknown.
- Toxicity threshold data for wildlife are extremely limited.

TABLE 1

Alternative flame retardants that have been detected in San Francisco Bay (from Klosterhaus et al. 2013a,b).

• indicates detection; x indicates lack of detection.

ALTERNATIVE FLAME RETARDANTS	WATER*	SEDIMENT	MUSSELS	SPORT FISH	BIRD EGGS	SEALS
HBCD		•	•	•	•	•
Dechlorane Plus (DP)		•	•	•	•	•
PBEB		•	•	x	x	•
DBDPE		x				
BTBPE		•	x	x	x	x
HBB		x	x	x	x	x
BEH-TBP**		x	x		x	
EH-TBB**		x	x	x	x	x
TDCPP or Chlorinated Tris	•	•	x		x	
TCPP	•	•	x		•	
TPhP	•	•	•		x	
TCEP	•				•	
TBP	•				x	
TBEP	x				•	
TEHP	x				x	
TPhP					x	
Tris(2,3-dibromopropyl) phosphate, Tricresyl phosphate, 2-Ethylhexyl-diphenyl phosphate, Tris(2-bromo-4-methylphenyl) phosphate					x	

* Qualitative detections via passive water samplers indicating presence or absence in Bay waters.
 ** Possibly not detected due to methodological issues.

TABLE 2

Possible additional target alternative flame retardants for monitoring in San Francisco Bay.

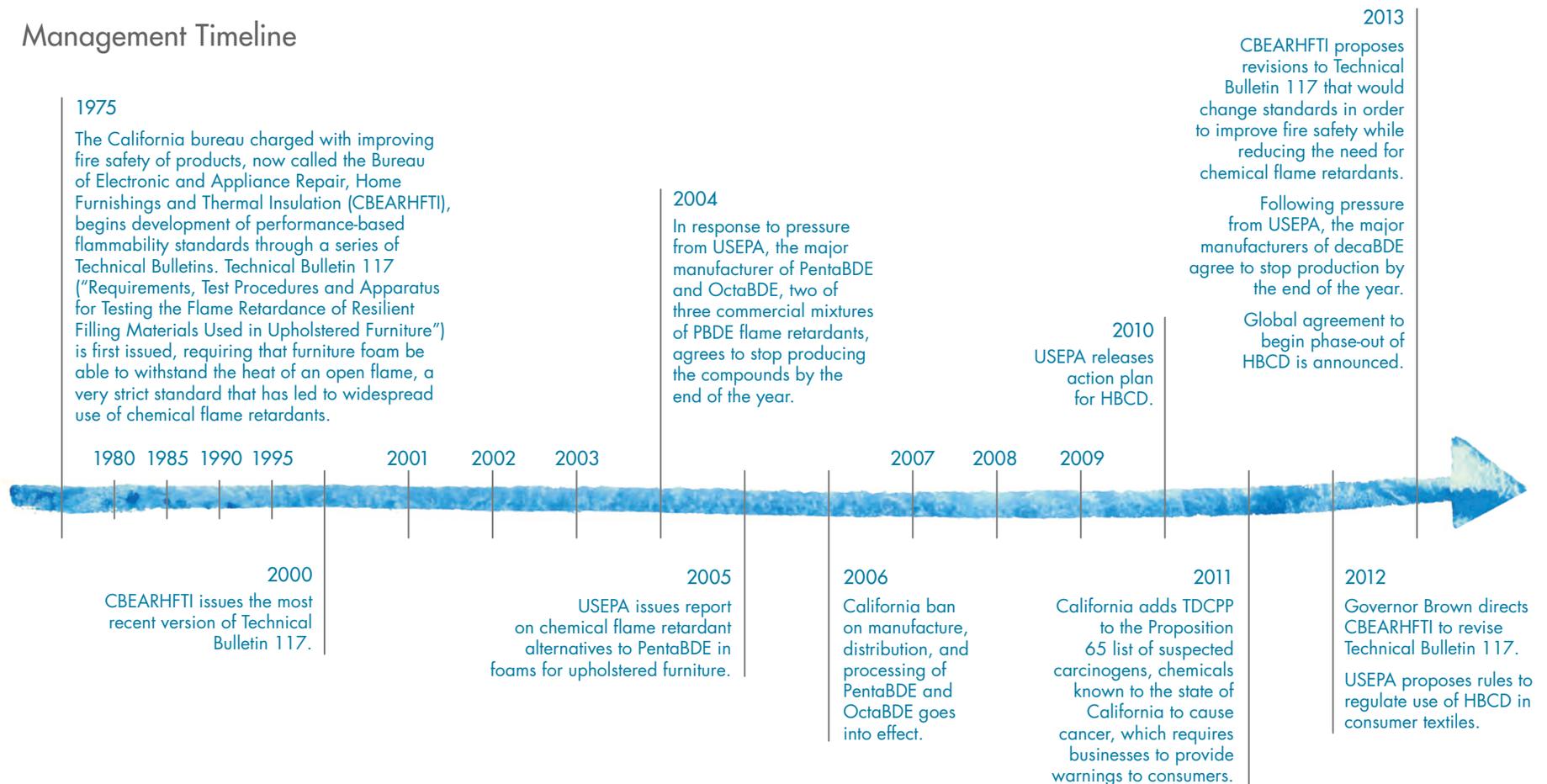
COMPOUND	REASON FOR MONITORING
V6	Newly identified, phosphate flame retardant used in polyurethane foam (Fang et al. 2013)
Phosphate flame retardant metabolites	Many phosphate flame retardants are not found in biota and appear to be metabolized rapidly; detection of metabolites would indicate exposure
Ethylene bis-tetrabromophthalimide – EBTEBPI	A widely used additive flame retardant with predicted high persistence and potential for bioaccumulation
1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane – TBECB or DBE-DBCH	Likely not used in high volume, but has been detected in environmental samples, with predicted high persistence, toxicity, and bioaccumulation; causes reproductive toxicity in American kestrels and thyroid disruption in juvenile brown trout

Alternative Flame Retardants

Key Information Gaps

- Additional compounds could be targeted for monitoring (TABLE 2).
- Some flame retardants are proprietary mixtures with unknown formulations, so other compounds may be present but not included on lists of potential analytes.
- Little is known about the toxicity of individual compounds, and even less is known about cumulative effects of complex mixtures.
- Trend monitoring will be needed to track changes in environmental concentrations in response to evolving regulation and use.

Management Timeline



Pharmaceuticals and Personal Care Products

CHRISTINE WERME,
Independent Consultant
(werme@sbcglobal.net)

TIER 2
LOW
CONCERN
Most Compounds
Tested

TIER 1
POSSIBLE
CONCERN
Bisphenol A
Phthalates

Quick Summary

Pharmaceuticals and personal care products (PPCPs) include a wide variety of prescription and over-the-counter drugs, cosmetics, sunscreens, fragrances in personal and home care products, and other products used in homes, medical facilities, and even agriculture. PPCPs enter the wastestream through excretion, bathing, laundering, and flushing of unused medicines. Although scientists have long been aware of their presence in the environment, only recently have analytical methods been developed to detect the low concentrations found in aquatic ecosystems such as the Bay. Of the thousands of chemicals used in these products, the RMP has targeted about 100 for analysis. The compounds detected in water samples include antibiotics, beta blockers, stimulants, nicotine metabolites, headache relievers, lipid reducers, antidepressants, anxiety reducers, hypertension relievers, plasticizers, and insect repellents. Many of these chemicals have also been detected in Bay sediment and wildlife samples. Concentrations of PPCPs in the Bay are lower than those found in wastewater-dominated rivers and streams where there is less dilution, and about the same as reported for other estuarine or marine areas. Risks are largely unknown due to the wide variety of chemical compounds, the generally low concentrations at which they are found, and the lack of information on the effects of these compounds on estuarine organisms. However, concentrations are generally below the thresholds that do exist.

What Are They?

- A wide variety of prescription, over-the-counter, and veterinary drugs and their metabolites; diagnostic agents; vitamins and other nutritional supplements; ingredients in cosmetics, sunscreens, and lotions; insect repellants; and fragrance ingredients used in many products.
- A few additional compounds are often measured along with PPCPs, including bisphenol A and plasticizers known as phthalates.

What Are They Used For?

- Pharmaceutical drugs are used as antibiotics, antidepressants, anti-epileptics, estrogenic steroids, and in many other human or veterinary health applications.
- Triclosan (PAGE 75) and triclocarban are antibacterial agents commonly added to soaps and other consumer products.
- Synthetic musks and other natural and artificial fragrance ingredients are used in cosmetics, perfumes, detergents, cleaning supplies, and other household products.
- Bisphenol A is used in plastics and epoxy resins and in the linings of food cans.
- Phthalates are added to plastics to increase flexibility and longevity. Some are also found in nail polish, home care products like treatments for wood floors, and in fragrance mixtures in personal care products and cleaning supplies.
- N,N-diethyl-m-toluamide, known as DEET, is the most widely used insect repellent.
- Siloxanes are common ingredients in personal care products like antiperspirants and deodorants, shampoos, conditioners, and cosmetics. They are also used in dry-cleaning.

How Are They Getting into the Bay?

- Municipal wastewater treatment plant effluent is probably the major pathway to the Bay, although more information is needed on other potential pathways.
 - PPCPs enter the sewage wastestream through excretion, bathing, laundering, and flushing of unused medicines.

- Municipal sewage systems are not engineered for removal of the wide variety of these chemical compounds, but standard treatment methodologies are effective at removing some PPCPs. Removal efficiencies vary by compound.
- Harrold et al. (2009) detected 18 of 39 target pharmaceuticals in influent, effluent, and water samples in the Lower South Bay, with findings comparable to similar studies in other regions.
- Urban stormwater, which flows directly into the Bay untreated, is another potential pathway.
- Flow through the Delta may be a source, particularly for veterinary pharmaceuticals used in agriculture.

What Happens to Them in the Bay?

General Properties

- Depending upon their individual physical and chemical characteristics, PPCPs may be subject to adsorption to sediment particles, degradation, volatilization to the atmosphere, or uptake into organisms.

Patterns of Occurrence in the Bay and in Other Aquatic Ecosystems

- Until recently, there were no reliable methods for quantifying PPCPs in ecosystems like the Bay, in which wastewater effluents are quickly diluted, and concentrations in sediment and wildlife samples are expected to be low (Klosterhaus et al. 2013a.)
- There are now occurrence data for about 100 PPCPs and metabolites in the Bay (Klosterhaus et al. 2013a,b).
- Chemicals detected in water samples make up a soup of antibiotics, beta blockers, stimulants, nicotine metabolites, headache relievers, lipid reducers, antidepressants, anxiety reducers, hypertension relievers, and insect repellent (TABLE 1).
 - The maximum concentration of a pharmaceutical in Bay water was 1,060 nanograms per liter (ng/L) for sulfamethoxazole, an antibiotic.
 - Sulfamethoxazole, valsartan (used to treat high blood pressure, heart failure, and progressive

Pharmaceuticals and Personal Care Products

kidney disease related to diabetes), erythromycin hydrate (an antibiotic degradation product), and gemfibrozil (used to lower blood lipid levels) were detected consistently in a special RMP PPCP study of five sites in the Bay.

- Other compounds detected in water samples included carbamazepine and caffeine. These compounds have low removal efficiencies by wastewater treatment plants and are persistent in the environment.
- The maximum concentration of a non-pharmaceutical PPCP was 459 ng/L of bis(2-ethylhexyl) phthalate, a plasticizer.
- PPCP concentrations in Bay water samples were generally highest in the southern Bay segments, where dilution is lowest, and residence times are highest.
- Fewer PPCPs have been detected in sediment samples than in water or wildlife (TABLE 1).
 - Pharmaceuticals detected in Bay sediment include stimulants, antibiotics, and a diuretic, with a maximum concentration of 678 parts per billion (ppb) for ciprofloxacin (an antibiotic).
 - The maximum concentration of other PPCPs in sediment was 605 ppb bis(2-ethylhexyl) phthalate.
 - Triclocarban, an antibacterial agent used in disinfectants and soaps, was unusual among PPCPs in that it was detected in sediment samples but not in water. The maximum measured concentration was 33 ppb.
- Compounds detected in biota include Benadryl®, the popular insect repellent DEET, antidepressants such as Zoloft®, other pharmaceuticals, and fragrance ingredients (TABLE 1).
 - The maximum concentration of pharmaceuticals in Bay mussels was about 90 ppb for both lomefloxacin, an antibiotic, and sulfamethazine, an antibiotic mostly used for veterinary applications.
 - Compounds measured in mussels at a majority of sites included amitriptyline, DEET, sertraline (Zoloft®), and dehydronifedipine.
 - The maximum concentration of other PPCPs in mussels was 2,620 ppb of di-n-butyl phthalate, a plasticizer.
 - In Bay cormorant eggs, maximum concentrations of bis(2-ethylhexyl) phthalate, a plasticizer, reached 1,880 ppb.
- The NOAA Mussel Watch California CEC Pilot Study (Mussel Watch) measured a variety of PPCPs in mussels from the Bay.
 - The antidepressant sertraline was detected frequently in California, with a maximum concentration in the Bay (FIGURE 1).
 - The antihistamine diphenhydramine (Benadryl®) was also found at relatively high levels in the Bay (FIGURE 2).

TABLE 1

PPCPs detected in Bay samples (from Klosterhaus et al. 2013b). Data collected as part of RMP studies, other research, and mussel samples collected in 2010 and analyzed as part of NOAA's Mussel Watch Program.

PHARMACEUTICALS		WATER	SEDIMENT	MUSSELS	EGG
COMPOUND	USE				
Albuterol	Bronchodilator – asthma, breathing issues	x			
Amitriptyline	Antidepressant – pain, minor depression	x		x	
10-hydroxy-amitriptyline	Metabolite of amitriptyline	x			
Amphetamine	Psychostimulant – fatigue, appetite	x	x	x	
Atenolol	Beta blocker – blood pressure, angina	x		x	
Benzoylcegonine	Analgesic and metabolite of cocaine	x			
Caffeine	Stimulant	x	x		
Carbamazepine	Mood stabilizer and anti-epileptic	x		x	
Ciprofloxacin	Antibiotic – diarrhea, nausea, vomiting		x		
Clarithromycin	Antibiotic – ulcers, tonsillitis, other infections	x			
Cocaine	Local, topical anesthetic	x	x	x	
Cotinine	Metabolite of nicotine	x			
Dehydronifedipine	Metabolite of diledipine (blood pressure)	x		x	
Desmethyldiltiazem	Metabolite of diltiazem	x			
Diazepam	Valium – anxiety, muscle spasms, seizures	x			
Digoxigenin	Steroid found in Digitalis – immuno-tag			x	
Diltiazem	Calcium channel blocker – blood pressure	x		x	
Diphenhydramine	Benadryl® – allergies, cold, nausea, hives	x		x	
Enalapril	ACE inhibitor – blood pressure, heart			x	
Enrofloxacin	Antibiotic – veterinary issues			x	
Erythromycin-H2O	Antibiotic degradation product	x	x	x	
Fluoxetine	Prozac – depression, panic disorders			x	
Gemfibrozil	Fibrate – high cholesterol, triglycerides	x			
Hydrocodone	Analgesic – pain relief, cough	x			
Ibuprofen	Analgesic – pain relief, inflammation	x			
Lomefloxacin	Antibiotic – urinary tract, other infection			x	
Meprobamate	Tranquilizer – tension, anxiety, nervousness	x			
Methylprednisolone	Corticosteroid – inflammation, allergy			x	
Metoprolol	Beta blocker – blood pressure, angina	x			
Naproxen	Anti-inflammatory – fever, pain	x			
Ofloxacin	Quinolone – ear infection			x	
Propoxyphene	Analgesic – no longer available in US	x			
Propranolol	Beta blocker – blood pressure, angina			x	
Ranitidine	Antihistamine – heartburn, ulcers			x	
Sertraline	Zoloft® – OCD, PTSD, other depression disorders			x	
Sulfamethazine	Antibacterial – veterinary			x	
Sulfamethizole	Antibacterial – urinary tract infection	x		x	
Sulfamethoxazole	Antibacterial – usually used in combinations	x	x		
Thiabendazole	Parasiticide – roundworm, pinworm	x	x		
Triamterene	Diuretic – hypertension, edema	x	x	x	
Trimethoprim	Antibacterial – urinary, ear infection	x	x		
Valsartan	Angiotensin receptor blocker – heart, stroke	x			
Verapamil	Calcium channel blocker – blood pressure, angina			x	
Virginiamycin	Antibiotic – veterinary			x	
OTHER PPCPs		WATER	SEDIMENT	MUSSEL	EGG
COMPOUND	USE				
N,N-diethyl-m-toluamide	DEET – insect repellent	x	x	x	
Celestolide	Musk (fragrance ingredient)			x	
Galaxolide	Musk (fragrance ingredient)			x	x
Tonalide	Musk (fragrance ingredient)			x	x
Versalide	Musk (fragrance ingredient)			x	
Bis(2-ethylhexyl) phthalate	Plasticizer	x	x	x	x
Butylbenzyl phthalate	Plasticizer	x	x		x
Di-n-butyl phthalate	Plasticizer, adhesives, printing inks	x	x	x	x
Triclocarban	Antibacterial soap		x	x	
Triclosan	Antibacterial soap, toothpaste, other consumer goods		x		

Pharmaceuticals and Personal Care Products

- The antibiotic lomefloxacin was detected throughout California, with a relatively high level in the Bay (FIGURE 3).
- Concentrations of PPCPs in the Bay are typically one-tenth to one-hundredth of those reported for sites in freshwater systems, which are often close to wastewater outfalls, and about the same as reported for other estuarine or marine areas, where wastewater outfalls may also occur but where dilution is greater (Klosterhaus et al. 2013a).
- Concentrations of PPCPs in Bay water were typically one-tenth of those at a Southern California ocean wastewater outfall.

Trends in the Bay and Nationally

- No general trend data are available for the Bay or nationally.
- Globally, the World Health Organization reports increasing use of pharmaceuticals across all income groups (Hoebert et al. 2011).
- Reductions in inputs, should they occur, would depend on source control, more prudent use, and source separation. Examples of these measures include reductions in product use in humans and livestock, controlled returns of unused products, consumer education, on-site treatment, and conceivably, separation of urine from the general waste stream.

Is There a Risk of Harm in the Bay?

- Risks are largely unknown due to the wide variety of chemical compounds, the generally low concentrations at which they are found, and the lack of information on the effects of these compounds on estuarine organisms. However, concentrations are generally below the thresholds that do exist.
 - All pharmaceuticals are inherently biologically active, and their presence in water, sediments, and wildlife samples may be indicative of potential effects, even at low concentrations.
 - Three of 15 measurements of sulfamethoxazole in Bay surface water samples were similar to or greater than those associated with a “predicted no effect concentration” calculated based on chronic toxicity to blue-green algae (Grung et al. 2008). These more contaminated samples were obtained from the southern arm of the Bay. Further study may be warranted to see if this antibiotic could be harming Bay algae.
- Triclocarban has been shown to be an endocrine disruptor in the laboratory and may promote development of antibiotic-resistant bacteria. Similar concerns exist for triclosan (PAGE 75).
- Synthetic musks are persistent and bioaccumulative. Few studies exist on potential adverse health effects.

FIGURE 1 (below)

The antidepressant sertraline, sold under the trade name Zoloft, was detected in 14 of 22 Mussel Watch stations in 2010. The highest concentrations (5.5 parts per billion or ppb) were in mussels from the San Francisco Bay Yerba Buena station (SFYB). High levels were also found at some Southern California sites. Red lines indicate limit of detection.

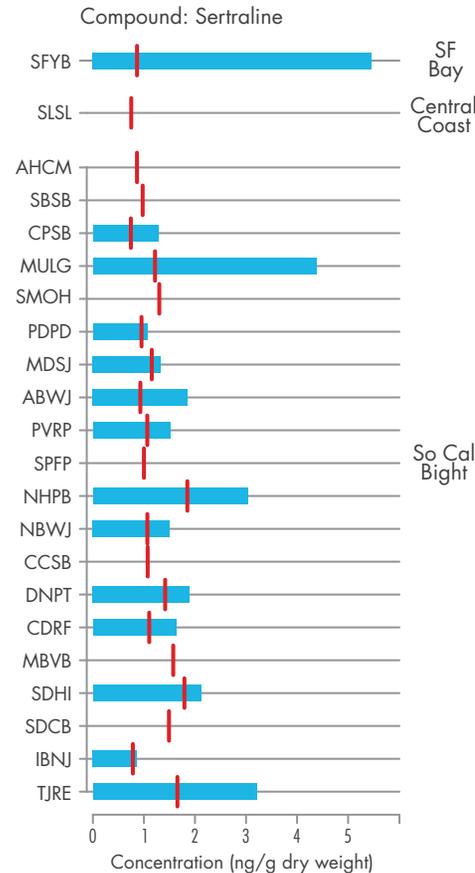
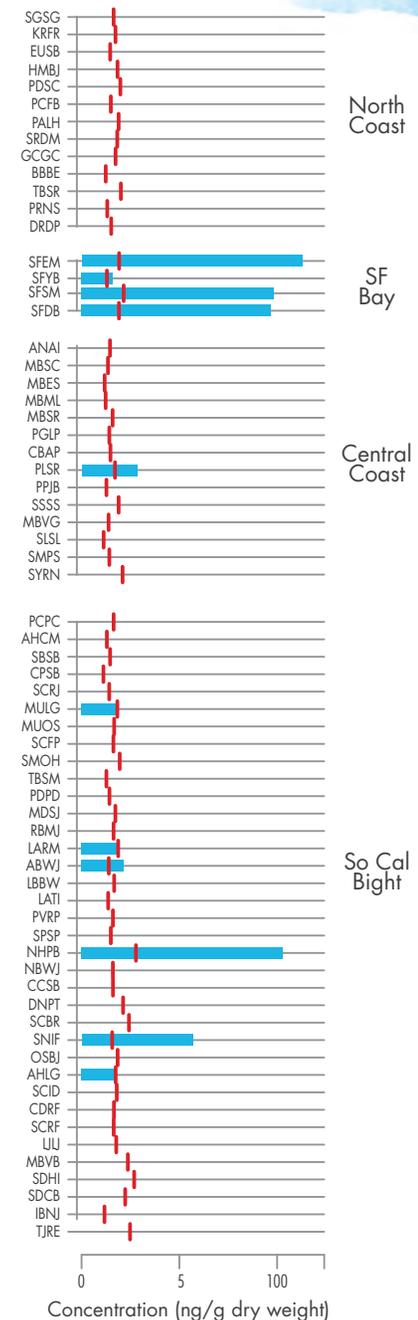


FIGURE 2 (right)

Diphenhydramine, widely known as Benadryl®, is an antihistamine used mostly to fight allergy symptoms. Mussel Watch detected it at only 11 of 68 stations. The highest concentration was in mussels from Emeryville (11 ppb). High levels were also detected at other Bay stations and at a Newport Harbor station in Southern California. Red lines indicate limit of detection.

Compound : Diphenhydramine



TIER 2

TIER 1

Pharmaceuticals and Personal Care Products

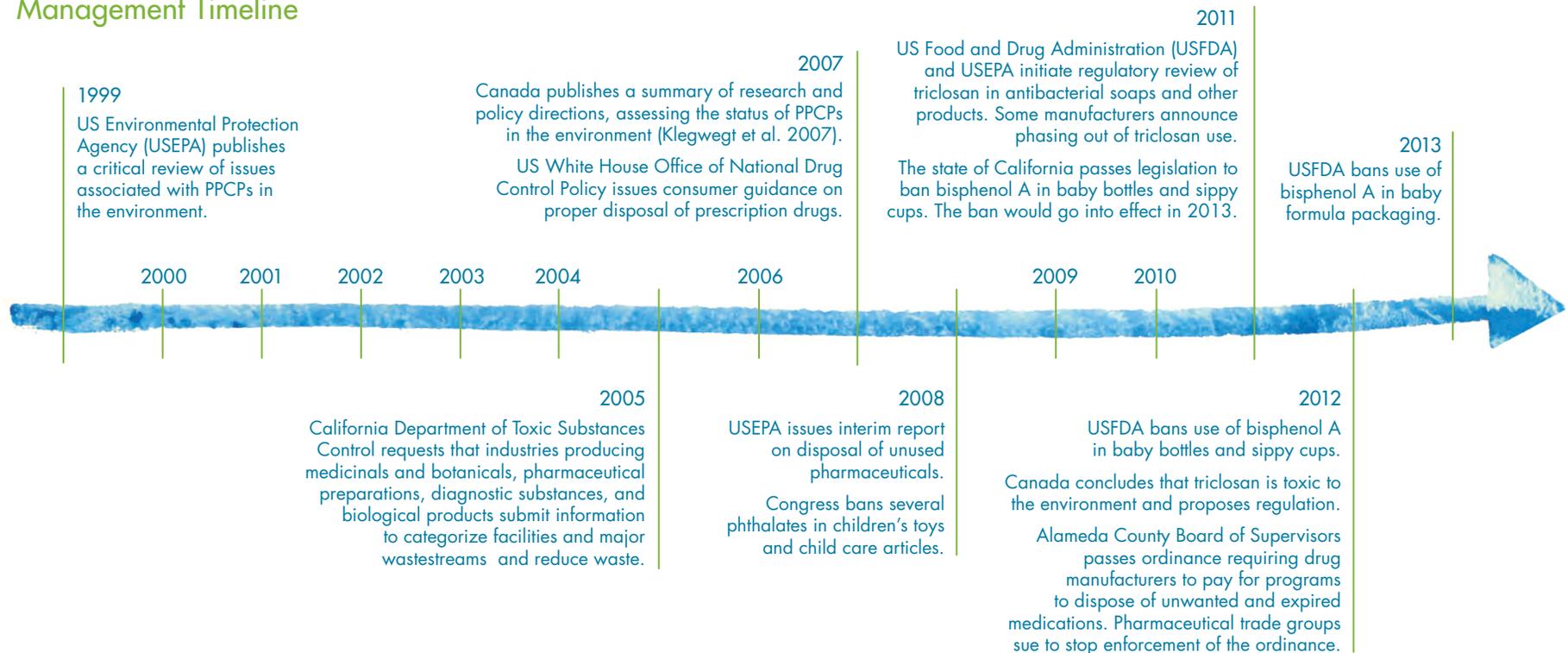
- Bisphenol A is a known endocrine disruptor.
- Many phthalates are known to be endocrine disruptors and may cause other health effects. Phthalates included on California's Proposition 65 list of chemicals known to be harmful include butylbenzyl phthalate (developmental effects), bis(2-ethylhexyl) phthalate (cancer, developmental effects, male reproductive toxicity), diisodecyl phthalate (developmental effects), di-n-butyl phthalate (developmental effects, male and female reproductive toxicity) and di-n-hexyl phthalate (male and female reproductive toxicity).
- A recent study (Brodin et al. 2013) reported behavior and feeding-rate alteration in fish from natural populations exposed to a psychoactive drug (the anxiety reducer oxazepam).

- The Science Advisory Panel for CECs in California's Aquatic Ecosystems identified the hormone-mimic bisphenol A and the synthetic musk galaxolide for monitoring in coastal embayments.

Key Information Gaps

- Information about occurrence, sources, fates, and potential effects of PPCPs is evolving. While most PPCPs examined in Bay samples were found at levels that do not appear to be harmful, for a few there is greater uncertainty (bisphenol A, bis(2-ethylhexyl) phthalate, butylbenzyl phthalate).
- Many basic questions remain.
 - What PPCPs are reaching the Bay and in what concentrations?
 - What are the sources and pathways?
- What is the fate of PPCPs in the Bay?
- What PPCPs are bioaccumulating in organisms?
- What are the acute and chronic effects?
- Which compounds are endocrine disruptors, and how may they affect marine life?
- How do observed concentrations compare to effect levels?
- How are inputs and Bay concentrations changing through time?
- Continued efforts to understand potential effects of mixtures, as well as of individual chemicals, is necessary.

Management Timeline



Triclosan

TIER 2
LOW
CONCERN

JAY DAVIS,
San Francisco Estuary Institute
(jay@sfei.org)

Quick Summary

Triclosan is an antimicrobial chemical used widely in personal care products, such as liquid hand soaps. Triclosan accumulates in Bay sediment. The concentrations observed have been well below effect thresholds, but potential risks are not fully understood. Doubts about the efficacy of triclosan in some of its uses and concern for its potential impacts on water quality call into question whether its uses should be curtailed.

What Is It?

- Synthetic chlorinated chemical that is a broad-spectrum antimicrobial agent.
- Kills or inhibits the growth of microorganisms, including bacteria and fungi.
- Structurally similar to triclocarban, another popular antimicrobial that is found in bar soaps and is also a concern in aquatic environments.

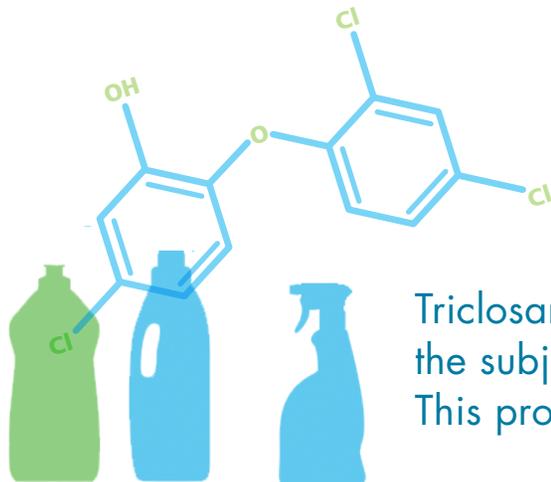
What Is It Used For?

- Antimicrobial used since the early 1960s in thousands of consumer and industrial products, including antibacterial liquid hand soaps (0.1-0.3% by weight), body washes, cosmetics, mouthwash, toothpaste, detergents, deodorants, and other products including furniture, cutting boards, sports equipment, floors, and carpets.
- Microban®, a slow release product that sometimes contains triclosan, is also incorporated into plastics used in children's toys, kitchen utensils, and other consumer and industrial products, and Biofresh®, another triclosan product, is embedded in some clothing.
- Estimated annual use of more than 300,000 kg/yr in the US (Halden and Paull 2005).
- The American Medical Association has not endorsed the necessity or efficacy of triclosan and other antibacterial agents in personal care products (WMI 2006). Physicians indicate that the best germ fighting measure continues to be the actual act of hand washing with regular soap, or for extra assurance, alcohol-based hand sanitizers.

- According to the US Food and Drug Administration, the only evidence of effectiveness is in toothpaste in preventing gingivitis (<http://www.fda.gov/forconsumers/consumerupdates/ucm205999.htm>).

How Is It Getting Into the Bay?

- Municipal wastewater treatment plant effluent is probably the major pathway to the Bay, although more information is needed on other potential pathways.
 - Over 95% of triclosan uses are in consumer products that are disposed of in residential drains, resulting in transport to municipal wastewater treatment plants.
 - Removal efficiencies in treatment plants typically range from 60% to >99.5%, depending on the type of treatment used.
 - Given the incomplete removal in treatment plants, triclosan is commonly detected in treatment plant effluent.
 - Concentrations in effluent from a Bay Area treatment plant in 2006 (ranging from <500 to 900 ng/L) (Jackson and Sutton 2008) were comparable to effluent concentrations observed in other studies.
 - Average concentrations in sewage sludge from two Bay Area treatment plants in 2008 (15-20 ppm) were similar to the nationwide average of 16 ppm (USEPA 2009 Targeted National Sewage Sludge Survey).
- Urban stormwater, which flows directly into the Bay untreated, is another potential pathway due to the use of triclosan-containing products for activities such as exterior cleaning and car washing.



Triclosan is a personal care product ingredient of particular interest that was the subject of a RMP fact sheet (www.sfei.org/news_items/factsheet-triclosan). This profile presents an update of the information in the fact sheet.

Triclosan

What Happens to It in the Bay?

General Properties

- The fate of triclosan in the Bay has not been studied, but predictions can be made based on information from other studies.
- Upon entry into the Bay, triclosan is expected to be quickly removed from the water column through binding to sediment particles, photodegradation, and biodegradation. Some of the degradation products are problematic, however (more on this below).
- Triclosan is expected to accumulate primarily in sediment (due to its high affinity for organic matter and sediment particles) where it can be taken up by sediment-dwelling organisms and passed up the food chain.
- Triclosan can persist in sediments with a half-life as long as 540 days and resists biodegradation under low oxygen conditions when it is associated with sediments (Halden and Paull 2005).
- Other degradation products include chloroform, chlorophenoxyphenols, chlorophenols (e.g., 2,4-dichlorophenol and 2,4,6-trichlorophenol), and 2,8-dichlorodibenzo-p-dioxin; some of these chemicals are probable human carcinogens. Triclosan is suggested as the largest source of lower chlorinated dioxins to aquatic environments (Buth et al. 2010).
- One transformation product, methyl triclosan, is more persistent than triclosan and has been found to accumulate in fish (Leiker et al. 2009).

Patterns of Occurrence in the Bay and in Other Aquatic Ecosystems

- In a 2008 Bay sediment survey, concentrations ranged from < 5 to 40 ppb (FIGURE 1) (unpublished data).

- In a 2010 RMP Bay survey, triclosan was not detected in surface water (< 60 ng/L) or sediment (< 62 ppb); however, typical concentrations in estuaries are below these detection limits (<1 to 26 ng/L in water and from below detection to 86 ppb in sediment). A more sensitive method would be needed to detect triclosan in Bay water.
- Triclosan was not detected in mussels collected from the Bay in 2010 (< 33 ng/g wet weight) (unpublished data).
- Sediment concentrations are comparable among the US estuaries that have been studied, including San Francisco Bay.
- Studies in other parts of the US indicate concentrations are generally highest in water and sediment near municipal wastewater treatment plant outfalls or waters with known inputs of raw wastewater (Glassmeyer et al. 2005).
- Triclosan was one of the most frequently detected wastewater contaminants in a 1999-2000 survey of US stream waters – detected at 58% of sites nationwide (Kolpin et al. 2002).
- Though few studies have investigated triclosan bioaccumulation, triclosan has been detected in the US and Europe in algae, fish tissues (bile, plasma), marine mammals (plasma), and humans (milk, blood, urine).

Trends in the Bay and Nationally (PAGE 3)

- No trend data are available for the Bay.
- Data from other parts of the US suggest that sediment concentrations were highest in the 1960s and 1970s, declined significantly with the adoption of activated sludge wastewater treatment, but may have recently begun rising (Cantwell et al. 2010).

Is There a Risk of Harm in the Bay?

- Laboratory studies have suggested that triclosan can act as an endocrine disruptor in fish and mammals, but concentrations in the environment are generally much lower than the exposure concentrations used in these studies.
- Algae appear to be the most sensitive to triclosan exposure (acute toxicity threshold 200 ng/L) (Chalew and Halden 2009).
- Most of the toxicity threshold data currently available are from acute effects studies, which are not indicative of the potential effects due to long-term, chronic exposure to concentrations that are typically found in aquatic environments.
- In chronic toxicity studies, effects on the endocrine system in amphibians and the structure and function of algal communities have been observed at concentrations occurring in the environment (Veldhoen et al. 2006; Wilson et al. 2003).
- Additional concerns include the potential for indirect effects on algal and aquatic plant grazers due to the toxicity of triclosan to algae and the combined effects of persistent antimicrobial compounds, such as triclosan and triclocarban, on microbial communities.
- Some of triclosan's transformation products are probable human carcinogens.

Triclosan

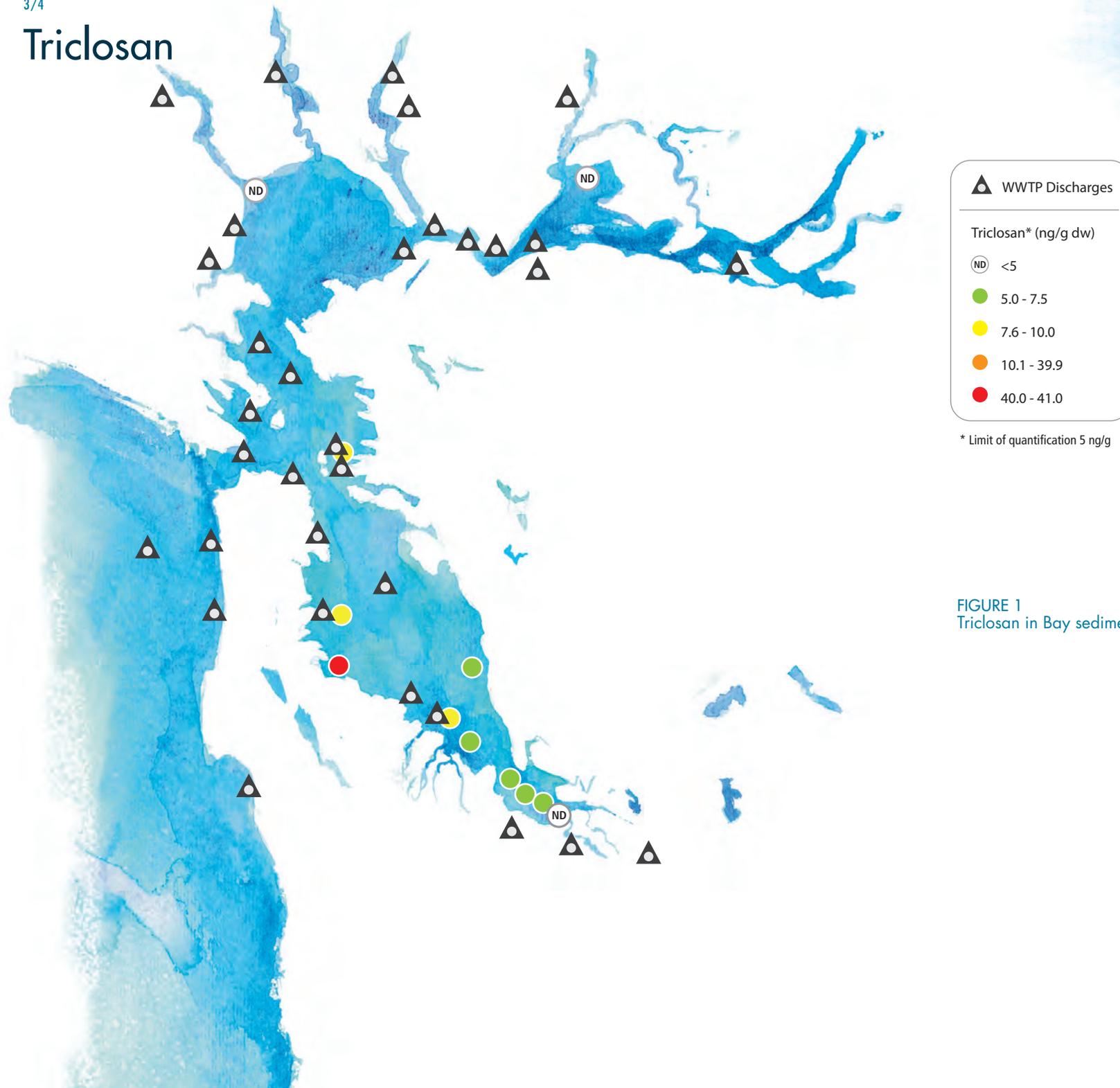


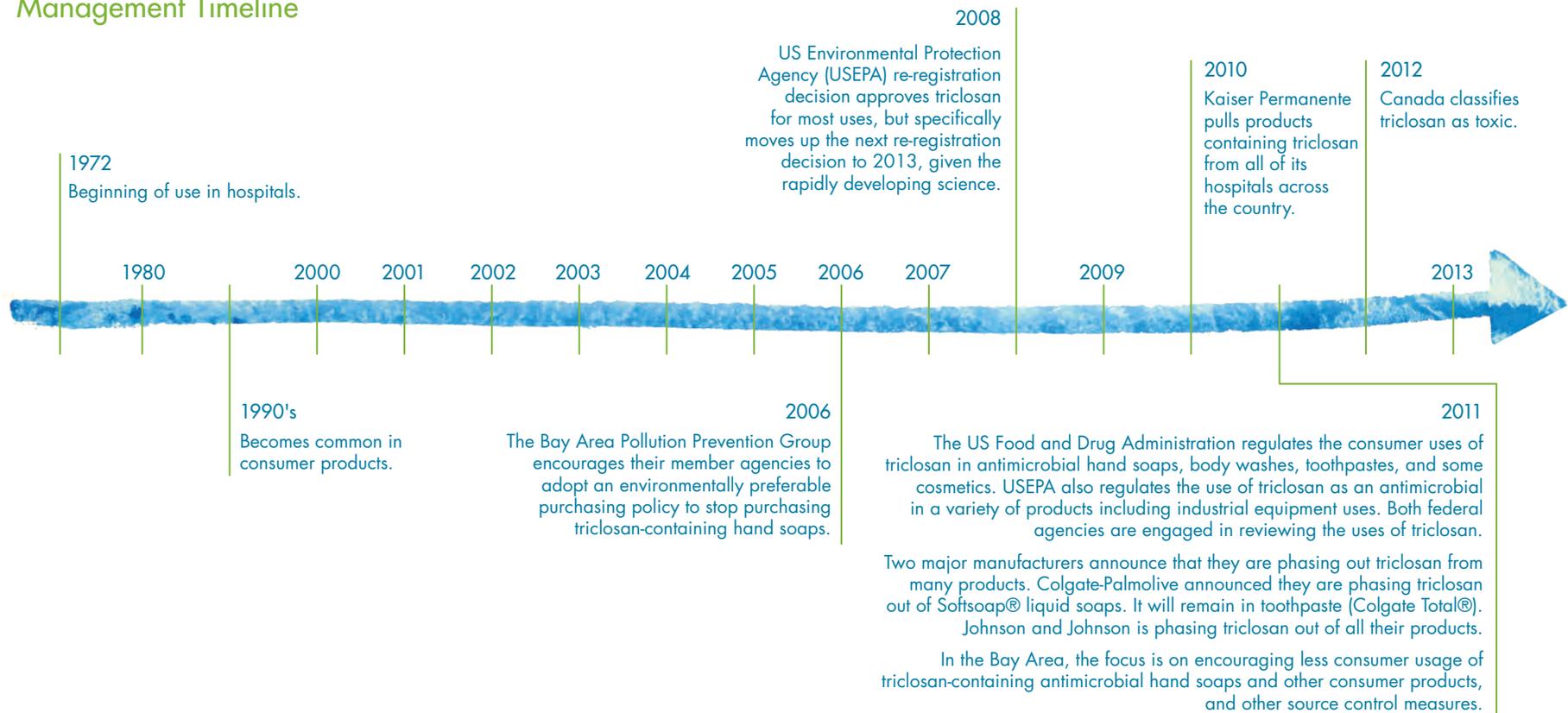
FIGURE 1
Triclosan in Bay sediment, 2008.

Triclosan

Key Information Gaps

- Relative contributions of stormwater runoff and municipal wastewater as pathways of triclosan to Bay surface waters.
- Potential chronic effects on algae and microbes due to long-term exposure to concentrations of triclosan and other antimicrobials that are typically found in aquatic environments.
- The potential for transfer of triclosan and methyl triclosan through the food web to act as a source of exposure to wildlife.
- Concentrations in sediment and biota influenced by Bay Area treatment plant outfalls, where exposures are anticipated to be highest.
- Potential development of widespread antimicrobial resistance due to the presence of triclosan in aquatic environments.
- The occurrence of potentially toxic degradation and transformation products in the Bay.
- The identity, extent of use, and potential environmental health impacts of chemicals used as replacements for triclosan.

Management Timeline



Pyrethroids

KELLY MORAN,
TDC Environmental
(kmoran@tdcenvironmental.com)

TIER 2
LOW
CONCERN
Most
Compounds

TIER 4
HIGH
CONCERN
Bay Area Urban
Creeks*

Quick Summary

Pyrethroids are a family of insecticides widely used both outdoors and indoors in urban areas to control insect pests like ants, fleas, bed bugs, and termites. Pyrethroids have been linked to incidents of toxicity to sensitive organisms in urban runoff, undiluted wastewater effluent, and in both water and sediment in urban creeks, but not in San Francisco Bay. Restrictions implemented in 2012 by state pesticide regulators should nearly (but perhaps not completely) eliminate pyrethroid-caused toxicity in urban runoff. Pesticide and water quality regulators continue to evaluate the need for additional management actions.

*

Pyrethroids are of low concern in the Bay, but high concern in Bay Area urban creeks

What Are They?

- A family of more than a dozen similar synthetic chemical compounds based on the chemical structure of pyrethrins, naturally occurring botanical insecticides derived from chrysanthemum flowers.
- Potent, broad-spectrum insecticides that control insects at relatively low application rates.
- Lethal to sensitive aquatic organisms (e.g., crustaceans) at concentrations < 10 nanograms per liter (ng/L) (Werner and Moran 2008; Weston and Jackson 2009).
- Photostable (stable in sunlight) “second generation” pyrethroids like bifenthrin, cypermethrin, cyfluthrin, and permethrin are most commonly detected in the environment.

What Are They Used For?

- Broad-spectrum insecticides widely used in agricultural and urban areas.
- Initially developed in the 1950s, pyrethroids grew in popularity when photostable second-generation pyrethroids were developed in the late 1970s and 1980s.
- In the early 2000s, with the phase-out of most allowable urban uses of organophosphate insecticides (e.g., chlorpyrifos and diazinon), pyrethroids became the primary class of insecticides available in the urban marketplace.
- Pyrethroids are safer for humans than organophosphates because mammals, unlike other classes of organisms, have more extensive enzyme systems capable of metabolizing and detoxifying the pyrethroids (EPA 2011).
- In urban areas, licensed professional applicators are the primary users of photostable second-generation pyrethroids, which are applied outdoors to control insects around buildings (particularly ants) and underground to control subterranean termites.
- Despite the large number of pyrethroid lawn, garden, and landscaping products available to non-professional consumers, these products comprise a relatively small fraction of the total quantity of pyrethroids used in urban areas.

- Pyrethroids are used indoors to control pet flea, head lice, and bed bug problems.
- In the early 2000s, USEPA approved sales of permethrin-treated mosquito-repellent clothing.
- Total California pyrethroids sales were about 455,000 kg in 2011 (CDPR 2013).

How Are They Getting Into the Bay?

- Urban runoff – and to a lesser extent agricultural runoff – which flows directly into the Bay untreated, are the pathways by which the highest concentrations of pyrethroids enter the Bay.
 - Urban runoff samples typically contain mixtures of pyrethroids that together often exceed toxicity thresholds for sensitive aquatic organisms (2-21 ng/L), sometimes by more than ten-fold. The most persistent of the pyrethroids, bifenthrin (concentrations sometimes >100 ng/L) is usually the leading contributor to the toxic potency in a water sample (e.g., Weston and Lydy 2010, 2012; Ensminger 2013).
 - Agricultural runoff can contain pyrethroids at concentrations sufficient to be toxic to the amphipod *Hyalella azteca* (i.e., >2 ng/L) but toxic levels occur less frequently than in urban runoff (e.g., Weston and Lydy 2010).
 - Professional structural pest control applications appear to be the primary source of pyrethroids in urban runoff. Landscaping applications are unlikely to be an important source. Nearly all of the urban use of second-generation pyrethroids other than bifenthrin and most (80%) of the urban use of bifenthrin are by professional applicators to control pests around buildings (TDC Environmental 2010).
 - Applications to control insects around buildings involve spraying impervious surfaces, like building walls and walkways, some of which drain directly to gutters and storm drains. Pyrethroids wash off from these impervious surfaces substantially more efficiently than from landscaped areas (Jorgenson et al. 2012).

Pyrethroids

- Municipal wastewater treatment plant effluent is likely a pathway to the Bay.
 - No Bay Area municipal wastewater treatment plant monitoring data have been published.
 - Limited published monitoring data from wastewater treatment plants elsewhere in California (Weston and Lydy 2010; Robertson-Bryan 2012; other unpublished data support the following points.
- Concentrations of pyrethroids in wastewater flowing into municipal wastewater treatment plants prior to treatment are similar to concentrations in urban runoff.
- Municipal wastewater treatment plants generally remove most, but not all, pyrethroids in wastewater.
- Pyrethroids have been detected in undiluted treatment plant effluent at concentrations less than 20 ng/L, much lower than concentrations in urban runoff, but sometimes above toxicity thresholds for sensitive aquatic organisms. Effluents may not necessarily cause toxicity due to dilution and changes in pyrethroid bioavailability in receiving waters.
 - Users wash some indoor pyrethroid products, such as pet flea shampoos and head lice treatments, down indoor drains immediately after use. Impregnated fabrics, like insect-repellent clothing and bed bug repellent mattress pads, gradually lose their pyrethroid content when machine or hand washed after use. Post-application cleanup, cleaning treated surfaces, seepage into underground sewer lines during subterranean termite treatments, spills, and improper disposal may also transfer pyrethroids into indoor drains and sewer lines, resulting in transport to municipal wastewater treatment plants (Moran and TenBrook 2011).

What Happens to Them in the Bay?

General Properties

- The fate of pyrethroids in the Bay has not been studied, but predictions can be made based on other studies of their environmental fate.
- After entry into the Bay, pyrethroids are expected to be removed from the water column through binding to sediment particles. The presence of pyrethroid-caused toxicity in water samples from urban creeks indicates that this binding process does not occur instantaneously.
- Pyrethroids likely accumulate primarily in sediment. Sediment-dwelling organisms are probably exposed to the Bay's highest pyrethroid concentrations.
- Pyrethroids persist in aquatic sediments; most have half-lives (time it takes for a 50% reduction) between 100 and 500 days. The half-life of bifenthrin in sediments is greater than 700 days (Gan et al. 2005, Budd et al. 2011).

Patterns of Occurrence in the Bay and in Other Aquatic Ecosystems

- In Bay sediment, total pyrethroid concentrations have generally been below 10 parts per billion (ppb), with only one sample from Suisun Bay showing a higher concentration (16 ppb). Bifenthrin and permethrin were among the pyrethroids most commonly detected, found in around 30 to 40% of samples.
- In the Southern California Bight in 2008, sediment pyrethroid concentrations were highest near urban runoff sources, where average total pyrethroid concentrations were 22 ppb. Consistent with other studies, bifenthrin was most commonly detected (32% of all samples) and the dominant contributor to pyrethroid toxic potency. Near urban runoff sources, total pyrethroid concentrations exceeded effects levels for the amphipod *Eohaustorius estuarius*, but the presence of pyrethroids did not directly correlate with toxicity measurements, suggesting that the presence of the many other anthropogenic chemicals in these sediments affected toxicity measurements (Lao et al. 2012).

Bifenthrin and permethrin were among the pyrethroids most commonly detected in Bay sediment

TABLE 1

A recent review of California urban watershed pyrethroid monitoring data published between 2003 and 2012 found that 14 pyrethroids have been detected in water and sediment (Ruby 2013).

allethrin
bifenthrin
cyfluthrin
cyhalothrin
cypermethrin
deltamethrin/tralomethrin
esfenvalerate/fenvalerate
fenpropathrin
fluvalinate
permethrin
phenothrin
prallethrin
resmethrin
tetramethrin

Pyrethroids

- Pyrethroids have been linked to toxicity to the amphipod *Hyalella azteca* in water and sediment samples from urban creeks in all of California's major urban areas (Ruby 2013; Holmes et al. 2008).
- A recent review of California urban watershed pyrethroid monitoring data published between 2003 and 2012 found that 14 pyrethroids have been detected in water and sediment (TABLE 1). For water samples where pyrethroids were detected, the average concentrations of bifenthrin, cyfluthrin, cypermethrin, and permethrin exceeded concentrations that cause acute toxicity to sensitive aquatic organisms (Ruby 2013).
- In urban areas, bifenthrin is the most frequently detected pyrethroid (64% of water samples, 69% of sediment samples) and the greatest contributor to toxic potency in both water and sediment samples (Ruby 2013).
- Pyrethroid concentration and toxicity data from San Francisco Bay Area urban creeks are similar to data from other California urban watersheds. In RMP sampling of an urban drainage in Hayward, the pyrethroids most frequently detected were permethrin (maximum 285 ng/L) and bifenthrin (maximum 46 ng/L).
- Agricultural watersheds generally contain fewer pyrethroids, lower pyrethroid concentrations, and less severe toxicity than urban watersheds (e.g., Weston and Lydy 2010). While no survey of Bay Area agricultural watersheds has been conducted, Central Valley sediment surveys found 16-20% of samples exhibited toxicity to *Hyalella azteca* that was attributed to pyrethroids (Weston et al. 2008, 2013).

Regulatory restrictions are likely to reduce pyrethroid use in urban areas, but users may shift to other insecticides, such as fipronil and indoxacarb, that are also highly toxic to aquatic organisms

- In a USGS survey of sediment samples from 36 urban and agricultural streambeds in 25 states, pyrethroids were detected in 78% of samples. Bifenthrin was the most frequently detected (58% of samples), followed by permethrin (31%), resmethrin (17%), and cyfluthrin (14%). Although toxicity was not measured, predicted toxic potency was greater for urban areas and attributed to bifenthrin, cyfluthrin and cypermethrin, while in agricultural areas the predicted toxic potency was primarily attributed to bifenthrin (Hladik and Kuivila 2012).

Trends in the Bay and Nationally

- Pyrethroids have been monitored in Bay sediments since 2008, but concentrations have not shown significant decreasing or increasing trends.
- California data indicate increases in pyrethroid usage and environmental concentrations starting in the early 2000s, coincident with the greater regulation of organophosphate insecticides.
- Regulatory restrictions are likely to reduce pyrethroids use in urban areas, but users may shift to other insecticides, such as fipronil and indoxacarb, that are also highly toxic to aquatic organisms.

Is There a Risk of Harm in the Bay?

- The crustacean *Americamysis bahia* appears to be the saltwater test organism most sensitive to pyrethroids (acute toxicity thresholds <10 ng/L). Although pyrethroids have not been measured in Bay waters, concentrations in tributaries sometimes exceed toxicity thresholds for freshwater organisms, and impacts to estuarine organisms might occur in the immediate areas near their entry to the Bay.
- Sediment concentrations in the Bay are likely lower than those that cause acute toxicity in test organisms. Pyrethroids were detected in 57 of 98 Bay sediment samples collected between 2008 and 2011. Of the eight pyrethroids detected in at least one sample, only two (allethrin and phenothrin) occurred at concentrations greater than 2 ppb. Although there are no relevant sediment toxicity data for these pyrethroids, they generally have aquatic toxicities similar to permethrin, which has a 10-day LC50 (concentration causing mortality to 50% of test organisms in a 10 day test) for the amphipod *Eohaustorius estuarius* of 140 ppb (Anderson et al. 2008). The most highly toxic pyrethroids detected (bifenthrin, cyfluthrin, cyhalothrin, and cypermethrin) were frequently below detection limits (0.03-0.6 ppb) and never exceeded 1.1 ppb individually or a total of 1.6 ppb. These concentrations are lower than the only available sediment toxicity thresholds for a chemical in this group, bifenthrin, for which the 10-day LC50 for the amphipod *Eohaustorius estuarius* is 8 ppb (Anderson et al. 2008).
- Both water and sediment pyrethroid concentrations in Bay Area urban creeks typically exceed toxicity thresholds for *Hyalella azteca* (BASMAA 2013; Weston and Lydy 2010, 2012; Ensminger 2013).
- Consistent with pyrethroid concentrations and similar to other California urban watersheds, 2011-2012 Bay Area testing found that 9 of 11 urban creek water samples were toxic to *Hyalella azteca* (BASMAA 2013).

TIER 2

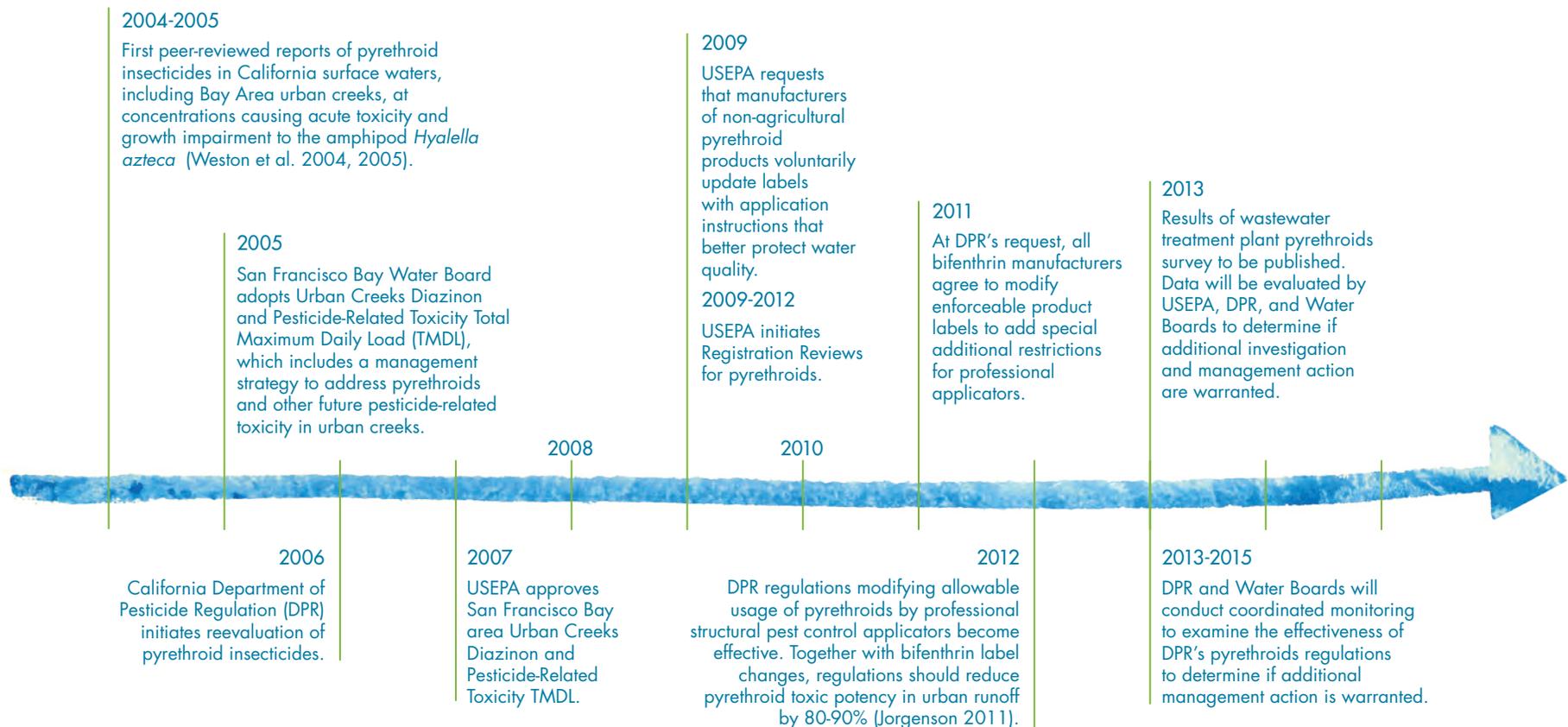
TIER 4

Pyrethroids

Key Information Gaps

- Potential for aquatic toxicity in water and sediment at Bay margins due to pyrethroid-containing urban runoff and wastewater effluents, accounting for dilution and bioavailability in these waters.
- Potential chronic effects on mysids and amphipods due to long-term exposure to concentrations found in Bay waters (if detected) and sediment.
- Potential environmental impacts of chemicals used as replacements for the pyrethroids, such as fipronil and indoxacarb. Limited available data indicate that concentrations of fipronil and its multiple toxic, stable degradation products are approaching effects thresholds in aquatic ecosystems (Ruby 2013) (PAGE 83).
- The results of a statewide survey of concentrations in influent, effluent, and biosolids from about 30 California wastewater treatment plants (including several Bay Area plants), anticipated in late 2013, will better characterize wastewater discharges and will provide more thorough insights on treatment plant removal efficiencies.
- Identification of the major sources of pyrethroids in wastewater.

Management Timeline



Fipronil

**TIER 3
MODERATE
CONCERN**

KELLY MORAN,
TDC Environmental
(kmoran@tdcenvironmental.com)

Quick Summary

Fipronil is a broad-spectrum insecticide with growing use to control pests around structures and fleas on pets. Fipronil and its multiple stable degradation products have been detected in Bay Area urban runoff, urban creeks, and Bay sediment. Nationally, fipronil has been detected in urban runoff, municipal wastewater effluent, water and sediment in urban creeks, and in estuary sediment. Observed concentrations are approaching and in some cases exceeding effect thresholds, suggesting an increasing potential for fipronil to pose risks to aquatic ecosystems.

What Is It?

- Synthetic broad-spectrum insecticide first approved for use in the late 1990s.
- A slow acting toxicant that insects can carry back to and share with colonies.
- Fipronil has at least four stable degradation products, three of which (fipronil sulfide, fipronil sulfone, and desulfinyl fipronil) can readily be measured with standard chemical analysis techniques.
- Fipronil and its stable degradation products are lethal to sensitive aquatic organisms (e.g., crustaceans and aquatic insects) at concentrations <1 microgram per liter ($\mu\text{g/L}$) (TABLE 1). Chronic toxicity to the crustacean *Americamysis bahia* has been reported at concentrations less than 0.003 $\mu\text{g/L}$ (USEPA 2007). For some aquatic species – such as *Americamysis bahia* – fipronil’s degradation products are more toxic than fipronil itself.

What Is It Used For?

- In 2003, the California Department of Pesticide Regulation (DPR) began to allow professional applicators to spray fipronil around buildings to control nuisance insects (the only significant outdoor use). Other uses are pet flea “spot-on” treatments, containerized insect control baits, and termite control solutions for injection into soil beneath structures.
- Not used on landscaping except in Southern California’s Coachella Valley, where professional applicators are authorized to make limited use of fipronil solely to control fire ants.
- No agricultural use in California.
- Total California sales were about 18,000 kg in 2011 and have tripled since 2003 (CDPR 2013).



Fipronil

How Is It Getting Into the Bay?

- Urban stormwater, which flows directly into the Bay untreated, is a pathway to the Bay due to use of fipronil outdoors around buildings.
- In samples from Bay Area storm drains and creeks in two watersheds collected between 2008 and 2011, Ensminger et al. (2013) measured fipronil concentrations up to 0.46 µg/L. Nine percent of Bay Area fipronil detections exceeded the US Environmental Protection Agency (USEPA) chronic aquatic invertebrate protection benchmark of 0.011 µg/L (USEPA 2013). Urban runoff concentrations measured in the Sacramento, Orange County, and San Diego regions were higher – up to 10 µg/L.
- In an intensive two-year sampling program in Sacramento and Orange Counties, median concentrations of fipronil plus its three degradation products in runoff were 0.014 to 0.441 µg/L (Gan et al. 2012).
- Applications to control insects around buildings involve spraying impervious surfaces, like building walls and walkways, from which fipronil and its degradation products can be washed into gutters and storm drains. In laboratory simulations, fipronil and its degradation products appeared in runoff from concrete surfaces at concentrations >140 µg/L one day after application, >30 µg/L two weeks after application, and >1 µg/L 56 days after application (Thuyet et al. 2012; Jiang et al 2010).

- Although there are no local monitoring data, municipal wastewater treatment plant effluent is probably also a pathway to the Bay.
- Fipronil and its degradation products were detected in both filtered effluent and effluent solids from eight of nine Columbia River Basin (Washington and Oregon) municipal wastewater treatment plants (Morace 2012). All fipronil detections exceeded USEPA's chronic aquatic invertebrate protection benchmark of 0.011 µg/L (USEPA 2013).
- The only indoor use of fipronil is a “spot-on” treatment for fleas and ticks on pets, which could subsequently be washed into the sewer system when the pet is bathed. Other possible pathways to the sewer system include post-application cleanup activities, seepage into underground sewer lines from subterranean termite treatments, spills, and improper disposal.

Applications to control insects around buildings involve spraying impervious surfaces, like building walls and walkways, from which fipronil and its degradation products can be washed into gutters and storm drains

TABLE 1

Toxicity thresholds for fipronil and its degradation products. All concentrations in µg/L.

CHEMICAL NAME	AMERICAMYSIS BAHIA		LOWEST USEPA PESTICIDE AQUATIC LIFE BENCHMARKS
	LC50	LOWEST OBSERVED EFFECT CONCENTRATION	
Fipronil	0.14	0.005	0.011 (invertebrates, chronic)
Fipronil Sulfone (MB46136)	0.56	0.0026	0.037 (invertebrates, chronic)
Fipronil Sulfide (MB45950)	0.077	0.0087	0.11 (invertebrates, chronic)
Desulfinyl Fipronil (MB46513)	1.5	–	0.59 (fish, chronic)

Fipronil

What Happens to It in the Bay?

General Properties

- The fate of fipronil in the Bay has not been studied, but predictions can be made based on information from other studies. Fipronil and its stable degradation products are likely to occur in both water and sediment in the Bay. Partitioning into sediment and breakdown by exposure to sunlight and microbial activity likely determine fipronil's ultimate fate in the Bay.
- In sediment, because the presence of organic carbon significantly reduces the uptake of fipronil and its degradation products by organisms, toxicity thresholds are expressed on the basis of sediment organic carbon content (e.g., micrograms of fipronil per gram of organic carbon).
- Limited data exist to characterize the fate of fipronil degradation products, which may have half-lives (time required for a 50% reduction) as long as 700 days in aquatic environments (USEPA 2007).

Patterns of Occurrence in the Bay and in Other Aquatic Ecosystems

- The RMP measured fipronil and its degradation products in Bay sediment in 2002-2003 and 2009-2012. The highest concentrations, up to 0.56 ppb for individual fipronil compounds, were measured in Lower South Bay. Toxicity data for saltwater benthic (sediment-dwelling) species are limited. One laboratory study found reduced reproduction in a saltwater benthic crustacean with addition of 30 ppb to sediment (Chandler et al. 2004). The highest concentrations observed in the Bay exceed the EC50 for immobilization (level causing immobilization in 50% of test organisms) of a freshwater benthic species, *Chironomus tentans*.
- Fipronil and its degradation products were detected in 100% of sediment samples collected in 2007-2009 from the Ballona Creek estuary (Los Angeles, CA). The highest measured fipronil concentration was 6 ppb. In most samples, the degradation product fipronil sulfone was present at higher concentrations, up to 9.8 ppb. In some cases, the total toxic potency of fipronil plus degradation products, exceeded the EC50 for *Chironomus tentans* (Bay et al. 2010).
- In 2012 monitoring of four Bay Area urban creeks, fipronil was detected in 100% of samples, at concentrations from 0.006 to 0.020 µg/L. Thirty-six percent of these discrete samples exceeded USEPA's chronic aquatic life protection benchmark of 0.011 µg/L (USEPA 2013).

- A recent review of California urban watershed fipronil monitoring data published between 2003 and 2012 found that fipronil was detected in 39% of water samples and 19% of sediment samples. Average observed levels of fipronil in water (0.09 µg/L) exceeded USEPA's chronic aquatic invertebrate protection benchmark of 0.011 µg/L, while average concentrations of fipronil degradation products were on the same order of magnitude as their lowest respective USEPA chronic aquatic protection benchmarks (0.037-0.590 µg/L) (Ruby 2013).

Trends in the Bay and Nationally

- In RMP sediment monitoring, higher concentrations of fipronil compounds were generally found in more recent (2009-2012) samples, compared to 2002-2003 samples, in which they were often not detected.
- Based on data from 10 nationwide urban sites, USGS identified a "widespread significant upward trend" in detection frequency and concentrations of fipronil and two degradation products from 2000-2008 (Ryberg et al. 2010).
- Since fipronil is an alternative to the pyrethroid insecticides, usage is likely to increase in response to regulatory restrictions on pyrethroids.

Is There a Risk of Harm in the Bay?

- Available monitoring data indicate that concentrations of fipronil and its degradation products could potentially be approaching effect levels for sensitive test organisms, particularly at the Bay margins, near discharge points.
- The persistence of fipronil degradation products could lead to accumulation in sediment.

Concentrations of fipronil and its degradation products could potentially be approaching effect levels for sensitive test organisms, particularly at the Bay margins, near discharge points

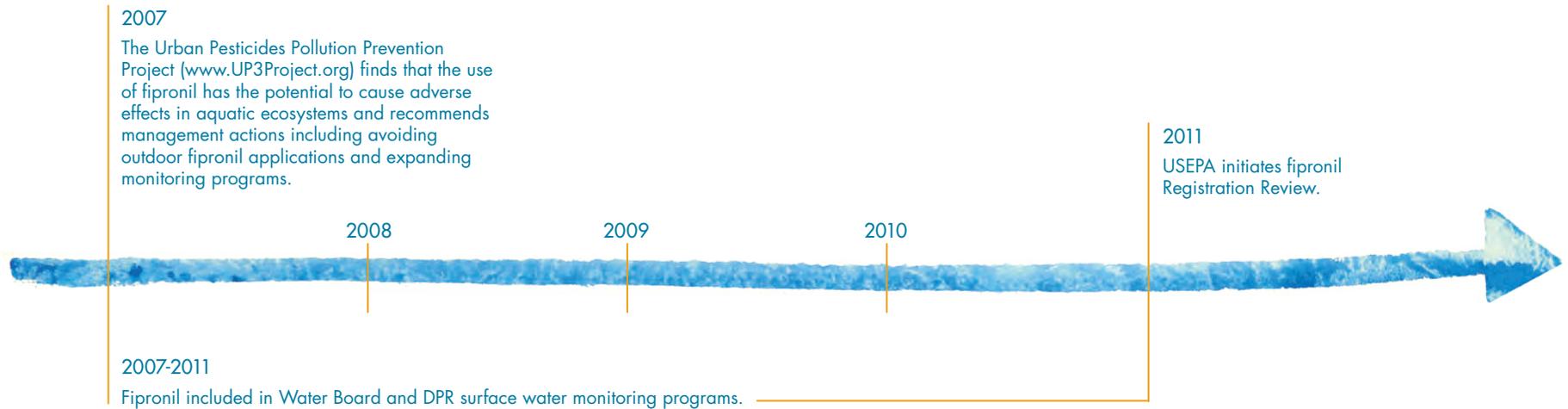
Fipronil

Key Information Gaps

- Aquatic toxicity and environmental fate data, particularly for fipronil degradation products.
- Monitoring data for fipronil and its stable degradation products in Bay water and sediment (particularly near discharge points, including Bay margins), urban creek sediment, and municipal wastewater effluent.
- Toxicity identification evaluation methods that allow evaluation of the potential for linkage between fipronil exposures and incidents of toxicity to testing organisms.
- Application rates and techniques that maintain pest control efficacy while reducing the quantity of fipronil in urban stormwater runoff.



Management Timeline



Currently Used Pesticides

KELLY MORAN,
TDC Environmental
(kmoran@tdcenvironmental.com)

TIER 1
POSSIBLE CONCERN
Other Currently Used Pesticide

TIER 2
LOW CONCERN
Pyrethroids*

TIER 3
MODERATE CONCERN
Fipronil

Quick Summary

The term “pesticides” includes all insecticides, herbicides, fungicides, rodenticides, and antimicrobials. Although both the US Environmental Protection Agency (USEPA) and the California Department of Pesticide Regulation (DPR) must approve pesticides prior to their first use, gaps in pesticide review procedures have resulted in pesticide water pollution. Currently used pesticides have been found throughout aquatic environments. Due to the lack of environmental chemical analysis methods for most currently used pesticides and limited availability of aquatic toxicity data, the potential risks are not fully understood.

*

Pyrethroids are of low concern in the Bay, but high concern in Bay Area urban creeks

What Are They?

- Any of more than 1,000 synthetic or natural organic or inorganic chemicals that are toxic to unwanted organisms.
- Some nanoparticles, such as nanosilver, are pesticides.
- Several dozen currently used pesticides are Clean Water Act priority pollutants (e.g., copper, silver, acrolein, and pentachlorophenol).
- Regulatory changes focused on protecting human health have driven a shift in the pesticide market away from pesticides like DDT that are passed up the food chain and into a multiplicity of new chemical families, some of which are highly toxic to aquatic organisms.

What Are They Used For?

- To control unwanted organisms, both indoors and outdoors.
- In agriculture, pesticides are most often used to protect crops from insects, competing weed growth, fungi, and nematodes.

- In urban areas, pesticides have hundreds of diverse uses, such as ant and termite control around buildings, weed and slug control in landscaping and along roads, wood preservatives, fungicides and biocides in building roofing and paints, swimming pool and drinking water biocides, pet flea control products, and antifouling treatments for boat hulls.
- Pesticides (particularly antimicrobials) are commonly incorporated into products that are not traditionally understood to contain pesticides, such as building materials and cleaning products.
- Although California is the nation’s leading agricultural state, more than half of all California pesticide use occurs in urban areas.
- California pesticide sales exceeded 280 million kg in 2011 (CDPR 2013).

How Are They Getting Into the Bay?

- Urban and agricultural stormwater runoff, in-Bay applications, and municipal wastewater treatment plant effluent are all pathways to the Bay (PAGE 16).



TIER 1

TIER 2

TIER 3

Currently Used Pesticides

What Happens to Them in the Bay?

- Pesticides and their degradation products (which are sometimes more toxic and persistent than their parent chemicals) may occur in water, sediments, and biota in the Bay ecosystem.
- Because environmental fate and aquatic toxicity data for estuarine environments are not routinely obtained before pesticides are approved for use, the fate of most currently used pesticides in the Bay is largely unknown.
- For most currently used pesticides, no published, validated environmental chemical analysis methods exist, which has greatly limited the availability of data to characterize patterns of occurrence in the Bay and in other aquatic ecosystems.
- While no trend data are available for the Bay, the general trend in pesticide design is away from chemicals that accumulate in the food web. Some currently used pesticides and their toxic degradation products (e.g., bifenthrin, indoxacarb), degrade slowly and may accumulate in sediment. Pesticides occurring in municipal wastewater discharges can be “virtually persistent” (have a persistent presence in the Bay) even if they degrade quickly because they are continuously discharged.

TABLE 1
Urban Pesticides Pollution Prevention Project Priority Pesticides List.

PESTICIDE	PRIORITY DISCHARGE PATHWAY			POTENTIAL POTW OPERATIONAL INTERFERENCE
	URBAN RUNOFF	POTW	DIRECT TO BAY	
PYRETHROID INSECTICIDES				
Allethrin	X	X		
Bifenthrin	X	X		
Cyfluthrin	X	X		
Cyhalothrin	X	X		
Cypermethrin	X	X		
Cyphenothrin	X	X		
Deltamethrin/Tralomethrin	X	X		
Esfenvalerate	X	X		
Etofenprox		X		
Permethrin	X	X		
Phenothrin	X	X		
Prallethrin	X	X		
Resmethrin	X	X		
Tetramethrin	X	X		
OTHER INSECTICIDES				
Carbaryl	X			
Fipronil	X	X		
Indoxacarb	X			
Malathion	X	X		
SWIMMING POOL, SPA, AND FOUNTAIN TREATMENTS				
Copper and Copper Compounds	X	X		
PHMB	X	X		
Silver	X	X		
ANTIMICROBIALS				
Copper		X		
Silver (including nanosilver)		X		X
Triclosan		X		
SEWER ROOT CONTROL				
Copper Sulfate		X		
Dichlobenil		X		X
Diquat Dibromide		X		X
Metam Sodium		X		X
WOOD PRESERVATIVES				
Copper and copper compounds	X		X	
Creosote			X	
Pentachlorophenol	X		X	
MARINE ANTIFOULING BIOCIDES				
Copper oxides			X	
Irgarol 1051			X	
Zinc Pyrithione			X	

Source: TDC Environmental 2010, as informally updated in 2011.

Currently Used Pesticides

Is There a Risk of Harm in the Bay?

- Due to the lack of environmental chemical analysis methods for most currently used pesticides and the limited availability of aquatic toxicity data, the potential risks are unknown.
- Past pesticide water pollution in the Bay (e.g., diazinon and chlorpyrifos), in effluents (e.g., copper-based root control products), and in creeks, where pesticides have been associated with fish kills (e.g., drinking water and swimming pool biocides), and are posing current challenges (e.g., pyrethroids), indicate that pesticides can harm aquatic ecosystems.
- Among emerging contaminants, pesticides are often ranked as the highest risk class of chemical compounds (e.g., von der Ohe 2011), which is unsurprising since they are specifically designed to kill organisms.
- No comprehensive list of pesticide priorities has ever been developed for the Bay, its urban and agricultural watersheds, or its wastewater discharges.
- The Urban Pesticides Pollution Prevention Project developed a simplified prioritization scheme to identify pesticides used in California urban areas that are most likely to threaten water quality (TABLE 1) (TDC Environmental 2010). Although the prioritization was not comprehensive, the ranking system is unique in its approach, which prioritizes pesticides based on use pattern, toxicity, and presence in the California urban market.
- In 2009, the Central Valley Water Board used DPR pesticide use reporting data and an earlier version of the UP3 Project urban pesticide priority list to develop a list of agricultural and urban pesticides that pose the highest overall relative risk to aquatic life in the Sacramento River, San Joaquin River, and Delta watersheds (TABLE 2).

TABLE 2
Central Valley Water Board List of High Overall
Relative Risk Level Pesticides

Abamectin
Bifenthrin
Chlorothalonil
Chlorpyrifos
Cyfluthrin
Cypermethrin
Deltamethrin
Diazinon
Diuron
Esfenvalerate
Fipronil
Lambda-Cyhalothrin
Malathion
Mancozeb
Maneb
(S)-Metolachlor
Oxyfluorfen
Paraquat Dichloride
Pendimethalin
Permethrin
Polyhexamethylene biguanide (PHMB)
Propanil
Propargite
Pyraclostrobin
Simazine
Tralomethrin
Trifluralin
Ziram

Source: Lu and Davis 2009.

TIER 1

TIER 2

TIER 3

TIER 1

Currently Used Pesticides

TIER 2

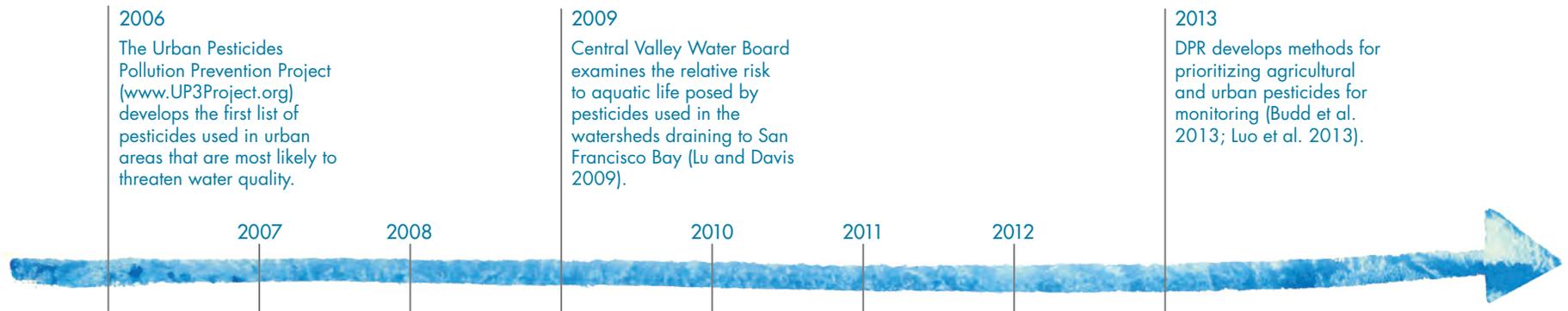
Key Information Gaps

TIER 3

- A robust system for prioritizing pesticides for development of environmental chemical analysis methods.
- Environmental fate and aquatic toxicity data for pesticides and their stable degradation products, particularly in estuarine environments.
- Monitoring data in San Francisco Bay waters and sediments (particularly near discharge and use points, including Bay margins and marinas), urban water and creek sediments, and municipal wastewater effluents.



Management Timeline



Nanoparticles or Nanomaterials

TIER 1 POSSIBLE CONCERN

MEREDITH WILLIAMS,
San Francisco Estuary Institute
(meredith@sefi.org)

Quick Summary

Nanomaterials are ultrasmall materials, 100 nanometers or less in size on at least one dimension. One nanometer is one millionth of a millimeter. Because of their size, nanomaterials have a range of unique physical, chemical, and electronic properties that can be used in a wide spectrum of applications. Some nanomaterials may also have unique toxic properties that have not been fully investigated.

What Are They?

- Nanomaterials are defined by size rather than composition and include both inorganic and organic materials.
- While we now synthesize a variety of unique, engineered nanomaterials for use in industry or in products, others occur naturally.

What Are They Used For?

- Nanomaterials are used in electronics; batteries; fuel cells; coatings for ceramic, glass, and plastic items; textile treatments; personal care products like sunscreens; and a host of other products.
- Some nanomaterials, including single-walled carbon nanotubes, can provide unique methods of drug delivery designed to target specific cells.
- Single-walled carbon nanotubes may also be used in electronics and energy applications, as well as in production of composite plastic polymers with enhanced strength or electrical or thermal properties.
- The high surface area to volume ratio and high reactivity of nanomaterials is useful commercially; one example is their use as metal catalysts that speed chemical reaction rates.
- Antibacterial consumer products containing silver nanoparticles are now common.

How Are They Getting Into the Bay?

- Given the wide range of applications and types of nanomaterials, these substances may be introduced to the environment via multiple pathways including municipal wastewater and urban runoff.
- In 2007, Silicon Valley was one of the top three nanotech development centers in the country.

- Inputs to municipal wastewater may occur as a result of normal transport and manufacturing operations, consumer use of nanomaterial-containing products, or by accidental release.
- Bench-scale studies have shown good removal of silver nanoparticles by conventional wastewater treatment. Wastewater treatment processes may also alter the chemical properties of engineered nanoparticles.

What Happens to Them in the Bay?

- Single-walled carbon nanotubes were not detected in Bay sediment collected in 2007 and 2010 (Schierz et al. 2012).
- No other nanomaterials have been analyzed in Bay samples.
- Significant gaps exist in the scientific understanding of transport, fate, and toxicity of nanomaterials.
- Analytical methods for nanomaterials in the environment are generally lacking.

Is There a Risk of Harm in the Bay?

- The highly reactive nature of nanoparticles is cause for concern for their potential toxicity.
- Some nanomaterials have been shown to increase the creation of reactive oxygen species, which can result in toxicity in aquatic organisms.
- The small size of some nanomaterials can allow them to compromise cells or cross cell membranes.

Management Timeline

- Launched in 2000, the National Nanotechnology Initiative encompasses 27 federal agencies overseeing a range of research and regulatory activities. The Initiative's Environmental, Health, and Safety Research Strategy, updated in 2011, provides guidance to federal agencies in developing research priorities.
- California's Department of Toxic Substances Control has issued two information requests to manufacturers and importers regarding analytical methods, fate and transport, and other information on carbon nanotubes (2010) and quantum dots, and nano forms of silver, iron, cesium oxide, titanium dioxide, and zinc oxide (2011).
- A 2011 report by the US Environmental Protection Agency (USEPA) Office of the Inspector General found that "USEPA has the statutory authority to regulate nanomaterials but currently lacks the environmental and human health exposure and toxicological data to do so effectively."
- USEPA, the National Science Foundation, and other federal agencies are beginning to address this data gap by funding research on the environmental implications of nanomaterials.
- Controlling nanomaterials in manufacturing settings where high dose exposure is more likely is a priority.

Chlorinated Paraffins

TIER 1
POSSIBLE
CONCERN

MEG SEDLAK,
San Francisco Estuary Institute
(meg@sfei.org)

Quick Summary

Chlorinated paraffins (CPs) are chlorine-containing compounds related to paraffin wax that are primarily used as lubricants and coolants in the metal forming and cutting industries. CPs accumulate in biota; however, concentrations observed to date in Bay seals, fish, and birds are very low. CPs are exceedingly difficult to analyze; toxicity and occurrence data are sparse. As a result, they are classified as Tier 1.

What Are They?

- CPs are chlorine-containing compounds related to paraffin wax. They are grouped into three classes: short-chained (carbon chain length between 10 and 13, SCCP); medium-chained (between 14 and 17, MCCP) and long-chained (greater than 17, LCCP).
- CPs are classified as highly persistent in the environment, bioaccumulative (accumulating in biota), and toxic to aquatic organisms (Environment Canada 2008, USEPA 2009). SCCPs are believed to be more toxic to aquatic organisms than MCCPs and LCCPs.

What Are They Used For?

- CPs have been used as lubricants in metal forming and cutting industries since the 1930s. They are also used as a plasticizer and as a flame retardant in plastics. Minor uses include paints, rubber formulation, adhesives and sealants.
- In 2009, the estimated annual use of CPs was more than 150 million pounds per year in the US. MCCPs have the largest use in North America. Production of CPs in China was almost 600 million pounds in 2002 (Bayen et al. 2006) and production in India appears to be growing as well.

How Are They Getting Into the Bay?

- It is not known how CPs enter the Bay; however, it is likely that wastewater treatment plant effluent is one pathway.
- The largest source of CPs to wastewater treatment plants is spent metal-cutting fluids and wash-off from metal-forming equipment and surfaces, followed by the leaching of CPs from polyvinyl chloride processes and products, rubber, adhesives, and paints (Environment Canada 2008).
- Landfill leachate is also a suspected source of CPs (Environment Canada 2008).

What Happens to Them in the Bay?

- CPs are viscous oils or solids. They have a strong tendency to adsorb to soil and sediment particles and to bioaccumulate (Bayen et al. 2006). They are very stable compounds.
- In a limited study of Bay biota, CPs were measured at very low concentrations in harbor seal blubber and bird eggs. CPs were not detected in sport fish.

Concentrations observed in Bay biota are substantially lower than elsewhere and well below available effect thresholds

Is There a Risk of Harm in the Bay?

- Limited toxicological information exists; however, the concentrations observed in the Bay are substantially lower than elsewhere and low relative to other legacy pollutants (Santos et al. 2006, Houde et al. 2008, and Bayen et al. 2006).
- CPs are known to cause narcosis and liver lesions (Cooly et al. 2001). Concentrations in Bay biota, however, are well below available effect thresholds.

Management

- CPs were a high production volume chemical (produced or imported in excess of 1 million pounds per year) in the late 1990s. Only one US firm produces CPs (Dover Chemical). As part of a settlement agreement with USEPA, Dover ceased production of SCCPs. SCCPs are also being phased out in Europe. MCCPs and LLCPs, however, remain widely used.
- SCCPs are a priority hazardous substances in the European Union and their use is restricted to less than 0.1% in metal working solutions and leather tanning operations. SCCPs are classified as compounds of very high concern under REACH (PAGE 19).

Polybrominated Dioxins and Furans

TIER 2
LOW
CONCERN

DONALD YEE,
San Francisco Estuary Institute
(don@sfei.org)

Quick Summary

Polybrominated dioxins and furans are brominated versions of the more commonly known chlorinated dioxins and furans. Polybrominated dioxins and furans are expected to accumulate in Bay sediments and biota, but have been found only at concentrations much lower than their chlorinated cousins. With the phase-out of PBDE flame retardants, polybrominated dioxins and furans from synthetic products will decrease, but some biologically produced forms will likely continue to be present.

In Bay samples, the most toxic polybrominated dioxin and furan compounds were not detected or found at very low concentrations

What Are They?

- Synthetic or naturally occurring brominated chemicals similar in structure and toxicity to chlorinated dioxins and furans.
- Polybrominated dioxins and furans are formed as by-products of brominated organic chemicals such as PBDEs (PAGE 63).
- They are also formed by combustion and environmental reactions of brominated chemicals and their degradation products.
- Some forms are naturally produced by algae.

What Are They Used For?

- The only deliberate uses for polybrominated dioxins and furans are in laboratory research.

How Are They Getting Into the Bay?

- Pathways for polybrominated dioxin and furan entry to the Bay are unknown, but may mirror those for PBDEs and other synthetic brominated chemicals.
- Measured loads in the literature have focused on areas with brominated materials in manufacturing, recycling, or incineration, generally not prevalent in the Bay Area.
- Samples in New York after the burning of the World Trade Center (Litten et al. 2003) had high concentrations, likely from combustion of brominated materials (Buser 1986). Production of polybrominated dioxins and furans may also occur in smaller structure fires, but, except in major disasters, the amounts will usually be small and dispersed.

What Happens to Them in the Bay?

- Polybrominated dioxins and furans are expected to bind to particles and settle into sediments, where they may be taken up by sediment-dwelling organisms and passed up the food chain.

- They are less persistent than the chlorinated dioxins and furans, with an estimated half-life in soil of three to six months (Melber and Kielhorn 1998).
- In Bay sediment and biota samples, the most toxic polybrominated dioxin and furan compounds were not detected or found at very low concentrations, much lower than those reported in the literature for areas with large expected sources.
- Some 1,3,7-tribromodibenzodioxin was found in the Bay, highest in South Bay and southern Central Bay. This is believed to be a degradation product of PBDEs (Steen et al. 2009, Arnoldsson et al. 2012).
- Polybrominated dioxins and furans in a sediment core from Osaka Bay in Japan decreased with depth, paralleling decreases in PBDEs in those cores and suggesting increasing concentrations over time (Takigami et al. 2005); concentrations in the Bay should show similar trends.

Is There a Risk of Harm in the Bay?

- Polybrominated dioxins and furans have modes of action similar to polychlorinated dioxins and furans (Melber and Kielhorn 1998).
- Bay polybrominated dioxins and furans are nearly a factor of 10 or more less toxic than polychlorinated dioxins and furans, so their risks are proportionally smaller, likely accounting for only around 5% of total dioxin-like activity in Bay sediments.

Management

- Polybrominated dioxins and furans should decrease with the phase-out of PBDEs, unless PBDEs are replaced with other brominated flame retardants.

On the Lookout for New CECs

Scientists and managers have been grappling with the challenge of identifying CECs among the thousands of chemicals in commerce. Some of the most influential assessments have been conducted by Derek Muir of Environment Canada (one of the science advisors on the RMP Emerging Contaminants Workgroup – [PAGE 51](#)) and Philip Howard. Howard and Muir (2010) screened over 22,000 chemicals in databases of chemicals in commerce maintained by the US Environmental Protection Agency and Environment Canada to identify new CECs. Each of the chemicals was evaluated for persistence, bioaccumulation, and toxicity. Over 600 chemicals were identified, comprising five general classes: brominated, chlorinated, fluorinated, silicone-related, and “others.” The RMP used a similar approach. Working with Dr. Muir and other advisers we have identified a suite of CECs. Several examples of chemicals that

are under consideration for RMP monitoring are presented below.

Brominated Compounds

Many of the CECs that are of greatest concern for San Francisco Bay are brominated compounds that are flame retardants. For example, ethylene bis-tetrabromophthalimide (EBTEBPI) is a high production volume chemical and an alternative for the DecaBDE formulation that is being phased out this year. Because flame retardants are used in high volumes, and are potentially persistent, readily accumulated by biota, and toxic, the RMP places a high priority assessing whether these compounds are a threat in the Bay. A special study on alternative flame retardants is planned for 2014. Not all brominated compounds are flame retardants. Muir and Howard identified in their top ten list of brominated compounds, 1,3,6,8-Tetrabromopyrene (TBrPy), a compound that is used in the manufacture of LEDs. It is estimated that 500,000 lbs of TBrPy are produced

annually (Howard and Muir 2010) and this compound has not been monitored in the environment.

Chlorinated Compounds

Many of the top candidates as new CECs are chlorinated pesticides (Howard and Muir 2010). Bis(4-chlorophenyl)sulfone is another type of chlorinated compound identified by Howard and Muir - a high production volume chemical that is used in the manufacture of plastics and pharmaceuticals. This compound has been detected in bird eggs in the Great Lakes and bird eggs and seals in the Baltic Sea.

Fluorinated Compounds

Perfluorinated compounds, such as PFOS, have been an area of concern since our first studies in 2007. Several of the fluorinated compounds identified in the Howard and Muir list are replacements for fluorinated compounds such as PFOS ([PAGE 55](#)). Fluorinated alkyl phosphates and fluorinated cyclic compounds are identified in the Howard and Muir top ten list. Fluorinated alkyl phosphates are frequently used

as additives in pesticides. Fluorinated cyclic compounds such as perfluoroperhydrophenanthrene are used in the electronics industry. Analytical techniques to measure these compounds are in development. Fluorinated alkyl phosphates have been detected in Canadian effluents in concentrations that are almost an order of magnitude lower than PFOS (D'Eon et al. 2009). The RMP is currently embarking on a pro bono study with AXYS Analytical to identify possible fluorinated compounds that undergo transformations to produce PFOS and PFOA in the environment

Silicone Compounds

Siloxanes and other silicone containing compounds are widely used in shampoos and deodorants as well as in lubricants, polymers, textiles, and medical devices. Siloxanes with cyclic structures such as D4 and D5 are widely used in these applications. Developing analytical methods for monitoring these compounds has been a challenge as a result of their ubiquitous use and high volatility. In addition,

the toxicity and potential for these compounds to bioaccumulate are not well understood. The RMP has monitored for D4, D5, and D6 in bivalves; the primary compound detected was D5 in concentrations ranging from approximately 20 to 90 ng/g dw.

Others

Other compounds identified by Howard and Muir as potential CECs include the fragrance ingredients such as traseolide and galaxolide (see also [PAGES 71-74](#)). An expert panel convened by the State Water Board recommended that galaxolide be monitored in enclosed bays and estuaries (Anderson et al. 2012). The RMP has monitored galaxolide in water and found concentrations substantially below the no effect concentration of 7,000 nanograms per liter. As part of the development of bioanalytical tools ([PAGE 51](#)), galaxolide is one of four chemicals that will be used to assess endocrine disruption. The RMP will consider evaluating additional fragrances in a future study.

← Photograph by Meg Sedlak.

References

Overview

Benotti MJ, Trenholm RA, Vanderford BJ, Holady JC, Stanford BD, Snyder SA. 2009. Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. *Environ Sci Technol* 43(3): 597-603.

Muir, D.C. and P.H. Howard. 2006. Are there other persistent organic pollutants? A challenge for environmental chemists. *Environmental Science and Technology* 40, 7157-7166.

Wilson, M.P. and M.R. Schwarzman. 2009. Toward a new U.S. chemicals policy: rebuilding the foundation to advance new science, green chemistry, and environmental health. *Environmental Health Perspectives*, 117, 1202-1209.

USEPA. 2013. TSCA Chemical Substances Inventory: Basic Information. <http://www.epa.gov/oppt/existingchemicals/pubs/tscainventory/basic.html>

US Department of Commerce. 2013. <http://www.bea.gov/index.htm>

Status and Trends Update

Brodberg et al. 2007. Report on the safety of consuming fish and shellfish from areas impacted by the M/V Cosco Busan oil spill in San Francisco Bay, CA. Office of Environmental Health Hazard Assessment, Sacramento, CA.

Buchanan, P.A., and Morgan, T.L., 2010. Summary of suspended-sediment concentration data, San Francisco Bay, California, water year 2007: U.S. Geological Survey Data Series 476, 30 p. (IP-006245).

Greenfield, B.K. and R.M. Allen. 2013. Polychlorinated biphenyl spatial patterns in San Francisco Bay forage fish. *Chemosphere*. 90:1693-1703.

Senn, D., et al. 2013. San Francisco Bay Nutrient Conceptual Model. RMP Publication. Richmond, CA.

CEC Monitoring

MONITORING CONTAMINANTS OF EMERGING CONCERN IN SAN FRANCISCO BAY

Benotti MJ, Trenholm RA, Vanderford BJ, Holady JC, Stanford BD, Snyder SA. 2009. Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. *Environ Sci Technol* 43(3): 597-603

Klosterhaus et al. 2013. Contaminants of Emerging Concern in San Francisco Bay: A Summary of Occurrence Data and Identification of Data Gaps. RMP Contribution #698. San Francisco Estuary Institute, Richmond, CA.

Kucklick et al. manuscript in prep.

Muir, D.C. and P.H. Howard. 2006. Are there other persistent organic pollutants? A challenge for environmental chemists. *Environmental Science and Technology*, 40, 7157-7166.

SFEI. 2012. Regional Monitoring Program Update. SFEI Contribution 678. San Francisco Estuary Institute, Richmond, CA.

Sutton et al. 2013. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. RMP Contribution #700. San Francisco Estuary Institute, Richmond, CA.

USEPA. 2013. TSCA Chemical Substances Inventory: Basic Information. <http://www.epa.gov/oppt/existingchemicals/pubs/tscainventory/basic.html>

Wilson, M.P. and M.R. Schwarzman. 2009. Toward a new U.S. chemicals policy: rebuilding the foundation to advance new science, green chemistry, and environmental health. *Environmental Health Perspectives*, 117, 1202-1209.

PFOS

Becker, A. M., S. Gerstmann, and H. Frank. 2008. Perfluorooctane surfactants in waste waters, the major source of river pollution. *Chemosphere* 72:115-121.

DeWitt, J.C., Peden-Adams, M.M., Keller, J.M., & Germolec, D.R. 2012. Immunotoxicity of perfluorinated compounds: recent developments. *Toxicologic pathology*, 40, 300-311.

Giesy, J. P. and K. Kannan. 2001. Global Distribution of Perfluorooctane Sulfonate in Wildlife. *Environmental Science & Technology* 35:1339-1342.

Hansen, K. J., L. A. Clemen, M. E. Ellefson, and H. O. Johnson. 2001. Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. *Environmental Science & Technology* 35:766-770.

Higgins, C. P., Field, J. A., Criddle, C. S., Luthy, R. G. 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environmental Science & Technology*, 39, 3946-3956.

Houtz, E. F., Sedlak, D. L. 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environmental science & technology*, 46, 9342-9349.

Kannan, K., E. Perrotta and N.J. Thomas. 2006. Association between perfluorinated compounds and pathological conditions in southern sea otters. *Environ. Sci. Tech.* 40: 4943-8.

Myers, A. L., P. W. Crozier, P. A. Helm, C. Brimacombe, V. I. Furdai, E. J. Reiner, D. Burniston, and C. H. Marvin. 2012. Fate, distribution, and contrasting temporal trends of perfluoroalkyl substances (PFASs) in Lake Ontario, Canada. *Environment International* 44:92-99.

Newsted, J. L., P. D. Jones, K. Coady, and J. P. Giesy. 2005. Avian toxicity reference values for perfluorooctane sulfonate. *Environmental Science and Technology* 39:9357-9362.

Plumlee, M. H., J. Larabee, and M. Reinhard. 2008. Perfluorochemicals in water reuse. *Chemosphere* 72:1541-1547.

Schultz, M. M., C. P. Higgins, C. A. Huset, R. G. Luthy, D. F. Barofsky, and J. A. Field. 2006. Fluorochemical Mass Flows in a Municipal Wastewater Treatment Facility. *Environmental Science & Technology* 40:7350-7357.

Sedlak, M., Allen, R. 2013. Sources of Perfluoroalkyl Substances to San Francisco Bay. Manuscript in preparation.

ALKYLPHENOLS

Billinghurst, Z., A.S. Clare, T. Fileman, J. McEvoy, J. Readman, and M.H. Dpledge. 1998. Inhibition of barnacle settlement by the environmental oestrogen 4-nonylphenol and the natural oestrogen 17 beta oestradiol. *Marine Pollution Bulletin* 36: 833-839.

Chiu, T.Y., Paterakis, N., Cartmell, E., Scrimshaw, M.D., Lester, J. N. 2010. A critical review of the formation of mono- and dicarboxylated metabolic intermediates of alkylphenol polyethoxylates during wastewater treatment and their environmental significance. *Critical Reviews in Environmental Science and Technology*, 40, 199-238.

Diehl, J., S.E. Johnson, K. Xia, A. West, and L. Tomanek. 2012. The distribution of 4-nonylphenol in marine organisms of North American Pacific Coast estuaries. *Chemosphere* 87:490-497.

Klosterhaus, S., R.M. Allen, and J. Davis. 2012. Contaminants of emerging concern in the San Francisco Estuary: alkylphenol ethoxylates. SFEI Contribution #657 San Francisco Estuary Institute, Richmond, CA.

Klosterhaus, S.L., R. Grace, M.C. Hamilton, and D. Yee. 2013a. Method validation and reconnaissance of pharmaceuticals and alkylphenols in surface waters, sediments, and mussels in an urban estuary. *Environment International* 54:92-99.

Schlenk, D., R. Lavado, J.E. Loya-Rosales, W. Jones, L. Maryoung, N. Riar, I. Werner, and D. Sedlak. 2012. Reconstitution studies of pesticides and surfactants exploring the cause of estrogenic activity observed in surface waters of the San Francisco Bay Delta. *Environmental Science and Technology* 46:9106-9111.

USEPA (United States Environmental Protection Agency). 2010. Nonylphenol (NP) and Nonylphenol Ethoxylates (NPEs) Action Plan. RIN 2070-ZA09. August 2010.

PBDEs

Arkoosh MR, Boylen D, Dietrich J, Anulacion BF, Ylitalo G, Bravo CF, et al. 2010. Disease susceptibility of salmon exposed to polybrominated diphenyl ethers (PBDEs). *Aquat Toxicol* 98(1): 51-59.

Crimmins BS, Pagano JJ, Xia X, Hopke PK, Milligan MS, Holsen TM. 2012. Polybrominated diphenyl ethers (PBDEs): turning the corner in Great Lakes trout 1980-2009. *Environ Sci Technol* 46(18): 9890-9897.

Dodder NG, Maruya KA, Lauenstein GG, Ramirez J, Ritter KJ, Schiff KC. 2012. Distribution and sources of polybrominated diphenyl ethers in the Southern California Bight. *Environ Toxicol Chem* 31(10): 2239-2245.

Grant PB, Johannessen SC, Macdonald RW, Yunker MB, Sanborn M, Dangerfield N, et al. 2011. Environmental fractionation of PCBs and PBDEs during particle transport as recorded by sediments in coastal waters. *Environ Toxicol Chem* 30(7): 1522-1532.

Henny CJ, Kaiser JL, Grove RA, Johnson BL, Letcher RJ. 2009. Polybrominated diphenyl ether flame retardants in eggs may reduce reproductive success of ospreys in Oregon and Washington, USA. *Ecotoxicology* 18(7): 802-813.

Ikonoum MG, Teas HJ, Gerlach R, Higgs D, Addison RF. 2011. Residues of PBDEs in northeastern Pacific marine fish: evidence for spatial and temporal trends. *Environ Toxicol Chem* 30(6): 1261-1271.

Kimbrough KI, Johnson WE, Lauenstein GG, Christensen JD, Apeti DA. 2009. An Assessment of Polybrominated Diphenyl Ethers (PBDEs) in Sediments and Bivalves of the U.S. Coastal Zone. (NOAA Technical Memorandum NOS NCCOS 94). Silver Spring, MD: National Oceanic and Atmospheric Administration.

Klasing S, Brodberg R. 2011. Development of Fish Contaminant Goals and Advisory Tissue Levels for Common Contaminants in Sport Fish: Polybrominated Diphenyl Ethers (PBDEs). Oakland, CA: Pesticide and Environmental Toxicology Branch, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency.

Neale JC, Gulland FM, Schmelzer KR, Harvey JT, Berg EA, Allen SG, et al. 2005. Contaminant loads and hematological correlates in the harbor seal (*Phoca vitulina*) of San Francisco Bay, California. *J Toxicol Environ Health Part A* 68(8): 617-633.

Rattner BA, Lazarus RS, Heinz GH, Karouna-Renier NK, Hale RC. 2011. Apparent Tolerance of Common Tern (*Sterna hirundo*) Embryos to a Pentabrominated Diphenyl Ether Mixture (DE-71).

She J, Holden A, Adelsbach TL, Tanner M, Schwarzbach SE, Yee JL, et al. 2008. Concentrations and time trends of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in aquatic bird eggs from San Francisco Bay, CA 2000-2003. *Chemosphere* 73(1 Suppl): S201-209.

She J, Petreas M, Winkler J, Visita P, McKinney M, Kopec D. 2002. PBDEs in the San Francisco Bay Area: measurements in harbor seal blubber and human breast adipose tissue. *Chemosphere* 46(5): 697-707.

ALTERNATIVE FLAME RETARDANTS

Birnbaum, L., and D. Staskal. 2004. Brominated flame retardants: Cause for concern? *Environmental Health Perspectives*, 112:9-17.

Chen, D., M.J. La Guardia, D.R. Luelien, E. Harvey, T.M. Mainor, and R.C. Hale. 2011. Do temporal and geographical patterns of HBCD and PBDE flame retardants in U.S. fish reflect evolving industrial usage? *Environmental Science and Technology* 45:8254-8261.

Dishaw, L.V., C.M. Powers, I.T. Ryde, S.C. Roberts, F.J. Seidler, T.A. Slotkin, and H.M. Stapleton. 2011. Is the PentaBDE replacement, tris (1,3-dichloro-2-propyl) phosphate (TDCPP), a developmental neurotoxicant? Studies in PC12 cells. *Toxicology and Applied Pharmacology* 256:281-289.

Fang, M., T.F. Webster, D. Gooden, E.M. Cooper, M.C. McClean, C. Carrigan, C. Makey, and H.M. Stapleton. 2013. Investigating a novel flame retardant known as V6: Measurements in baby products, house dust, and car dust. *Environmental Science and Technology* 47:4449-4454.

Gauthier, L.T., and R.J. Letcher. 2009. Isomers of Decchlorane Plus flame retardant in the eggs of herring gulls (*Larus argentatus*) from the Laurentian Great Lakes of North America: Temporal changes and spatial distribution. *Chemosphere* 75:115-120.

Gauthier, L.T., D. Potter, C.E. Hebert, and R.J. Letcher. 2009. Temporal trends and spatial distribution of non-polybrominated diphenyl ether flame retardants in the eggs of colonial populations of Great Lakes herring gulls. *Environmental Science and Technology* 43:312-317.

Hoguet, J., J.M. Keller, J.L. Reiner, J.R. Kucklick, C.E. Bryan, A.J. Moors, R.S. Pugh, and P.R. Becker. 2013. Spatial and temporal trends of persistent organic pollutants and mercury in beluga whales (*Delphinapterus leucas*) from Alaska. *Science of the Total Environment* 449:285-294.

Klosterhaus, S.L., R. Grace, M.C. Hamilton, and D. Yee. 2013b. Method validation and reconnaissance of pharmaceuticals and alkylphenols in surface waters, sediments, and mussels in an urban estuary. *Environment International* 54:92-99.

Klosterhaus, S.L., H.M. Stapleton, M.J. La Guardia, and D.J. Greig. 2012. Brominated and chlorinated flame retardants in San Francisco Bay sediments and wildlife. *Environment International* 47:56-65.

Klosterhaus, S., D. Yee, M. Sedlak, A. Wong, and R. Sutton. 2013a. Contaminants of emerging concern in San Francisco Bay: a summary of occurrence data and identification of data gaps. RMP Contribution 698. San Francisco Estuary Institute, Richmond, CA.

Meeker, J.D., and H.M. Stapleton. 2010. House dust concentrations of organophosphate flame retardants in relation to hormone levels and semen quality parameters. *Environmental Health Perspectives* 118:318-323.

Shen, L., E.J. Reiner, P.A. Helm, C.H. Marvin, B. Hill, X. Zhang, K.A. MacPherson, et al. 2011. Historic trends of Decchloranes 602, 703, 604, Decchlorane Plus and other nonbromene derivatives and their bioaccumulation potential in Lake Ontario. *Environmental Science and Technology* 45:3333-3340.

Stapleton, H.M., N.G. Dodder, J.R. Kucklick, C.M. Reddy, M.M. Schantz, P.R. Becker, et al. 2006. Determination of HBCD, PBDEs and MeO-BDEs in California sea lions (*Zalophus Californianus*) stranded between 1993 and 2003. *Marine Pollution Bulletin* 52:522-531.

Yang, R., H. Wei, J. Guo, and A. Li. 2012. Emerging brominated flame retardants in the sediment of the Great Lakes. *Environmental Science and Technology* 46:3119-3126.

PHARMACEUTICALS

Brodin, T., J. Fick, M. Jonsson, and J. Klaminder. 2013. Dilute concentrations of a psychiatric drug alter behavior of fish from natural populations. *Science* 333:814-815.

Grung M., T. Kallqvist, S. Sakshaug, S. Skurtveit, and K.V. Thomas. 2008. Environmental assessment of Norwegian priority pharmaceuticals based on the EMEA guideline. *Ecotoxicology and Environmental Safety* 71:328-340.

Harrold, K.H., D. Yee, M. Sedlak, S. Klosterhaus, J.A. Davis, M. Woudneh, and P. Riley. 2009. Pharmaceutical concentrations in wastewater treatment plant influent and effluent and surface waters of Lower South San Francisco Bay. SFEI Contribution 549. San Francisco Estuary Institute, Oakland, CA.

Hoebert, J., R. Laing, and P. Stephens. 2011. The world medicines situation 2011: pharmaceutical consumption. World Health Organization, Geneva, Switzerland.

Klegwegt, S. S.A. Smyth, J. Parrot, K. Schaefer, E. Lagacé, M. Payne, E. Topp, A. Beck, A. McLaughlin, and K. Ostapyk, editors. 2007. Pharmaceuticals and personal care products in the Canadian environment. Research and policy directions. NWRI Scientific Assessment Report Series No. 8. 53p.

Klosterhaus, S.L., R. Grace, M.C. Hamilton, and D. Yee. 2013a. Method validation and reconnaissance of pharmaceuticals and alkylphenols in surface waters, sediments, and mussels in an urban estuary. *Environment International* 54:92-99.

Klosterhaus, S., D. Yee, M. Sedlak, A. Wong, and R. Sutton. 2013b. Contaminants of emerging concern in San Francisco Bay: a summary of occurrence data and identification of data gaps. RMP Contribution 698. San Francisco Estuary Institute, Richmond, CA.

References (cont)

TRICLOSAN

Buth, JM et al. 2010. Dioxin photoproducts of triclosan and its chlorinated derivatives in sediment cores. *Environ Sci Technol*. 44: 4545-4551.

Cantwell MG et al. 2010. Temporal trends of triclosan contamination in dated sediment cores from four urbanized estuaries: Evidence of preservation and accumulation. *Chemosphere*. 78:347-352.

Chalew, T E., Halden, R.U. 2009. Environmental exposure of aquatic and terrestrial biota to triclosan and triclocarban. *Journal of the American Water Resources Association*, 45, 4-13.

Emerging Contaminants Workgroup of the Santa Clara Basin Watershed Management Initiative (WMI). 2006. White Paper; Environmental Emergence of Triclosan.

Glassmeyer ST et al. 2005. Transport of chemical and microbial compounds from known wastewater discharges: Potential for use as indicators of human fecal contamination. *Environ Sci Technol*. 39:5157-5169.

Halden RU, Paull DH. 2005. Co-occurrence of triclocarban and triclosan in US water resources. *Environ Sci Technol*. 39:1420-1426.

Jackson J, Sutton R. 2008. Sources of endocrine-disrupting chemicals in urban wastewater, Oakland, CA. *Sci Tot Environ*. 405:153-160.

Kolpin DW et al. 2002. Pharmaceuticals, Hormones and Other Organic Wastewater Contaminants in US Streams, 1999-2000: A National Reconnaissance. *Environ Sci Technol*. 36:1202-1211.

Leiker TJ et al. 2009. Identification of methyl triclosan and halogenated analogues in male common carp (*Cyprinus carpio*) from Las Vegas Bay and semipermeable membrane devices from Las Vegas Wash, Nevada. *Sci Tot Environ*. 407:2102-2114.

Veldhoen N et al. 2006. The bactericidal agent triclosan modulates thyroid-associated gene expression and disrupts postembryonic anuran development. *Aquatic Toxicol*. 80: 217-227.

Wilson BA et al. 2003. Effects of three pharmaceutical and personal care products on natural freshwater algal assemblages. *Environ Sci Technol*. 37:1713-1719.

PYRETHROIDS

Anderson BS et al. 2008. Relative sensitivities of toxicity test protocols with the amphipods *Eohaustorius* estuarius and *Ampelisca abdita*. *Ecotoxicol. Environ. Safety* 69(1): 24-31.

Bay Area Stormwater Management Agencies Association (BASMAA) 2013. Regional Monitoring Coalition Urban Creeks Monitoring Report Water Year 2012.

Budd R et al. 2011. Removal mechanisms and fate of insecticides in constructed wetlands. *Chemosphere* 83(11): 1581-1587.

California Department of Pesticide Regulation (CDPR) 2013. Pesticides Sold in California For Year: 2011.

Ensminger MP et al. 2013. Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008-2011. *Environ Monit Assess* 185(5): 3697-3710

Gan J et al. 2005. Distribution and persistence of pyrethroids in runoff sediments. *J Environ Qual* 34(3): 836-841.

Hladik ML, Kuivila KM 2012. Pyrethroid insecticides in bed sediments from urban and agricultural streams across the United States. *J Environ Monitor* 14(7): 1838-1845.

Holmes RW et al. 2008. Statewide investigation of the role of pyrethroid pesticides in sediment toxicity in California's urban waterways. *Environ Sci Technol* 42(18): 7003-7009.

Jorgenson BC 2011. Off-Target Transport of Pyrethroid Insecticides in the Urban Environment: An Investigation into Factors Contributing to Washoff and Opportunities for Mitigation. Agricultural and Environmental Chemistry. Davis, CA, University of California Davis. Ph.D. [Note: replace with Jorgenson & Young journal paper if accepted before this is published.]

Jorgenson BC et al. 2012. Factors Contributing to the Off-Target Transport of Pyrethroid Insecticides from Urban Surfaces. *J Agr Food Chem* 60(30): 7333-7340.

Lao W et al. 2012. Pyrethroids in Southern California coastal sediments. *Environ Toxicol Chem* 31(7): 1649-1656.

Moran KD, TenBrook PL 2011. Sources of Pyrethroid Insecticides in California's Urban Watersheds: A Conceptual Model. In *Pesticide Mitigation Strategies for Surface Water Quality*; Goh KS, Gan J, Bret B, Eds. American Chemical Society: Washington, DC, 287-308.

Robertson-Bryan, Inc. 2012. Easterly Wastewater Treatment Plant Water Quality Monitoring Plan. Final Report for Monitoring Pyrethroids in Effluent and Receiving Water. Prepared for the City of Vacaville Utilities Department.

Ruby, A. 2013. Review of Pyrethroid, Fipronil and Toxicity Monitoring Data from California Urban Watersheds. Prepared for the California Stormwater Quality Association. Santa Cruz, CA.

TDC Environmental 2010. Pesticides in Urban Runoff, Wastewater, and Surface Water: Annual Urban Pesticide Use Data Report 2010. Urban Pesticide Pollution Prevention Project report prepared for the San Francisco Estuary Partnership.

U.S. Environmental Protection Agency (EPA) 2011. Pyrethrins/Pyrethroid Cumulative Risk Assessment. Office of Pesticide Programs.

Werner, I., & Moran, K. 2008. Effects of pyrethroid insecticides on aquatic organisms. In *Synthetic Pyrethroids: Occurrence and Behavior in Aquatic Environments ACS Symposium Series* (Vol. 991), pp. 310-335.

Weston DP et al. 2004. Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of California's Central Valley. *Environ Sci Technol* 38(10): 2752-2759.

Weston DP et al. 2005. Aquatic Toxicity Due to Residential Use of Pyrethroid Insecticides. *Environ. Sci Technol* 39(24): 9778-9784.

Weston DP et al. 2008. Sediment Toxicity in Agricultural Areas of California and the Role of Hydrophobic Pesticides. *Synthetic Pyrethroids*. Gan J, Spurlock F, Hendley P, Weston D, Eds.; American Chemical Society: Washington, DC, 26-54

Weston DP, Jackson CJ 2009. Use of Engineered Enzymes to Identify Organophosphate and Pyrethroid-Related Toxicity in Toxicity Identification Evaluations. *Environ Sci Technol* 43(14): 5514-5520.

Weston DP, Lydy MJ 2010. Urban and Agricultural Sources of Pyrethroid Insecticides to the Sacramento-San Joaquin Delta of California. *Environ Sci Technol* 44(5): 1833-1840.

Weston DP, Lydy MJ 2012. Stormwater input of pyrethroid insecticides to an urban river. *Environ Toxicol Chem* 31(7): 1579-1586.

Weston DP et al. 2013. Identifying the cause of sediment toxicity in agricultural sediments: the role of pyrethroids and nine seldom-measured hydrophobic pesticides. *Chemosphere* 90(3): 958-964.

FIPRONIL

Bay S et al. 2010. Toxicity Identification Evaluation of Sediment (Sediment TIE) in Ballona Creek Estuary: Final Report. Technical Report 634. Costa Mesa, CA: Southern California Coastal Water Research Project.

California Department of Pesticide Regulation (CDPR) 2013. Pesticides Sold in California For Year: 2011.

Chandler, G. T., Cary, T. L., Volz, D. C., Walse, S. S., Ferry, J. L., Klosterhaus, S. L. 2004. Fipronil effects on estuarine copepod (*Amphiascus tenuiremis*) development, fertility, and reproduction: A rapid life-cycle assay in 96-well microplate format. *Environmental toxicology and chemistry*, 23, 117-124.

Ensminger MP et al. 2013. Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008-2011. *Environ Monit Assess* 185(5): 3697-3710.

Gan J et al. 2012. Occurrence of Fipronil and Its Biologically Active Derivatives in Urban Residential Runoff. *Environ Sci Technol* 46 (3): 1489-1495.

Jiang W et al. 2010. Wash-off potential of urban use insecticides on concrete surfaces. *Environ Toxicol Chem* 29(6): 1203-1208.

Morace JL 2012. Reconnaissance of Contaminants in Selected Wastewater-Treatment Plant Effluent and Stormwater Runoff Entering the Columbia River, Columbia River Basin, Washington and Oregon, 2008-10. USGS Scientific Investigations Report 2012-5068.

Ruby A 2013. Review of Pyrethroid, Fipronil, and Toxicity Monitoring Data from California Urban Watersheds. Prepared for the California Stormwater Quality Association.

Ryberg KR et al. 2010. Trends in pesticide concentrations in urban streams in the United States, 1992-2008. U.S. Geological Survey Scientific Investigations Report 2010-5139, 101 p.

Thuyet DQ et al. 2012. Wash off of imidacloprid and fipronil from turf and concrete surfaces using simulated rainfall. *Sci Tot Environ* 414: 515-524.

U.S. Environmental Protection Agency (USEPA) Office of Pesticide Programs 2007. Ecological Risk Assessment for Current and Proposed Residential and Crops Uses of Fipronil.

U.S. Environmental Protection Agency (USEPA) Office of Pesticide Programs 2013. Aquatic Life Benchmarks. http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm Accessed 3/26/13.

CURRENTLY USED PESTICIDES

Budd R. et al. 2013. Method for Prioritizing Urban Pesticides for Monitoring California's Urban Surface Waters. Prepared by the California Department of Pesticide Regulation Environmental Monitoring Branch.

California Department of Pesticide Regulation (CDPR) 2013. Pesticides Sold in California For Year: 2011.

Lu Z, Davis G. 2009. Relative-Risk Evaluation for Pesticides Used in the Central Valley Pesticides Basin Plan Amendment Project Area. Prepared by the Regional Water Quality Control Board, Central Valley Region.

Luo Y. et al. 2013. Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas. Prepared by the California Department of Pesticide Regulation Environmental Monitoring Branch.

TDC Environmental 2010. Pesticides in Urban Runoff, Wastewater, and Surface Water: Annual Review of New Scientific Findings 2010. Urban Pesticide Pollution Prevention Project report prepared for the San Francisco Estuary Partnership.

von der Ohe PC et al. 2011. A new risk assessment approach for the prioritization of 500 classical and emerging organic microcontaminants as potential river basin specific pollutants under the European Water Framework Directive. *Sci Total Environ* 409(11): 2064-2077.

NANOMATERIALS

EPA Needs to Manage Nanomaterial Risks More Effectively Report No. 12-P-0162 December 29, 2011 <http://www.epa.gov/oig/reports/2012/20121229-12-P-0162.pdf>

Schierz, A., A. N. Parks, K. M. Washburn, G. T. Chandler and P. L. Ferguson. 2012. "Characterization and Quantitative Analysis of Single-Walled Carbon Nanotubes in the Aquatic Environment Using Near-Infrared Fluorescence Spectroscopy." *Environmental Science and Technology* 46(22): 12262-12271

CHORINATED PARAFFINS

Bayen, S., Obbard, J. and G. Thomas. 2006. Chlorinated Paraffins: A review of analysis and environmental occurrence. *Environment International* 32, p 915-929.

Cooley, H., Fisk, A., Wiens, S., Tomy, G., Evan, R. and D. Muir. 2001. Examination of the behavior and liver and thyroid histology of juvenile rainbow trout (*Oncorhynchus mykiss*) exposed to high dietary concentrations of C10, C11, C12, C14- polychlorinated n-alkanes. *Aquatic Toxicology*. 54 p 81-99.

Environment Canada. 2008. Proposed Risk Management Approach for Chlorinated Paraffins. <http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=D048964A-1>

Houde, M., Muir, D., Tomy, G., Whittle, M., Teixeira, C. and S. Moore. Bioaccumulation and trophic magnification of short- and medium-chain chlorinated paraffins in food webs from Lake Ontario and Lake Michigan. *Environ. Sci. Technol.* Vol. 42. P. 3893-3899.

Santos, F. J., Parera, J., Galceran, M.T. 2006. Analysis of polychlorinated n-alkanes in environmental samples. Analytical and bioanalytical chemistry, 386, 837-857.

USEPA. 2009. Short-Chain Chlorinated Paraffins (SCCPs) and Other Chlorinated Paraffins Action Plan. http://www.epa.gov/opptintr/existingchemicals/pubs/sccps_ap_2009_1230_final.pdf

POLYBROMINATED DIOXINS

AND FURANS

Arnoldsson, K., P. L. Andersson and P. Haglund (2012). "Photochemical Formation of Polybrominated Dibenzodioxins from Environmentally Abundant Hydroxylated Polybrominated Diphenyl Ethers." *Environ Sci Technol* 46(14): 7567-7574.

Buser, H. R. (1986). "Polybrominated dibenzofurans and dibenzodioxins: thermal reaction products of polybrominated diphenyl ether flame retardants." *Environmental Science & Technology* 20(4): 404-408.

Litten, S., D. J. McChesney, M. C. Hamilton and B. Fowler (2003). "Destruction of the World Trade Center and PCBs, PBDEs, PCDD/Fs, PBDD/Fs, and Chlorinated Biphenyls in Water, Sediment, and Sewage Sludge." *Environmental Science & Technology* 37(24): 5502-5510.

Melber, C. and J. Kihlhorn (1998) "Environmental Health Criteria 205: Polybrominated Dibenzodioxins and Dibenzofurans."

Steen, P. O., M. Grandbois, K. McNeill and W. A. Arnold (2009). "Photochemical Formation of Halogenated Dioxins from Hydroxylated Polybrominated Diphenyl Ethers (OH-PBDEs) and Chlorinated Derivatives (OH-PBCDEs)." *Environmental Science & Technology* 43(12): 4405-4411.

Takigami, H., S. Sakai and A. Brouwer (2005). "Bio/chemical Analysis of Dioxin-like Compounds in Sediment Samples from Osaka Bay, Japan." *Environmental Technology* 26(4): 459-470.

ON THE LOOKOUT FOR NEW CECS

Anderson, P., Denslow, N., Drewes, J., Olivieri, A., Schlenk, D., Scott, G. and S. Snyder. 2012. Monitoring Strategies for Chemicals of Emerging Concern (CECs) in California's Aquatic Ecosystems. 692. Costa Mesa, CA.

D'Eon, J., Crozier, P., Furdulj, V., Reiner, E., Libelo, L., and S. Maybury. 2009. Perfluorinated phosphonic acids in Canadian surface waters and wastewater treatment plant effluent: Discovery of a new class of perfluorinated acids. *Environmental Toxicology and Chemistry*. Vol. 28. No. 10. P 2101-2107.

Howard PH and Muir DC. 2010. Identifying new persistent and bioaccumulative organics among chemicals in commerce. *Environ Sci Technol* 44(7): 2277-2285.

Howard PH, Muir DC. 2011. Identifying new persistent and bioaccumulative organics among chemicals in commerce II: pharmaceuticals. *Environ Sci Technol* 45(16): 6938-6946.

RMP Committee Members and Participants

RMP Steering Committee

Small POTWs, Karin North, City of Palo Alto
Medium-sized POTWs, Daniel Tafolla, Vallejo Sanitation and Flood Control District
Large POTWs/BACWA, Jim Ervin, City of San Jose Refineries, Peter Carroll, Tesoro Golden Eagle Refinery Industry, Dave Allen, USS-POSCO
Cooling Water, Steve Bauman, Mirant Delta LLC
Stormwater Agencies, Adam Olivieri, EOA, Inc.
Dredgers, John Coleman, Bay Planning Coalition
San Francisco Bay Regional Water Quality Control Board, Tom Mumley
US Army Corps of Engineers, Rob Lawrence
RMP Steering Committee Chair in bold print

RMP Technical Review Committee

POTWs/BACWA, Nirmela Arsem, East Bay Municipal Utility District
Rod Miller, San Francisco Public Utilities Commission
South Bay Dischargers, Tom Hall, EOA Inc.
Refineries, Bridgette DeShields, Integral Corporation
Industry, Dave Allen, USS-POSCO
Stormwater Agencies, Chris Sommers, EOA, Inc.
Dredgers, John Prall, Port of Oakland
San Francisco Bay Regional Water Quality Control Board, Karen Taberski
USEPA, Luisa Valiela
City of San Jose, Eric Dunlavey
City/County of San Francisco, Michael Kellogg
US Army Corps of Engineers, Robert Lawrence
RMP Technical Review Committee Chair in bold print

RMP Science Advisors

CONTAMINANT FATE WORKGROUP
Dr. Joel Baker, University of Washington - Tacoma
Dr. Frank Gobas, Simon Fraser University
EMERGING CONTAMINANTS WORKGROUP
Dr. Lee Ferguson, Duke University
Dr. Jennifer Field, Oregon State University
Dr. Phil Gschwend, Massachusetts Institute of Technology
Dr. Derek Muir, Environment Canada
Dr. David Sedlak, University of California - Berkeley

EXPOSURE AND EFFECTS WORKGROUP

Dr. Michael Fry, US Fish and Wildlife Service
Dr. Harry Ohlendorf, CH2M Hill
Dr. Daniel Schlenk, University of California – Riverside
Dr. Steve Weisberg, Southern California Coastal Water Research Project

SOURCES PATHWAYS AND LOADING WORKGROUP

Dr. Barbara Mahler, US Geological Survey
Dr. Roger Bannerman, Wisconsin Department of Natural Resources
Dr. Kelly Moran, TDC Environmental
Dr. Mike Stenstrom, University of California – Los Angeles

RMP Participants

MUNICIPAL DISCHARGERS

Burlingame Waste Water Treatment Plant
Central Contra Costa Sanitary District
Central Marin Sanitation Agency
City of Benicia
City of Calistoga
City of Palo Alto
City of Petaluma
City of Pinole/Hercules
City of Saint Helena
City and County of San Francisco
City of San Jose/Santa Clara
City of San Mateo
City of South San Francisco/San Bruno
City of Sunnyvale
Delta Diablo Sanitation District
East Bay Dischargers Authority
East Bay Municipal Utility District
Fairfield-Suisun Sewer District
Las Gallinas Valley Sanitation District
Marin County Sanitary District #5, Tiburon
Millbrae Waste Water Treatment Plant
Mountain View Sanitary District
Napa Sanitation District
Novato Sanitation District
Rodeo Sanitary District
San Francisco International Airport
Sausalito/Marin City Sanitation District
Sewerage Agency of Southern Marin
Sonoma County Water Agency
South Bayside System Authority
Town of Yountville
Union Sanitary District

Vallejo Sanitation and Flood Control District
West County Agency

INDUSTRIAL DISCHARGERS

C & H Sugar Company
Chevron Products Company
Conoco Phillips (Tosco-Rodeo)
Crockett Cogeneration
Rhodia, Inc.
Shell – Martinez Refining Company
Tesoro Golden Eagle Refinery
USS – POSCO Industries
Tosco, Rodeo
Valero Refining Company

COOLING WATER

GenOn Energy

STORMWATER

Alameda Countywide Clean Water Program
Caltrans
City and County of San Francisco
Contra Costa Clean Water Program
Fairfield-Suisun Urban Runoff Management Program
Marin County Stormwater Pollution Prevention Program
San Mateo Countywide Water Pollution Prevention Program
Santa Clara Valley Urban Runoff Pollution Prevention Program
Vallejo Sanitation and Flood Control District

DREDGERS

Alameda Point
BAE Systems
Chevron Richmond Long Wharf
City of Benicia Marina
Conoco Phillips (Tosco-Rodeo)
Marin Yacht Club
Marina Bay Yacht Harbor
Marina Vista Harbor Homeowners Association
Napa Yacht Club
Port of Oakland
Port of San Francisco
San Francisco Marina
San Rafael Yacht Harbor
Sausalito Yacht Harbor
US Army Corps of Engineers
Vallejo Ferry Terminal
Valero Refining Co.

Credits & Acknowledgements

Editors

Jay Davis, Meg Sedlak,
Rebecca Sutton, Christine Werme

Contributing Authors

Jay Davis, Meg Sedlak,
David Senn, Naomi Feger,
Ellen Willis-Norton

RMP Data Management

Cristina Grosso, John Ross, Amy
Franz, Don Yee, Adam Wong

Creative Direction, Design & Illustration

Linda Wanczyk

Information Graphics

Linda Wanczyk, Patty Frontiera,
Don Yee, Kelly Moran

Information Compilation

David Gluchowski, John Ross,
Dave Schoellhamer, Lester
McKee, Nicole David

Graphics Assistance

Joanne Cabling

Reviewers

Derek Muir, David Sedlak, Jennifer Field,
Lee Ferguson, Phil Gschwend, Luisa Valiela,
Peter Carroll, Denise Greig, Don Yee,
Lester McKee, Mike Connor, Keith Maruya,
Patti TenBrook, Dave Tamayo, Tom Mumley,
Gail Krowech, Ellen Willis-Norton,
Nicole David

Printing information

Marilyn Leoncavallo at Bay Area Graphics
www.bayareagraphics.com

THE PAPER.
REINCARNATION™ IS THE MOST
ENVIRONMENTALLY
FRIENDLY PAPER STOCK AVAILABLE.

- ★ 100% Recycled, 60% Post-consumer
Waste Processed Chlorine Free
- ★ FSC Certified
- ★ Ancient Forest Friendly
- ★ Manufactured with electricity that is
offset with Green-e® certified renewable
energy certificates

← Photograph by Tim Davis.

RMP

Regional Monitoring Program
for Water Quality in San Francisco Bay

A program of the San Francisco Estuary Institute

4911 Central Avenue, Richmond, CA 94804

p: 510-746-SFEI (7334), f: 510-746-7300

www.sfei.org

For an electronic copy of this report
and other RMP information, please visit
www.sfei.org



Printed on 100% Recycled, 60% Post-consumer Waste Processed Chlorine Free Paper

alkylphenol perfluorooctane sulfonate erythromycin hydrate
tris (1,3-dichloro-2-propyl) phosphate ranitidine sertraline
diuron fenpropathrin triclosan bis(4-chlorophenyl)sulfone
polybrominated diphenyl ether hexabromocyclododecane
ziram 1,2-bis (2,4,6, tribromophenoxy) ethane bifenthrin
bis (hexachlorocyclopentadieno) cyclooctane nanomaterials
gemfibrozil tris (1,3-dichloro-2-propyl) phosphate maneb
triclocarban 4-nonylphenol bisphenol a diphenhydramine
fipronil caffeine sulfamethoxazole n,n-diethyl-m-toluamide
carbamazepine bis(2-ethylhexyl) phthalate cypermethrin
single-walled carbon nanotubes galaxolide siloxanes
chlorinated paraffins dehydronifedipine ciprofloxacin D5
esfenvalerate permethrin di-n-butylphthalate oxazepam
chlorothalonil perfluoroperhydrophenanthrene cocaine
traseolide nanosilver polybrominated dibenzo-p-dioxins
cotinine 1,3,6,8-tetrabromopyrene indoxacarb cyfluthrin
diphenhydramine ethylenebis-tetrabromophthalidimide V6
chlorophenoxyphenols valsartan phenothrin mancozeb