Contaminants of Emerging Concern

IN SAN FRANCISCO BAY

A STRATEGY FOR FUTURE INVESTIGATIONS

2017 REVISION

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Executive Summary

More than 100,000 chemicals have been registered or approved for commercial use in the US. For many of these chemicals, major information gaps limit evaluations of their potential risks, and environmental monitoring of these chemicals has not been required by regulatory agencies. Nevertheless, researchers and government agencies have begun to collect occurrence, fate, and toxicity data for a number of these chemicals.

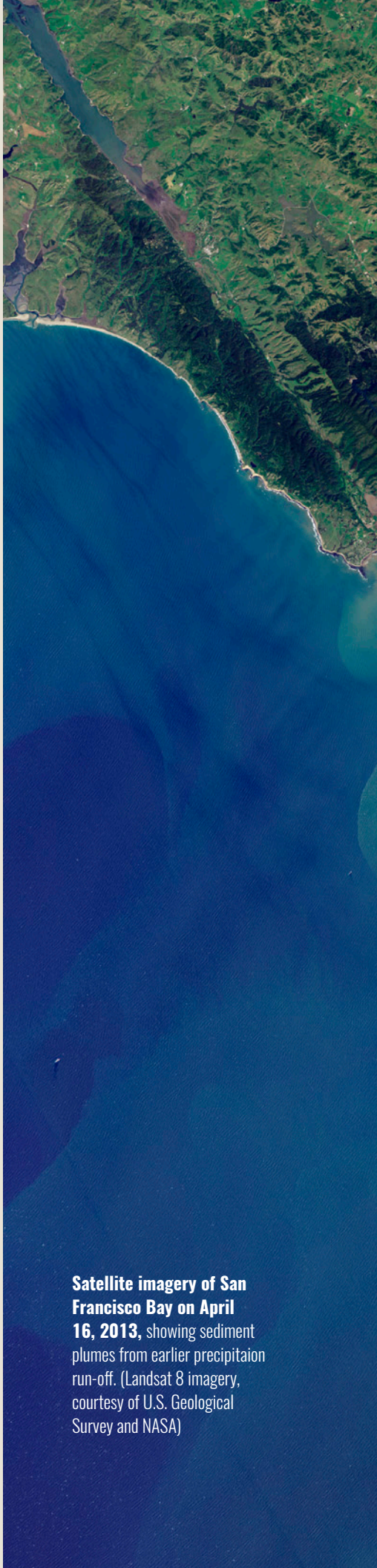
As a result, a growing number of chemicals have been classified as contaminants of emerging concern (CECs), broadly defined as synthetic or naturally occurring chemicals that are not regulated or commonly monitored in the environment but have the potential to enter the environment and cause adverse ecological or human health impacts. The primary challenge for scientists and regulators is investigating and managing this ever-expanding number of emerging contaminants to ensure that they do not harm human and ecological health.

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has been investigating CECs since 2001, and established a formal workgroup to address the issue in 2006. The RMP Emerging Contaminants Workgroup (ECWG) includes representatives from RMP stakeholder groups, regional scientists, and an advisory panel of expert researchers that work together to address the Workgroup's guiding management questions.

- Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?
- What are the sources, pathways, loadings, and processes leading to CEC pollution in the Bay?
- Have the concentrations of CECs in the Bay increased or decreased?
- Which management actions may be effective in reducing CEC levels?

The overarching goal of the ECWG is to develop cost-effective strategies to identify and monitor CECs to support management actions to minimize impacts to the Bay. The ECWG guides an annual process of contaminant evaluation and long-term planning and optimization to respond to new RMP data and the rapidly evolving body of science on CECs.

Following this process over the past decade, the RMP has generated one of the world's most comprehensive datasets for CECs in an estuarine ecosystem. While RMP stakeholders are the primary audience and user of RMP data and communications, the Program informs broader decision-making through outreach to state and federal agencies.



Satellite imagery of San Francisco Bay on April 16, 2013, showing sediment plumes from earlier precipitaion run-off. (Landsat 8 imagery, courtesy of U.S. Geological Survey and NASA)

The RMP first published a formal CEC Strategy in 2013 as part of a continuous effort to refine approaches for supporting the management of CECs in San Francisco Bay. Periodic revision of the Strategy is essential given the rapid evolution of the science surrounding emerging contaminants; this document is the second revision of the RMP's CEC Strategy. The Strategy described herein consists of three major elements.

First, for CECs known to occur in the Bay, the RMP prioritizes CECs using a tiered risk-based framework (Section 2.2). This prioritization framework guides future monitoring proposals for each of these contaminants (Section 3.0), the results of which, in turn, provide key data to update evaluations of potential risk. The criteria listed below are used for placement in each tier.

Criteria used for placement in each tier:

Tier IV (High Concern) • Bay occurrence data suggest a high probability of a moderate or high level effect on Bay wildlife (e.g., frequent detection at concentrations greater than the EC_{10} or another effects threshold). No CECs are currently assigned to Tier IV for the Bay.

Tier III (Moderate Concern) • Bay occurrence data suggest a high probability of a low level effect on Bay wildlife (e.g., frequent detection at concentrations greater than the predicted no effect concentration (PNEC) or no observed effect concentration (NOEC) but less than EC_{10}, the effect concentration where 10% of the population exhibit a response, or another low level effects threshold). CECs in Tier III include: PFOS; fipronil; and nonylphenols and nonylphenol ethoxylates.

Tier II (Low Concern) • Bay occurrence data suggest a high probability of no effect on Bay wildlife (i.e., Bay concentrations are well below toxicity thresholds and potential toxicity to wildlife is sufficiently characterized). CECs in Tier II include: pyrethroids (in the Bay - however, pyrethroids are a significant concern in Bay Area urban creeks); many pharmaceuticals and personal care products (PPCPs); hexabromocyclododecane (HBCD); and polybrominated dioxins and furans (PBDD/Fs). PBDEs, once considered a moderate concern for the Bay, have declined in response to management actions, and can now be classified as low concern CECs.

Tier I (Possible Concern) • Uncertainty in measured or predicted Bay concentrations or in toxicity thresholds suggests uncertainty in the level of risk to Bay wildlife. CECs in Tier I include: alternative flame retardants (including brominated, chlorinated, and phosphate compounds); bisphenol A; bis(2-ethylhexyl) phthalate (BEHP or DEHP) and butylbenzyl phthalate (BBzP); microplastic; tissue contaminants identified via recent broadscan study (2,2'-dichlorobenzil, dichloroanthracenes, 4-tert-butylamphetamine, methyl triclosan); other current use pesticides; poly- and perfluorinated alkyl substances (PFAS) other than PFOS; PCB-11; polyhalogenated carbazoles; short-chain chlorinated paraffins; and single-walled carbon nanotubes.

The tier designation for a CEC may also indicate whether levels are decreasing or increasing over time, via ↓ and ↑ symbols, respectively. Declines may be linked to specific management actions designed to prevent pollution, with continued monitoring appropriate for tracking recovery. Other contaminants may be expected to increase over time, for example due to expanded manufacturing and use, or increases in population. Consideration of broader chemical or functional classes is an integral approach responsive to both manufacturing substitutions, market shifts, and data limitations.

The second element of the RMP CEC Strategy involves review of the scientific literature and other CEC monitoring programs as a means of identifying new CECs for which no Bay occurrence data yet exist (Section 4.0). Initial monitoring to establish the presence of these newly identified CECs in the Bay is needed to evaluate the risks they may pose. Contaminants recently identified via this process include common fragrance ingredients and dyes.

Finally, the third element of the Strategy consists of exploratory techniques collectively referred to in this document as non-targeted monitoring. The RMP has conducted two types of non-targeted monitoring projects. The first, broadscan analyses of Bay samples, is designed to identify unexpected, previously unidentified CECs that are present in the Bay (Section 5.1). The other, bioanalytical tools, is expected to establish protocols that can be used to evaluate whether Bay samples have the potential to elicit specific biological effects, such as estrogenic endocrine disruption, in exposed organisms (Section 5.2).

The RMP's multi-faceted approach to addressing the challenge of CECs is designed to be flexible and adaptive to new data from both the RMP and other sources. Based on the Strategy, a multi-year plan indicating monitoring and science priorities is outlined (Section 6.0). A series of special studies are recommended for PFAS including the moderate concern PFOS, and a more limited range of studies are suggested for two other moderate concern contaminants, fipronil and nonylphenols and nonylphenol ethoxylates. Targeted special studies are also recommended for the following classes of compounds: alternative flame retardants, pharmaceuticals, plastic additives, personal care and cleaning product ingredients, and current use pesticides. Continued exploration of Bay matrices via non-targeted analysis is also suggested. Finally, recommendations for inclusion or exclusion of contaminant monitoring within routine RMP Status and Trends monitoring activities are also provided.

Early industry at the edge of the Bay. The Standard Oil refinery at Point Richmond, 1910. (Courtesy of the Richmond Public Library)

1 Introduction

1.1 The CEC Challenge and San Francisco Bay

More than 100,000 chemicals have been registered or approved for commercial use in the US. These substances include more than 85,000 industrial chemicals, 9,000 food additives, 3,000 cosmetics ingredients, 1,000 different pesticide active ingredients, and 3,000 pharmaceutical drugs (Muir and Howard 2006; Benotti et al. 2009; USEPA 2017) (Figure 1). Globally, chemical production is projected to continue growing by about 3% per year, and to double every 24 years (Wilson and Schwarzman 2009). The primary challenge for regulators and scientists is managing this ever-growing amount and variety of chemicals to ensure that they do not adversely impact human and ecological health.

San Francisco Bay, critical habitat for a multitude of estuarine species and a recipient of continuous inputs of chemical pollution from the surrounding urban environment, is a prime example of an ecosystem that merits investigation of the potential impacts of anthropogenically derived compounds on biota. Early identification of emerging pollution issues is particularly important in the Bay, because the ecosystem can act as a long-term trap for persistent contaminants, with recovery taking decades or longer when contamination is extensive.

Only a very small fraction of the large number of chemicals in use is routinely monitored in environments like San Francisco Bay. These generally include legacy pollutants – compounds that tend to meet the criteria of being persistent, bioaccumulative, and toxic – such as polychlorinated biphenyls (PCBs), chlorinated pesticides, and other chemicals on the United States Environmental Protection Agency (USEPA) list of 128 regulated priority pollutants. The risks these historically prioritized contaminants pose

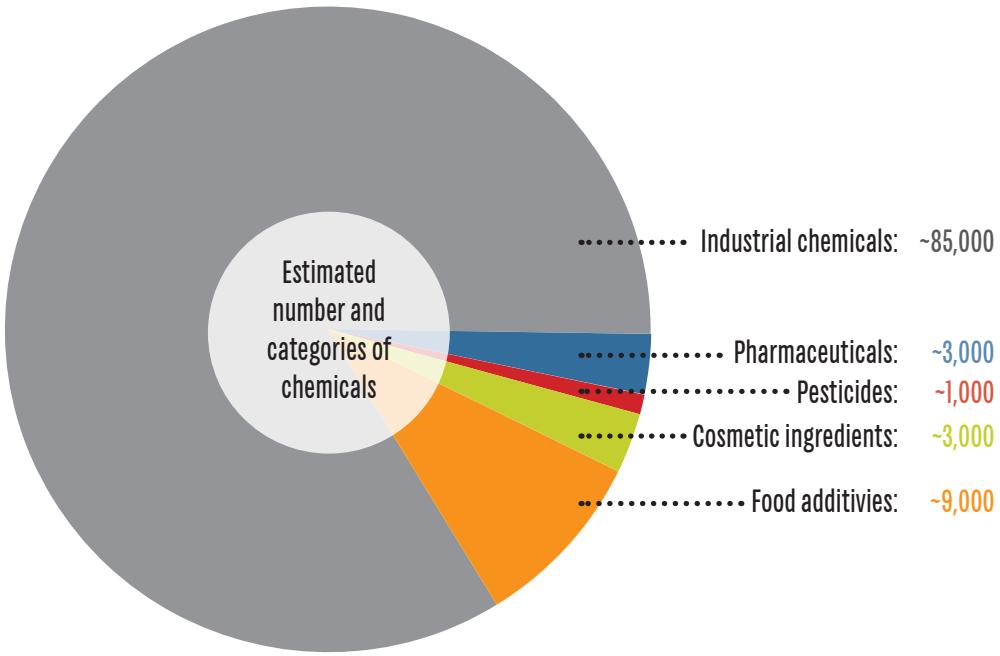


Figure 1. Estimated number and categories of chemicals in commerce registered for use in the United States over the past 30 years. Adapted from Muir and Howard (2006).

Ridgeways Rail at Pt. Isabel. (Courtesy of Becky Matsubara, March, 2017, CC)

to ecological and human health are relatively well understood, and monitoring is conducted to support risk reduction actions. However, for most chemicals currently in use, major information gaps limit the ability of scientists to assess their potential risks, and monitoring of these chemicals has not been required by regulatory agencies.

Over the last decade, researchers and government agencies have begun to collect occurrence, fate, and toxicity data for a variety of chemicals, including pharmaceuticals and personal care product ingredients (PPCPs), current use pesticides, and persistent industrial chemicals such as flame retardants and poly- and perfluorinated alkyl substances (PFAS). Analytical methods have progressed to the point that it is possible to measure trace quantities (below parts per trillion) of many contaminants in water, which has led to frequent detection of a variety of previously unmonitored or unmeasurable chemicals in the environment. Some of these chemicals have been classified as contaminants of emerging concern (CECs), often due to their high volume use, potential for toxicity in non-target species, and the increasing number of studies that report their occurrence in the environment. 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.

Determining which of the thousands of CECs pose the greatest threats to the Bay ecosystem is a formidable challenge. For most chemicals in use, a number of limitations prevent researchers from assessing their potential risks.

- The identities of chemicals used in commercial formulations, their applications, and product-specific uses are often unknown, characterized as confidential business information, or not readily available for other reasons.
- Sensitive methods that can reliably measure these chemicals at environmentally-relevant concentrations often do not exist. Development of new analytical methods is expensive, so researchers tend to focus their method development efforts on chemicals that are well-established concerns.
- The potential toxicological impacts of the majority of chemicals in use are largely unknown. Little to no information exists on chronic toxicity for realistic exposures, toxicity in non-target species, or sensitive toxicological endpoints such as endocrine disruption. Knowledge of toxic modes of action for most CECs is lacking, and details of toxicity studies conducted by chemical manufacturers are often not available for public review.

The combination of such large obstacles and limited resources makes it difficult for researchers and regulators to prioritize CECs for monitoring and control. For the majority of chemicals in use today, occurrence, persistence, and toxicity data are still needed to establish exposure and risk thresholds that protect the beneficial uses of aquatic ecosystems. Nevertheless, scientists and policymakers working to assess and protect the Bay from pollution have investigated a number of CECs for which data are available and that have the potential to impact the Bay.

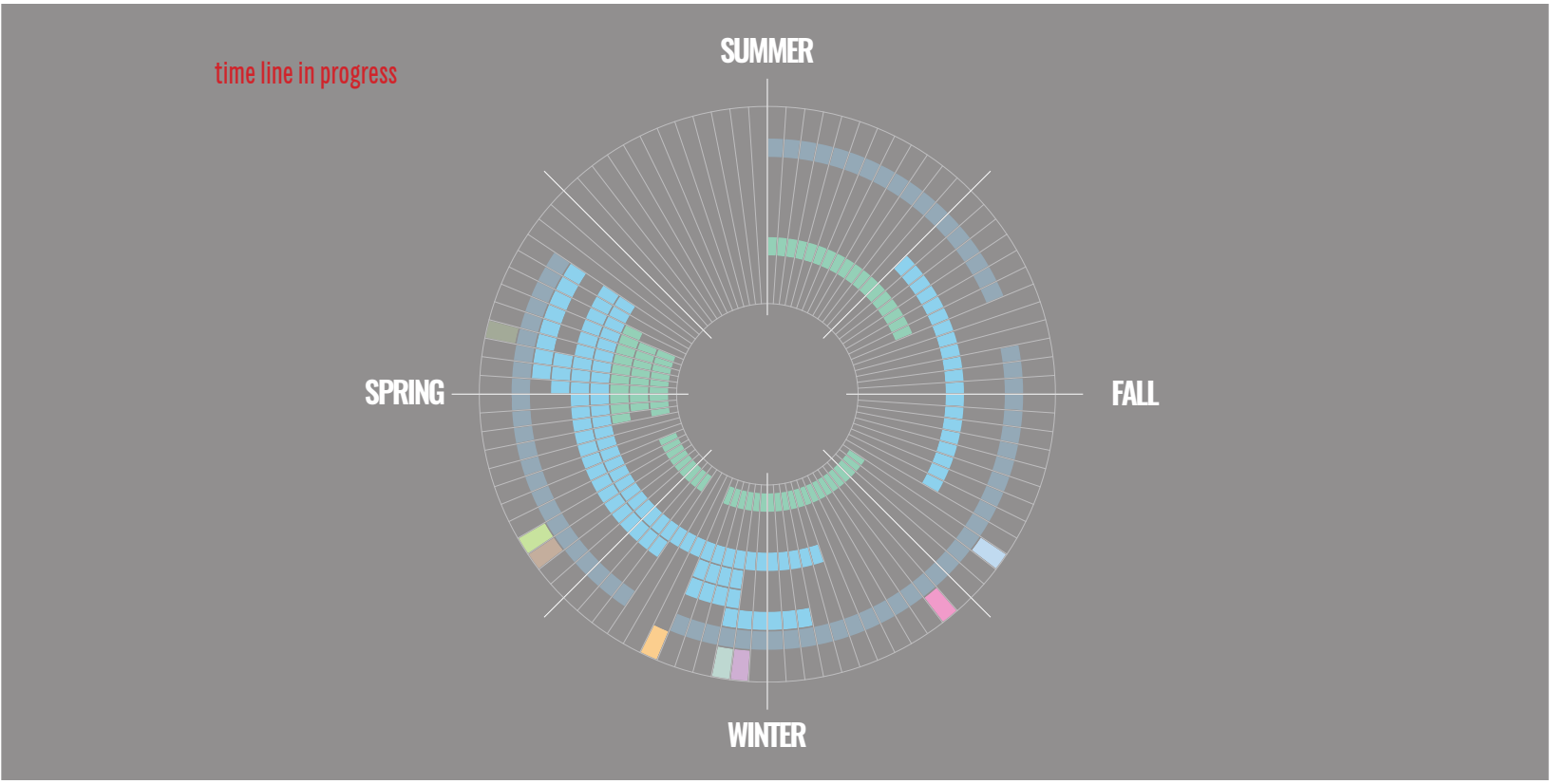
Vineyards in Napa Valley. (Courtesy of WineCountry Media, November, 2015, CC)

1.2 The RMP Emerging Contaminants Workgroup and Annual CEC Evaluation Process

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has been monitoring CECs since 2001, and developed a formal workgroup to address the issue in 2006. The RMP Emerging Contaminants Workgroup (ECWG) includes representatives from RMP stakeholder groups, local scientists, and an advisory panel of expert researchers that work together to protect the health of the Bay by addressing the Workgroup's guiding management questions (Section 1.3). The overarching goal of the ECWG is to develop cost-effective CEC identification and monitoring strategies in support of management efforts to minimize impacts to the Bay.

The ECWG plays a key oversight role in the RMP's annual cycle of CEC monitoring and evaluation. Each spring, the ECWG meets to discuss the CEC Strategy and review recent findings. At this meeting, the ECWG evaluates special study proposals for the coming year, recommending those that should be advanced to the RMP's Technical Review and Steering Committees for review and approval. A follow-up teleconference can be used to address remaining issues prior to review by the RMP Committees during their summer meetings.

Starting in the summer, the CEC science leads that manage the ECWG begin an annual evaluation of new information, including Bay monitoring data and new toxicity findings in the scientific literature, to consider revisions to the classification of CECs within the RMP's Tiered Prioritization Framework (Section 2.1). This risk-based framework guides future monitoring proposals for each of the listed contaminants (Section 3.0), the results of which, in turn, provide key data to update evaluations of potential risk. Recommendations for changes to the Tiered Prioritization Framework, as well as for contaminants appropriate to add to routine



Status and Trends monitoring, are reported to the ECWG as part of a draft CEC Strategy Update or Revision document (such as this one), completed prior to the spring meeting. Also included is a Multi-Year Plan intended to guide future monitoring and science activities; all RMP Multi-Year Plans, including a draft ECWG Multi-Year Plan, are reviewed together as part of a fall RMP Steering Committee meeting. After ECWG stakeholders and experts have reviewed and improved the draft CEC Strategy document, it is finalized. Meanwhile, scientists begin developing the next year's special study proposals, guided by the Multi-Year Plan, to be reviewed at the spring ECWG meeting.

With this process, the RMP has generated one of the world's most comprehensive datasets for CECs in an estuarine ecosystem. CECs investigated to date include poly- and perfluorinated alkyl substances (PFAS), alkylphenols, current use pesticides, pharmaceuticals and personal care product ingredients (PPCPs), and flame retardants including polybrominated diphenyl ethers (PBDEs) and their replacements. Among the CECs studied to date by the RMP, PBDEs, some PFAS, and pyrethroid pesticides have been added to the RMP Status and Trends monitoring program.

An inherent strength of the RMP CEC process is the consideration of individual chemicals as members of broader classes defined by chemical similarities (e.g., phthalates) or function or purpose in society (e.g., pesticides). Members of a chemical class may have similar properties with respect to persistence, bioaccumulation, or toxicity; a class-based approach can alert the RMP to potential concerns of a poorly studied compound that is chemically similar to a well-established toxicant. Members of a functional class may be substituted within formulations or other products in response to the phase-out or ban of a toxic compound; in this case, a class-based approach can indicate which chemicals may see increasing use as substitutes and may merit future monitoring. Similar class-based approaches have been adopted by several science and regulatory agencies as a means of systematically evaluating chemicals of concern.

Ideally, the CEC monitoring conducted by the RMP informs management actions that result in declines of high and moderate concern contaminants in Bay matrices. When contamination has fallen significantly below available thresholds of concern, the ECWG may determine that the contaminant should be reclassified in the tiered framework. As noted above, reclassification is typically outlined in a CEC Strategy Update or Revision document, and discussed during the ECWG meeting, to achieve consensus. In 2017, it is proposed that PBDEs be reclassified, from Moderate Concern (Tier III) to Low Concern (Tier II) contaminants, as levels in Bay matrices have declined below available toxicity thresholds (see Section 3.3).

1.3 CEC Management Questions and Stakeholder Interactions

RMP focus areas are guided by management questions to ensure that all RMP monitoring and science activities support the overarching RMP goal of informing management decisions. For many years, the CEC focus area was guided by a single management question:

MQ1 *Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?*

In response to the increasing demand for policy-relevant information about CECs in the region, three new questions have been brought forward in 2017, following consultation with ECWG experts and stakeholders:

MQ2 *What are the sources, pathways, loadings, and processes leading to CEC pollution in the Bay?*

MQ3 *Have the concentrations of CECs in the Bay increased or decreased?*

MQ4 *What are the effects of management actions?*

Management question 2 reflects the goal of tracing contaminants back to their sources, providing information to guide pollution prevention activities. Management question 3 focuses on temporal trends in contaminants, which may be influenced by management actions or independent changes in chemical manufacturing and use, as well as by secondary drivers such as climate change. Understanding the likely causes of apparent trends can lead to more effective solutions for pollution problems. Management question 4 is written broadly, as management actions can have positive and negative impacts. Responses to this question can even encompass reviews of functional substitutes for CECs at the source (e.g., within consumer products) as a means of exploring the potential for a management action to lead to "regrettable substitution," when a chemical of concern is replaced by another compound with problematic properties.

RMP stakeholders provide general guidance through development of management questions and review of the Strategy, and specific direction during the review of special study proposals and discussion of new findings. The spring ECWG meeting is a key venue for stakeholders to direct efforts on CECs; supplemental communication occurs throughout the year via teleconferences, the ECWG listserv, and meetings with stakeholder groups. Members of key state and federal agencies also engage with the ECWG and provide broader context regarding data needs and decision-making.

RMP data and communications are specifically designed to inform management decisions. Relevant policymaking bodies include the following:

- ***RMP Stakeholders*** – As the primary audience for RMP data and communications, stakeholders benefit directly from the RMP's focus on CECs. For example, wastewater and stormwater agencies use RMP findings to support voluntary educational efforts to reduce pollution within their service areas. Regionally, RMP CECs activities are an integral part of the

San Francisco Estuary Partnership's 2016 Estuary Blueprint (or Comprehensive Conservation and Management Plan; http://www.sfestuary.org/ccmp/).

- ***San Francisco Bay Regional Water Quality Control Board*** – As the RMP's regulatory stakeholder, the Water Board is leading region-wide efforts to reduce the harmful effects of CECs in the Bay through development of CEC Action Plans. Water Board staff are now drafting Action Plans for the CECs identified as moderate concerns for the Bay: the perfluorochemical PFOS, nonylphenol ethoxylates, and the pesticide fipronil. An Action Plan for PBDEs, until recently considered a moderate concern, is also being drafted. The RMP will provide the scientific support needed to develop and update CEC Action Plans and the related management strategies of local stakeholders.

- ***California Department of Pesticide Regulation (DPR)*** – Regulatory shifts relating to pesticide formulation and application can be a powerful means of preventing environmental contamination. The RMP strives to coordinate its monitoring efforts relating to current use pesticides with DPR priorities, leveraging available resources to inform statewide pesticide policies. For example, findings from RMP monitoring may influence ongoing efforts by DPR aimed at reducing environmental contamination and ecological impacts of fipronil and

(Below) **Edge of the SF Bay.** (Photo by Shira Bezalel, SFEI)

imidacloprid, two insecticides that are currently in wide use in urban settings. In 2016, the RMP monitored the influent and effluent from eight Bay municipal wastewater treatment plants for fipronil and its degradates, as well as imidacloprid (Sadaria et al. 2016). The study revealed the ubiquity and persistence of these contaminants despite treatment. Scientists from the RMP study team, which included DPR, assessed the concentrations and concluded that the primary source of contamination is likely pet flea control products.

- ***DTSC Safer Consumer Products Program*** – California is implementing a ground-breaking green chemistry approach to guide chemical and product manufacturers toward safer product design. The Department of Toxic Substance Control's Safer Consumer Products Regulations, established in 2013, define a process to evaluate whether there are safer alternatives to a chemical of concern in a product, and allow the agency to implement appropriate controls. RMP scientists regularly provide data to the program regarding environmental detections as well as insights on ecological toxicity and chemical source or use information.

- ***US Environmental Protection Agency*** – RMP data can also be used to inform federal regulation of industrial chemicals or pesticides. RMP staff seek out opportunities to bring Bay detection information and insights to the attention of the USEPA, typically in the form of comment letters regarding proposed actions such as Significant New Use Rules or pesticide re-registration.

1.4 Report Objectives

This strategy document has been revised as part of a continuous effort to refine approaches for supporting the management of CECs in San Francisco Bay. The specific objectives of this report are to:

- describe the general approach for identifying and prioritizing CECs with the potential to adversely impact beneficial uses of San Francisco Bay (Section 2.0);
- outline the current strategy to monitor CECs in the Bay based on the RMP's evaluation of their relative risk (Section 3.0);
- summarize the process for identifying new CECs suitable for initial study based on current literature and regional lists of prioritized water contaminants (Section 4.0);
- summarize the non-targeted, screening studies completed or now underway to identify additional CECs present in Bay media (Section 5.0);
- provide a multi-year plan for future monitoring and science (Section 6.0); and,
- provide recommendations to other RMP programs regarding CECs (Section 6.0).

The Strategy outlined here is part of an iterative process designed to ensure that the RMP remains ahead of the curve regarding CECs, specifically by tracking new information as it becomes available and communicating key findings to the ECWG, RMP stakeholders, and the broader policymaker community.

2 General Approach to Identify and Prioritize CECs

2.1 RMP CEC Strategy: Three Elements

The RMP has developed a three-element strategy to direct CEC monitoring and science in the Bay. First, for those CECs known to occur in the Bay, the RMP has established priorities using a tiered prioritization framework (Section 2.2). This risk-based framework guides future monitoring proposals for each of these contaminants (Section 3.0), the results of which, in turn, provide key data to update evaluations of potential risk. Second, RMP staff review the scientific literature and data from other regional CEC aquatic monitoring programs as a means of identifying new CECs for which no Bay occurrence data yet exist (Section 4.0). Initial monitoring to establish the presence of these newly identified CECs in San Francisco Bay is needed to evaluate the risks they may pose. Finally, the RMP has launched two types of non-targeted monitoring projects, one designed to identify previously unknown CECs present in Bay matrices (Section 5.1), the other to establish bioassays useful for identifying presence of contaminants that may elicit specific impacts to wildlife, such as estrogenic effects (Section 5.2). The RMP's multi-faceted approach to addressing the CEC challenge is designed to be flexible and adaptive to new information.

The RMP's approach is largely consistent with the recommendations from a Science Advisory Panel assembled by the California State Water Resources Control Board in 2009 to provide guidance for CEC monitoring in the State's receiving waters (Anderson et al. 2012). However, there are three notable differences. The first centers around the RMP's role in providing applied science to support management decisions. All RMP studies are designed to respond to information needs from water quality managers and other policymakers aiming to make sound, science-based decisions to protect the Bay. Stakeholders ensure that the RMP maintains this tight focus on applied science through development of management questions for each focus area, and through annual review of individual special study proposals via the ECWG and Technical Review and Steering committees.

A second distinctive element of the RMP approach to CECs is its emphasis on chemical or functional classes. By focusing on broader classes of chemicals, the RMP maintains a forward-looking approach that is designed to identify potential concerns before they cause harm to the Bay.

A third important difference from the statewide guidance is greater flexibility in the criteria for selecting CECs to monitor. The guidance in Anderson et al. (2012) limits monitoring to CECs with established quantitative risk thresholds. The RMP follows a more flexible approach that can include monitoring of CECs for which uncertainty regarding risk exists and thresholds have not yet been established. In some cases, monitoring information is of value to managers and can lead to pollution prevention actions even in the absence of robust estimates of risk thresholds. Recent examples of actions of this kind include the bans and use reductions for plastic microbeads in 2016 and for PBDE mixtures in 2004-2006. The microbead bans were established simply in response to an awareness of the presence of these non-essential consumer product components in the Bay and other aquatic ecosystems. The PBDE actions occurred in response to an alarming increase in concentrations in aquatic food webs and in humans, even though quantitative thresholds for risks to humans and wildlife were still in development.

The Bay edge, near the Oakland International Airport. (Courtesy of Google Earth, accessed March, 2017)

2.2 The RMP's Tiered Prioritization Framework

For those CECs for which monitoring in Bay water, sediment, or biota has occurred, and for which relevant toxicity information may be available, a risk-based screening method can be used to assign appropriate levels of concern regarding the potential to impact San Francisco Bay. The classification of each CEC guides both RMP monitoring and management actions. The RMP assigns each CEC or CEC class to a tier in the prioritization framework, based on available Bay occurrence data and toxicity information (framework in Table 1; CEC tier assignments in Table 2).

Criteria used for placement in each tier:

Tier IV (High Concern) • Bay occurrence data suggest a high probability of a moderate or high level effect on Bay wildlife (e.g., frequent detection at concentrations greater than the EC_{10} or another effects threshold).

Tier III (Moderate Concern) • Bay occurrence data suggest a high probability of a low level effect on Bay wildlife (e.g., frequent detection at concentrations greater than the PNEC or NOEC but less than EC_{10}, the effect concentration where 10% of the population exhibit a response, or another low level effects threshold).

Tier II (Low Concern) • Bay occurrence data suggest a high probability of no effect on Bay wildlife (i.e., Bay concentrations are well below toxicity thresholds and potential toxicity to wildlife is sufficiently characterized).

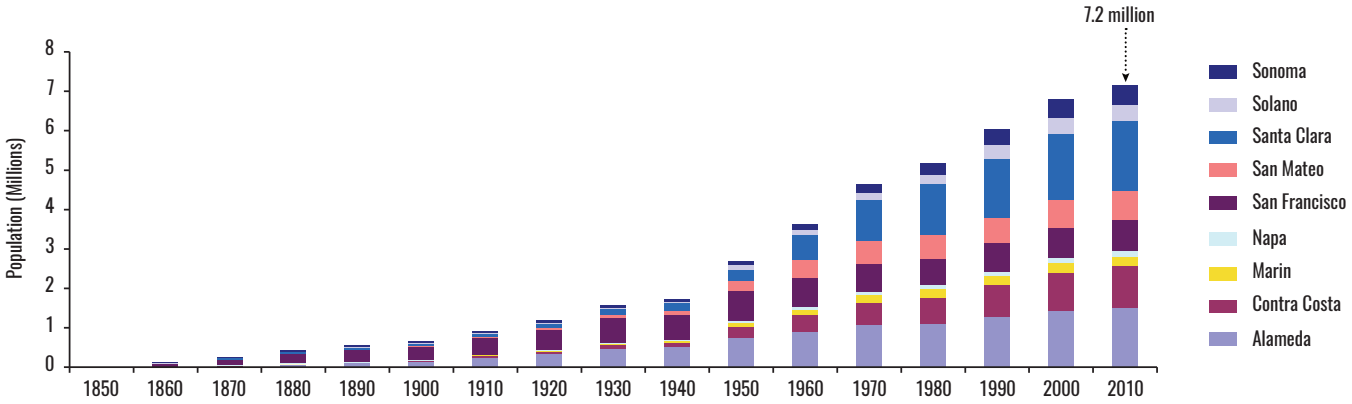
Tier I (Possible Concern) • Uncertainty in measured Bay concentrations or toxicity thresholds suggest uncertainty in the level of effect on Bay wildlife.

The tier designation for a CEC may also be modified to indicate whether levels are decreasing or increasing, via ↓ and ↑ symbols, respectively. Decreases may be linked to specific management actions designed to prevent pollution, with continued monitoring appropriate for tracking recovery. For example, PBDE bans and phase-outs have led to declines in contaminant levels in multiple Bay matrices (Sutton et al. 2015a). Continued RMP monitoring of this class of contaminants is useful in tracking further declines. Other contaminants may be expected to increase over time, perhaps due to expanded manufacturing and use or increases in population. Levels of many pharmaceuticals in Bay matrices are likely to grow along with our population; while pharmaceuticals are generally considered of low concern for the Bay, periodic monitoring is essential given this expected trend.

The assignments for established CECs that have been monitored in the Bay are provided in Table 2. A CEC is only assigned to a tier in the framework if it has been analyzed in Bay samples. Secondary factors that may impact tier assignments for each CEC include trends in use of the chemical or trends in Bay

concentrations. The tier assignments for each CEC in this report were based on available information and will be updated at least annually as new information on the levels or potential risk of the CEC becomes available.

The Bay integrates inputs from a variety of pollution pathways, including discharges of wastewater, stormwater, and flows from the Sacramento-San Joaquin Bay Delta. Typically, the RMP evaluates the presence and levels of contaminants in Bay water, sediment, or biota first; should detections suggest concern is warranted, further work to characterize relevant pathways may be indicated. Modeling capabilities specific to CECs are also under development to aid in interpretation of monitoring results.



(above) **Bay Area population increase over time, 1850-2010.**

(left) **A portion of the South Bay, 1939 and 2015.** (Courtesy USDA NAIP and ESRI imagery)

Table 1. The RMP Conceptual Tiered CEC Prioritization Framework for San Francisco Bay.

	RISK LEVEL DESCRIPTION	MONITORING STRATEGY	WATER QUALITY MANAGEMENT ACTIONS
TIER IV HIGH CONCERN	Bay occurrence data suggest a high probability of a moderate or high level effect on Bay wildlife.	Studies to support TMDL or alternative management plan.	303(d) listing.* TMDL or alternative management plan.* Aggressive control/treatment actions for all controllable sources.
TIER III MODERATE CONCERN	Bay occurrence data suggest a high probability of a low level effect on Bay wildlife.	Consider including in Status and Trends monitoring. Special studies of fate, effects, sources, pathways, and loadings.	Action plan/strategy. Aggressive pollution prevention. Low-cost control/treatment actions.
TIER II LOW CONCERN	Bay occurrence data suggest a high probability of no effect on Bay wildlife.	Low-cost source identification and control. Low-level pollution prevention. Track product use and market trends.	Discontinue or conduct periodic screening level monitoring in water, sediment, or biota. Periodic screening level monitoring for chemical(s) detected in wastewater or stormwater to track trends.
TIER I POSSIBLE CONCERN	Potential for concerns or uncertainty in measured Bay concentrations or toxicity thresholds suggest uncertainty in the level of effect on Bay wildlife.	Screening level monitoring to determine presence in water, sediment, or biota. Screening level monitoring for presence in wastewater or stormwater.	Maintain (ongoing/periodic) effort to identify and prioritize emerging contaminants of potential concern. Track international and national efforts to identify high priority CECs. Develop biological screening methods and identify available analytical methods.

*Subject to Regional Water Quality Control Board action with public review.

2.3 Identifying New CECs as Candidates for Initial Monitoring

The risk-based framework described above requires measured environmental concentrations to evaluate CECs and determine if there is a potential for concern in the Bay, yet many chemicals in commerce have never been the subject of local monitoring studies. To expand the suite of chemicals to screen for risk, the RMP has employed two additional approaches to identify potential CECs appropriate for Bay monitoring.

- ***Literature reviews and results from other monitoring programs:*** RMP scientists' extensive and ongoing review of the scientific literature on CECs can uncover additional compounds with potential to impact the Bay ecosystem. In addition, the results of approaches adopted by other state or regional agencies to prioritize CEC monitoring and management actions for aquatic ecosystems may reveal additional candidates for the RMP to consider. Details on this approach are provided in Section 4.

- ***Non-targeted monitoring:*** Novel non-targeted methods can also be used to identify previously unmonitored CECs.

    - *Non-targeted chemical screening:* The RMP conducted non-targeted screening analyses of Bay mussels and harbor seal blubber collected in 2010 in collaboration with the National Institute of Standards and Technology (NIST). The broadscan screening method focused on halogenated, hydrophobic compounds present in the tissue. In 2016, a similar broadscan analysis was applied to water and treated wastewater samples to identify previously unmonitored polar compounds. These non-targeted analyses are useful for creating an inventory of detectable compounds in tissues or abiotic matrices and can be used as a screening tool for directing targeted chemical analysis or toxicity identification evaluations. More information on these studies is provided in Section 5.1.

    - *Bioanalytical screening assays:* Another useful means of identifying potential pollution concerns is via biological responses following exposure to a matrix of interest, with all its associated contaminants. Existing bioanalytical tools show promise, but many have not yet been adapted and/or validated for environmental (i.e., receiving water) matrices, nor have they been adequately linked to effects at higher levels of biological organization. In 2013, the RMP sponsored a study to develop a bioanalytical tool to evaluate the estrogenicity of ambient estuarine waters from the Bay and effluent from Bay Area wastewater treatment plants. Successful application of this tool would result in identification of estrogenic water or effluent samples; further examination of such samples may reveal specific estrogenic contaminants that merit further investigation. More information on this study is provided in Section 5.2.

Initial monitoring to establish CEC levels in the Bay is essential to determine which level of concern each CEC merits using the tiered risk and management action framework (Table 2). Targeted contaminant monitoring (element one of the CEC strategy) is informed by close attention to the evolving science of CECs and the priorities of other monitoring programs (element two), as well as non-targeted studies using novel techniques (element three). Prior to formal establishment of the RMP's three-element CEC strategy (Sutton et al. 2013), efforts to identify new candidates for monitoring were summarized in the RMP synthesis document, "Contaminants of Emerging Concern in San Francisco Bay: A Summary of Occurrence Data and Identification of Data Gaps" (Klosterhaus et al. 2013a).

Shira Bezalel (SFEI)

Table 2. Current status of CECs in the tiered risk and management action framework for San Francisco Bay (see Section 2.2).

	CONTAMINANT CLASS	RATIONALE
TIER III MODERATE CONCERN	PFOS	Bird egg concentrations have been greater than PNEC and are currently in the range of concentrations linked to reproductive effects in wild birds; high concentrations in seal blood; high volume use of precursors; recent monitoring suggests declines in birds and seals.
	Fipronil	Sediment concentrations are in the range of toxicity thresholds for degradates; use is high and increasing in urban areas.
	Nonylphenols and Nonylphenol ethoxylates	Bay concentrations below most toxicity thresholds; possible impacts on larval barnacle settlement; possible synergistic effects with pyrethroids; estrogenic activity; previously high volume use in one product type, laundry detergent, may be decreasing.
TIER II LOW CONCERN	PBDEs	Concentrations in Bay wildlife and sediment have decreased over time, with detections now typically below thresholds of potential concern; tern egg concentrations are below reproductive toxicity threshold; sport fish concentrations are below protective human health thresholds for fish consumption; uncertainty regarding impacts on harbor seals; production and use phased out in US.
	PBDD/Fs	Low concentrations; synthetic sources declining with PBDE phase-out.
	HBCD	Concentrations are low; reduction in use anticipated worldwide.
	Pharmaceuticals and Personal care product ingredients*	Concentrations below toxicity thresholds, toxicity to aquatic species sufficiently characterized; levels expected to increase with population.
	Pyrethroids**	Detected infrequently and in low concentrations in Bay sediment; of concern in watersheds, as tributary sediment concentrations are comparable or higher than toxicity thresholds; previously high volume use may be decreasing; lower impact professional application methods have been prescribed via state regulations.

	CONTAMINANT CLASS	RATIONALE
TIER I **POSSIBLE CONCERN**	Alternative Flame Retardants (organophosphates including TPhP, hydrophobic brominated and chlorinated [Dechlorane-type] compounds, metabolites)	Detection of several in water, sediment, and/or tissue; limited toxicity data for aquatic species; endocrine disrupting properties; additive/synergistic exposure effects unknown; high volume use or potentially increasing use as PBDE replacements.
	Bisphenol A	Analyzed but not detected in surface waters (< 2500 ng/L) or sediments (< 2600 ng/g), PNEC=60 ng/L.
	Bis(2-ethylhexyl) phthalate (BEHP or DEHP)	Sediment concentrations in the same range as low apparent effects threshold (but threshold not directly linked to DEHP).
	Butylbenzyl phthalate (BBzP)	Sediment concentrations exceed low apparent effects threshold (threshold not directly linked to BBzP or effects in macrobenthos).
	Microplastic	Detected in Bay surface water; uncertainty in toxicity to Bay wildlife.
	Newly identified tissue contaminants • 2,2'-dichlorobenzil • dichloroanthracenes • 4-tert-butylamphetamine • methyl triclosan	Detected in Bay wildlife tissue samples via non-targeted analysis; uncertainties in toxicity data.
	Other pesticides***	Concentrations below toxicity thresholds; uncertainty in toxicity to Bay wildlife.
	PFAS other than PFOS	Detection of several compounds in Bay matrices; indications of contamination with as-yet unidentified PFAS; no evident declines in PFOA and other long- and short-chain PFAS, the latter likely due to increasing use; toxicity to aquatic species not sufficiently characterized.
	PCB 11	Ubiquitous contaminant and has been detected in Bay water, urban runoff, sediments, but not bioaccumulative like the more highly chlorinated PCB congeners (minor congener in small fish and bivalves); uncertainty in toxicity thresholds.
	Polyhalogenated carbazoles	Ubiquitous contaminant detected in Bay sediment, bivalves, fish, birds, and seals; uncertainty in toxicity thresholds.
	Short-chain chlorinated paraffins	Concentrations below toxicity thresholds; uncertainties in toxicity data; high volume use.
	Single-walled carbon nanotubes	Not detected; toxicity information not available.

*For full list of PPCPs considered in this group see Klosterhaus et al. 2013a, Appendix Tables B1 and B2

**Pyethroids are of high concern in Bay Area creeks and streams.

***For full list of pesticides considered in this classification see Klosterhaus et al. 2013a, Appendix Table B6

3 The RMP CEC Prioritization Framework and Monitoring Recommendations

The tiered prioritization framework identifies chemical-specific monitoring activities that will likely improve the evaluation of CEC risks to the Bay. Monitoring strategies for addressing individual CECs, grouped by relative risk assigned via the tiered framework, are outlined below.

3.1 Tier IV (High Concern) Monitoring Recommendations

At this time, no CECs have been assigned to Tier IV (High Concern).

3.2 Tier III (Moderate Concern) Monitoring Recommendations

Tier III CECs are those for which occurrence data suggest a high probability of low level effects on Bay wildlife (e.g., frequent detection at concentrations greater than the PNEC or NOEC but less than EC_{10}, the effect concentration where 10% of the population exhibit a response, or another low level effects threshold). In addition, these compounds may share modes of action with other Bay contaminants, or cause synergistic effects in combination with other contaminants. Because significant management actions may be prudent for Tier III CECs, studies to inform these actions are given a high priority. Regular monitoring of relevant matrices as part of Status and Trends work is recommended. In some cases, studies to elucidate the fate, effects, sources, pathways, and loadings of Tier III CECs may be needed. Where declines have been observed or are expected, monitoring to track recovery is appropriate.

Cormorants building a nest on the East span of the Bay Bridge. (Courtesy of Becky Matsubara, September, 2016, CC)

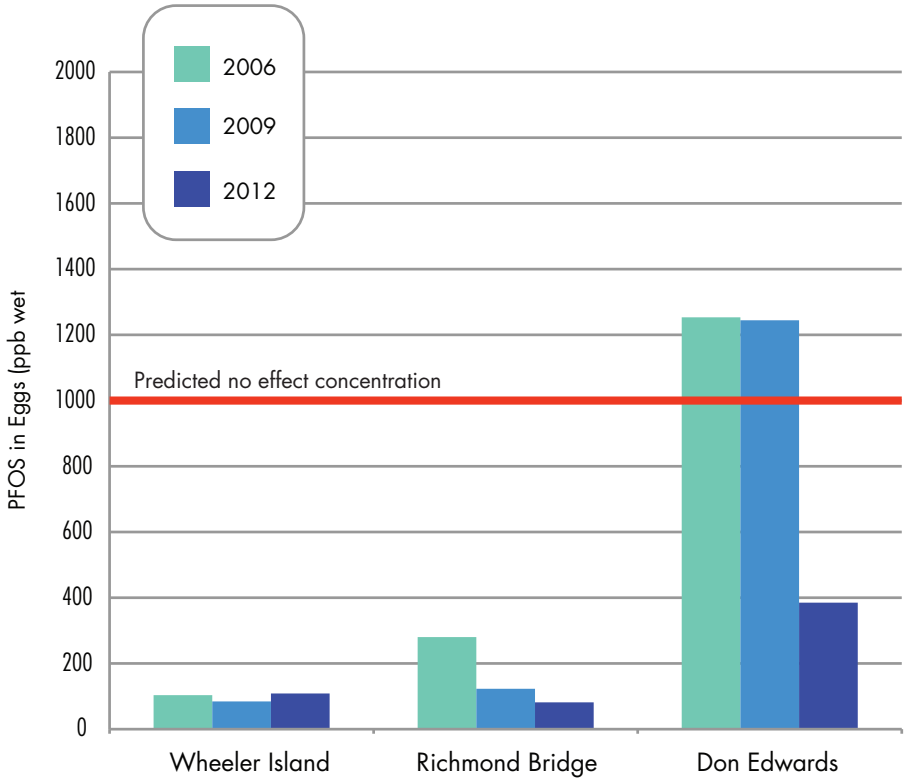
PFOS

TIER III
MODERATE CONCERN

Perfluorooctane sulfonate (PFOS) is a fully fluorinated 8-carbon chain compound that is part of a much larger class of compounds referred to as the poly- and perfluoroalkyl substances (PFAS). PFAS including PFOS were widely used for over 50 years in the US due to their chemical stability, useful surfactant properties, and their unique property of being able to repel both oil and water. PFOS is very stable in the environment, binds to proteins, and bioaccumulates primarily in the blood and liver (it does not selectively accumulate in fatty tissues as do many other organic contaminants). In early 2000, PFOS was widely detected in biota and people; as a result, in 2002, US manufacturers voluntarily phased out the manufacture of PFOS and some related PFAS compounds.

The RMP has analyzed bivalves, sport and prey fish, bird eggs, and seals for PFOS. In general, low to nondetectable PFOS concentrations have been observed in Bay bivalves (Dodder et al. 2014) and sport fish (Davis et al. 2012; Sun et al. 2017). For example, in the most recent round of Bay sport fish monitoring in 2014, PFOS was detected at concentrations ranging from 2.5 to 14.2 ppb, consistent with prior results; however, PFOS was detected more frequently (in 76% of fish vs. 19% in samples collected in 2009). More frequent detections may in part be attributed to the inclusion of fish from Artesian Slough in the Lower South Bay, an area that is known to have elevated concentrations of PFOS in biota. California has not established fish consumption guidelines for PFOS; however, the Minnesota Department of Public Health has established a fish consumption guideline of no restrictions (i.e., more than one meal per week) for consumption of fish containing less than 40 ppb PFOS (MDH 2008).

In contrast to the low concentrations observed in bivalves and fish, concentrations of PFOS in bird eggs and harbor seal blood are quite high relative to other monitoring sites around the world. The RMP has



Average PFOS concentrations in cormorant eggs from the South Bay in 2006. (from the Pulse, 2013, SFEI)

monitored PFOS in bird eggs triennially since 2006. Concentrations of PFOS in South Bay bird eggs suggest a possible decline, from means of approximately 1,200 ppb (2006/2009) to 390 ppb (2012). Although bird egg concentrations declined below a PNEC of 1,000 ppb (Newsted et al. 2005), they remain at levels that have been linked to impaired hatchling success in tree swallows in Minnesota (Custer et al. 2012). Currently unknown attributes of bird biology, including temporal variations in foraging behavior, may be a factor in the apparent decline. A second factor may be the shorter half-lives of PFAS in birds versus marine mammals (on the order of weeks rather than years) (Sedlak and Greig 2012).

Similarly, the most recent seal monitoring suggests a possible decline of PFOS in seal blood from means of approximately 700 ppb (2011) to 180 ppb (2014) (Sedlak et al. submitted). Similar to birds, the highest concentrations were observed in the South Bay ~1,000 ng/mL, followed by Central Bay, 80 ng/mL. Background concentrations observed in seals from Tomales Bay in the Point Reyes National Seashore were 12 ng/mL. There are few studies of the toxicological effects of perfluorinated compounds on marine mammals; however, PFOS studies in other mammals suggest that these concentrations may be of concern (e.g., Kannan et al. 2006).

The lack of a decline in the longer-chained PFAS (C9 and above) and the increased frequency of detection of these compounds in harbor seals and bird eggs suggest that it will be useful to monitor these compounds over time as replacements for PFOS and PFOA are used. These analytes are typically included at no additional cost in analyses from commercial laboratories.

It is also important to note that there has been significant regulatory action at both the State and Federal levels on PFOS. For example, the California Office of Environmental Health Hazard Assessment is currently

Harbor seals swimming in Mission Bay. (Courtesy of Britta Helse, November, 2009, CC)

responding to public comments on its intent to list PFOS and the structurally similar perfluorooctanoic acid (PFOA) as Proposition 65 reproductive and developmental toxicants. At the federal level, USEPA issued in May 2016 a health advisory for PFOS and PFOA in drinking water.

USEPA requires water quality monitoring of drinking water supplies serving over 10,000 people for unregulated contaminants every five years. USEPA included the following PFAS in the most recent national monitoring of drinking water supplies (2012-2016 survey): PFOS, PFOA, perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), and perfluorononanoic acid (PFNA). Of the nine counties surrounding the Bay, only Alameda County had detections of any PFAS, specifically low levels of PFHxS in two samples from the City of Pleasanton. Much of the Bay Area drinking water is derived from remote reservoirs in the Sierra Nevada and is unlikely to have significant PFAS concentrations.

While Bay Area drinking water does not appear to be contaminated, PFOS was detected in Bay Area wastewater via an RMP study in collaboration with California's Department of Toxic Substances Control (Houtz et al. 2016). Higher levels were observed at two facilities, SFO Airport and Fairfield-Suisun, impacted by industrial firefighting agents that contain these chemicals. PFOS has also been detected in stormwater; a recent study by UC Berkeley researchers of 10 Bay Area watersheds indicated that concentrations in stormwater ranged from 2.6 to 26 ng/L (Houtz and Sedlak 2012).

Recent RMP monitoring suggests PFOS levels may be declining in birds and harbor seals. However, concentrations are above a threshold of concern identified for birds, suggesting the potential for low level effects in wildlife. For this reason, PFOS is listed as a Moderate Concern (Tier III ↓) CEC for the Bay.

Cormorants, pelicans, and gulls near Tiburon, with ferry. (Courtesy of Ingrid Taylar, September, 2007, CC)

PFOS STUDY RECOMMENDATIONS

We recommend that the following matrices continue to be monitored for PFOS, as well as a dozen other PFAS measured simultaneously by many analytical laboratories at no additional charge: bird eggs, sport fish, and harbor seals. Bird eggs and sport fish monitoring can be conducted via inclusion within RMP Status and Trends analyses. Harbor seal monitoring would require a special study.

Fipronil and Degradates

TIER III
MODERATE CONCERN

Fipronil is a phenylpyrazole pesticide that is widely used in urban environments to control ants, fleas, and ticks. As an alternative to pyrethroids, the use of fipronil has increased dramatically in the last decade (CDPR 2017). It is present in the environment as fipronil, as well as degradates, primarily fipronil sulfide, fipronil sulfone, and desulfinyl fipronil. Fipronil and its degradates have been detected in Bay watersheds in concentrations that exceed the USEPA aquatic life benchmark for chronic toxicity to freshwater invertebrates (Ensminger et al. 2013; USEPA 2013).

The RMP has routinely monitored fipronil and its degradates in Bay sediment since 2009. Concentrations of fipronil and its degradates ranged as high as 0.56 ng/g dw (estimated) for fipronil sulfone in a Lower South Bay sample in 2010; with approximately 1% organic carbon (OC) in that sample, the reported maximum organic carbon normalized fipronil sulfone concentration would be 56 ng/g OC, above the EC_{50} (immobilization) for the freshwater species *Chironomus tentans,* which is 40 ng/g OC (Maul et al. 2008). An earlier laboratory study found reduced reproduction in a saltwater benthic crustacean with addition of fipronil at a concentration of 65 ng/g dry weight in salt marsh sediment (Chandler et al. 2004). The 2014 sediment monitoring data featured detections of this degradate at levels comparable to these toxicity thresholds.

As part of a 2016 special study, the RMP monitored influent and effluent from eight Bay municipal wastewater treatment plants for fipronil and its degradates (Sadaria et al. 2016). The study revealed the ubiquity and persistence of fipronil and degradates during conventional wastewater treatment, with no obvious differences observed among secondary versus advanced facilities. Scientists from the

A dog shakes off while still in the water. Domestic pets are often treated with flea control applications containing Fipronil**.** (Courtesy of ClaraS, December, 2009, CC)

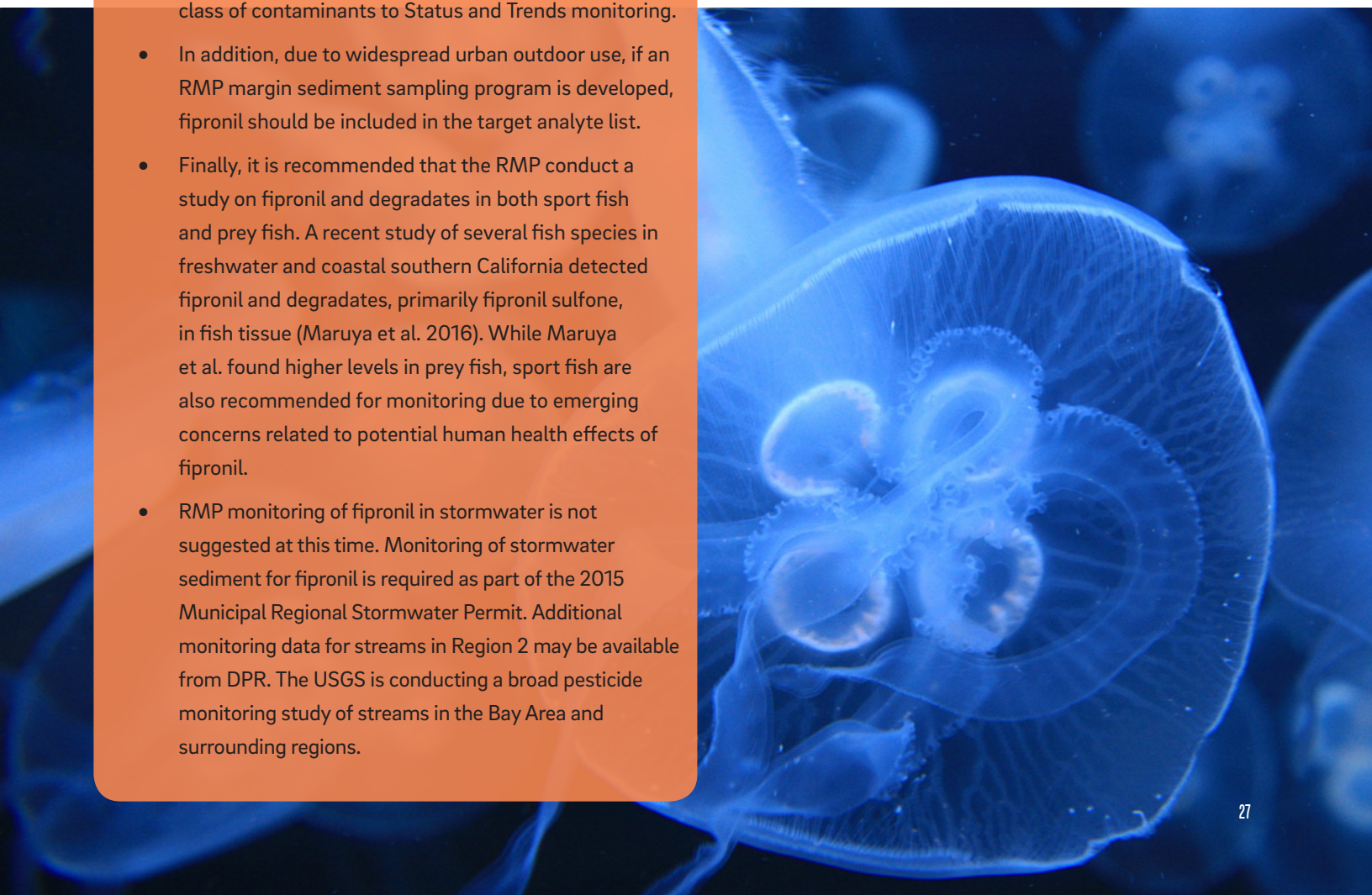
RMP study team, which included the California Department of Pesticide Regulation (DPR), assessed the concentrations and concluded that a primary source of contamination is likely to be pet flea control products. Fipronil is undergoing reviews by DPR and USEPA aimed at reducing environmental contamination and the ecological impacts of the pesticide; the RMP study will provide scientific data to inform these review processes.

Fipronil and its degradates were not detected in ambient Bay water collected in 2013; however, the analytical technique employed for this particular study typically requires sample filtration, which would have eliminated particle-bound contaminants. The 2016 study of wastewater found that particle-bound fipronil and degradates were an important component of influent but not effluent.

Based on the increasing use of fipronil, and the detection of fipronil and degradates in Bay sediment at levels at levels of potential concern, we classify this contaminant as a Moderate Concern (Tier III ↑) for the Bay. Should DPR and/or USEPA take actions likely to lead to reductions in use or environmental contamination, the temporal trend classification may be reversed.

FIPRONIL and DEGRADATES STUDY RECOMMENDATIONS

- It is recommended that the RMP continue to monitor Bay sediment for fipronil and degradates by adding this class of contaminants to Status and Trends monitoring.
- In addition, due to widespread urban outdoor use, if an RMP margin sediment sampling program is developed, fipronil should be included in the target analyte list.
- Finally, it is recommended that the RMP conduct a study on fipronil and degradates in both sport fish and prey fish. A recent study of several fish species in freshwater and coastal southern California detected fipronil and degradates, primarily fipronil sulfone, in fish tissue (Maruya et al. 2016). While Maruya et al. found higher levels in prey fish, sport fish are also recommended for monitoring due to emerging concerns related to potential human health effects of fipronil.
- RMP monitoring of fipronil in stormwater is not suggested at this time. Monitoring of stormwater sediment for fipronil is required as part of the 2015 Municipal Regional Stormwater Permit. Additional monitoring data for streams in Region 2 may be available from DPR. The USGS is conducting a broad pesticide monitoring study of streams in the Bay Area and surrounding regions.



Moon jellyfish at the Aquarium of the Bay, San Francisco. (Courtesy of Cliff, May, 2012, CC)

Nonylphenols (NPs) and Nonylphenol Ethoxylates (NPEs)

TIER III
MODERATE CONCERN

NPs are a class of compounds consisting of nine-carbon chains, variously branched, and attached to a benzene ring opposite a hydroxyl functional group. NPs are a breakdown product of NPEs, industrial surfactants once commonly found in laundry detergents. Current industrial uses of NPEs are unknown and potentially broad (Maruya and Sutton 2017); federal efforts are underway to reduce use of this class of chemicals.

NPs and mono- and diethoxylates NP1EO and NP2EO have been detected in Bay sample collected in 2010 and prior years; no recent monitoring has occurred. Many other NPEs have been registered for use in the US but have not been the subject of targeted analyses by the RMP. In surface waters, 4-NP concentrations were less than 100 ng/L, and NP1EO and NP2EO have not been detected. Most NP effects are associated with water concentrations ranging from 1 to 1000 µg/L, according to a recent OEHHA review (2009). However, there are some reports of effects at environmental concentrations below 1 µg/L (e.g., Billinghurst et al. 1998). Most studies on aquatic impacts are derived from freshwater species; more information on toxicity to estuarine and marine species is needed.

In sediment, 4-NP, NP1EO, and NP2EO were all consistently detected at moderately high concentrations, including a median of 35 ng/g dry weight for 4-NP. Of note, an integrated World Health Organization risk assessment for NPs includes a freshwater sediment PNEC of 39 ng/g dry weight (WHO 2004).

In transplanted mussels, detection of these contaminants was sporadic, but the maximum concentrations of 4-NP, NP1EO, and NP2EO – 1,290, 300, and 1,420 ng/g dry weight, respectively – were high relative to

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A Brown Pelican feeding on a herring, Mission Bay. (Need to obtain permission, Phil McGrew on Flickr, 2013)

other contaminants detected in these bivalves. Maximum concentrations of 4-NP, NP1EO, and NP2EO in resident Bay mussel samples collected in 2010 as part of the statewide Mussel Watch study were lower – 223, 300, and 67 ng/g dry weight, respectively – but still high relative to other contaminants found in Bay mussels. A temporal trend study of archived Mussel Watch resident mussels collected from San Francisco Bay and two other California locations from 1995 to 2009 suggests a declining trend in levels of 4-NP and NP1EO, with Bay levels of both contaminants at 500 ng/g dry weight or less for the sample collected in 2009 (Maruya et al. 2015).

In small fish and cormorant eggs, maximum concentrations of NPs and NPEs, 420 and 228 ng/g wet weight, respectively, were also relatively high compared to other contaminants that accumulate in these species. Concentrations of NPs in small fish were comparable to those in small fish from other California estuaries (Diehl et al. 2012). Concentrations of NPs and NPEs detected in Bay samples were generally an order of magnitude or more below concentrations expected to elicit toxic effects in aquatic organisms (Klosterhaus et al. 2012). An exception is a study suggesting the potential for impacts on barnacle settlement due to exposure to NP concentrations of 60 ng/L in water (Billinghurst et al. 1998).

NPs and some NPEs are estrogenic. Studies suggest that effects from estrogenic compounds may be additive or synergistic; thus organisms living near wastewater discharges may be the most susceptible, particularly since they can be continuously exposed to many estrogenic substances in wastewater effluent. A particular cause for concern for NPs and NPEs is the potential for synergistic effects in combination with other pollutants. Schlenk et al. (2012) found that mixtures of pesticides with environmentally relevant concentrations of NPs, NPEs, and related octylphenols and octylphenol ethoxylates resulted in significantly greater production of vitellogenin, an egg yolk precursor protein, in adult male Japanese medaka *(Oryzias latipes)* in *in vivo* exposures. The authors suggested that this type of combined estrogenic potency may have a role in the decline of key fish populations in the Bay-Delta (known as the "pelagic organism decline").

NPs and NPEs STUDY RECOMMENDATIONS

- Only a few members of this chemical class have been examined in Bay matrices. Preliminary results of a non-targeted analysis of ambient Bay water samples indicate many other members are present (L. Ferguson, personal communication). A special study of margin sediment is recommended to measure a broader array of analytes in this depositional environment, to determine which members of the class should be prioritized for further study.
- A special study to evaluate temporal trends in NPs and NPEs in archived tissue and/or sediment samples is suggested as a means of establishing whether levels are declining over time.
- Should declines be evident, a synthesis of findings may indicate the need to reclassify this contaminant in the tiered risk framework.which may provide data useful to the RMP.

To address the concern of additive or synergistic estrogenicity, the RMP has funded a project for 2017 to screen the overall estrogenicity of Bay waters using the bioanalytical screening tool currently in development (Section 5.2). This tool has already been used to evaluate a treated wastewater effluent from a secondary treatment facility in the Bay Area, and revealed no significant estrogenic signal. Use of the bioanalytical tool may be incorporated into Status and Trends monitoring as a regular means of evaluating estrogenicity.

This contaminant class is considered a Moderate Concern (Tier III) for the Bay due to its presence in the Bay at levels of concern for particularly sensitive species, and the potential for additive or synergistic estrogenicity or toxicity in combination with other contaminants. However, NPs and NPEs have not been evaluated in Bay matrices in some time. Active federal efforts to encourage use of NPE alternatives in laundry detergent suggest levels may have declined in receiving waters throughout the US. Consistent with this expectation, a temporal trend analysis of NP and 4-NP1EO in resident Bay bivalves collected from 1995 to 2009 suggests levels have declined (Maruya et al. 2015).

3.3 Tier II (Low Concern) Monitoring Recommendations

Tier II CECs include: polybrominated diphenyl ethers (PBDEs), which had been previously classified as Tier III contaminants; a related family, the polybrominated dioxins and furans (PBDD/Fs); the alternative flame retardant hexabromocyclododecane (HBCD); pharmaceuticals and personal care product ingredients (PPCPs; compounds listed in Klosterhaus et al. 2013a); and pyrethroid pesticides. Existing data for these compounds suggest the limited possibility of low level effects on Bay wildlife (i.e., Bay concentrations are well below toxicity thresholds and potential toxicity to wildlife is sufficiently characterized).

For compounds of low concern, periodic special studies to monitor those Bay matrices most relevant to the CEC's chemistry and potential impacts are recommended. For PBDEs, which have been monitored via Status and Trends for a number of years and only now are found at low enough concentrations to merit a Low Concern (Tier II) designation, more limited Status and Trends analyses are suggested to continue for at least two more monitoring cycles for key matrices.

PBDEs

TIER II
LOW CONCERN

The identification of the Bay as a ***PBDE*** contamination "hot spot" led the RMP to initiate studies probing the occurrence and effects of these flame retardant chemicals in the ecosystem. PBDEs are flame retardants once common in foam furniture, electronics, and many other products. Two commercial mixtures, PentaBDE and OctaBDE, were banned in California in 2006. However, they are still found in many consumer goods made before the ban went into effect, and in the wastestream. The third and final commercial formulation, DecaBDE, was phased out of US production in 2013. DecaBDE may still be present in imported products and consumer goods made before the phaseout.

RMP data on PBDEs have been summarized in a recent synthesis (Sutton et al. 2014) and journal publication (Sutton et al. 2015a), and demonstrate that levels have declined substantially from the first identification of these chemicals in the Bay. Concentrations in Bay sport fish are considered safe for human consumption, based on comparison to thresholds developed by the California Office of Environmental Health Hazard Assessment (Klasing and Brodberg 2011). Shiner surfperch collected in 2014 had a median PBDE concentration of 4.4 ppb wet weight (range: 2.6 – 9.2 ppb ww); OEHHA suggests three servings of fish per week are safe when PBDE levels are below 100 ppb ww. A toxicity study sponsored by the RMP suggests

current PBDE levels are unlikely to pose reproductive risks to Bay birds (Rattner et al. 2011, 2013). PBDE levels in all Bay species undergoing routine monitoring have declined over the last ten years, likely a response to state and federal management actions to ban or phase-out their production and use (Sutton et al. 2015a). Blubber collected from seven Bay harbor seals captured as part of a 2014 RMP special study exhibited total PBDE concentrations ranging between 270 and 1100 ng/g lipid weight (Sutton et al. 2015b), generally lower than observed in the blubber of five deceased adult harbor seals collected from San Francisco Bay in 2007 and 2008 (range 530-5075, median 770 ng/g lipid; Klosterhaus et al. 2012), and significantly lower than observed in three deceased adult harbor seals collected from San Francisco Bay in 1997 and 1998 (1944, 2985, 8325 ng/g lipid; She et al. 2002).

Current levels of PBDEs in the Bay appear to be lower than available toxicity thresholds, suggesting these contaminants no longer pose low level risks to wildlife. In studies with fish, increased susceptibility to pathogenic microorganisms (Arkoosh et al. 2010) has been observed in subyearling Chinook salmon (Oncorhynchus tshawytscha) with PBDE concentrations comparable to those found in Bay fish collected prior to 2009. Subsequent declines suggest that Bay fish would not experience impaired immune function due to PBDE contamination, but no specific tissue-based ecotoxicity thresholds are available. A study of polychaete larval settlement and growth found BDE-47 exposure triggered effects in three species at a sediment concentration of 3.0 ng/g dry weight, and no effect at a concentration of 0.5 ng/g (Lam et al. 2010). Among Bay sediment samples collected in 2014, just one exceeded 0.5 ng/g BDE-47; prior Status and Trends monitoring revealed one ambient Bay sample and two Bay margin "hot spot" samples exceeded 3.0 ng/g BDE-47.

Abandoned couches and mattresses. (Courtesy of Kamal Hamid, 2007, CC)

There is little available information concerning potential adverse impacts of PBDEs on harbor seals. A previous study of California harbor seals found correlation between higher PBDE levels in blood samples and higher white blood cell counts, suggesting that high levels of contaminants might be linked to increased rates of infection (Neale et al. 2005). These harbor seals generally had higher levels of PBDE contamination than the Bay harbor seals captured in 2014 (Sutton et al. 2015b). A study of grey seals found blubber contamination correlated with thyroid hormone endocrine disruption at levels above 1,500 ng/g lw (Hall et al. 2003); the highest level of PBDE contamination observed in the 2014 Bay seals, 1,100 ng/g lw, is below this concentration. Study of another marine mammal population, killer whales in the Northeast Pacific, suggests via a food web bioaccumulation model that a total sediment PBDE concentration of 1.0 ng/g could be considered a protective benchmark, as the model predicts PBDE concentrations in resident killer whales below the toxicity reference value established by Hall et al. (2003) for the majority of the population (Alava et al. 2016). Bay sediment samples often exceed this conservative threshold. Based on the limited evidence available, it would appear that PBDE contamination may no longer be a significant threat for Bay harbor seals.

(Below) **Shiner surfperch.** (Courtesy of Pat Kight, CC)

The reduced potential for low level risks for Bay wildlife, along with the observation of decreasing levels in Bay matrices, led to the new classification of PBDEs as declining contaminants of Low Concern (Tier II ↓) for the Bay.

PBDEs STUDY RECOMMENDATIONS

- Status and Trends monitoring of sediment (currently conducted every four years; est. annual cost $27,000) is recommended for at least two more cycles, as an essential means of evaluating whether BDE-209, derived from the recently phased-out DecaBDE, declines as expected. The DecaBDE commercial mixture was phased out of US production in 2013; previous sediment monitoring does not yet indicate a decline.

- Continued monitoring of Bay sport fish (on a five-year cycle; est. annual cost $12,000 for shiner surfperch) and cormorant eggs (triennially; est. annual cost $2,000) is recommended to track recovery in the form of continuing declines in Bay biota. Birds appear to be especially sensitive to PBDE exposures, and there are limited data concerning adverse impacts outside of reproduction for Bay-relevant species. Continued sport fish monitoring is recommended to assure that public health is not impacted via fish consumption.

- Status and Trends monitoring of bivalves may be discontinued, given resource constraints (est. annual cost $8,000). The bioavailability of PBDE congeners has already been established and contamination trends can be tracked in higher trophic level organisms. Because water measurements have not provided valuable information beyond that provided by other indicators, monitoring of PBDEs in water has already been eliminated.

PBDD/Fs

TIER II ↓
LOW CONCERN

Polybrominated dioxins and furans (PBDD/Fs) are brominated versions of the more commonly known chlorinated dioxins and furans. They are formed as by-products of brominated organic chemicals such as PBDEs, or by combustion and environmental reactions of brominated chemicals and their degradation products. Some forms are naturally produced by algae.

PBDD/Fs are expected to accumulate in Bay sediment and biota, but have been found only at concentrations much lower than their chlorinated cousins. The most toxic forms were not detected or were found at very low concentrations in sediment and biota, much lower than those reported in the literature for areas with large expected sources. Some 1,3,7-tribromodibenzodioxin was found in the Bay, with highest concentrations in South Bay and southern Central Bay. This compound is believed to be a degradation product of PBDEs (Steen et al. 2009; Arnoldsson et al. 2012).

PBDD/Fs are significantly less toxic than polychlorinated dioxins and furans, and less persistent. With the phase-out of PBDE flame retardants, PBDD/Fs from synthetic products will decrease, though some biologically produced forms will likely continue to be present. For these reasons, PBDD/Fs have been classified as declining contaminants of Low Concern, (Tier II ↓); monitoring is not considered a priority for the Bay.

(Above) **Shore edge with algae at Coyote Hills.** (Photo by Shira Bezalel, SFEI)

(Below) **Bay mussels collected for analysis.** (Photo by Zephyr Sylvester, SFEI)

HBCD

TIER II ↓
LOW CONCERN

This brominated flame retardant has been a subject of two RMP special studies. ***HBCD*** was detected in Bay sediment from 2007 at total concentrations ranging from 0.1 to 2 ng/g dry weight (median 0.3 ng/g dry weight; Klosterhaus et al. 2012). In biota, cormorant eggs contained the highest concentrations of total HBCD (22–39 ng/g lipid weight), followed by shiner surfperch (3–25 ng/g lipid weight), harbor seal adults and pups (4–19 and 2–12 ng/g lipid weight, respectively), and white croaker (<6–5 ng/g lipid weight; Klosterhaus et al. 2012). Study of Bay sediment, deployed bivalves, and harbor seal blubber from 2014 revealed concentrations from below detection to 0.33 ng/g dry weight (median 0.12 ng/g dry), below detection to 1.8 ng/g dry weight (median 0.29 ng/g dry), and 4.4 to 27 ng/g lipid weight (median 6.1 ng/g lipid), respectively (Sutton et al. 2015b; Sutton et al. in prep). All measured concentrations were comparable to or lower than those measured in biota in other ecosystems (reviewed in Klosterhaus et al. 2012). Levels in wildlife were also significantly lower than toxicity thresholds reported in the literature (Kuiper et al. 2007; Marvin et al. 2011; Marteinson et al. 2012a).

HBCD is a high production volume chemical; however, reductions in use are expected as a result of its addition to the Stockholm Convention list of banned persistent organic pollutants, albeit with a five-year phase-out period for use in polystyrene building insulation. For these reasons, HBCD has been classified as a declining contaminant of Low Concern, (Tier II ↓); monitoring is not considered a priority for the Bay.

PPCPs

TIER II
LOW CONCERN

Pharmaceuticals and personal care product ingredients (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. Over 100 of these chemicals have been analyzed in Bay surface water, sediment, and mussel tissue (chemicals listed in Klosterhaus et al. 2013a). Concentrations of PPCPs in the Bay were typically one or more orders of magnitude lower than those reported for sites in freshwater systems, which have often been located near wastewater outfalls, and were in closer agreement to concentrations reported for other marine and estuarine environments, where wastewater discharges are also common but dilution occurs to a greater extent (Klosterhaus et al. 2013b). The concentrations of PPCPs detected in Bay samples were generally low and an order of magnitude or more below concentrations expected to elicit toxic effects in aquatic organisms. Exceptions include two antibiotics, sulfamethoxazole and erythromycin, both intermittently detected above an aquatic PNEC.

Sunscreen use. (Courtesy of Alex Livit, CC)

RMP collaborations have led to recent findings relating to triclosan, a PPCP of special interest. Hensley et al. (2015) reported triclosan levels in effluent from Palo Alto Regional Water Quality Control Plant that averaged 313 ± 72 ng/L in July 2011 and 58 ± 4 ng/L in January 2012 (n=4 each). Kerrigan et al. (2015) measured triclosan levels at 68 ± 26 ng/L in the Lower South Bay, and 17 ± 9 ng/L in the Sacramento River. Observed concentrations remain below available aquatic toxicity thresholds (e.g., a PNEC of 115 ng/L; EC 2012).

Kerrigan et al. (2015) also reported sediment levels up to 6 ng/g dw in sediment (n=10). Sediment cores revealed little triclosan present prior to mass production in the 1960s, and significant increases in recent decades, indicating persistence in this matrix. A collaboration with the National Institute of Standards and Technology to examine tissue samples for halogenated, hydrophobic compounds via non-targeted analysis (see Section 5.1) tentatively identified the triclosan metabolite methyl triclosan in transplanted bivalves (Sutton and Kucklick 2015). Methyl triclosan, an under-monitored biomarker for exposure to triclosan, has potential concerns relating to persistence, bioaccumulation, and toxicity (e.g., Bedoux et al. 2012).

The RMP will monitor small fish in San Francisco Bay for triclosan and methyl triclosan in 2017. Meanwhile, in 2016 the US Food and Drug Administration announced a ban on triclosan and 18 other antimicrobial compounds in over-the-counter hand soaps, to go into effect in 2017.

Continued review of the literature may highlight additional PPCPs that merit investigation. For example, a recent study found that exposure to environmentally relevant concentrations of the benzodiazepine anxiolytic drug, oxazepam, altered behavior and feeding rate of wild European perch *(Perca fluviatilis)* (Brodin et al. 2013). Metformin, a common treatment for type 2 diabetes, has been widely detected in aquatic ecosystems and was found to cause estrogenic effects and reduced fecundity in fish at low levels (Niemuth and Klaper 2015). A number of other PPCPs are identified as appropriate candidates for environmental monitoring based on estimated persistence and bioaccumulative potential (Howard and Muir 2010, 2011).

In general, few PPCP toxicity studies have evaluated effects due to long-term exposures to environmentally relevant concentrations, particularly via sediment. An improved understanding of the potential for impacts due to exposure to typical mixtures of contaminants is also needed to thoroughly assess the risk of PPCPs and other compounds to Bay wildlife. Surface water and sediment near wastewater outfalls in the Bay may exhibit higher concentrations and an increased likelihood of impacts.

While the RMP has not conducted a special study to monitor the Bay for PPCPs in a number of years, continuing work on this contaminant class is recommended for two reasons: the ever-growing Bay Area population is likely to discharge more and more of this contamination into the Bay, and the ever-expanding array of PPCP analytes that can be probed by academic or commercial laboratories allows for a more comprehensive evaluation of risks to the Bay. In 2016, the RMP took on a coordinating role with BACWA in a voluntary effort on the part of six local wastewater treatment facilities to test influent and effluent for pharmaceutical contaminants. Should the participating facilities approve RMP use of the resulting data, a report on measured levels relative to toxicity thresholds may help identify future targets for study. Meanwhile, wastewater agencies have played a major role in promoting pharmaceutical take-back programs, now active in counties around the Bay, as a means of preventing a portion of pharmaceutical pollution from going down the drain.

STUDY RECOMMENDATIONS

- Periodic monitoring in water and sediment is recommended to determine whether levels of any contaminants exceed toxicity thresholds, whether due to changes in consumer use, increases in population, or newly developed analytical methods.

Drug store vitamins and supplements. (Creative Commons)

Pyrethroids

TIER II
LOW CONCERN

Pyrethroids are neurotoxic insecticides currently applied in large amounts in California (CDPR 2017). They have the potential to impact the health of aquatic arthropods and fish, and are toxic at low levels. The RMP began monitoring Bay sediment samples for pyrethroid pesticides in 2008. The specific compounds studied include: allethrin, bifenthrin, cyfluthrin, lambda cyhalothrin, cypermethrin, deltamethrin, esfenvalerate/fenvalerate, fenpropathrin, cis-permethrin, trans-permethrin, phenothrin, prallethrin, resmethrin, tetramethrin, and tralomethrin. In Bay sediment, total pyrethroid concentrations have generally been below 10 ng/g dry weight, with only one sample from Suisun Bay showing a higher concentration (16 ng/g dry weight). Bifenthrin and permethrin were among the pyrethroids most commonly detected, found in around 30 to 40% of samples. The maximum sediment concentration measured for bifenthrin was 1 ng/g dry weight, five times lower than the lowest observed effect concentration (LOEC) of 5 ng/g dry weight (Amweg et al. 2005). The maximum sediment concentration measured for permethrin was 3 ng/g dry weight, 24 times lower than the LOEC of 73 ng/g dry weight (Amweg et al. 2005). The most highly toxic pyrethroids detected (bifenthrin, cyfluthrin, cyhalothrin, and cypermethrin) never exceeded 1.1 ng/g dry weight individually or a total of 1.6 ng/g dry weight. These concentrations are lower than the LOEC of 5 ng/g dry weight for bifenthrin, the only available sediment toxicity thresholds for a chemical in this group.

These compounds were measured in stormwater discharges beginning in 2008. This testing revealed a different story, with maximum measurements of bifenthrin (46 ng/L) and permethrin (285 ng/L) exceeding the PNECs of 4 ng/L and 10 ng/L, respectively. Pyrethroids remain a high concern for tributaries in the surrounding watersheds, where monitoring is ongoing. Regulatory restrictions implemented by the California Department of Pesticide Regulation in 2012 are expected to result in lower levels of contamination.

Pyrethroids have been classified as declining contaminants of Low Concern (Tier II↓) for the Bay (though they remain a significant concern in Bay Area urban creeks) because they are detected infrequently and at concentrations well below established LOECs, and because recent regulatory actions are expected to reduce environmental contamination.

Pesticide spraying. (Creative Commons)

PYRETHROID STUDY RECOMMENDATIONS

- Inclusion of pyrethroids in margin sediment monitoring efforts is recommended, given the levels of concern detected in stormwater.
- Further pyrethroid Status and Trends monitoring in surface waters and sediment is not recommended, as concentrations are not likely to be high.

3.4 Tier I (Possible Concern) Monitoring Recommendations

Possible Concern (Tier I) CECs are those for which there is considerable uncertainty as to their potential to impair beneficial uses of the Bay. Many lack sufficient toxicity information specific to aquatic species. For a few, analytical methods may be insufficient to detect concentrations relevant to toxicity thresholds. For Tier I CECs, the RMP typically conducts special studies to monitor relevant Bay matrices.

Alternative Flame Retardants

TIER I
POSSIBLE CONCERN

Flame retardant chemical additives are incorporated into a wide range of consumer goods to meet regulatory or voluntary flammability standards. Following state bans and nationwide phase-outs of PBDEs, one of the most commonly used flame retardants historically, alternative chemicals saw greater use. For the diverse array of bromine-, chlorine-, and phosphate-containing compounds that have replaced PBDEs, considerable data gaps concerning production and use, environmental occurrence, and toxicity remain. Some of these chemicals have been in use for decades, while others are relatively new. One of these compounds, hexabromocyclododecane (HBCD), has been classified as a Low Concern (Tier II↓) contaminant and was discussed earlier.

Several non-PBDE flame retardants have been detected in Bay samples analyzed as part of two RMP Special Studies (Klosterhaus et al. 2012; Sutton et al. in prep), but with the exception of some phosphate compounds in water, sediment, and tissue samples, they have been detected at concentrations at least one order of magnitude lower than PBDEs.

Brominated flame retardants detected in Bay sediment and/or wildlife include 2,4,6-tribromophenyl allyl ether (TBP-AE), bis(2,4,6 tribromophenoxy) ethane (BTBPE), BEH-TBP and EH-TBB (or TBPH and TBB, the brominated components of the PentaBDE replacement commercial mixture, Firemaster 550), hexabromobenzene (HBBZ), pentabromobenzyl acrylate (PBBA), pentabromobenzyl bromide (isomer 2)/polybrominated biphenyl 101 (coeluants; PBBB-2/BB-101), 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (DBE-DBCH, also known as TBECH), and tetrabromo-o-chlorotoluene (TBCT). Brominated flame retardants that were analyzed but not detected in Bay samples include decabromodiphenylethane (DBDPE, a Deca-BDE replacement), N,N'-ethylenebis(tetrabromophthalimide) (EBTEBPI), hexachlorocyclo-pentadiene (HCCPD), hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO), pentabromobenzene (PBBZ), pentabromoethylbenzene (PBEB), and 2,3,5,6-tetrabromo-p-xylene (TBPX).

Chlorinated flame retardants detected at low levels in Bay sediment and/or wildlife include Dechlorane Plus (DP) and a handful of related compounds including mono-dechlorinated Dechlorane Plus, Dechlorane 601, 602, 603, 604, and 604CB. Many other dechlorane-related compounds were not detected.

Phosphate flame retardants detected in water and/or sediment include triethyl phosphate (TEP), tris (2-chloroethyl) phosphate (TCEP), tris (1-chloro-2-propyl) phosphate (TCPP), tris (1,3-dichloro-2-propyl) phosphate (TDCPP, also known as chlorinated tris), triphenyl phosphate (TPhP), tri-n-butyl phosphate (TnBP), tri-iso-butyl phosphate (TiBP), tricresyl phosphate (TCrP), tris (2-butoxyethyl) phosphate (TBEP), tris (2-ethylhexyl) phosphate (TEHP), 2-ethylhexyl diphenyl phosphate (EHDPP), tris (2,3-dibromopropyl) phosphate (TDBPP), tris (3,5-dimethylphenyl) phosphate (T35DMPP), and tris (2-isopropylphenyl) phosphate (T2iPPP).

TDCPP, TCPP, and TPhP have been detected in Bay sediment at estimated concentrations that are comparable to the PBDE and PCB concentrations in the same samples. Phosphate flame retardants are water soluble, with TCPP typically found at the highest concentrations. Concentrations of TPhP in some southern Bay samples approached a marine PNEC of 370 ng/L (ECHA 2014). The RMP has funded a Special Study for 2017 to examine phosphate flame retardants in ambient Bay water, in part to more comprehensively evaluate levels of TPhP in water and determine whether they are of potential concern.

Bivalve and harbor seal blubber samples analyzed contained fewer phosphate flame retardants, and were typically dominated by TCPP, TDCPP, TCEP and TPhP. It is hypothesized that phosphate flame retardants may be taken up by organisms and then metabolized; however, testing for a handful of known metabolites revealed no detections.

For most of these flame retardant contaminants, the risks are unknown due to a lack of information on toxicity. While some aquatic toxicity thresholds exist, few sediment thresholds have been established, and there is particularly little information on risks posed to marine mammals. Many of these flame retardant chemicals have been found to have endocrine disrupting properties in laboratory tests, but potential risks to Bay wildlife are not well understood. The effects of long-term exposure to low levels of these contaminants, particularly in mixtures, are largely unknown.

In general, a lack of information on toxicity has resulted in the designation of alternative flame retardants as Possible Concern (Tier I) contaminants for the Bay. At present, a lack of information concerning temporal contamination trends prevents additional designation of this class of compounds as likely to be increasing or decreasing in San Francisco Bay. As noted previously, increased use of some of these compounds followed bans and phase-outs of PBDEs. However, recent changes to California's flammability standards have reduced the use of flame retardants in some consumer goods, which may result in lower levels of contamination in the Bay. For the phosphate-based class, additional use as chemical components of plastic means there is an additional source of this contaminant that is unlikely to be affected by changes in flammability standards.

(Below) **Edge of the SF Bay.** (Photo by Shira Bezalel, SFEI)

ALTERNATIVE FLAME RETARDANTS STUDY RECOMMENDATIONS

- Periodic study of a subset of these alternative flame retardants may be useful to identify the presence of a temporal trend in contaminant levels. In particular, TPhP and other phosphate flame retardants in ambient Bay water are suggested as targets of periodic monitoring.

Bisphenol A (BPA)

TIER I
POSSIBLE CONCERN

Bisphenol A is used in plastics, epoxy resins, thermal paper, and in the linings of food cans. BPA is a known endocrine disruptor and is banned in some products, such as infant food packaging. Some companies have chosen to phase out its use voluntarily, with many products now marked BPA-free. Bay studies on BPA to date have been limited and have had high detection limits. BPA is one of the chemicals that was assessed as part of the RMP-funded effort to develop a bioanalytical tool to identify estrogenic activity (Section 5.2). The RMP has funded a Special Study for 2017 to analyze ambient Bay water samples for bisphenol A and a number of other bisphenols using a method with a detection limit below existing toxicity thresholds.

BISPHENOL A STUDY RECOMMENDATIONS

- Following monitoring of ambient Bay water for bisphenols, it is suggested that sediment levels be examined, as many of these contaminants are known to partition into sediment.

Food cans awaiting recycling. (Courtesy of Kamal Hamid, 2007, CC)

Bis(2-Ethylhexyl) Phthalate (BEHP or DEHP) and Butylbenzyl Phthalate (BBZP)

TIER I
POSSIBLE CONCERN

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. Many phthalates are known to be endocrine disruptors and may cause other health effects; several are included on California's Proposition 65 list of chemicals known to cause cancer or reproductive or developmental harm.

Phthalates have been detected in water, sediment, mussels, and cormorant eggs. Bis(2-ethylhexyl) phthalate and butylbenzyl phthalate were detected above sediment low apparent effects threshold (LAET) and high apparent effects threshold (HAET) values (PTI Environmental Services 1988; Vidal and Bay 2005); however, there is uncertainty regarding the application of these thresholds to Bay sediment because they do not have a strong causal linkage to specific chemicals, and in some cases are not directly linked to effects on macrobenthos. For this reason, they are considered Possible Concern (Tier I) contaminants in the Bay.

PHTHALATE STUDY RECOMMENDATIONS

- It is suggested that relevant Bay matrices such as sediment be examined for phthalates in the future, to assure that these widely used chemicals have not exceeded toxicity thresholds in the Bay. Previous monitoring for these CECs provided a significant amount of data, but samples were collected 15 or more years ago.

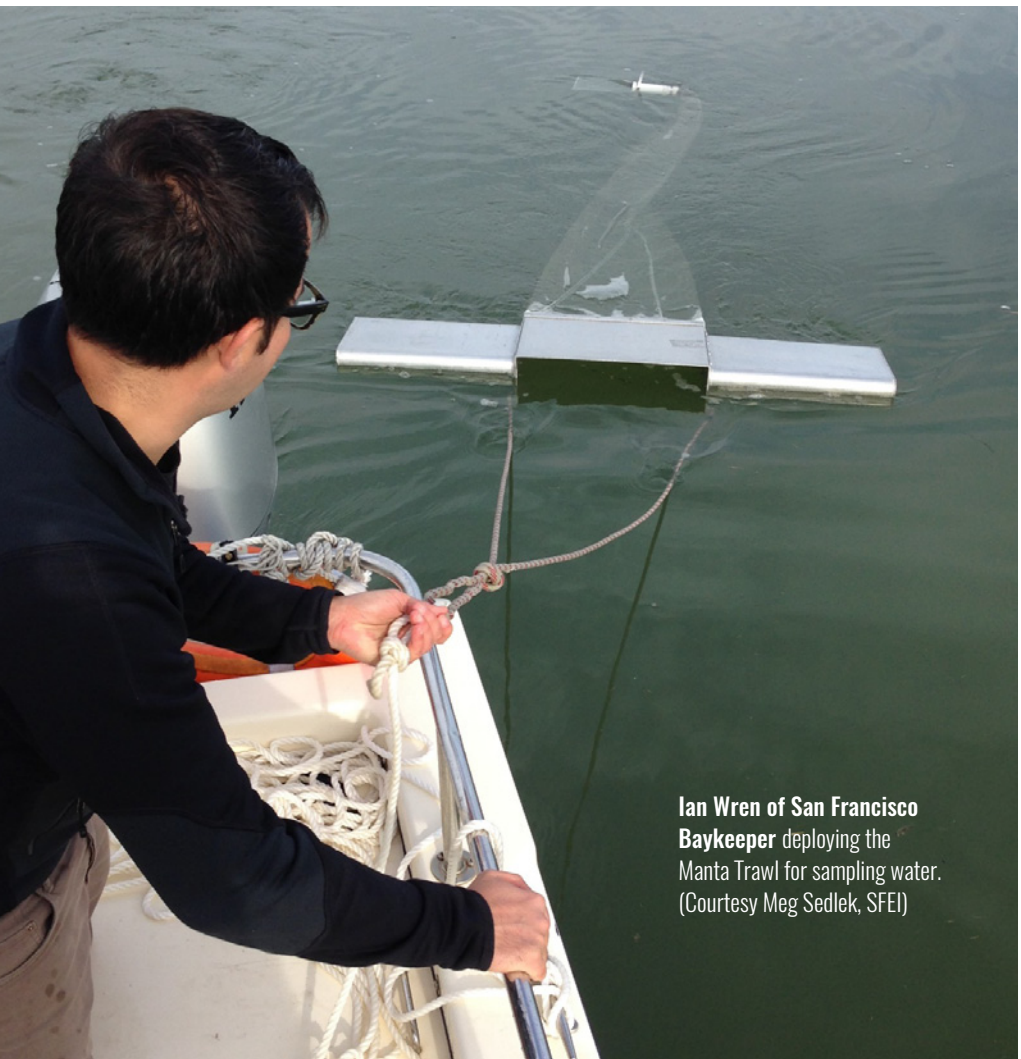
Microplastic

TIER I
POSSIBLE CONCERN

Accumulated debris at the edge of SF Bay. (Photo by Shira Bezalel, SFEI)

Motivated by recent state and federal efforts to ban microbeads in personal care products, the RMP funded a study to characterize Bay surface waters and wastewater treatment plant effluents for microplastic contaminants. Microplastic is a term used to describe plastic particles that are 5 mm or smaller. Nine Central and South Bay surface water samples were collected and samples of effluent were collected from eight facilities discharging to the Bay. Microplastics in samples were visually characterized by size, type (e.g., fiber, fragment, etc.), and abundance.

Microplastics were widely detected in the Central and South Bays, and found at levels higher than other water bodies near highly urbanized regions of the US (e.g., Eriksen et al. 2013; Yonkos et al. 2014). Bay WWTPs were found to discharge microparticles at levels higher than New York WWTPs (Mason et al. 2016). Because the visual identification of plastic particles was not confirmed using spectroscopic techniques, not all particles detected are known to be plastic. The existing monitoring data do not suggest a difference in the concentration of microplastics in effluent for WWTPs employing secondary vs. advanced secondary treatment. Fragments and fibers were seen in the greatest abundance in both Bay surface water and effluent. Microbeads in personal care products, a recent policy focus, consist primarily of small plastic fragments, and to a lesser extent the more iconic, colorful, bead-like small pellets; the RMP findings indicate microbeads can be found in the Bay, and are likely discharged via treated wastewater.



Ian Wren of San Francisco Baykeeper deploying the Manta Trawl for sampling water. (Courtesy Meg Sedlek, SFEI)

Microplastic contamination of aquatic ecosystems is associated with a number of potential concerns. Wildlife can consume microplastics; ingestion can lead to physical harm, exposure to contaminants in the plastic, and bioaccumulation of contaminants in higher trophic organisms (Fendall and Sewell 2009; Desforges et al. 2015; Seltenrich 2015). However, no clear toxicity thresholds exist for this contaminant, leading to its assignment as a Possible Concern (Tier I) contaminant for San Francisco Bay.

The RMP has created a separate Microplastics Workgroup that has developed a strategy specific to this contaminant (Sutton and Sedlak 2017) and will oversee future studies.

Newly Identified Tissue Contaminants

TIER I
POSSIBLE CONCERN

San Francisco Bay wildlife were tested for previously unmonitored contaminants using a non-targeted analysis that screens mainly for long-lived, fat-soluble, chlorine and bromine-rich chemicals (Section 5.1). The non-targeted analysis of tissue samples revealed that most of the Bay chemical contamination was from high priority contaminants that the RMP already monitors, such as PCBs, or closely related compounds. However, Bay mussels and harbor seals contained five contaminants not previously identified in Bay wildlife, and for which toxicity is largely unknown: 2,2′-dichlorobenzil, 9,10- dichloroanthracene and a similar, unspecified dichloroanthracene, 4-tert-butylamphetamine, methyl triclosan (Sutton and Kucklick 2015).

The chemicals identified in this study have been the subject of little or no targeted tissue monitoring elsewhere in the world, and have not been identified in non-targeted studies of wildlife in other areas, with the exception of dichloroanthracenes observed in freshwater species exposed to combustion byproducts (Myers et al. 2014). Relevant toxicity thresholds have not been established for these contaminants, so they have been designated a Possible Concern (Tier I) contaminant for San Francisco Bay.

Current Use Pesticides

TIER I
POSSIBLE CONCERN

Current use pesticides include 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 use, gaps in pesticide review procedures have resulted in pesticide water pollution. Many currently used pesticides have been detected in aquatic environments; however, lack of analytical methods for others, including relevant transformation products, limits environmental detections. In addition, the lack of availability of aquatic toxicity data for many pesticides and transformation products limits a full understanding of the potential risks to the Bay.

To prioritize pesticides for further study, DPR has developed a Surface Water Protection Program (SWPP) Monitoring Prioritization Model (cdpr.ca.gov/docs/emon/surfwtr/sw_models.htm) that uses pesticide application data from its Pesticides Use Reporting (PUR) database and pesticide chemical toxicity benchmarks to run a watershed-based pesticide prioritization algorithm. Because the PUR database does not include information on use of pesticides marketed to consumers, DPR also conducts marketplace surveys of these products to assess relative availability of different active ingredients. A synthesis of these exercises specific to the South and Lower South Bay region suggests the need to monitor a number of current use pesticides in margin sediment, including fipronil, pyrethroids, pyriproxyfen (a hormone mimic), etofenprox (a pyrethroid ether), and oxyfluorfen and pendimethalin, both herbicides. A longer list of pesticides was identified as priorities for water monitoring.

Imidacloprid is an insecticide toxic to aquatic invertebrates at low levels, and for which no ambient Bay detection information exists. As noted previously, the RMP monitored the influent and effluent from eight Bay municipal wastewater treatment plants for imidacloprid in 2016. The study revealed the ubiquity and persistence of this contaminant despite treatment. Scientists from the RMP study team, which included DPR, assessed the per capita influent concentrations and concluded that the primary source of contamination is likely pet flea control products. The RMP will conduct a study on imidacloprid, its degradates, and other pesticides in the neonicotinoid class in ambient Bay water in 2017. This study is designed to provide data needed to classify imidacloprid in the tiered risk framework.

Quaternary ammonium compounds (QACs), a class that includes a number of antimicrobial pesticides, are cationic surfactants for which no Bay data are yet available. QACs have been found at high concentrations in sediments of river or estuarine environments receiving WWTP effluents (Kreuzinger et al. 2007; Lara-Martín et al., 2010; Li and Brownawell, 2010). In the NY/NJ Harbor complex, QACs are found in sediments at higher levels than other classes of organic contaminants that have been monitored (Li and Brownawell, 2010; Lara-Martín et al., 2010). While studies indicate some QACs are toxic to aquatic life when dissolved at low levels in water (e.g., Beck et al. 2000; Peréz et al. 2008; Rico et al. 2013), their toxicity when associated with sediment is unknown, and may be reduced due to reduced bioavailability. The ECWG has previously expressed interest in a special study targeting this class of compounds in sediment.

Much of the pesticide-related work of the RMP focuses on urban use pesticides. However, the region also supports agricultural lands, particularly in the North Bay. Agricultural pesticides may be prioritized for study using the DPR Monitoring Prioritization Model.

PESTICIDE STUDY RECOMMENDATIONS

- A screen of current use pesticides is recommended for South and Lower South Bay margin sediment and water, guided by DPR prioritization exercises. The Bay margins are more likely to be depositional sediment environments reflecting recent and current pesticide uses, while ambient Bay sediment is less likely to be depositional. Future studies of different Bay regions and matrices should be informed by DPR expertise.
- QACs are recommended as target analytes in sediment.
- A study focusing on agricultural pesticides is recommended for portions of the Bay influenced by local agriculture, such as the area in and around the Napa River. The DPR Monitoring Prioritization Model would inform selection of pesticide targets. The potential contribution of pesticides applied in the Central Valley and reaching the Bay via the Delta must be considered when selecting targets and designing the study; there is likely to be some overlap in pesticides prioritized for monitoring in North Bay and Central Valley watersheds, with notable differences reflecting differences in crops and other factors specific to each location.

Avocets feeding in the tidal flats at low tide, Palo Alto Baylands. (Courtesy of Jitze Couperus, March, 2017, CC)

Other PFAS

TIER I
POSSIBLE CONCERN

In addition to PFOS, the RMP routinely monitors 12 other PFAS, a small fraction of the 3,000 plus that are currently in use. PFOA, a full fluorinated eight-chain-carbon molecule (referred to as a C8 compound), is frequently detected in environmental samples; however, it is less bioaccumulative than PFOS. Historically, PFOA was widely used in such diverse applications as the manufacture of fluoropolymers (e.g., Teflon), stain/water repellant coatings for textiles and food packaging, and fire-fighting foams.

An independent human health science panel found that there was a probable link between PFOA exposure and high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer, and pregnancy-induced hypertension (C8 Panel; see C8panel.org). As mentioned previously, the Office of Environmental Health Hazard Assessment is currently in the process of listing PFOA and PFOS as Proposition 65 reproductive and developmental toxicants. In addition, a health advisory for PFOS and PFOA in drinking water has now been established. In the most recent drinking water survey by USEPA, 14 water systems that serve over 1.4 million people in California had PFOA concentrations ranging from 0.0041 to 0.035 ppb. This is below the threshold for PFOA of 0.07 ppb; however, the threshold is applicable to a combined threshold of PFOS and PFOA, so it is possible that there are exceedances. At present, human exposure from Bay contamination is not a significant concern.

As noted above, PFOA is thought to have a low bioaccumulation potential in fish and wildlife (Martin et al. 2003, 2004). In Bay biota, PFOA concentrations are generally an order of magnitude lower than PFOS concentration (Sedlak and Greig 2012; Sedlak et al. submitted). However, in some animals, concentrations of PFOA, unlike PFOS, are not showing significant declines (Sedlak et al. submitted). In addition, the other longer chained compounds such as PFNA (C9), PFDA (C10), PFUnDA (C11) and PFDoDA (C12) are also not showing appreciable declines. In the most recent sport fish sampling (2014), several longer-chained PFASs such as PFDA, PFUnDA and PFDoDA were detected for the first time. The continued present of these longer chained compounds suggests on-going sources.

Eight major manufacturers of PFOA agreed to phase out production of PFOA by 2015, typically replacing it with shorter chained compounds such as C6 and C4 that are thought to be less bioaccumulative and toxic. A 2014 study of wastewater effluent from Bay Area treatment plants indicated a significant increase in the shorter chained PFAS (C4, C5, and C6) in comparison to a RMP effluent study in 2009 (Houtz et al. 2016). These shorter chained compounds are detected infrequently in Bay biota and sediment (Sedlak and Grieg 2012; Sedlak et al. submitted). Perfluoroalkyl ether carboxylic acids have also been identified as PFOA alternatives.

PFAS precursor compounds such as the polyfluoroalkyl phosphate esters (PAPs), fluorotelomer acrylate polymers, and fluorotelomer sulfonate-based substances can degrade to PFAS including PFOA. One of the more well-known compounds, GenX, perfluoro-2-propoxypropanoic acid (PFPrOPrA), a PFOA replacement, was recently detected in a North Carolina watershed downstream of a PFAS manufacturer at very high concentrations (upwards of 630 ng/L; Sun et al. 2016).

In addition, precursors such as perfluorooctane sulfonamide (FOSA), perfluorooctane sulfonamide acetate (FOSAA), N-ethyl perfluorooctane sulfonamidoacetate (N-EtFOSAA), N-methyl perfluorooctane

sulfonamidoacetate (N-MeFOSAA) and the perfluorooctane sulfonamide ethanol-based phosphate diesters (SAmPAP) can be transformed in the environment to PFOS (Higgins et al. 2005; Benskin et al. 2012). Shorter chained analogs of these precursors can be converted to their respective perfluorosulfonates. Similarly, the fluorotelomer alcohols, sulfonates, and polymers may be converted into PFOA and other PFAS (Houtz and Sedlak 2012).

Several researchers have monitored for PFAS and precursors in San Francisco Bay sediment, effluent, and stormwater. In a small, pro bono study evaluating effluent and sediment in San Francisco Bay, relatively high concentrations of the polyfluoroalkyl phosphate diesters (diPAPs) that can degrade to

PFAS STUDY RECOMMENDATIONS

- A number of novel PFAS have been identified in environmental matrices including: perfluoralkyl ether carboxylates and sulfonates; perfluorobutane sulfonamide (FBSA); chlorinated polyfluorinated ether sulfonates; and perfluoroethylcyclohexanesulfonate (PFECHS). One of the challenges of analyzing for these compounds will be finding analytical laboratories that are able to conduct the work. Following completion of the PFAS Synthesis and Strategy, potential follow-up studies might focus on one or more of the following novel PFAS.
    - Perfluoralkyl ether carboxylates (PFECA) and sulfonates (PFESA) are a high priority as they are believed to be replacements and have been identified in water (Strynar et al. 2015; Sun et al. 2016). For example, perfluoro-2-propoxypropanoic acid (PFPrOPrA, trade name GenX) is widely believed to be a replacement for PFOA (Sun et al. 2016). A number of these perfluoroalkyl ether carboxylic and sulfonic acids have been identified in surface waters in North Carolina (Strynar et al. 2015). Little is known about the toxicity or fate of these comounds.
    - Chlorinated polyfluorinated ether sulfonate (F-53B) has been used as a mist suppressant for metal plating in China for several decades (Wang et al. 2013). High concentrations of F-53B have been identified in water in China at concentrations comparable to PFOS (ng/L). There is some speculation that this type of compound will be used as a replacement for PFOS (Wang et al. 2013); again very little information is available on the toxicity and fate of this compound. Given the large number of metal-finishing operations in the Bay Area, it may be prudent to conduct monitoring of this compound in water.
    - PFECHS was originally identified as a chemical of concern by Howard and Muir (2010) based on high production volume and chemical properties. Used as an erosion inhibitor in aircraft hydraulic fluids, it has been detected in fish tissue from the Great Lakes and China (De Silva et al. 2011; Wang et al. 2016), albeit in concentrations slightly lower than PFOS. Given the high number of aviation facilities in the Bay Area (three international commercial airports, two federal facilities [Moffett and Travis] and eight general aviation towered airports), it is possible that PFECHS may be a significant food web contaminant. At present, very little is known about the toxicity of this contaminant, although it appears endocrine disruption can occur at concentrations that are higher than what is typically seen in the environment (Houde et al. 2016). A study evaluating prey fish is suggested.

perfluorocarboxylates were detected in three sediment samples, with concentrations between three and 24 times higher than the highest concentration of PFOS in sediment collected in the Bay (Sedlak et al. submitted). Much lower concentrations of diPAPs were observed in effluent. The sum of PFOS precursors detected at one sediment site were higher than the PFOS sediment concentrations. In a prior study of San Francisco Bay sediment, researchers at Stanford University found similar results with concentrations of the PFOS precursors that were of the same magnitude as PFOS (Higgins et al 2005). These findings suggest that the precursors may be a significant source of PFOS and PFOA to the Bay.

Many PFAS in Bay Area stormwater, effluent, and Bay sediment remain uncharacterized, (Houtz and Sedlak 2012, Higgins et al. 2005, Houtz et al. 2016) and may be composed of the precursors noted above and/or other diverse members of this large chemical family. In a study of Bay Area stormwater runoff, up to 60% of the total perfluorinated compounds were unidentified. Similar percentages of unidentifiable perfluorinated compounds were observed in effluent from eight Bay Area wastewater treatment facilities (Houtz et al. 2016).

Little information exists regarding the environmental toxicity of precursors and the shorter-chained PFAS. As a result, this class of chemicals is considered a Possible Concern (Tier I) contaminant for the Bay. At present, the RMP is preparing a PFAS synthesis document that will evaluate whether there is sufficient information to change the classification of any of these contaminants.

A school of anchovies at the Aquarium of the Bay, San Francisco. (Courtesy of Cliff, May, 2012, CC)

Newspaper ink. (Creative Commons)

PCB 11

TIER I
POSSIBLE CONCERN

PCB 11, also known as 3,3'-dichlorobiphenyl, is inadvertently manufactured in the production of pigments used for inks, dyes, paints, and textiles. PCB 11 is a previously overlooked PCB that can enter waterways via effluent from pigment manufacturing and also through consumer products like printed paper and cardboard. PCB concentrations in the low ppb range have been measured in printed newspaper, magazines, cardboard, plastic bags and cereal boxes (Rodenburg et al. 2010). PCB 11 can volatilize and partition into the air as well as leach out of consumer products and enter wastewater effluent and stormwater flows. In urban and densely populated areas, these consumer products can potentially represent a significant load to the environment. Recently, PCB 11 has been reported in various urban areas in the water column and air such as the Delaware River and Chicago ambient air.

The prevalence of PCB 11 in urban areas including the Bay was discovered through analysis of the full 209 PCB congeners in environmental samples. This was possible through analytical improvements that have made these measurements more routine and economical. PCB 11 has been measured in RMP water and sediment samples since 2009. PCB 11 is a major PCB component of Bay water (composing 3.7% of total PCBs, 6th most abundant PCB congener, with a median concentration of 11 pg/L, maximum 34 pg/L), urban runoff (2.8% of total PCBs, 8th most abundant PCB congener, median 129 pg/L, maximum 825 pg/L), and is also in the top 40 for Bay sediment (0.9% of PCBs, 31st most abundant congener, median concentration of 0.09 ug/kg dw, maximum 0.9 ug/kg dw). However, while PCB 11 was measured in small fish (median 0.022 ng/g ww, maximum 0.076 ng/g ww) and bivalves (median 0.28 ng/g dw, maximum 0.719 ng/g dw), it was not among the top 40 PCB congeners in these tissue samples. PCB 11 is also a dominant congener in municipal wastewater effluent. Based on the RMP data, it appears that PCB 11 enters the Bay in wastewater and urban runoff, but does not accumulate in the food web.

Not much is known about the toxicity of PCB 11, and currently, we have not found reported toxicity thresholds at environmentally relevant concentrations. Other PCBs are carcinogens, suspected neurotoxins, endocrine disruptors, and may affect development. PCB 11 has been shown to exhibit toxic effects similar to effects observed from other PCBs in *in vitro* studies in human and rat cells. Another *in vivo* study in rats showed PCB 11 was quickly absorbed through inhalation and eliminated from the liver in hydroxylated form (Rodenburg et al. 2015). There is growing concern that inhalation of airborne PCBs, like PCB 11, can be another exposure route, leading to more stable and toxic metabolites (Zhu et al. 2013). Additionally, more research on potential risk to invertebrates and lower trophic organisms is needed based on concentrations measured in the water column and sediment.

PCB 11 was not included in the RMP 40 list of congeners because it is not present in Aroclor mixtures, does not bioaccumulate in the food web, and does not exhibit dioxin-like toxicity because of its lower number of chlorines. From a management and risk perspective, PCB 11 should not be grouped with the Aroclor-derived PCBs because it derives from different sources and has no relationship with the PCBs that accumulate in fish and cause impairment of the Bay. The PCB TMDL was meant to address impairment through bioaccumulation in the food chain leading to health risk to humans, fish, birds, and seals. Therefore, although PCB 11 and other congeners with similar characteristics do contribute to total PCB

loads into the Bay, PCB 11 is grouped separately from the RMP 40 used to support the PCB TMDL, and instead classified as an emerging contaminant.

The lack of information on toxicity has resulted in the designation of PCB 11 as a Possible Concern (Tier 1) contaminant for the Bay.

PCB 11 STUDY RECOMMENDATIONS

- Currently, the full 209 congener PCB analysis is being conducted on sediment samples collected as part of the RMP Margins Special Study. Water and bivalve samples are analyzed every 10 and 2 years, respectively, for the full 209 PCBs as part of the RMP Status and Trends Monitoring. We recommend continuing this analysis because of the widespread prevalence of PCB 11 in the Bay, and additional research may provide more information on relevant toxicity thresholds. We recommend reviewing the PCB 11 data to understand distribution of concentrations in the Bay and potentially to identify hotspots.
- Since it is expected that PCB 11 is coming from urban sources, it may be advisable to screen a subset of wastewater and stormwater samples for PCB 11 (and preferably the full set of 209 PCB congeners) to understand the sources and pathways of this contaminant to the Bay.

Polyhalogenated Carbazoles

TIER I
POSSIBLE CONCERN

Polyhalogenated carbazoles (PHCZs) are a recently discovered class of environmental contaminants that have chemical properties similar to polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs), including the potential to be persistent, bioaccumulative, and toxic. Information concerning potential sources of PHCZs is lacking; studies indicate that PHCZs are derived from both natural (such as marine fungus) and anthropogenic sources. Halogenated indigo dyes and polymer production for electronics may be potential anthropogenic sources of PHCZs (Fang et al. 2016; Wu et al. 2017).

A recent study of San Francisco Bay identified PHCZs to be ubiquitous in sediment and wildlife. PHCZs were detected in all samples of sediment (range 1.7-20.5 ng/g dw, with a median 9.3 ng/g dw), transplanted bivalves (median 33.7 ng/g lw), sport fish (median 53 ng/g lw), cormorant eggs (median 155 ng/g lw), and harbor seal blubber (median 164 ng/g lw). The median sediment concentrations of PHCZs measured in the Bay (9.3 ng/g dw) was lower than reported surface sediment concentrations in the Saginaw River basin (Michigan, US, median 18.9 ng/g dw) and the Great Lakes (median 38 ng/g dw), but much higher than reported concentrations in the North Sea estuary (Germany, median 0.21 ng/g dw) and Lake Tai of China (median 1.5 ng/g dw) (Wu et al. 2017). Concentrations in bivalves measured in six sites in the Bay ranged between 8.3 and 76.1 ng/g lw, greater than concentrations of bivalves from the reference site, indicating that the elevated concentration are likely due to urban influence (Wu et al. 2017).

The chlorinated carbazole, 36-CCZ (3,6-dichlorocarbazole), was the dominant congener in sediment, bivalves, sport fish, and harbor seal blubber samples. The data suggest the biomagnification potential of PHCZ to be driven by chlorinated PHCZs. Other dominant congeners in Bay samples were 136-BCZ (1,3,6-tribromocarbazole) and 36-BCZ (3,6-dibromocarbazole). The congener composition of bivalves was

closely correlated with the composition in sediment, and contained elevated concentration of 1368-BCZ (1,3,6,8-tetrabromocarbazole) compared to other species. Fish and harbor seals shared similar composition profiles. Cormorant eggs had a different congener pattern, and the dominant congener was 136-BCZ (Wu et al. 2017).

While there is limited information about the toxicity of PHCZs, the compounds are structurally similar to polychlorinated dibenzofurans, polychlorinated dibenzo-p-dioxins, and polychlorinated biphenyls (PCBs), which are known to be carcinogenic, persistent, and bioaccumulative. A number of studies have reported dioxin-like activity from specific PHCZs congeners, as well as developmental, cardiotoxic, and mutagenic activities (Wu et al. 2017), resistance to degradation and bioaccumulation characteristics (Mumbo et al. 2015). A study on the developmental toxicity of a few PHCZs using an in vivo zebrafish embryonic model found deformation phenotypes associated with exposure to 36-BCZ and 1368-BCZ at the ppm level (Fang et al. 2016). In this study, higher toxicities were measured for 2,7-dichlorocarbazole (27-CBZ) and 2,3,6,7-tetrachlorocarbazole (2367-CBZ), with lethal toxicities in the ppm range and clear observable deformities in the ppb range (Fang, 2016).

The lack of information on the toxicity, especially for sediment, has resulted in the designation of PHCZs as a Possible Concern (Tier I) contaminant for the Bay.

Cormorant feeding newly hatched chicks on the East span of the Bay Bridge. (Courtesy of Becky Matsubara, September, 2016, CC)

PHCZs STUDY RECOMMENDATIONS

- Pro bono collaborations to examine a) pollution pathways, and b) temporal trends may be warranted, in particular because these studies may help to elucidate the potential sources of the contamination. A study of wastewater effluent and stormwater runoff could help determine the relative contributions of these pathways, and indicate whether the contamination is due to legacy or current uses. Temporal trends, examined in archived sediment or tissue samples or via sediment cores, may also provide information on whether PHCZs present as a result of current or legacy sources and processes.

Short-Chain Chlorinated Paraffins

(SCCP, C_{10}-C_{13} congeners)

TIER I

POSSIBLE CONCERN

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. Seal blubber contained the highest ΣSCCP concentrations (25-50 ng/g wet weight), followed by cormorant eggs (4-6 ng/g wet weight), and then sport fish (<1-1 ng/g wet weight). Relatively low concentrations of these compounds have been detected in sediment as well.

Short-chain chlorinated paraffin production stopped in 2012 as part of a settlement negotiated with USEPA (2012). Low levels in Bay samples and a halt to production suggest this contaminant class is not a high priority for RMP monitoring. However, sparse data on toxicity mean SCCPs are considered Possible Concern (Tier I) contaminants in the Bay. Of note, medium- and long-chain chlorinated paraffins have not been the subject of RMP monitoring studies.

Sea lions and seals at Pier 39, San Francisco. (Courtesy of Ken Lund, 2004 CC)

Single-walled Carbon Nanotubes

(SWNT)

TIER I

POSSIBLE CONCERN

Single-walled carbon nanotubes may be used in electronics and energy applications, drug delivery applications, as well as in production of composite plastic polymers with enhanced strength or electrical or thermal properties. These nanomaterials were not detected in any Bay sediment or mussel samples analyzed (Dodder et al. 2014). To our knowledge, SWNT have not been analyzed in environmental matrices outside of California, nor are they well characterized with respect to aquatic toxicity. No other nanomaterials have been analyzed in Bay samples. Analytical methods for the analysis of other nanomaterials in environmental samples are not currently available. Existing information does not support prioritizing monitoring for SWNT or other nanomaterials at this time. Limited toxicity data support classification of SWNT as Possible Concern (Tier I) contaminants for the Bay.

4 Identification of CECs by Review of Literature and Regional CEC Monitoring Programs

4.1 Ongoing Review of the Scientific Literature on CECs

It is important that scientific literature regarding CECs is routinely reviewed to identify new chemicals, new methods, and new collaborators. RMP staff actively read the scientific literature, regularly attend scientific conferences, and confer with leading CEC scientists to obtain feedback on existing RMP studies, to identify new CECs, and to forge new partnerships, including pro bono collaborations.

Identification of the highest priority CECs is a challenge for regulators, managers and researchers around the world. Recently, several research groups have been engaged in screening large chemical inventories to identify CECs that are likely to be persistent, bioaccumulative and toxic in the environment and should be monitored. One of the most comprehensive and relevant endeavors is the work conducted by Drs. Muir and Howard (Muir and Howard 2006; Howard and Muir 2010, 2011, 2013). In one recent publication (Howard and Muir 2010), this research team combined the Canadian Domestic Substance List (11,317 chemicals) with the USEPA Toxic Substance Control Act Inventory Update Rule database (14,376 chemicals) and a list of substances of commercial "unknown or variable composition complex reaction products and biological materials" (UVCBs; 3,059 substances). With the elimination of duplicate listings, 22,263 chemicals were evaluated. Chemical-physical models, more limited toxicology models, and expert judgment were used to predict the behavior of these compounds in the environment and their potential for bioaccumulation and toxicity.

Based on this review, Howard and Muir (2010) identified 610 CECs to be monitored. The authors used production volume, persistence, and potential for bioaccumulation to rank the 610 chemicals into the top ten brominated, chlorinated, fluorinated, silicone-related and "other" compounds for which data are lacking and urgent study is recommended. A similar study focusing on pharmaceuticals identified an additional 58 high production volume compounds as candidates for monitoring, along with 364 pharmaceuticals produced at lower volumes (Howard and Muir 2011).

Journals are regularly reviewed as another means of identifying potential monitoring targets. For example, a recent study used non-targeted analysis to identify brominated azo dyes with mutagenic properties as major contaminants of household dust (Peng et al. 2016); this class of compounds may merit investigation in Bay sediment samples. Broader review of the literature may be guided by themes relating to chemical or functional class. Finally, active solicitation of new ideas from external experts can reveal additional contaminants worthy of study, as well as opportunities for collaboration.

Pro bono opportunities that leverage existing RMP sample collection efforts are of particular interest. A recent study on a new class of contaminants, polyhalogenated carbazoles (PHCZs; Wu et al. 2017), is a notable example of such a collaboration. These contaminants are classified as a Possible Concern (Tier I) for the Bay.

4.2 Reviewing Other State and Regional Strategies to Monitor CECs

RMP staff review a number of other state and regional efforts to develop effective strategies for monitoring CECs in the environment. Through these exchanges, the RMP can observe the different approaches to identifying and prioritizing CECs employed elsewhere; these observations may suggest possible improvements to the RMP CEC strategy. The dialogues are also an important means of staying abreast of the latest scientific developments in the field. The following is a brief description of the CEC strategies for California, Oregon, Washington, and the Great Lakes region.

California Pilot CECs Study Design

The Southern California Coastal Water Research Project (SCCWRP) has crafted a pilot CEC monitoring study design (Dodder et al. 2015) in response to recommendations by the Science Advisory Panel for CECs convened on behalf of the California Water Resources Control Board (Anderson et al. 2012). This pilot study design identifies individual chemicals for targeted monitoring based on estimated risk to ecosystem health in three general types of waterways – inland freshwater, coastal embayment, and open ocean. Monitoring is also suggested for wastewater effluent and MS4 receiving water (stormwater) pollution pathways. Finally, the pilot study design suggests use of bioanalytical monitoring tools and non-targeted analysis to screen for known and unknown contaminants.

For the coastal embayment scenario, the pilot study design recommends monitoring ambient Bay water for eight CECs, including pesticides (bifenthrin, fipronil, permethrin, chlorpyrifos), chemicals associated with consumer products (bisphenol A, galaxolide), and natural hormones (17β-estradiol, estrone) (see Appendix Table A2). For Bay sediment, two flame retardant chemicals (BDE-47, BDE-99), three pesticides (bifenthrin, fipronil, permethrin), and PFOS were prioritized for monitoring. In biological tissues, monitoring of the PBDEs and PFOS is recommended. To characterize the contribution of pollution pathways, the CECs listed above were recommended for monitoring in wastewater effluent and stormwater; other CECs that may be of interest in these pathways include PPCPs (diclofenac, ibuprofen, triclosan), phthalates (DEHP, BBzP), and 4-nonylphenol (see Appendix Table A2). Elements of this pilot study design have been incorporated into ongoing monitoring activities in southern California and in the Russian River watershed.

Biomonitoring California

By measuring chemicals (or metabolites) in a person's 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 collaborative effort 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 December 2015, includes dozens of CECs within the following classes: PFAS, PBDEs and their metabolites, alternative flame retardants, PPCPs (e.g., phthalates, parabens, cyclosiloxanes, and triclosan), BPA and related compounds, pesticides (e.g., pyrethroids), and perchlorate (Biomonitoring California 2015). It also includes legacy contaminants like PCBs, PAHs, and heavy metals, as well as diesel exhaust and tobacco smoke.

Oregon

Oregon's Department of Environmental Quality was charged by the state legislature with developing a Persistent Priority Pollutant (P3) List as part of state water pollution prevention efforts. To guide its assessment and prioritization process, the agency convened a Science Workgroup of experts in the fields of fate and transport, hydrology, human health, aquatic life, and wildlife toxicology. The agency compiled a list of 2,000 chemicals largely drawn from other state, federal and international lists of persistent, bioaccumulative, and toxic (PBT) compounds. Each of these substances was evaluated using USEPA chemical property estimation models to estimate persistence, bioaccumulative potential and toxicity, and each was given an overall numeric score for ranking purposes; the final P3 List consisted of a total of 118 chemicals (Mullane et al. 2009). The 69 "current use" P3 chemicals are composed of 16 pesticides (including bifenthrin, chlorpyrifos, fipronil, and others), 17 consumer-related products (including siloxanes, galaxolide and other musks, triclosan, cholesterol, others), 7 halogenated flame retardants (BDE-47, 99, 100, 153, 209, hexabromocyclododecane, tetrabromobisphenol A), 4 industrial chemicals (benzotrichloride, octachlorostyrene, pentachloroanisole, 2,4,6-tris-(1,1-dimethylethyl)phenol), 14 polycyclic aromatic hydrocarbons, 5 inorganic and organic metals, and 6 PFASs (including PFOS, PFOA, others). The 49 "legacy" P3 chemicals are pesticides, polychlorinated biphenyls (PCBs), polychlorinated naphthalenes, and dioxins and furans. The P3 List has been used to direct wastewater effluent monitoring, which in a few cases has revealed the need for pollution prevention plans.

Washington

To reduce PBT compound use, release, and exposures in the state, Washington's Department of Ecology established a PBT Rule in 2006 (Washington 2006). The Rule defines specific criteria for a chemical to be considered PBT and provides a list of chemicals that meet these criteria, as well as procedures to update this list periodically. The current list includes 17 chemicals, 8 chemical groups, and 2 metals of concern. The list features a number of legacy contaminants as well as brominated flame retardants (PBDEs, hexabromocyclododecane, tetrabromobisphenol A), perfluorooctane sulfonate (PFOS), and industrial chemicals (hexachlorobutadiene, 1,2,4,5-tetrachlorobenzene). Chemicals identified as PBTs may become part of ambient environment monitoring efforts. In addition, they may become the subject of Chemical Action Plans, which are comprehensive plans to identify, characterize, and evaluate all uses and releases of a chemical, and to recommend actions to protect human health and the environment. While Chemical Action Plans are not regulations themselves, they may spur new legislation or rulemaking efforts in the state.

The Washington State Department of Ecology, in collaboration with King County Department of Natural Resources and other organizations, also launched an effort to assess toxic chemicals contaminating the Puget Sound (Washington Department of Ecology and King County, 2011). The assessment was designed to provide scientific information that could be used to guide decisions about how best to direct and prioritize resources and strategies for controlling toxic chemicals in the Puget Sound basin. Target chemicals were identified by a Chemicals of Concern Workgroup composed of regional experts who selected a manageable list of compounds that were known or suspected to cause harm to Puget Sound and broadly representative of pathways of contamination. The final list of 17 chemicals includes a number of metals and legacy contaminants, as well as PBDEs, bis(2-ethylhexyl) phthalate, the herbicide triclopyr, and nonylphenols. Toxic chemical loading to Puget Sound via major pathways such as surface water runoff, wastewater treatment plant effluent, and direct air deposition, was then estimated for each compound (Washington Department of Ecology and King County, 2011).

Great Lakes

The independent, binational International Joint Commission tackles issues regarding the use and quality of US-Canada boundary waters like the Great Lakes. To address CECs, the Commission established a Chemicals of Emerging Concern Work Group, which in 2011 drafted a coordinated strategy for assessing exposures and effects of toxic substances in the Great Lakes (Chemicals of Emerging Concern Work Group, 2011). The Work Group noted that prior evaluation of CEC risks has taken a largely empirical, exposure-based approach, through monitoring of Great Lakes media and biota for selected chemicals including synthetic musks, fluorinated surfactants, PBDEs and other flame retardants, alkylphenol ethoxylates, chlorinated paraffins, pharmaceuticals, and current use pesticides. Because available information tends to be relatively "exposure-rich and effects-poor," the Work Group focused on determining the effects of CECs. The resulting draft strategy relies on an ecological risk assessment framework to guide the design of a biomonitoring program that would use *in situ* effects-based monitoring via standardized methodologies to be developed.

The Great Lakes draft strategy incorporates both prospective and retrospective techniques: prospective methods that incorporate improved predictive approaches would be valuable in providing screening level information, while retrospective methods would be important for diagnostic purposes and establishing causality between chemical exposure and adverse effects. The strategy is augmented through use of the Adverse Outcome Pathway conceptual framework that displays existing knowledge concerning the link between a direct molecular initiating event of a toxic substance (i.e., exposure) to an adverse outcome relevant to ecological risk assessment. Where endpoints of direct concern to risk assessment (survival, growth, development, reproduction) are lacking, the Adverse Outcome Pathway provides a basis for making the link between a broader array of mechanism-specific responses triggered by CECs and impacts of ecological concern. The Work Group recommends incorporating effects-based monitoring as a complement to existing chemical-based approaches. The Work Group does not supply a specific list of CECs recommended for study.

More recently, US and Canadian agencies, working together under the Great Lakes Water Quality Agreement, have identified the first set of chemicals of mutual concern for the Great Lakes (ECCC 2016).

Designated chemicals or chemical classes are: hexabromocyclododecane (HBCD), polybrominated diphenyl ethers (PBDEs), perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), long-chain perfluorinated carboxylic acids (LC-PFCAs), mercury, polychlorinated biphenyls (PCBs), and short-chain chlorinated paraffins (SCCPs). These chemicals are potentially harmful to human health or the environment. Once a chemical is designated, Canada and the United States have committed to develop and implement strategies to address the chemical, reporting every three years on its status.

4.3 CECs Recommended for Initial Study

A review of the literature and the CECs prioritized by other regional water quality programs suggests a few candidates for potential study:

- PPCPs – Pharmaceuticals (e.g., ibuprofen) and fragrance ingredients (e.g., galaxolide) have been identified in the scientific literature or prioritized for monitoring by water quality monitoring programs for persistence, bioaccumulation, and/or toxicity. These compounds and related chemical classes are expected to be the subject of future RMP special studies.

- Dyes – Recent detection of brominated azo dyes in household dust (Peng et al. 2016) suggests these compounds may be present in the environment. DTSC's Priority Product Work Plan guiding current efforts of the Safer Consumer Products Branch has identified azo dyes as potential candidate chemicals in three product categories: personal care products, clothing, and consumable office products such as ink cartridges. There is a dearth of data on the presence of dyes or their breakdown products in the environment. Therefore, a special study targeting dyes in Bay matrices may inform DTSC's green chemistry efforts.

5 Non-targeted Monitoring Approaches to CEC Identification

Using the chemical-specific, targeted monitoring paradigm described in Section 3.0, the RMP has monitored a number of chemicals and chemical classes in the Bay. However, given the significant data gaps concerning chemical production and use, and the sheer number of chemicals in commerce, we cannot assume that we have identified all appropriate CECs for monitoring. To provide a measure of assurance that the RMP is not missing unexpected yet potentially harmful contaminants simply because of failures to predict their occurrence based on incomplete use information or exposure prioritization criteria, two alternative tools are used: broadscan screening (also known as non-targeted analysis) and bioanalytical assays.

5.1 Broadscan Screening

Investigations using non-targeted analysis to screen for CECs are useful for creating an inventory of bioaccumulative compounds in tissues or compounds present in abiotic matrices. Findings from such investigations can be used to inform targeted chemical monitoring or toxicity studies. The RMP has completed one broadscan project and initiated another; future special studies are also recommended on matrices not yet characterized with these techniques, such as sediment.

In 2010, the RMP began a collaboration with the National Institute of Standards and Technology (NIST) and other researchers to use non-targeted analysis to identify contaminants present in San Francisco Bay harbor seal blubber and mussel samples (Sutton and Kucklick 2015). Two dimensional gas chromatography time-of-flight mass spectrometry was used by the NIST scientists to conduct a broad scan of Bay samples, comparing signals found to those present in the NIST Mass Spectral Library, a resource containing information on over 200,000 compounds.

This analysis focused on organic compounds with chlorine or bromine atoms, which are not very water-soluble and tend to build up in fatty tissues in wildlife and people. Most of the compounds identified in Bay harbor seals and mussels were well-known, "legacy" pollutants, including PCBs, organochlorine pesticides, and chemicals that form when these pollutants break down in the environment. Both seals and mussels also contained some unusual compounds that are related to DDT.

In seals, this non-targeted approach identified three new contaminants: 2,2′-dichlorobenzil, 9,10-dichloroanthracene and a similar, unspecified dichloroanthracene (Sutton and Kucklick 2015). To confirm the identities, pure forms of the chemicals were subjected to the same analytical method. These newly identified compounds were found at very low levels relative to legacy pollutants. New contaminants found in Bay mussels include methyl triclosan, derived from the antibacterial ingredient triclosan, as well as 4-tert-butylamphetamine, likely derived from amphetamine drugs (Sutton and Kucklick 2015). These identities have not yet been confirmed using pure compounds. These contaminants were also found at very low levels relative to legacy pollutants.

In addition, naturally-forming, brominated compounds such as "Q1" (2,3,3′,4,4′,5,5′-heptachloro-1′-methyl-1,2′-bipyrrole) were detected in both seals and mussels, and were most abundant in mussels in less-polluted Bodega Bay (Sutton and Kucklick 2015). While these natural compounds have been detected worldwide in ocean food webs, little is known about their toxicity.

The detection of these compounds suggests that the original or "parent" contaminants may not always be the most important chemical to monitor in wildlife. The RMP has found the parent amphetamine compound previously, but has not targeted 4-tert-butylamphetamine for analysis. Similarly, while a few studies have characterized triclosan contamination in the Bay, relatively little information exists for methyl triclosan (Klosterhaus et al. 2013a). The chemicals identified in this study have been the subject of little or no targeted tissue monitoring elsewhere in the world, and have not been identified in non-targeted studies of wildlife in other areas (e.g., Hoh et al. 2012; Shaul et al. 2015), with the exception of dichloroanthracenes observed in freshwater species exposed to combustion byproducts (Myers et al. 2014). The potential for these newly identified compounds to cause health impacts at current levels is unknown. According to the RMP's tiered CEC monitoring framework, the five Bay contaminants newly identified via this study may be considered of Possible Concern (Tier I) because more information about toxicity is needed to determine their risk to aquatic life (see Section 3.4).

It is possible that this non-targeted analysis may have missed other unexpected Bay contaminants. Some may be identifiable but not present in the NIST Mass Spectral Library, while others may provide a signal (chemical mass spectrum or "fingerprint") that cannot be identified. Some contaminants may also build up in Bay species other than the ones examined here.

In addition, the focus on fat-soluble compounds in this study leaves a significant data gap regarding water-soluble contaminants in the Bay. To fill this data gap, the RMP initiated a special study in 2016 designed to probe polar, water-soluble organic compounds that were not covered by the previous non-targeted tissue analysis. For this study, non-targeted analysis using Orbitrap liquid chromatography high resolution mass spectrometry can allow identification of more water-soluble (polar) organic contaminants in ambient Bay water (collected via grab and passive sampling), as well as in treated wastewater effluent, anticipated to be a major source of these compounds to the Bay. Polar organic contaminants are of significant concern to the water quality of the San Francisco Bay, as they may exhibit meso-range transport, be difficult to remove through treatment strategies, and cause effects on wildlife through endocrine disruption and other mechanisms. Detergents, plastic additives, and medications are examples of products that can contain such water-soluble, polar organic contaminants.

Completion of this study will make the Bay the first ecosystem to be studied via non-targeted methods for both water- and fat-soluble contaminants. Should the study identify the presence of unexpected and potentially concerning water-soluble contaminants, this may indicate the need for a follow-up RMP special study designed to assess the contaminants quantitatively. It could also point to ecotoxicity data gaps or suggest new management priorities. In contrast, because of the comprehensive nature of the non-targeted methods proposed herein, should few unexpected contaminants be identified, the RMP would then have considerable evidence that existing polar organic CEC monitoring is already focusing on the highest priority contaminants for the Bay.

Bay matrices not yet examined via non-targeted analysis include sediment, stormwater, and other tissue samples such as bird eggs. To track changes in chemical production and use as well as rapidly improving analytical methods, non-targeted analysis must be repeated on matrices of interest every 5-10 years. Routine use of this technique may be incorporated into Status and Trends monitoring.

5.2 Bioanalytical Screening Assays

Bioanalytical assays are tools designed to screen for classes of chemicals that share a common mode of toxic action in the environment. Existing bioanalytical tools, which indicate whether tested matrices have the potential to elicit biological responses in cells, show promise as a complementary monitoring technique. However, many of these tools have not yet been adapted and/or validated for environmental (i.e., receiving water) matrices, nor have they been adequately linked to effects at higher levels of biological organization.

To remedy this data gap, in 2013 the RMP sponsored a project to quantitatively link cellular effects (e.g., changes in hormones that affect genetic signaling and processing) to organism effects (e.g., growth, reproduction, and survival). Researchers at University of Florida and SCCWRP used the common silverside *(Menidia beryllina),* a model estuarine fish, to evaluate the estrogenic effects of endocrine disrupting compounds including estrone (E1), 17β-estradiol (E2), and 4-nonylphenols (4-NPs). Effects of exposure were characterized during two life stages: early life and juvenile. The juvenile period occurs just before gonadal differentiation, another window of vulnerability to endocrine disruptors. The *in vivo* endpoints examined were survival and growth of larvae (7-day grow out assay), gonadal tissue differentiation, and growth of juveniles (28 day assay). Molecular gene expression endpoints were also included for genes related to brain development (brain aromatase in larvae) and sex differentiation and reproduction (both life stages). Commercially available *in vitro* assays for human estrogen receptor alpha transactivation were used to screen for estrogenic effects.

The results established quantitative linkages between the screening levels in *in vitro* assays and higher order responses in fish that are influenced by estrogen, such as growth and gonadal sex differentiation (Denslow et al. 2017). The most sensitive endpoints at the molecular level were for genes known to contain strong estrogen response elements in their control regions, including vitellogenin (Vtg), choriogenin (chg), and the brain aromatase (Cyp19b). As expected, the *in vitro* responses occurred at far lower exposure levels than *in vivo* responses. This means the bioassays can be used as a monitoring tool that provides a margin of safety, ranging from approximately 20-50 for potent estrogen E2 to 2-5 for weaker estrogens, for aquatic systems. A margin of safety is particularly important given some organisms may be more sensitive to estrogenic chemicals than *Menidia.*

In addition to the individual chemicals, the research team also exposed larvae and juvenile fish to diluted effluent from a wastewater treatment plant that uses secondary treatment and discharges into San Francisco Bay. Exposure to diluted effluent resulted in little to no observed effects on either life stage. Likewise, the *in vitro* ER transactivation assay response revealed very low equivalent concentrations of estrogenic chemicals (< 5 ng/L) in the diluted effluent. This research element highlights a key strength of this type of bioassay, the fact that it can be used to assess the cumulative effects of exposure to multiple CECs with common modes of action.

The RMP has provided additional funds for 2017 for the research team to refine the bioanalytical tool and then subject Bay water and sediment samples to testing. The RMP Exposure and Effects Workgroup (EEWG) will provide oversight of this study. Should estrogenic water or sediment samples be identified using these bioassay tools, followup chemical analyses may be indicated. Long-term plans for use of these tools may be established by the EEWG following completion of this special study. Future work could also include developing similar tools that explore other (non-estrogenic) modes of action, such as glucocorticoid activity. However, it is important to note that several more years of research and development are likely to be necessary before bioanalytical screening assays become routine monitoring tools.

San Francisco Bay. (Photo by Shira Bezalel, SFEI)

6 Conclusion: RMP CEC Multi-Year Plan and Status and Trends Monitoring Recommendations

Assembled below are special studies supported by this strategic examination of CECs in the Bay, structured as a multi-year plan (Table 6). Relevant pro bono and Status and Trends monitoring contributions have been identified, as have relevant studies from other RMP workgroups. The rationale for specific Status and Trends recommendations is presented as well.

Table 6. RMP CEC Research Strategy – Multi-Year Plan

Element	Study	Funder	Questions addressed
CEC Strategy			
MODERATE CONCERN CECs (Tier III)			
PFOS/PFAS	Perfluorinated Compounds in Harbor Seals	RMP	1,3,4
	Sediment, Effluent Precursor Monitoring	AXYS	1,2,4
	CECs in Municipal Wastewater[1]	RMP	1,2,4
	Effluent TOF analysis	DTSC	1,2,4
	Perfluorinated and Polyfluorinated Compounds in San Francisco Bay: Synthesis and Strategy	RMP	1,2,3,4
	Identify Unknown PFAS in Harbor Seals and Archived Margin Sediment	RMP	1,3,4
	PFAS and Novel Compounds in Archived Eggs		1,3,4
	Novel PFAS Study, Informed by Synthesis and Strategy and Additional Studies	RMP	1,4
	Trunkline Influent	RMP	1,2,4
	RMP Status and Trends[2]	RMP S&T	1,3,4
NP/NPE	Archived Margin Sediment	RMP	1,2
	Archived Tissue	RMP	1,3,4
	Synthesis		1,2,3,4
Fipronil	Fipronil, Fipronil Degradates, and Imidacloprid in Municipal Wastewater	RMP	1,2
	Fipronil, Fipronil Degradates, and Imidacloprid in Biosolids	ASU	1,2
	CECs in Municipal Wastewater[1]	RMP	1,2
	Fish	RMP	1
	RMP Status and Trends[2,3]	RMP	1,3,4

2013	2014	2015	2016	2017	2018	2019	2020	2021
20	20	20	48	50	65	65	80	65
	26							
	(30)							
		27.5						
		(50)						
				56				
					78			
						65		
							125	
								100
	F		E		E	F		E
					54			
						75		
								50
			30					
			(8)					
		27.5						
						50		
	S				S			

Element	Study	Funder	Questions addressed
LOW or POSSIBLE CONCERN CECs (Tier II & I)			
PBDE[4]	PBDE Summary Report	RMP	1,2,3,4
	RMP Status and Trends[2]	RMP S&T	1,3,4
Alt. Flame Retardants	Monitoring Alternative Flame Retardants in SF Bay Water, Effluent, Stormwater, Sediment and Biota	RMP	1,2,3,4
	Phosphate Flame Retardants in Ambient Bay Water	RMP / ECCC	1,3,4
	Conceptual Model	RMP	1,2
Pharmaceut-icals	Pharmaceutical Contamination in Wastewater	RMP / POTWs	1,2,3
	Pharmaceutical Compounds in Ambient Bay Water & Sediment	RMP	1,3
	Antibiotics in Sediment Cores	U Minn	1,3
Bisphenols/ Phthalates	Bisphenol Compounds in Ambient Bay Water	RMP / SIU	1,4
	Bisphenol Compounds in Archived Sediment	RMP	1,4
	Phthalates in Bay Matrices		1,3
Personal Care/ Cleaning	Triclosan in Small Fish	RMP	1
	Musks in Water and Sediment	RMP	1
	Quats in Archived Sediment	RMP	1
	Siloxanes in Bivalves	ECCC	1
Pesticides	Current Use Pesticides in Ambient Bay Water	RMP	1,2
	Imidacloprid, Imidacloprid Degradates and other Neonicotinoids in Ambient Bay Water	RMP	1
	DPR Priorities in Water and Sediment	RMP	1,2,3
	Emerging Concerns	RMP	1
	Napa River Agricultural Pesticides		1,2
SDPA/BZT	Water, Sediment	ECCC	1
OH-BDEs / Triclosan	Water, Sediment Cores	U Minn	1,3
Polyhalagenated Carbazoles	Sediment, Tissue	SIU	1
NON-TARGETED & OTHER STUDIES			
Non-targeted	Non-targeted Analysis of Water-soluble CEC Compounds	RMP / Duke / AXYS	1,2
	Sediment (Polar and Nonpolar Compounds) and Related Studies	RMP	1,2
	Follow-up Targeted Study	RMP	1
	Tissue (Polar and Nonpolar Compounds)	RMP	1
	Follow-up Targeted Study		1
	RO Concentrate		2

2013	2014	2015	2016	2017	2018	2019	2020	2021
36								
	S, B,F		B, E		S, E	F		E
	104							
	(2)			47				60
						80		
			(68)		30			
							150	
				(8)				
		(25)		50				
						50		
								50
				41				
					63			
						50		
	(5)							
15								
				40				
					63			
							75	
								100
	(3)							
	(125)							
		(15)	(20)	(40)				
			52 (10) (6)					
					118			
						80		
							120	
								80
					59			

Element	Study	Funder	Questions addressed
RELEVANT STUDIES IN OTHER WORKGROUPS			
Bioassay (EEWG)	Linkage of In Vitro Estrogenic Assays with In Vivo End Points	RMP / SCCWRP / UF	1,2
	Development of Glucocorticoid Bioanalytical Screens	RMP / SCCWRP / UF	1
RMP-funded Special Studies Subtotal – ECWG			
RMP-funded Special Studies Subtotal – Other Workgroups			
Pro-Bono & Externally Funded Studies Subtotal			
OVERALL TOTAL			

CEC Multi-Year Plan Table Notes

1 – The 2015 CECs in Municipal Wastewater study was a $55k study that included analyses of PFOS/PFAS and fipronil; in this table the budget for this study has been split between these two contaminant groups.

2 – When a CEC is proposed for inclusion in the the RMP Status and Trends monitoring, there is a letter in the cell denoting the matrix for which monitoring is proposed: W = water; S = sediment; B = bivalve; E = eggs; F = fish.

3 – Analysis of fipronil and fipronil degradates is a proposed recommendation for inclusion in the RMP Status and Trends monitoring effort. The current Status and Trends monitoring budget does not include these analyses.

4 – PBDEs were considered Moderate Concern CECs (Tier III) until 2017.

2013	2014	2015	2016	2017	2018	2019	2020	2021
70	56 (125)			45				
						100 (100)	100 (100)	
71	**150**	**75**	**130**	**284**	**560**	**510**	**545**	**500**
70	**56**	**0**	**0**	**45**	**0**	**100**	**100**	**0**
0	**165**	**90**	**112**	**48**	**TBD**	**100+**	**100+**	**TBD**
141	**371**	**165**	**242**	**377**	**560**	**710+**	**745+**	**500+**

Status and Trends Monitoring Recommendations for CECs

CECs that have been, or are recommended to be, part of routine Status and Trends monitoring are listed below by matrix of interest.

- Water – None. PBDEs were at one time measured in this matrix via Status and Trends monitoring; resulting data were considered less valuable than measurements in other matrices, so this component of Status and Trends monitoring was eliminated.

- Sediment – Fipronil and degradates; PBDEs. Routine monitoring of sediment for fipronil is essential to determine the impacts of potential management actions. Monitoring of sediment for PBDEs is recommended for at least two more cycles, as an essential means of evaluating whether BDE-209, derived from the recently phased-out DecaBDE, declines as expected. The DecaBDE commercial mixture was phased out of US production in 2013; previous sediment monitoring does not yet indicate a decline.

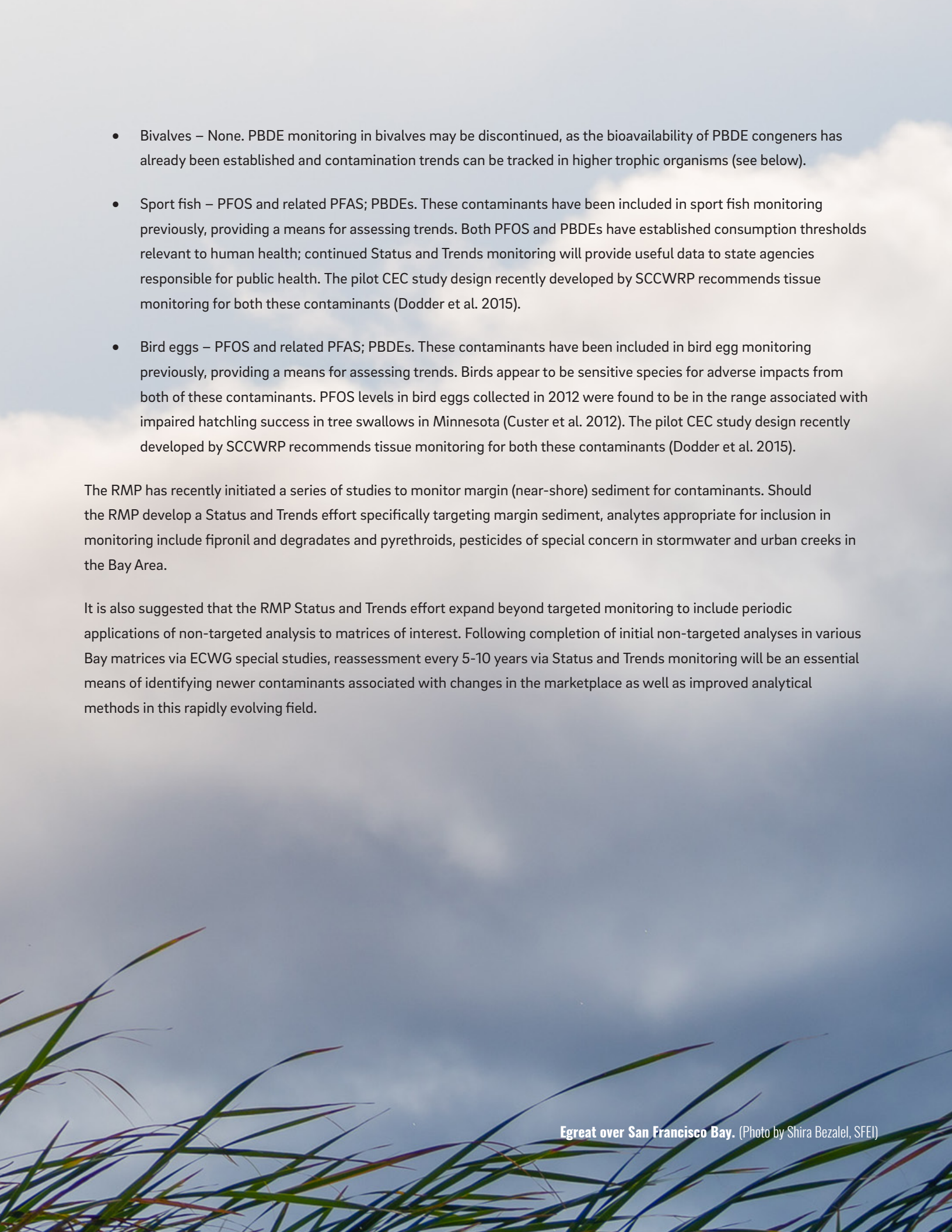
- Bivalves – None. PBDE monitoring in bivalves may be discontinued, as the bioavailability of PBDE congeners has already been established and contamination trends can be tracked in higher trophic organisms (see below).

- Sport fish – PFOS and related PFAS; PBDEs. These contaminants have been included in sport fish monitoring previously, providing a means for assessing trends. Both PFOS and PBDEs have established consumption thresholds relevant to human health; continued Status and Trends monitoring will provide useful data to state agencies responsible for public health. The pilot CEC study design recently developed by SCCWRP recommends tissue monitoring for both these contaminants (Dodder et al. 2015).

- Bird eggs – PFOS and related PFAS; PBDEs. These contaminants have been included in bird egg monitoring previously, providing a means for assessing trends. Birds appear to be sensitive species for adverse impacts from both of these contaminants. PFOS levels in bird eggs collected in 2012 were found to be in the range associated with impaired hatchling success in tree swallows in Minnesota (Custer et al. 2012). The pilot CEC study design recently developed by SCCWRP recommends tissue monitoring for both these contaminants (Dodder et al. 2015).

The RMP has recently initiated a series of studies to monitor margin (near-shore) sediment for contaminants. Should the RMP develop a Status and Trends effort specifically targeting margin sediment, analytes appropriate for inclusion in monitoring include fipronil and degradates and pyrethroids, pesticides of special concern in stormwater and urban creeks in the Bay Area.

It is also suggested that the RMP Status and Trends effort expand beyond targeted monitoring to include periodic applications of non-targeted analysis to matrices of interest. Following completion of initial non-targeted analyses in various Bay matrices via ECWG special studies, reassessment every 5-10 years via Status and Trends monitoring will be an essential means of identifying newer contaminants associated with changes in the marketplace as well as improved analytical methods in this rapidly evolving field.



Egreat over San Francisco Bay. (Photo by Shira Bezalel, SFEI)

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7 Appendix: RMP CEC monitoring for target analytes identified in pilot CEC study guidance (Dodder et al. 2015)

Table A1. CECs recommended for study in coastal embayments.

Compound	SCCWRP CEC Pilot Study Guidance: Embayments	RMP SF Bay CEC Tier (Table 2)	RMP Status & Trends Monitoring	RMP Approach
Flame Retardants				
PBDEs (BDE-47 and 99)	sediment, tissue	Low (II)	sediment, sport fish, bird eggs	Extensive dataset; concentrations declining in sediment and wildlife.
Hormones				
17β-estradiol and Estrone	water			No Bay data; bioanalytical tools will be used in a 2017 special study to characterize the estrogenicity of water and sediment sites of highest potential concern.
Pesticides				
Bifenthrin and Permethrin (Pyrethroids)*	water, sediment	Low (II)		Hydrophobic; based on Bay sediment concentrations, detection is not expected in water.
Chlorpyrifos*	water		water	Not formally classified as a CEC by the RMP; water monitoring occurs every ten years, with recent levels below 1 ng/L (2009-2011); levels are expected to continue declining due to DPR actions.
Fipronil	water, sediment	Moderate (III)	sediment	Not detected in water; sediment monitoring to continue.
PPCPs & Plastic Additives				
Bisphenol A	water	Possible (I)		Not detected in previous monitoring using a method with a high detection limit; a special study to examine bisphenols in ambient water samples will take place in 2017.
Galaxolide (HHCB)*	water	Low (II)		Detected at low levels in Bay wildlife; a special study to monitor margin sediment and water is proposed for 2018.
PFAS				
PFOS	sediment, tissue	Moderate (III)	sport fish, bird eggs	Detected at elevated concentrations in seals and bird eggs; other studies have detected PFOS in Bay sediment; a special study to analyze margin sediment and harbor seal blood is proposed for 2018.

* Additional data provided in Klosterhaus et al. 2013a.

Table A2. CECs recommended for effluent and stormwater discharged to embayments.

Compound	SWRCB CEC Pilot Study Guidance: Pathways	RMP SF Bay CEC Tier (Table 2)	RMP Approach
Flame Retardants			
PBDEs (BDE-47 and 99)	effluent, stormwater	Low (II)	Recent data include findings from a 2014 special study that measured PBDEs in 3 effluents and during storms at 2 stormwater sites. Ongoing monitoring in stormwater from selected sites.
Hormones			
17β-estradiol and Estrone	effluent, stormwater		Bioanalytical tools applied to a secondary effluent indicated low levels of estrogenicity. Little to no targeted chemistry data in pathways.
Pesticides			
Bifenthrin and Permethrin (Pyrethroids)	effluent, stormwater	High (IV)**	Effluents from 32 facilities have been monitored for pyrethroids. Ongoing monitoring in stormwater from a variety of sites.
Chlorpyrifos	effluent, stormwater		Ongoing monitoring in stormwater from a variety of sites.
Fipronil	effluent, stormwater	Moderate (III)	A 2016 special study detected fipronil and degradates in influent and effluent of 8 facilities. Ongoing monitoring in stormwater from a variety of sites.
PPCPs & Plastic Additives			
Bisphenol A	effluent, stormwater	Possible (I)	Detected in effluent from single WWTP in past study; a BACWA study may provide more data. Detected in 3/4 stormwater samples; unpublished data.
Diclofenac	stormwater	Low (II)	No effluent data available in the Bay Area. Detected in four stormwater samples; unpublished data.
Galaxolide (HHCB)	effluent, stormwater	Low (II)	No Bay Area effluent or stormwater data available.
Ibuprofen	stormwater	Low (II)	Detected in an effluent in one study, not detected in another; a BACWA study may provide more data. Detected in 3/4 stormwater samples; unpublished data.
Triclosan	stormwater	Low (II)	Detected in effluent in past studies; a BACWA study may provide more data. Not detected in four stormwater samples; unpublished data.
PFAS			
PFOS	effluent, stormwater	Moderate (III)	A 2015 special study on effluent from 8 WWTPs detected PFOS, with higher concentrations at 2 facilities linked to AFFF. An independent study also detected PFOS in stormwater.

**Classified as High Concern for Bay tributaries, but Low Concern for ambient Bay water.