Contaminants of Emerging Concern in San Francisco Bay:

A Strategy for Future Investigations

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Executive Summary

More than 100,000 chemicals have been registered or approved for commercial use in the U.S. For many of these chemicals, major information gaps limit the ability of scientists to assess their potential risks, and environmental monitoring of these chemicals is not required. The primary challenge for regulators and scientists is managing this ever-growing variety of chemicals to ensure that they do not adversely impact human and environmental health.

Over the last decade, researchers and government agencies have begun to collect occurrence, fate, and toxicity data for a number of chemicals. Some of these chemicals have been classified as contaminants of emerging concern (CECs), often due to 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 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 Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has been investigating 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, regional scientists, and an advisory panel of expert researchers that work together to address the workgroup's guiding management question – Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay? The overarching goal of the ECWG is to develop cost-effective strategies to identify and monitor CECs to minimize impacts to the Bay. 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 (PFASs), alkylphenols, current use pesticides, pharmaceuticals and personal care products (PPCPs), and flame retardants including polybrominated diphenyl ethers (PBDEs) and their replacements.

This strategy document was developed as part of a continuous effort to refine approaches for supporting the management of CECs in San Francisco Bay. The strategy is consistent with recommendations from the California State Water Resources Control Board's nationally-recognized expert panel on monitoring CECs in the State's aquatic systems. The RMP CEC

strategy described herein consists of three major elements.

First, for CECs known to occur in the Bay, the RMP has evaluated relative risk using a tiered risk and management action framework (Section 2.2). This risk-based framework guides future monitoring proposals for each of these contaminants (Section 3.0), the results of which may provide key data to update initial evaluations of potential risk. The criteria listed below were used for placement in each tier.

Tier I (Possible Concern) – Uncertainty in measured or predicted Bay concentrations or in toxicity thresholds suggests uncertainty in the level of effect on Bay wildlife. CECs in Tier I include: alternative flame retardants (BEH-TEBP, EH-TBB, DBDPE, PBEB, BTBPE, HBB, DP, TDCPP, TCEP, TCPP, TBEP, TPhP, other organophosphates); bisphenol A; bis(2-ethylhexyl) phthalate (BEHP or DEHP) and butylbenzyl phthalate (BBzP); poly- and perfluorinated alkyl substances (PFASs) other than PFOS; short-chain chlorinated paraffins; other pesticides; and single-walled carbon nanotubes.

Tier II (Low Concern) – Bay occurrence data or predicted environmental concentrations (PECs) 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; many PPCPs; hexabromocyclododecane (HBCD); and polybrominated dioxins and furans (PBDD/Fs).

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; nonylphenols and nonylphenol ethoxylates; and PBDEs.

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.

The second element of the RMP CEC strategy involves review of the scientific literature and other 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 the Bay is needed to evaluate the risks they may pose.

Finally, the third element of the strategy consists of non-targeted monitoring. The RMP has launched two types of non-targeted monitoring projects. The first, involving broadscan analyses of Bay biota samples, is designed to identify previously unknown CECs present in Bay organisms (Section 5.1). The other is expected to establish a bioassay useful for identifying the presence of contaminants with estrogenic effects (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 internal and external sources. Based on the strategy, a five-year plan indicating research priorities is outlined (Section 6.0).

1.0 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 U.S. These substances include more than 84,000 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 2013a) (Figure 1). Globally, chemical production is projected to continue growing by about 3% per year, and 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 environmental health.

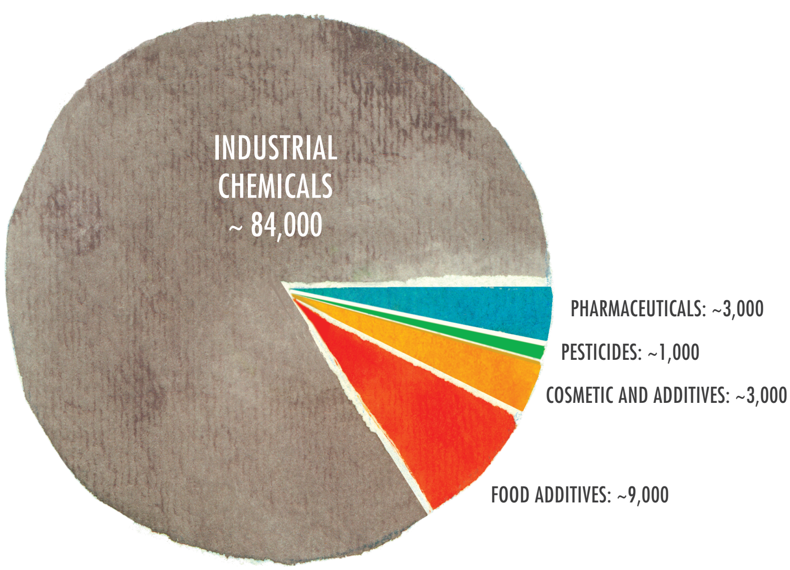

Figure 1. Estimated number and categories of chemicals in commerce registered for use in the United States over the past 30 years. Adapted from Muir and Howard (2006).

San Francisco Bay, critical habitat for a number 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 synthetic compounds on biota. Early identification of emerging pollution issues is particularly important in the Bay, because it can become a long-term trap for persistent contaminants, with recovery taking decades or more 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 to ecosystem and human health are relatively well understood, and monitoring is conducted as part of 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 is not required.

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 products (PPCPs), current use pesticides, and persistent industrial chemicals such as flame retardants and poly- and perfluorinated alkyl substances (PFASs). 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 are relevant 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 characterized as confidential business information or are 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 high priority chemicals.
- 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.

Such large obstacles and limited resources make 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 studied a number of CECs with the potential to impact the Bay.

1.2 The RMP Emerging Contaminants Workgroup

The Regional Monitoring Program for Water Quality in the San Francisco Bay (RMP) has been investigating 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 address the workgroup's guiding management question – Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay? The overarching goal of the ECWG is to develop cost-effective CEC identification and monitoring strategies in an effort to minimize impacts to the Estuary. The ECWG works toward this goal by evaluating available information on chemical occurrence, fate, toxicity, volume used, potential sources, and analytical method capability, and then recommends CECs for investigation in special studies. Each year the highest priority studies are conducted, and the results guide whether or not these CECs are added to routine monitoring by the RMP.

Using 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 compounds, alkylphenols, current use pesticides, PPCPs, and flame retardants including PBDEs and their replacements. Among the CECs studied to date by the RMP, PBDEs, PFASs and pyrethroid pesticides have been added to the routine monitoring program.

1.3 Report Objectives

This strategy document was developed as part of a continuous effort to refine approaches for supporting the management of CECs in San Francisco Bay. The specific objectives of the report were to:

- provide 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); and,
- summarize the non-targeted, screening studies now underway to identify additional CECs present in Bay media (Section 5.0).

The strategy outlined here is part of an iterative process designed to ensure that the RMP is keeping up with the state of the science regarding CECs, specifically by tracking new information as it becomes available and communicating relevant information to the ECWG.

2.0 General Approach to Identify and Prioritize CECs

2.1 Recommendations from a Science Advisory Panel for Monitoring CECs in California's Aquatic Ecosystems

In response to the CEC challenge, in 2009 the California State Water Resources Control Board assembled a panel of nationally recognized experts to develop a strategy for monitoring CECs in the State's aquatic systems. This Science Advisory Panel was tasked with identifying potential sources and evaluating the fate and effects of CECs, as well as with providing guidance for developing monitoring programs that assess those chemicals with the highest potential to cause effects in the State's receiving waters. The final report, "Monitoring

Strategies for CECs in California's Aquatic Ecosystems," was released in 2012, and provides the results from the Panel's deliberations (Anderson et al. 2012).

The Advisory Panel supplied the following products, which are intended to assist the State in developing a monitoring process for CECs:

- a conceptual, risk-based screening framework to assess and identify CECs for monitoring in California receiving waters;
- application of the risk-based screening framework to identify a list of CECs for initial monitoring (Table 1);
- an adaptive, phased monitoring approach with interpretive guidelines that direct and update management actions commensurate with potential risk; and
- identification of research needs, including development of bioanalytical screening methods, linking molecular responses with higher order effects, and filling key data gaps.

These products are discussed in more detail in the RMP's synthesis document, Contaminants of Emerging Concern in San Francisco Bay: A Summary of Occurrence Data and Identification of Data Gaps (Klosterhaus et al. 2013a).

In accordance with the State Panel's approach, the RMP has developed its own three-pronged strategy to direct CEC monitoring and research in the Bay. First, for those CECs known or predicted to occur within the Bay environment, the RMP has evaluated relative risk using a tiered risk and management action framework (Section 2.2). This risk-based framework guides future monitoring proposals for each of these contaminants (Section 3.0), the results of which may provide key data to update initial evaluations of potential risk. Second, the RMP reviews 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 organisms (Section 5.1), the other to establish a bioassay useful for identifying presence of contaminants with 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.

Table 1. The California State Panel's monitoring recommendations for CECs in Coastal Embayments and the associated RMP Strategy.

Recommendations for Surface Waters	RMP Strategy
17-beta estradiol (hormone)	Address through implementation of bioanalytical tools.
Estrone (hormone)	Address through implementation of bioanalytical tools.
Bisphenol A (PPCP*)	Not detected (ND) in Bay samples; however, detection limit was high. Use method with lower detection limit when monitoring again. Address through implementation of bioanalytical tools.
HHCB - Galaxolide (PPCP*)	Detected in pooled Bay samples from 1999-2000 and in later Bay POCIS passive sampling study. Special study of PPCPs under consideration.
Bifenthrin (pesticide)	Hydrophobic compound; based on Bay sediment concentrations, expect ND in water. Monitor stormwater.
Permethrin (pesticide)	Hydrophobic compound; based on Bay sediment concentrations, expect ND in water. Monitor stormwater.
Chlorpyrifos (pesticide)	Legacy contaminant; monitored in water as part of S&T. Low levels detected in the Bay. Not considered a CEC in the Bay (intensively studied when use was higher in the 1990s).
Fipronil (pesticide)**	Monitor fipronil and its degradates in Bay as part of special studies focusing on areas where the highest sediment concentrations have been found.
Recommendations for Sediments	**RMP Strategy**
Bifenthrin (pesticide)	Monitored in sediment as part of S&T since 2008; low levels detected. Also addressed by sediment toxicity testing.
Permethrin (pesticide)	Monitored in sediment as part of S&T since 2008; low levels detected. Also addressed by sediment toxicity testing.
BDE-47, 99 (flame retardants)	Monitored in sediment as part of S&T since 2002.
PFOS (PFAS*)	Monitored as part of special studies. Consult with ECWG regarding incorporation into S&T sediment monitoring.
Fipronil (pesticide)**	Fipronil and its degradates monitored in sediment as part of S&T since 2009; possible increasing concentration trend.
Recommendations for Tissue	**RMP Strategy**
BDE-47, 99 (flame retardants)	Monitored in bivalves, cormorant and tern eggs, sport fish as part of S&T. Also monitored in seals.

PFOS (PFAS*)	Monitored in cormorant eggs as part of S&T since 2006. Consider incorporating into other S&T studies and/or special studies (e.g., seals).

*PPCP=pharmaceutical and personal care product; PFAS=perfluoroalkyl substance
** Fipronil added during Advisory Panel Meeting – State of California Pilot Study: Monitoring Constituents of Emerging Concern (CECs) in Aquatic Ecosystems. September 12-13, 2013: Costa Mesa, CA.

2.2 The RMP's Tiered Risk and Management Action Framework

For those CECs for which monitoring in Bay water, sediment, stormwater runoff, or wildlife 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 degree of concern associated with a particular chemical or chemical class guides both RMP monitoring and management actions. The RMP assigned each CEC or CEC class to a tier in the program's risk and management action framework, based on available Bay occurrence data and toxicity information (framework in Table 2; CEC tier assignments in Table 3). The criteria listed below were used for placement in each tier.

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

Tier II (Low Concern) – Bay occurrence data or PECs 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 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 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}, the effect concentration where 10% of the population exhibit a response or another effects threshold).

The assignments for established CECs that have been monitored in the Bay are provided in Table 3. 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 continually updated as new information on the potential risk of the CEC becomes available.

Table 2. The Conceptual Tiered Risk and Management Action Framework for San Francisco Bay. The framework is based on the framework proposed by a statewide work group in 2009 for prioritizing and monitoring CECs (California Ocean Protection Council et al. 2009).

Risk Level Description	**Monitoring Strategy**	**Water Quality Management Actions**
Tier I (Possible Concern) – Potential for concerns or uncertainty in measured or predicted 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 runoff.	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.
Tier II (Low Concern) – Bay occurrence data or predicted environmental concentrations suggest a high probability of no effect on Bay wildlife.	Discontinue or conduct periodic screening level monitoring in water, sediment, or biota. Periodic screening level monitoring for chemical(s) detected in wastewater or runoff to track trends.	Low-cost source identification and control. Low-level pollution prevention. Track product use and market trends.
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, and sources, pathways, and loadings.	Action plan/strategy. Aggressive pollution prevention. Low-cost control/treatment 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.

*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 or predicted 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: The State Panel also recommended conducting investigations using non-targeted methods to identify unmonitored CECs. These methods include chemical screening and development of bioanalytical tools.

    - Non-targeted chemical screening: The RMP initiated non-targeted screening analyses of Bay mussels and harbor seals in 2010 in collaboration with the National Institute of Standards and Technology (NIST) and other researchers. 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 this ongoing study is provided in Section 5.1.

Table 3. Current status of CECs in the tiered risk and management action framework for San Francisco Bay. (See Section 2.2)

Management Tier	**Compound(s)**	**Rationale**
Tier III: Moderate Concern	PFOS	Bird egg concentrations have been greater than PNEC, high concentrations in seal blood, high volume use of precursors
	Fipronil	May be above toxicity thresholds at some sites for calculated pore water concentrations, need better ambient data and/or toxicity thresholds for sediment matrices to better assess risk
	Nonylphenols, Nonylphenol ethoxylates	Bay concentrations below most toxicity thresholds, possible impacts on larval barnacle settlement, possible synergistic effects with pyrethroids, high volume use, estrogenic activity
	PBDEs	Detected in Bay wildlife, toxicity in mammalian models, bird egg concentrations below toxicity threshold, sport fish concentrations below CA fish contaminant goal, possible immune system impacts on fish, possible blood impacts on seals, use declining
Tier II: Low Concern	Pyrethroids	Detected infrequently and in low concentrations in Bay sediment; of concern in watersheds, tributary sediment concentrations comparable or higher than toxicity thresholds, toxic at low concentrations, high volume use
	Pharmaceuticals, Personal care product ingredients*	Concentrations below toxicity thresholds, toxicity to aquatic species sufficiently characterized
	HBCD	Concentrations are low; likely reduction in use
	PBDD/Fs	Low concentrations; synthetic sources declining with PBDE phase-out

Tier I: Possible Concern	Alternative Flame Retardants (BEH-TEBP, EH-TBB, DBDPE, PBEB, BTBPE, HBB, DP, TDCPP, TCEP, TCPP, TBEP, TPhP, other organophosphates)	Detection of some in sediments or bird eggs, toxicity for some in mammalian models, limited toxicity data for aquatic species, high volume use or 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 the specific chemical)
	Butylbenzyl phthalate	Sediment concentrations greater than low apparent effects threshold (but threshold not directly linked to the specific chemical or effects in macrobenthos)
	PFASs other than PFOS	Detection of some compounds, possible impacts to marine mammals from PFOA, toxicity to aquatic species not sufficiently characterized
	Short-chain chlorinated paraffins	Concentrations below toxicity thresholds, uncertainties in toxicity data, high volume use
	Other pesticides**	Concentrations below toxicity thresholds, uncertainty in toxicity to Bay wildlife
	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

**For full list of pesticides considered in this classification see Klosterhaus et al. 2013a, Appendix Table B6. The RMP is evaluating current use agricultural pesticides applied in the Bay Area.

- Bioanalytical screening assays: The State Panel also recommended a shift away from a chemical-specific monitoring paradigm to one in which biological responses are measured to address the thousands of chemicals that are potentially present in receiving waters. Existing bioanalytical tools show promise but 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. The RMP sponsored a study starting in 2013 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 ongoing study is provided in Section 5.2.

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), summarizes the outcomes of RMP efforts to identify new candidates for monitoring to date. 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 3).

3.0 The RMP CEC Risk Framework and Monitoring Recommendations

The tiered risk and management action framework prioritizes chemical-specific monitoring activities that will likely improve the evaluation of CEC risks to the Bay. Monitoring strategies for addressing individual CECs or CEC classes, grouped by relative risk assigned via the tiered framework, are outlined below. Also described are plans for initial monitoring of newly identified CECs for which levels in Bay media and wildlife are unavailable, a data gap that prevents assignment to a tier within the risk-based framework.

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 should be given a high priority. Regular monitoring of all relevant matrices as part of Status and Trends work is recommended. In some cases, studies to elucidate the fate, effects, and sources, pathways, and loadings of Tier III CECs may be needed.

- PFOS: As part of a series of special studies, PFOS has been monitored in Bay sediments, ambient water, storm water runoff, sport fish, small fish, bivalves and harbor seals. In addition, the RMP has monitored PFOS in bird eggs triennially since 2006. In 2006 and 2009, concentrations of PFOS in bird eggs from the South Bay were above a PNEC of 1,000 ng/mL (Newsted et al. 2005); however, the most recent sampling in 2012 found a lower average concentration of 385 ng/g (1 gram is approximately equivalent to 1 mL). Currently unknown attributes of bird biology, including temporal variations in foraging behavior, may be a factor in the observed decline. Conversely, concentrations of PFOS in seal blood have remained relatively constant over time. Similar to birds, the highest concentrations have been 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. Concentrations of PFOS in Bay sediments, ambient water, and storm water are in the range of concentrations observed in urbanized locations nationally. The RMP is focused on identifying possible sources of PFOS to the Bay and is currently conducting a pro bono study to monitor PFOS, PFOA, and their precursors in effluent and Bay sediment. It has been well established that 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). Similarly the fluorotelomer alcohols, sulfonates, and polymers may be converted into PFOA (Houtz and Sedlak 2012). In a study of San Francisco Bay sediment, researchers at Stanford University found concentrations of the precursors that were of the same magnitude as PFOS, suggesting that the precursors may be a significant source to the Bay (Higgins et al 2005). Similarly, researchers at University of California at Berkeley (Houtz and Sedlak 2012) observed that precursors could be responsible for an additional 70% of the PFAS's load. In addition to this special study, we recommend that the following matrices continue to be monitored for PFOS, as well as a dozen other PFASs measured simultaneously by the analytical laboratory at no additional charge: stormwater, bird eggs, harbor seals, and a subset of RMP Status and Trends water and sediment samples (e.g., 10 samples distributed throughout the Bay). PFASs were infrequently detected in bivalves and sport fish.

- Fipronil: Fipronil is a phenylpyrazole pesticide that is widely used in urban environments to control fire ants, fleas, and ticks. As an alternative to pyrethroids, the use of fipronil has increased dramatically in the last decade; it has tripled in sales in California since 2003 to 18,000 kilograms annually (CDPR 2013). It is present in the environment as fipronil, as well as its degradates, 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 invertebrates (Ensminger et al. 2013; USEPA 2013b). The RMP has been routinely monitoring fipronil and its degradates in Bay sediment since 2009, and the concentrations suggest an increasing trend. Concentrations of fipronil and its degradates ranged as high as 0.56 ng/g for fipronil sulfone in a Lower South Bay sample; with approximately 1% organic carbon (OC) in that sample, the reported maximum organic carbon normalized 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). One laboratory study found reduced reproduction in a saltwater benthic crustacean with addition of 30 ng/g to sediment (Chandler et al. 2004). It is recommended that the RMP continue to monitor Bay sediment and watershed tributary water for fipronil, as well as expanding the monitoring on a pilot basis to evaluate ambient Bay waters. Currently concentrations of fipronil products are near the limits of detection in tributary water samples, so initial monitoring in the ambient Bay will focus on areas where the highest sediment concentrations have been found. In addition, given that most of the expected uses and sources originate from land, if an RMP margins sampling program is developed, fipronil should be included in the target analyte list.

- Nonylphenols (NPs), Nonylphenol Ethoxylates (NPEs): NPs and mono- and diethoxylates NP1EO and NP2EO have been detected in Bay samples. In surface waters, NP concentrations were less than 100 ng/L, and NP1EO and NP2EO have not been detected. In sediment, NPs, NP1EO and NP2EO were all consistently detected at moderately high concentrations, including a median of 35 ng/g dry weight for NPs. In transplanted mussels, detection of these contaminants was sporadic, but the maximum concentrations of NPs, NP1EO and NP2EO – 1,290, 300, and 1,420 ng/g dry weight, respectively – were high relative to other contaminants detected in these bivalves. Maximum concentrations of NPs, 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 that are found in Bay mussels. 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). At this time, the State Panel report does not recommend monitoring for NPs in estuaries (Anderson et al. 2012) nor are they included on Oregon or Washington priority lists (see Section 4.2).

  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 estrogenic, and a breakdown product of NPEs. 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 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 and NPEs resulted in significantly greater production of vitellogenin, an egg yolk precursor protein, in adult male Japanese medaka (*Oryzias latipes*) in *in vivo* exposures, and 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").

To address the concern of additive or synergistic estrogenicity, the RMP plans to evaluate the contribution NPs makes toward the overall estrogenicity of wastewater treatment plant effluent and Bay waters using the bioanalytical screening tool in development (Section 5.2). Once the *in vitro* bioassay has been validated using specific estrogenic CECs like NPs, it will be used to assess the estrogenicity of effluent and ambient water samples, the role of NP and NPE contamination, and the need for further study.

- PBDEs: 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. RMP data on PBDEs have been summarized in a recent report, and suggest risks may have declined substantially from the first identification of these chemicals in the Bay (Yee et al. 2013). Concentrations of these contaminants 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). A toxicity study sponsored by the RMP suggests current PBDE levels are unlikely to pose 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 (Yee et al. 2013).

  However, current levels of PBDEs may pose risks to harbor seals (Neale et al. 2005), especially pups experiencing fasts after weaning (Greig et al. 2011). 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. 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). In Bay sediment, 37% of samples exceeded 0.5 ng/g BDE-47, while one Bay sample and two Bay margin "hot spot" samples exceeded 3.0 ng/g BDE-47. The high frequency of Bay sediment BDE-47 levels between these values suggests the potential for low level adverse effects to benthic organisms.

Despite the declining levels in biota and the reduced concern with respect to sport fish consumption and adverse effects in bird populations, the potential for low-level risks for seals, fish, and benthic organisms led to the classification of PBDEs as Tier III (Moderate Concern).

Continued monitoring of Bay sport fish (on a five-year cycle), cormorant and tern eggs (triennially), and bivalves (biennially) is recommended to track expected declines in Bay biota in response to bans and phase-outs of PBDEs. A seal monitoring study has been approved for 2014. Continued biennial monitoring of sediment is also recommended, as the phase-out of DecaBDE, source of the dominant sediment congener BDE-209, will not be complete until the end of this year, and many previously manufactured products containing PBDEs are still in use today. It may also be valuable to track sediment PBDE contamination relative to contamination with alternative flame retardants (Section 4.1). Because water measurements have not provided valuable information beyond that provided by other indicators, monitoring of PBDEs in water has been reduced to once every four years and could be eliminated.

3.3 Tier II (Low Concern) Monitoring Recommendations

Tier II CECs include pyrethroid pesticides, the alternative flame retardant hexabromocyclododecane (HBCD), pharmaceuticals and personal care product ingredients (PPCPs; compounds listed in Klosterhaus et al. 2013a), and polybrominated dioxins and furans (PBDD/Fs). Existing data for these compounds suggest the possibility of low-level effects on Bay wildlife (e.g., detection at concentrations that may be comparable to some effects threshold(s) but well below other effects thresholds). For compounds of low concern, periodic special studies to monitor those Bay matrices (water, sediment, biota, effluent and stormwater) most relevant to the CEC's chemistry and potential impacts are recommended, in conjunction with RMP Status and Trends work.

- Pyrethroids: Pyrethroids are neurotoxic insecticides currently applied in high volumes in California. 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 in 2008 and 2010. Stormwater 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 have been assigned to Tier II (Low Concern) for the Bay because they are detected infrequently in sediment, and when detected, are at concentrations well below established LOECs. In contrast, sediment and stormwater samples from tributaries contain levels comparable to or higher than toxicity thresholds, reflecting their high volume use and toxicity at low concentrations. Continued biennial monitoring in Bay sediment is recommended to verify that recent regulatory restrictions implemented by the California Department of Pesticide Regulation have resulted in lower levels of contamination. Monitoring a subset of sediment sites may be sufficient for this purpose. Pyrethroid monitoring in surface waters is not recommended as concentrations are not likely to be high. Pyrethroids remain a high concern for the surrounding watersheds, where monitoring is ongoing.

- HBCD: This brominated flame retardant has been detected in Bay sediment at total concentrations ranging from 0.1 to 2 ng/g dry weight (median 0.3 ng/g dry weight). 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). These 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). In fact, HBCD is generally not considered acutely toxic to aquatic life due to the compound's low solubility (Marvin et al. 2011). HBCD is a high production volume chemical; however, reductions in use may be forthcoming 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 monitoring is not considered a priority for the Bay.

- PPCPs: 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. 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 or stormwater outfalls in the Bay may exhibit higher concentrations and an increased likelihood of impacts.

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). 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). Development of a proposal to monitor a new set of PPCPs not previously investigated in the Bay is a recommended activity for 2015.

Some PPCPs can induce estrogenic effects in wildlife. The RMP is working to develop bioanalytical screening tools to identify estrogenic compounds in wastewater treatment plant effluent and ambient Bay water samples (Section 5.2). These tools may play a key role in identifying individual PPCPs that merit more focused study, and will also allow a more general assessment of the aggregate estrogenicity of real-world exposures to PPCP mixtures. The RMP recommends revisiting this CEC class in 2015, after completing testing of these bioanalytical tools, at which point a new monitoring proposal may be warranted.

- PBDD/Fs: 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. Additionally, 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, but some biologically produced forms will likely continue to be present. At present, there is no plan to continue monitoring these compounds in the Bay.

3.4 Tier I (Possible Concern) Monitoring Recommendations

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 (BEH-TBP, EH-TBB, DBDPE, PBEB, BTBPE, HBB, DP, TDCPP, TCEP, TCPP, TBEP, TPhP, other organophosphates): Several non-PBDE flame retardants have been detected in Bay samples (Table 4), but with the exception of some organophosphate compounds in sediment, they have been detected at concentrations at least one order of magnitude lower than PBDEs. Non-PBDE flame retardants detected in Bay wildlife include hexabromocyclododecane (HBCD), Dechlorane Plus (DP), pentabromoethylbenzene (PBEB), tris(1-chloropropyl) phosphate (TCPP), tris(2-chloroethyl)phosphate (TCEP), tris(2-butoxyethyl)phosphate (TBEP), and triphenylphosphate (TPhP). Bis(2,4,6 tribromophenoxy) ethane (BTBPE) was detected in Bay sediment but not biota. Brominated flame retardants that were analyzed but not detected in Bay samples were BEH-TBP and EH-TBB (or TBPH and TBB, the brominated components of the PentaBDE replacement commercial mixture, Firemaster 550), decabromodiphenylethane (DBDPE, a Deca-BDE replacement), and hexabromobenzene (HBB). The organophosphates 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. Several other organophosphate flame retardants were analyzed in cormorant eggs but were not detected (tripropylphosphate, tris(2,3-dibromopropyl) phosphate, tributyl phosphate (TBP), tricresyl phosphate, 2-ethylhexyl-diphenyl phosphate, tris(2-bromo-4-methylphenyl) phosphate, tris(2-ethylhexyl) phosphate (TEHP)). It is hypothesized that some of these may be taken up by aquatic organisms (e.g., TDCPP) but are easily metabolized.

Table 4. Summary of existing data on alternative flame retardants in San Francisco Bay.

+ indicates previous detection; - indicates previous non-detection

Alternative Flame Retardants	Water*	Sediment	Mussels	Sport Fish	Bird Eggs	Seals
HBCD		+	+	+	+	+
Dechlorane Plus (DP)		+	+	+	+	+
PBEB		+	+	-	-	+
DBDPE		-				
BTBPE		+	-	-	-	-
HBB		-	-	-	-	-
BEH-TBP**		-	-		-	
EH-TBB**		-	-	-	-	-
TDCPP or Chlorinated Tris	+	+	-		-	
TCPP	+	+	-		+	
TPhP	+	+	+		-	
TCEP	+				+	
TBP	+				-	
TBEP	-				+	
TEHP	-				-	
TPrP					-	
Tris(2,3-dibromopropyl) phosphate, Tricresyl phosphate, 2-Ethylhexyl-diphenyl phosphate, Tris(2-bromo-4-methylphenyl) phosphate					-	

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

In addition to quantitative measurements, passive water samplers (POCIS) deployed by RMP as part of the NOAA Mussel Watch Contaminants of Emerging Concern (CECs) Early Warning Network: California Pilot Project indicated the presence of several organophosphate flame retardants in San Francisco Bay waters: TCPP, TDCPP, TCEP, TBP, and TPhP (Klosterhaus et al. 2013a). TBEP and TEHP were not detected. Dozens of additional flame retardants have never been the subject of Bay monitoring efforts.

A proposal to conduct monitoring in 2014 for a select group of alternative flame retardants in relevant Bay matrices has been approved. Suggested matrices include water, appropriate for water-soluble, phosphate flame retardants; sediment, a sink for hydrophobic compounds; bivalves, filter feeders known to accumulate organic contaminants; harbor seals, top predators with tissues that will indicate which compounds will bioaccumulate; and stormwater and wastewater treatment plant effluent, useful for determining pathways of contamination. Selection of the flame retardants and matrices to investigate will be informed by a variety of factors, including chemical information on fate and transport, previous monitoring data, production and use trends, and availability of affordable analytical methods. Some of the flame retardants identified will be part of the existing Tier I group described above, while others will be newly identified CECs. A few potential candidates for study include:

- TDCPP, TCPP, and TPhP in sediment – Previous monitoring has indicated levels comparable to PBDEs in sediment samples, suggesting periodic monitoring to assess temporal trends in concentration would be appropriate. Lower concentrations in wildlife are consistent with the hypothesis that organisms are able to metabolize and excrete these compounds; monitoring of biota is considered a lower priority.

- PBEB, HBB, BTBPE, DBDPE in sediment and biota – AXYS Analytical currently offers semi-quantitative analysis of these compounds as part of its regular PBDE analysis. Obtaining measurements of these alternative flame retardants on a subset of samples already intended for PBDE analysis may be particularly cost-effective. BTBPE and DBDPE were identified by Howard and Muir (2010) as good candidates for environmental monitoring based on predicted persistence and bioaccumulative potential. However, in previous monitoring, DBDPE and HBB were not detected in Bay samples.

  - BEH-TBP and EH-TBB (or TBPH and TBB, brominated components of Firemaster 550) in sediment and biota – These compounds were not detected in previous monitoring, but it was suggested that matrix interference compromised the measurements (Klosterhaus et al. 2012). Should analytical improvements be available, it would be useful to conduct a second round of monitoring.

  - Ethylene bis-tetrabromophthalidimide (EBTEBPI) in sediment and biota – This compound was identified by Howard and Muir (2010) as a likely candidate for monitoring based on predictions of its persistence and bioaccumulative potential. It is a high production volume chemical and an alternative for DecaBDE, which is being phased out this year. AXYS Analytical will be developing capabilities for alternative flame retardant analysis in 2013, and has identified this chemical as a likely candidate for methodological development.

  - 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH or DBE-DBCH) in sediment and biota – This flame retardant was also identified by Howard and Muir (2010) as a likely candidate for monitoring based on predictions of its persistence and bioaccumulative potential. It has been detected in Arctic wildlife (Tomy et al. 2008) and causes reproductive toxicity in American kestrels (Marteinson et al. 2012b). TBECH has also been identified as an androgen agonist (Larsson et al. 2006). However, no effects on plasma sex hormones were observed in exposed juvenile brown trout (Gemmill et al. 2011); instead, TBECH was found to modulate the thyroid axis in these fish at environmentally relevant concentrations (Park et al. 2011). AXYS Analytical will be developing capabilities for alternative flame retardant analysis in 2013, and has identified this chemical as a likely candidate for methodological development.

- <u>Bisphenol A</u> (BPA): Bay studies on BPA to date have been limited and have had high detection limits. Use of a method with lower detection limits is being explored. BPA is one of the chemicals being assessed as part of the RMP effort to develop a bioanalytical tool to identify estrogenic activity (Section 5.2).

- Bis(2-ethylhexyl) Phthalate (BEHP or DEHP) and Butylbenzyl Phthalate (BBzP): Bis(2-ethylhexyl) phthalate and butylbenzyl phthalate were detected above sediment low apparent effects threshold (LAET) and high apparent effects threshold (HAET) values; 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. Monitoring for these CECs is a low priority given the existence of a reasonable amount of monitoring data for the Bay.

- Poly- and Perfluorinated Compounds (PFASs) other than PFOS: Perfluorinated chemicals comprise a large and very diverse class of compounds. A pro bono study is underway that would evaluate perfluorinated sulfonates, perfluorinated carboxylates, and perfluorinated precursors in effluent and Bay sediment. The precursors include the perfluoroctane sulfonamides (FOSAMs) and the perfluorooctane sulfonamidoethanol-based phosphates (SAmPAP) esters that have been shown to degrade to PFOS and the fluorotelomer alcohols that have been shown to degrade to PFOA. Recent studies suggest that PFAS precursors may be present in Bay stormwater and sediment in concentrations on par with PFOS and PFOA (Higgins et al. 2005; Houtz and Sedlak 2012). This work will help to identify sources of PFOS, which is a Tier III CEC. In addition, with the phase out of PFOS, PFOA and other C8 fluorinated compounds, it will be important to assure that other perfluorinated substitutes are not accumulating. The RMP will continue to evaluate the PFC literature to identify strategic studies for San Francisco Bay.

- Short-chain Chlorinated Paraffins (SCCP, C_{10}-C_{13} congeners): Relatively low concentrations of these compounds have been detected in sediment and biota. 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). 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. Medium- and long-chain chlorinated paraffins have not been the subject of monitoring studies in the Bay.

- Other Pesticides: The RMP has begun a study using California Department of Pesticide Regulation records to examine agricultural pesticide applications that drain directly to the Bay. The results of this analysis will allow identification and prioritization of current use pesticides of emerging concern that are not already the subject of focused, local monitoring or management actions. A proposal to monitor select pesticides in the Bay will be developed based on the forthcoming analysis.

- Single-walled Carbon Nanotubes (SWNT): These nanomaterials were not detected in any Bay sediment or mussel samples analyzed. To our knowledge, SWNT have not been analyzed in environmental matrices from other locations, 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.

4.0 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.

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. Perhaps 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; Howard and Muir 2011). In a recent publication, 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 as well as toxicology models were used to predict the behavior of these compounds in the environment and their potential for bioaccumulation and toxicity. In addition to the models, expert judgment was used to evaluate the compounds such as the rule of thumb that persistent chemicals tend to be highly halogenated, highly branched, and nitroaromatic whereas bioaccumulative substances tend to have log octanol-water partition coefficients great than three. Compounds with log octanol-water partition coefficients greater than eight were reviewed individually; bioaccumulation tends to decrease in compounds with log octanol-water partition coefficients great than six (Howard and Muir 2010). Compounds with high molecular weights were not considered bioaccumulative.

Based on this review, Howard and Muir identified 610 CECs to be monitored. Some of these compounds have been relatively well studied such as the polychlorinated biphenyls, the polybrominated biphenyls, PBDEs, and PFOS and were not the focus of the review. Instead 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. The Appendix summarizes these results and indicates chemicals that the RMP should consider for future study.

Top journals are regularly reviewed as another means of identifying potential monitoring targets. Broader review of the literature may be guided by themes relating to functional class in commerce, such as alternative flame retardants or PPCPs. Finally, active solicitation of new ideas from external experts can reveal additional contaminants worthy of study, as well as opportunities for collaboration.

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.

Southern California: The Southern California Coastal Water Research Project (SCCWRP) has endorsed a CEC monitoring strategy recommended by the Science Advisory Panel for CECs convened on behalf of the California Water Resources Control Board (Anderson et al. 2012), as mentioned previously. This strategy targets specific chemicals for monitoring based on estimated risk to ecosystem health in three general types of waterways – inland river, coastal embayment, and open ocean. In addition, the strategy calls for development of bioanalytical monitoring tools to screen for known and unknown contaminants based on mode of action. For the Bay discharge scenario, the Panel recommended monitoring seven different CECs in Bay receiving waters, including pesticides (bifenthrin, permethrin, chlorpyrifos), chemicals associated with consumer products (bisphenol A, galaxolide), and natural hormones (17β-estradiol, estrone). To characterize the source contribution, the seven CECs above were recommended for monitoring in treated municipal wastewater effluent and at locations currently receiving stormwater runoff. For Bay sediment, the two flame retardants (BDE-47, BDE-99) and two pyrethroids (bifenthrin, permethrin) were prioritized for monitoring. In biological tissues, the group is prioritizing monitoring of PBDEs and PFOS. SCCWRP is currently working with the State Water Board to develop a statewide monitoring effort, incorporating regional monitoring already being performed (e.g., as part of the Southern California Bight Survey and the RMP) to implement these recommendations.

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 May 2013, includes a dozens of CECs within the following classes: PFASs, 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 2013). 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, 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 sulfonates (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.

4.3 New 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 additional study:

- PPCPs – A number of additional drugs (e.g., oxazepam) and fragrance ingredients (e.g., musks) have been identified in the scientific literature or prioritized for monitoring by state agencies for persistence, bioaccumulation, and/or toxicity. These newly identified compounds may become part of a study proposal, to be developed in 2015, to monitor the Bay for a broader set of PPCP compounds.

- Alternative Flame Retardants – Howard and Muir (2010) and others have identified a number of different non-PBDE flame retardants with potential to persist and bioaccumulate in the environment. Some of these may prove to be good candidates for study in Bay matrices, as outlined previously (Section 4.4).

- Tetrabromobisphenol A (TBBPA) is a high production volume flame retardant highlighted by Howard and Muir (2010) and included on Oregon and Washington lists of water contaminants of concern (Washington 2006; Mullane et al. 2009). However, because TBBPA is most often used as a reactive flame retardant, detections in the environment are low (Covaci et al. 2009). The TBBPA that does escape into the environment may also degrade to BPA under anaerobic conditions (e.g., Voordeckers et al. 2002). Therefore, monitoring for TBBPA is not recommended; however, BPA monitoring may be useful for probing the aggregate contamination possibly resulting from both BPA and TBBPA sources.

5.0 Non-targeted Monitoring Approaches to CEC Identification

Using the chemical-specific, targeted monitoring paradigm described in Section 4.0, the RMP has identified individual compounds to monitor in the Bay based on toxicity, persistence and potential for bioaccumulation; however, given the sheer number of chemicals in commerce and limited resources (both time and money), it will not be possible for the Program to monitor every chemical with potential concerns individually. As a result, the RMP is seeking to identify

CECs through two alternative methods: broadscan screening, in which compounds that are accumulating in biota are identified, and bioassays. The RMP is currently completing a two-year broadscan study of compounds accumulating in San Francisco Bay bivalve and seal tissues. In 2013, The RMP will begin a two-year study of classes of compounds acting through a common mode of action (e.g., endocrine disruption) that may cause adverse impacts to organisms.

5.1 Non-targeted Screening

Investigations using non-targeted analysis to screen for newly discharged CECs are useful for creating an inventory of bioaccumulative compounds in tissues or compounds present in abiotic matrices (e.g., sediment, wastewater). Findings from such investigations can be used to direct targeted chemical monitoring or toxicity identification evaluations.

In 2010, the RMP initiated non-targeted screening analyses of San Francisco Bay harbor seal and mussel samples in collaboration with the National Institute of Standards and Technology (NIST) and other researchers. The primary method for sample analysis is two-dimensional gas chromatography (GCxGC) time-of-flight (TOF) mass spectrometry (GCxGC TOF/MS). The instrument being used for this work, the LECO Pegasus 4D GCxGC TOF/MS (LECO St. Joseph, MI), has a unique capability to separate chemicals of interest from a very complex mixture and identify the chemicals using comprehensive mass spectral libraries. Both fat-soluble (non-polar) and more polar chemical contaminants will be screened for in the samples. As some of the compounds found in Bay organisms will not be present in existing NIST/EPA/NIH mass spectral libraries, NIST scientists are augmenting these libraries with spectra of chemicals identified by Howard and Muir (2010) as likely to be persistent and bioaccumulative, and also considered amenable to gas chromatography analysis.

A list of CECs newly identified in non-polar fractions of Bay seal blubber, then verified and quantified using GC-MS/MS, is presented in Table 5. The majority of compounds selected for confirmation were not confirmed by GC-MS/MS analysis, indicating that false-positive results can easily arise. Confirmed compounds were present at low levels relative to legacy persistent organic pollutants. The full results from this study, including concentrations of each of the compounds identified in both seal and mussel samples, are expected in 2013, after which a proposal for further study may be developed. It would be prudent to consider revisiting using this technique as chemical use changes over time and our analytical abilities improve.

Table 5. Compounds identified in San Francisco Bay seal blubber samples using Broadscan Analyses, then confirmed and quantified (ng/g wet weight).

Sample	2,2'-dichlorobenzil	9,10-dichloroanthracene	dichloro PAH*
Blank	<LOD	<LOD	<LOD
HS10**	0.14	0.83	1.50
6050	1.95	8.78	13.1
2125	3.32	1.29	4.37
2028	1.23	4.88	7.75
2120	1.58	17.8	13.8
2118	3.91	10.5	18.8

* "Dichloro PAH" is a dichloroanthracene compound with unknown chlorine substitution.

** Harbor seal blubber sample from Alaska, NIST Environmental Specimen Bank

5.2 Bioanalytical Screening Assays

Bioanalytical tools are very much in their infancy. Existing tools show promise but 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. The RMP has not previously applied these types of tools to monitoring chemical contaminants in San Francisco Bay.

As a result, the RMP is sponsoring the development of bioanalytical tools for the Bay that will link cellular effects a (e.g., changes in hormones that affect genetic signaling and processing) to organism effects (e.g., growth, reproduction, and survival). The research will be conducted by researchers at University of Florida and SCCWRP. The work will use silversides (*Menidia beryllina*), a model estuarine fish, to evaluate the estrogenic effects of four endocrine disrupting compounds recently recommended for monitoring in California's estuaries by the State's Science Advisory Panel for CECs: estrone (E1), bisphenol A (BPA), 4-nonylphenols (4-NPs), and galaxolide (HHCB).

In year one, the project will identify responsive bioassays that can be correlated to measured effects in fish. There are a few molecular biomarkers already developed for silversides including vitellogenin, ER alpha (esr1), ER beta a (esr3), and androgen receptor (AR), among others. The research group will validate these assays and will develop additional molecular assays for the following genes: IGF-1; StAR; GH; brain aromatase (cyp19b); and two genes involved in testis differentiation, anti-Mullerian hormone (amh) and doublesex and mab-3 related transcription factor 1 (dmrt1). These genes have been determined in studies of other fish to be responsive to estrogens *in vivo*. Traditional *in vivo* endpoints for early life stages of silversides will include: development, growth, and survival and for juveniles: growth, survival, and biochemical endpoints such as plasma vitellogenin and hormone concentrations and hepatic gene expression for at least five genes per life stage.

Exposure experiments will be divided up between the laboratories at the University of Florida and SCCWRP, and each will perform a positive control. Each lab will study the effects of exposure during two life stages: early life and juvenile. The juvenile period occurs just before gonadal differentiation, another window of vulnerability to endocrine disruptors. The groups will also perform histopathology on the gonads to distinguish males from females, and if a sequence for genetic marker is identified, the groups will correlate its expression with the sex of the fish.

Assuming successful completion of year one activities, in year two, fish will be exposed to field collected samples from San Francisco wastewater treatment plants and ambient estuarine waters from the Bay as well as select locations in southern California.

A key strength of this type of bioassay is that it can be used to assess the cumulative effects of exposure to multiple CECs with common modes of action. These tools may prove particularly relevant for identifying potential harm caused to organisms living near outfalls and likely exposed to a variety of estrogenic chemicals at concentrations relatively higher than found in the greater Bay. Identification of especially estrogenic water or effluent samples using these bioassay tools followed by chemical analyses may also reveal estrogenic contaminants that merit chemical-specific monitoring studies.

Long-term plans for use of these tools will be established once they have been shown to be effective means of detecting estrogenicity. Future work could also include developing similar tools that explore other (non-estrogenic) modes of action. 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.

6.0 Conclusion: RMP CEC Research Plan

Assembled below are Status and Trends monitoring and other recommended studies that have grown out of this strategic look at CECs in the Bay, structured as a five-year research plan (Table 6).

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

	2013	2014	2015	2016	2017
Monitoring Strategy for CECs Assigned to Risk and Management Action Tiers (Section 3.0)					
Water	PFASs; Fipronil; Alt. flame retardants		PBDEs; Pesticides (TBD)		
Sediment		PFASs (sources); Fipronil; PBDEs; Pyrethroids; Alt. flame retardants		PBDEs	
Stormwater & Effluent		PFASs; Alt. flame retardants; Pyrethroids (stormwater)			
Bivalves		PBDEs; Alt. flame retardants			PBDEs
Sport Fish		PBDEs			
Bird Eggs			PBDEs; PFASs		
Seals		Alt. flame retardants	PBDEs		
CECs Identified through Review of Literature & Other CEC Monitoring Programs (Section 4.0)					
New info tracking	Alt. flame retardants	Design study on PPCPs not yet examined in the Bay	Ongoing	Ongoing	Ongoing
Non-targeted Approaches to CEC Identification (Section 5.0)					
NIST screening	Identify chemicals	Follow-up monitoring study TBD			
Bioanalytical tools	E1, BPA, 4-NPs, HHCB	Water, effluent testing	Follow-up monitoring study TBD		
Supporting RMP Activities					
Special Studies	CEC Synthesis & Strategy; PBDE Synthesis; Agricultural Pesticide Project				

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Appendix. Top candidates for monitoring according to Howard and Muir (2010).

Top ten brominated compounds

Chemical	Use	Method exists?	RMP Study Proposed?
Tetrabromobisphenol A (TBBPA)	Most widely used flame retardant today. Used in epoxy resins (additive and reactive) and raw material to manufacture other flame retardants. Applications in electronics.	Method available. Has been prioritized by other CEC monitoring programs. No Bay data.	No. Likely degrades to BPA.
1,2,3,4,5-Pentabromo-6-chlorocyclohexane (PBCC)	Flame retardant in polystyrene	Possible method. No environmental data.	
1,3,6,8-Tetrabromopyrene (TBrPy)	Building block for LEDs	Possible method. No environmental data.	
Hexabromocyclododecane (HBCD or HBCDD)	Flame retardant	Low concentrations observed in Bay.	No. Low concentrations, global phase-out underway.
1,2-Dibromo-4-(1,2-Dibromoethyl)-Cyclohexane (β-TBECH or DBE-DBCH)	Flame retardant	Method exists. Detected in Beluga whale blubber.	Yes
Bis(2-ethylhexyl) tetrabromophthalate (BEH-TBP or TBPH)	Flame retardant (component of Firemaster 550), substitute for PentaBDE	Method exists. Not detected in Bay sediments; possible matrix interference for Bay biota.	Yes
1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE)	Flame retardant, substitute for PentaBDE and DecaBDE	Detected in Bay sediment but not in Bay biota.	Yes
1,1'-(Ethane-1,2-diyl)bis(pentabromobenzene) (DBDPE)	Flame retardant, substitute for DecaBDE	Not detected in Bay sediment; compromised results for Bay biota.	Yes
Octabromo-1,3,3-trimethyl-3-phenylindane (OBTMPI or OBIND)	Flame retardant, substitute for DecaBDE	No environmental data.	
Ethylene bis(tetrabromophthalimide) (EBTEBPI)	High production volume flame retardant for high impact polystyrenes, thermoplastic polyesters, polycarbonates. Possible DecaBDE replacement.	Possible method.	Yes

Top ten chlorinated compounds

Chemical	Use	Method exists?	RMP Study Proposed?
Hexachlorocyclopentadiene	Intermediate in production of pesticides (e.g., endosulfan) as well as dyes, resins, flame retardants, plastic, etc.	Yes. Detected in air samples from Great Lakes.	Consider evaluating as part of pesticide studies
Bis-(4-chlorophenyl) sulfone	High production volume chemical that is used to manufacture plastics; also used as an intermediate in pharmaceutical production	Yes. Detected in Great Lake bird eggs.	
Triclocarban	Antimicrobial used in bar soap and other personal care products	Yes. Widely detected in environment. Detected in Bay sediment and mussels, ND in Bay water.	Consider evaluating as part of PPCP studies
Pentachlorothiophenol	Peptizing agent (reduce viscosity) for rubber	Possible method.	
3,5-Dichloro-2,4,6 trifluoropyridine	Pesticide intermediate	Possible method.	Consider evaluating as part of pesticide studies
Dibutyl chlorendate	Reactive flame retardants in plastics	Possible method	No – reactive flame retardants are not as readily released from products as additive flame retardants
Dechlorane Plus	Flame retardant	Yes. Measured in SF Bay at low levels.	Yes
Heptachlorocylcopentene	Pesticide intermediate	Yes.	
Heptachlorocylcopentane		Possible method.	
2-Chloropyridine	Pesticide intermediate	Possible method.	Consider evaluating as part of pesticide studies

Top ten fluorinated compounds

Chemical	Use	Method exists?	RMP Study Proposed?
4-Chloro-3-nitrobenzotrifluoride	Crop protection	Possible method.	
Perfluoroperhydrophenanthrene	Wide applications in electronics industry (e.g., soldering agent for printed circuit boards) as well as used as internal eye fluid in human retina replacements.	Possible method.	
3,4-dichlorobenzotrifluoride	Pesticide/drug intermediate?	Possible method.	Consider evaluating as part of pesticide studies
Bromopentafluorobenzene	Intermediate	Possible method.	
1-Chloro-2,6-dinitro-4-(trifluoromethyl)benzene	Crop protection and intermediate for pesticide and polymers	Possible method.	Consider evaluating as part of pesticide studies
1,3,5-Tris[(3,3,3-trifluoropropyl)methyl]cyclotrisiloxane	Fluorinated cyclic siloxane. Monomer for production of polyfluorosilicones.	Possible method.	
Benzenamine, 3-chloro-2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)	Pesticide intermediate?	Possible method.	Consider evaluating as part of pesticide studies?
2-Chloro-4-trifluoromethyl-3'-acetoxy diphenyl ether	Pesticide intermediate	Possible method.	Consider evaluating as part of pesticide studies
Potassium decafluoro(pentafluoroethyl) cyclohexanesulphonate	Fluorinated product found in consumer products and surface treatment agents	Possible method.	
Perfluoroalkyl (C6-C12) phosphonic acid	Fluorinated product found in consumer products and surface treatment agents	Possible method.	

Top ten silicone-related compounds

Chemical	Use	Method exists?	RMP Study Proposed?
Dodecamethylpentasiloxane	Appears to be used in consumer products such as antiperspirants, deodorants, skincare lotions, cosmetics, etc.	Possible method.	Consider evaluating as part of PPCP studies
Dodecamethylcyclohexasiloxane	Used in personal care products, petroleum processing and laundry detergents, anti-foam agent, lubricant	Yes. Some Great Lakes measurements.	Consider evaluating as part of PPCP studies
Hexadecamethyl heptasiloxane		Method under development.	
Decamethylcyclopentasiloxane (D5)	Extensively studied. Used in personal care products, aerosol products, dry cleaning agent.	Yes. Detected in SF Bay bivalves.	Consider evaluating as part of PPCP studies
Octamethylcyclotetrasiloxane (D4)	Extensively studied. Used widely: preparation of silicon oils, fermentation processes, paper coatings and sizing, food washing solutions, adhesives, etc.	Yes. Detected in SF Bay bivalves.	Consider evaluating as part of PPCP studies
Octadecamethyloctasiloxane		Method under development.	
Phenyltris(trimethylsiloxy)silane		Possible method.	
2,4,6,8 Tetravinyl-2,4,6,8-tetramethylcyclotetrasiloxane		Possible method.	
Trisiloxane	Pesticide adjuvant	Possible method.	Consider evaluating as part of pesticide studies
Heptamethyl-phenyl-cyclotetrasiloxane		Possible method.	

Top ten "other" compounds

Chemical	Use	Method exists?	RMP Study Proposed?
2,4,6-Tri-tert-butylphenol	Used as an intermediate in the manufacture of antioxidants for rubber	Possible method.	
Triphenyl borane	Intermediate in formation of triphenylborane amine compounds that are catalysts for polymerization of acryclic esters	Possible method.	
Galaxolide (HHCB)	Fragrance ingredient used in soaps, detergents, and other personal and home care products	Yes.	Consider evaluating as part of PPCP studies
1,1-Bis(3,4-dimethylphenyl)ethane	Used in electronics/electrical industry?	Possible method.	
Celestolide (ADBI; musk dimethyl indane)	Fragrance ingredient used in soaps, detergents, and other personal and home care products	Yes. Detected in Great Lakes.	Consider evaluating as part of PPCP studies
2-(2H-Benzotriazol-2-yl)-4,6-ditertpentylphenol	Used as UV stabilizer in films, outdoor furniture and clear coat for automobiles	Possible method.	
Traseolide (ATII: musk methyl ketone)	Fragrance ingredient used in soaps, detergents, and other personal and home care products	Yes. Detected in Great Lakes.	Consider evaluating as part of PPCP studies
Diisopropyl-1,1'-biphenyl	Used as a PCB replacement for dielectric fluids in capacitors	Possible method.	
Triphenyl phosphite	Intermediate. Stabilizer for resins, metal scavenger and diluent for epoxy resins.	Possible method.	
Triphenyl phosphine	Widely used in organic synthesis; catalyst for formation of ethylene and propylene	Possible method.	