**Contaminants of Emerging Concern in San Francisco Bay:**

**A Strategy for Future Investigations**

**DRAFT REPORT**

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RMP Contribution xxx

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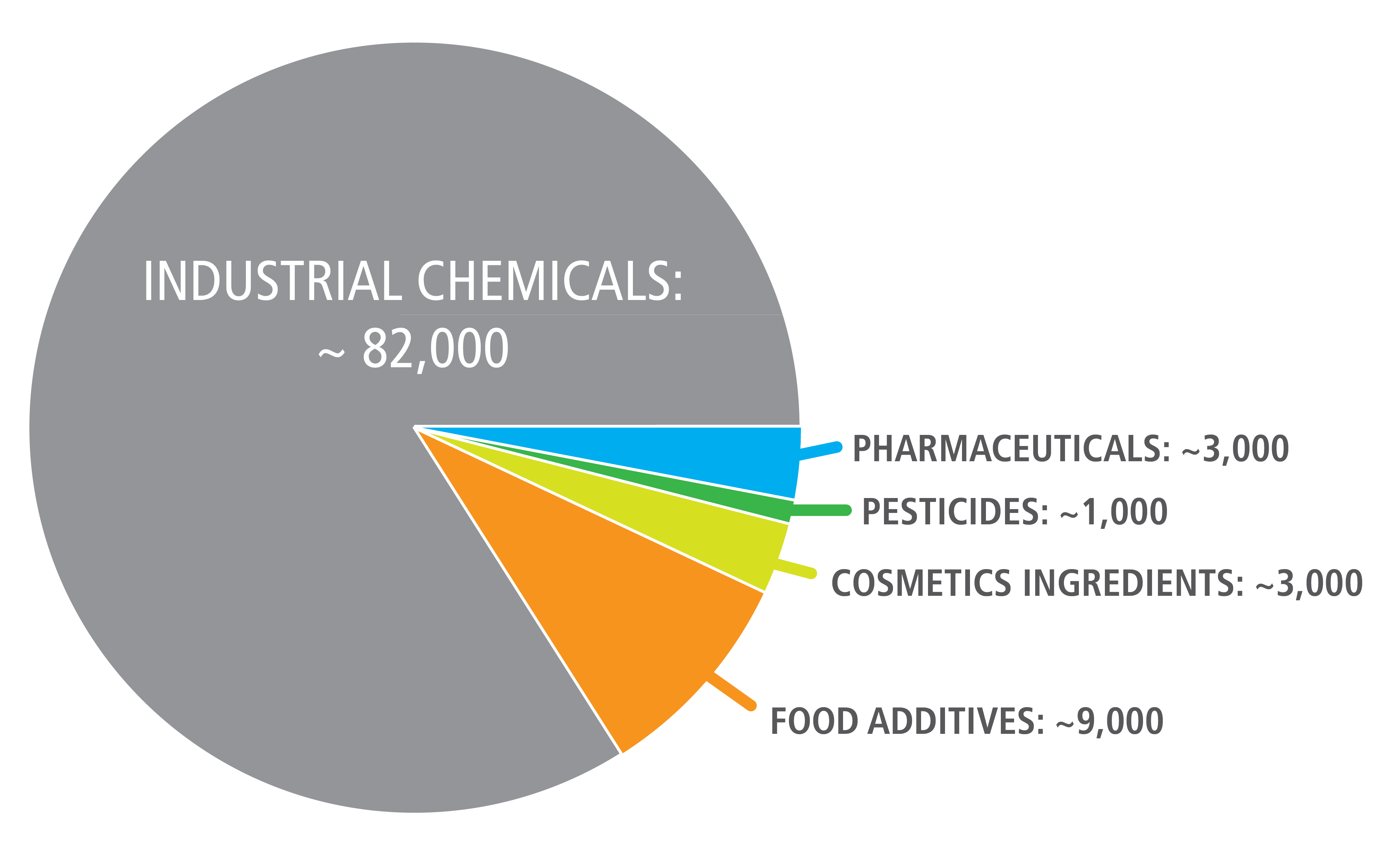
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1. Introduction
   1. The CEC Challenge

Over the past 30 years 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) (Figure 1). For industrial chemicals alone, production and import in the U.S. totaled 27 trillion pounds in 2005, an 80% increase from 2002 (Wilson and Schwarzman 2009). Global chemical production is projected to continue growing by about 3% per year, and double every 24 years. 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).**

Only a very small fraction of the large number of chemicals in use is routinely monitored in the environment. These generally include persistent, bioaccumulative, and toxic compounds such as polychlorinated biphenyls (PCBs), chlorinated pesticides, heavy metals such as mercury, 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 established, and compliance 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 does not routinely occur. As a result, many chemicals that have not been adequately tested for their potential impacts to humans and wildlife are continuously released into the environment.

Over the last decade, researchers and government agencies have begun to collect occurrence, fate, and toxicity data for a variety of chemicals that have not yet been regulated for environmental impacts. Analytical methods have 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 chemicals in the environment. Some of these chemicals have been classified as contaminants of emerging concern (CECs). CECs can be broadly defined as any synthetic or naturally occurring chemical that is not regulated or commonly monitored in the environment but has the potential to enter the environment and cause adverse ecological or human health impacts. Pharmaceuticals and personal care products (PPCPs), current use pesticides, and industrial chemicals such as flame retardants and perfluorinated compounds (PFCs, more recently termed poly- and perfluorinated substances (PFASs)) constitute the majority of chemicals that are commonly considered CECs 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.

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

* The identities of chemicals used in commercial formulations, their applications, and product-specific uses are characterized as confidential business information or are not readily available due to other reasons.
* Methods to reliably measure most chemicals in use do not exist. Development of new analytical methods for new chemicals is expensive, so researchers tend to focus their method development efforts on chemicals deemed to be the highest priority.
* Little to no information exists on chronic toxicity for realistic exposures, toxicity in non-target species (particularly for pharmaceuticals), or sensitive toxicological endpoints such as endocrine disruption. Knowledge of toxic modes of action for most CECs is minimal, and details of toxicity studies conducted by chemical manufacturers are typically not available for public review.

Such large obstacles make it difficult for researchers and regulators to pre-emptively target CECs for monitoring and control. For the vast majority of chemicals in use today, occurrence, persistence, and toxicity data are still needed to establish exposure and risk thresholds to protect the beneficial uses of aquatic ecosystems.

* 1. 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 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 so that potentially problematic chemicals can be identified as early as possible and thus minimize impacts to the Estuary. The ECWG works toward this goal by evaluating available information on chemical occurrence, fate, toxicity, volume use, 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 most comprehensive datasets for CECs in aquatic ecosystems. CECs investigated to date include perfluorinated compounds (PFCs or more recently termed poly- and perfluorinated substances (PFASs)), alkylphenols, more than 100 pharmaceuticals and personal care products (PPCPs), and a variety of flame retardants including polybrominated diphenyl ethers (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. 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 3.0),
  + Outline the current strategy to monitor CECs in the Bay based on the RMP’s evaluation of their relative risk (Section 4.0),
  + Summarize the process for identifying new CECs suitable for initial study based on reviews of the literature and regional lists of prioritized water contaminants (Section 5.0), and
  + Summarize the non-targeted, screening studies now underway to identify additional CECs present in Bay media (Section 6.0).

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.

1. General Approach to Identify and Prioritize CECs
   1. Recommendations from a Science Advisory Panel for Monitoring CECs in California’s Aquatic Ecosystems

To respond to the CEC challenge, the California State Water Resources Control Board assembled a nationally recognized expert panel 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, and ultimately 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 - Summary of CEC Data for San Francisco Bay (Klosterhaus et al. 2013).

In keeping with the State Panel’s approach, the RMP has developed its own 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. The RMP also conducts on-going reviews of the scientific literature and 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 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 data from both internal and external sources.

**Table 1. The California State Panel recommendations for CECs in Coastal Embayments and 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) | ND in Bay samples; however, high detection limits. Need to identify methods with lower detection limits before monitoring again. |
| HHCB - Galaxolide (PPCP\*) | ND in Bay POCIS. Consider special study of fragrances? |
| Bifenthrin (pesticide) | Have monitored since 2009 as part of S&T in sediments; low levels detected. Monitor storm water runoff. |
| Permethrin (pesticide) | Have monitored since 2009 as part of S&T in sediments; low levels detected. Monitor storm water runoff. |
| Chlorpyrifos (pesticide) | Legacy contaminant; monitored in water as part of S&T. Low levels in the Bay. |
| **Recommendations for Sediments** |  |
| Bifenthrin (pesticide) | Monitored in sediment as part of S&T since 2008. |
| Permethrin (pesticide) | Monitored in sediment as part of S&T since 2008. |
| PBDEs 47, 99 (flame retardants) | Monitored in sediment as part of S&T since 2002. |
| PFOS (PFC) | Monitored as part of special studies. Consider incorporating into S&T sediment monitoring. |
| **Recommendations for Tissue** |  |
| PBDEs 47, 99 (flame retardants) | Monitored routinely in bivalves, cormorants and tern eggs, sportfish as part of S&T. |
| PFOS (PFAS\*) | Monitored routinely 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=perfluorinated chemical

* 1. The RMP’s Tiered Risk and Management Action Framework

For those CECs with an established presence in Bay water, sediment, stormwater runoff, or wildlife, and for which relevant toxicity information is 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 its RMP monitoring strategy, as well as appropriate management actions to consider. The RMP assigned each CEC or CEC class to a tier in its 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 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).

**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 EC10, 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 EC10, the effect concentration where 10% of the population exhibit a response or another effects threshold).

**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. |

A CEC is only assigned to a tier in the framework if it has been analyzed in Bay samples or a predicted environmental concentration (PEC) has been estimated. To estimate exposure for the coastal embayment scenario appropriate for San Francisco Bay, PECs were derived from measured environmental concentrations obtained in the effluent-dominated inland waterway scenario with a ten-fold dilution to simulate embayment dilution.

The assignments for established CECs that have been monitored in the Bay are provided in Table 3. 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. The assignments provide guidance to the San Francisco Bay Regional Water Quality Control Board in their consideration of management actions for CECs in the Bay.

* 1. Identifying New CECs as Candidates for Initial Monitoring

The risk-based framework described above requires measured or predicted environmental concentrations to evaluate CECs for concerns relevant to 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 adopted a three-pronged approach to identify potential CECs appropriate for Bay monitoring.

* + Literature reviews and results from other monitoring programs: RMP scientists’ extensive and on-going review of the scientific literature on CECs can uncover additional compounds with potential to impact the Bay ecosystem. In addition, the results of alternative 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 Chemical Screening: The State Panel recommended conducting a pilot investigation using non-targeted analysis to screen for unmonitored CECs. These methods 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

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

|  |  |  |
| --- | --- | --- |
| **Management Tier** | **Compound(s)** | **Rationale** |
| Tier III: Moderate Concern | PFOS | Bird egg concentrations greater than PNEC, high concentrations in seal blood, high volume use of precursors |
| Fipronil | May be above toxicity thresholds at some sites for calculated porewater concentrations, need better ambient data and/or toxicity thresholds for sediment matrices to better assess risk |
| Nonylphenol, | Bay concentrations below most toxicity thresholds, possible impacts on larval barnacle settlement, possible synergistic effects with pyrethroids, high volume use, estrogenic activity |
| Nonylphenolethoxylates |
| Tier II: Low Concern | 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 and behavioral impacts on fish, use declining |
| Pyrethroids | Detected infrequently and in low concentrations in Bay sediments, of concern in watersheds, tributary sediment concentrations comparable or higher than toxicity thresholds, toxic at low concentrations, high volume use |
| Pharmaceuticals, | Concentrations below toxicity thresholds, toxicity to aquatic species sufficiently characterized |
| Personal care product ingredients\* |
| HBCD | Concentrations are low; possible reduction in use |
| Tier I: Possible Concern | Alternative Flame Retardants (TBPH, TBB, DBDPE, PBEB, BTBPE, HBB, DP, TDCPP, TCEP, TCPP, TBEP, TPP 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 | Sediment concentrations comparable to high apparent effects threshold (but threshold not directly linked to specific chemicals) |
| (BEHP or DEHP) |
| Butylbenzyl phthalate | Sediment concentrations greater than low apparent effects threshold (but threshold not directly linked to specific chemicals or effects in macrobenthos) |
| PFCs 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, high volume use |

\*For full list of PPCPs considered to be in this classification see Klosterhaus et al. 2013, Appendix Tables B1 and B2

\*\*For full list of pesticides considered to be in this classification see Klosterhaus et al. 2013, Appendix Table B6. RMP will convene a workshop in 2013 to address current use pesticides.

toxicity identification evaluations. 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. More information on this ongoing study is provided in Section 5.1.

* + 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 has sponsored a study starting in 2013 to develop a bioanalytical tool to evaluate the estrogenicity of four endocrine disrupting compounds (i.e., estrone, bisphenol A, 4-nonylphenol, and galaxolide) as well as ambient estuarine waters from the Bay and effluent from Bay Area wastewater treatment plants. Successful application of this tool may result in identification of specific estrogenic contaminants that merit further investigation. More information on this ongoing study is provided in Section 5.2.

The RMP synthesis document - Summary of CEC Data for San Francisco Bay (Klosterhaus et al. 2013) - 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 of these merits using the tiered risk and management action framework (Table 3).

1. The RMP CEC Monitoring Strategy

The tiered risk and management action framework enables effective prioritization of chemical-specific monitoring activities likely to have the greatest impact in improving 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 suggestions 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. These proposals will be reviewed at the April 2013 Emerging Contaminant Workgroup meeting.

* 1. Tier IV (High Concern) Monitoring Recommendations

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

* 1. Tier III (Moderate Concern) Monitoring Recommendations

Tier III CECs are those for which 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 EC10, 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 adverse effects in combination with other contaminants. Because significant management actions may be prudent for Tier III CECs, studies to inform these actions should be prioritized. Regular monitoring of all relevant matrices as part of Status and Trends work is recommended. In some cases, studies to elucidate the fate, effects, sources, pathways, and loadings of Tier III CECs may be needed.

* 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 in bird eggs from the South Bay were above a PNEC of 1,000 ng/mL ([Newsted et al. 2005](#_ENREF_1)); however, the most recent sampling in 2012 showed a decline in concentration to 385 ng/g (1 gram is approximately equivalent to 1 mL). Conversely, concentrations of PFOS in seal blood have remained relatively constant over time. Similar to birds, the highest concentrations are 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 are 12 ng/mL. Concentrations of PFOS in Bay sediments, ambient water, and storm water are in the range of concentrations observed nationally. The RMP is focused on identifying possible sources of PFOS to the Bay and is currently developing at a study to monitor PFOS, PFOA and their precursors in effluent, storm water (if possible given the lack of precipitation to date) and Bay sediments. 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 degrade in the environment to PFOS (Benskin et al. 2012, Higgins et al. 2005). Similarly the fluorotelomer alcohols, sulfonates, and polymers are known to degrade to PFOA (Houtz and Sedlak 2012). In a study of San Francisco Bay sediments, researchers at Stanford University identified 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 PFASs load. In addition to this special study, we recommend that the following matrices continue to be monitored for PFASs: storm water, water, sediment, bird eggs, and harbor seals. It is recommended that a subset of the RMP Status and Trends water and sediment samples be analyzed for PFASs (e.g., 10 samples distributed throughout the Bay). PFASs were infrequently detected in bivalves and sportfish tissues.
* 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 use in California since 2003 to 18,000 kilograms annually (CDPR 2013). It is present in the environment as fipronil, as well as its degradation products, fipronil sulfide, fipronil sulfone, and desulfinyl fipronil. Fipronil and its degradation products have been detected in Bay watersheds in concentrations that exceed toxicity thresholds (Ensminger et al. 2012; USEPA 2013). The RMP has been routinely monitoring fipronil and its degradates in Bay sediments since 2009, and the concentrations show an increasing trend. Concentrations of fipronil and its degradates in the most recent sampling event in 2012 ranged as high as 2.09 ng/g for the fipronil sulfone for a location in Lower South Bay; with 0.92% organic carbon (OC) in that sample, the reported maximum organic carbon normalized sulfone concentration would exceed 220 ng/g OC, well above the EC 50 (immobilization) for the fresh water species *Chironomus tentans,* which is 40 ng/g OC (Maul et al 2008). There are no available sediment toxicity data for salt water species, but in water, the salt water organism *Americamysis bahia* is more sensitive to fipronil and its degradates than the fresh water organism *Chironomus tentans*, so it might be be expected that saltwater sediment toxicity thresholds would be equal to or lower than those freshwater. It is recommended that the RMP continue to monitor sediments and watershed tributaries for fipronil, as well as expanding the program on a pilot basis to evaluate ambient Bay waters. Currently concentrations of fipronil products are near the limits of detection in tributary samples, so initial monitoring in the ambient Bay will focus on areas where the highest sediment concentrations have been found to date. 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.
* Nonylphenol (NP), Nonylphenol Ethoxylates (NPEs): NP 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 sediments, NP, NP1EO and NP2EO were all consistently detected at moderately high concentrations, including a median of 35 ppb for NP. In mussels, detection of these contaminants was sporadic, but the maximum concentrations of NP, NP1EO and NP2EO of 1,290, 300, and 1,420 ng/g dry weight were high relative to other contaminants that are detected in these bivalves. Maximum concentrations of NP, NP1EO, and NP2EO in resident Bay mussel samples collected in 2010 as part of the statewide Mussel Watch study were lower – 223, 300, and 67 ng/g dry weight, respectively – but still high relative to other contaminants that are found in Bay mussels. In small fish and cormorant eggs, maximum concentrations of NP and NPEs were 420 and 228 ng/g wet weight, respectively, also relatively high compared to other contaminants that accumulate in these species. Concentrations of NP 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 the San Francisco 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 NP in estuaries (Anderson et al 2012) nor is it included in Oregon or Washington priority lists (see Section 4.2).

NP is an estrogenic compound, 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 that have been identified in wastewater effluent. Another 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 vitellogenin production 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.

To address the moderate concerns associated with these compounds, the RMP will evaluate NP for estrogenicity using the bioanalytical screening tool now in development (Section 5.2). Once the bioassay has been validated using specific estrogenic CECs like NP, it will be used to assess the estrogenicity of effluent and ambient water samples, and may provide findings useful in determining the contribution NP makes toward the overall estrogenicity of Bay waters, and the need for further study.

* 1. Tier II (Low Concern) Monitoring Recommendations

Tier II CECs include PBDEs, the alternative flame retardant hexabromocyclododecane (HBCD), pyrethroid pesticides, and pharmaceuticals and personal care product ingredients (PPCPs; listed in Klosterhaus et al. 2013). 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 a compound of low concern, periodic special studies to monitor those Bay matrices (water, sediment, biota, effluent and stormwater) most relevant to its chemistry and concerns are recommended, in conjunction with RMP’s Status and Trends work.

* 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 (Sutton 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, submitted); however, they may pose risks to harbor seals (Neale et al. 2005), especially pups experiencing fasts after weaning (Greig et al. 2011). While PBDE levels in Bay water and sediment have shown little change with time, levels in all Bay species that have been monitored have declined over the last ten years, likely a response to state and federal management actions to ban or phase-out their production and use (Sutton et al. 2013).

The declining levels in biota, together with reduced concern with respect to sport fish consumption and adverse effects in bird populations, led to the classification of these contaminants as Tier II (Low Concern).

Continued monitoring of Bay sport fish (triennially), 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 monitoring study on seals (to be developed) is recommended for 2015. Continued biennial monitoring of sediment is also recommended, as the phase-out of DecaBDE, source of dominant sediment congener BDE-209, will not be complete until the end of this year. 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 have been reduced to once every four years.

* 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. The maximum sediment concentration measured for bifenthrin was 1 ppb, five times lower than the lowest observed effect concentration (LOEC) of 5 ppb (Amweg et al. 2005). The maximum sediment concentration measured for permethrin was 3 ppb, 24 times lower than the LOEC of 73 ppb (Amweg et al. 2005).

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 predicted no effect concentrations (PNECs) of 4 ng/L and 10 ng/L, respectively.

Pyrethroids have been assigned to Tier II (Low Concern) for San Francisco Bay because they are detected infrequently in Bay sediments, 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. 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 ppb (median 0.3 ppb). 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 or lower than those measured in other biota (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. 2012). 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 consideration for addition to the Stockholm Convention list of persistent organic pollutants. For these reasons, HBCD monitoring is not considered a priority for the Bay.
* PPCPs: These chemicals have been analyzed in Bay surface waters, sediments, and mussel tissue. Concentrations of PPCPs in the Bay were typically one or more orders of magnitude lower than those typically reported for sites in freshwater systems, which are often 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 the San Francisco 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 sediments. Addressing these data gaps, along with developing an improved understanding of the potential for impacts due to exposure to the vast number and types of chemicals typically present in urban aquatic environments (i.e., effects of chemical mixtures) are needed to thoroughly assess the risk of PPCPs and other compounds to Bay wildlife. Surface waters and sediments 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.

Many PPCPs can induce estrogenic effects in wildlife. The RMP is working to develop a bioanalytical screening tool to identify estrogenic compounds in effluent and ambient Bay water samples (Section 5.2). This tool will 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 development of this bioanalytical tool, at which point a new monitoring proposal may be warranted.

* 1. 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 recommends special studies to monitor relevant Bay matrices.

* Alternative Flame Retardants (TBPH, TBB, DBDPE, PBEB, BTBPE, HBB, DP, TDCPP, TCEP, TCPP, TBEP, other organophosphates): Several non-PBDE flame retardants have been detected in Bay samples, but with the exception of some organophosphate compounds in sediments, 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), bis(2,4,6 tribromophenoxy) ethane (BTBPE), tris(1-chloropropyl) phosphate (TCPP), tris(2-chloroethyl)phosphate (TCEP), tris(2-butoxyethyl)phosphate (TBEP), and triphenylphosphate (TPP). Brominated flame retardants that were analyzed but not detected in Bay samples were TBB and TBPH (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 TPP have been detected in Bay sediments 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, tricresyl phosphate, 2-ethylhexyl-diphenyl phosphate, tris(2-bromo-4-methylphenyl) phosphate, tris(2-ethylhexyl) phosphate). It is hypothesized that some of these may be taken up aquatic organisms (e.g., TDCPP) but are easily metabolized. Dozens of additional flame retardants have never been the subject of Bay monitoring efforts.

Development of a proposal to conduct monitoring in 2014 for a select group of alternative flame retardants in relevant Bay matrices is recommended. Suggested matrices include sediment, which harbors hydrophobic compounds; bivalves, filter feeders known to accumulate organic contaminants; and harbor seals, top predators with tissues that will indicate which compounds will bioaccumulate. 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 TPP in sediment – Previous monitoring has found levels comparable to PBDEs in sediment samples, suggesting periodic monitoring to assess trends in concentration with time would be appropriate. Lower detections in wildlife are consistent with the hypothesis that organisms are able 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 measurements 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.
* TBB and TBPH (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 (EBTPI) 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) 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. 2011b). 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.
* Bisphenol A (BPA): San Francisco Bay studies on BPA to date have been limited and have had unusually elevated detection limits. Use of a method with lower detection limits is being explored now. 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 sediments 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.
* Per- and Polyfluorinated Compounds (PFASs) other than PFOS: Perfluorinated chemicals comprise a large and very diverse class of compounds. A study for 2014 is proposed which would evaluate perfluorinated sulfonates, perfluorinated carboxylates, and perfluorinated precursors. 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 (C10-C13 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.
* Other Pesticides: The RMP will convene a workgroup meeting of pesticide experts in 2013 to develop a strategy to identify and prioritize 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 workgroup’s recommendations.
* 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.

1. Identification of CECs by Review of Literature and Regional CEC Monitoring Programs
   1. On-going Review of the Scientific Literature on CECs

By the sheer nature of evaluating contaminants of emerging concern, it is important that the scientific literature is routinely reviewed to identify new chemicals, new methods and new collaborators. RMP staff actively read the scientific literature and regularly attend scientific conferences 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 successful and most relevant endeavors is the work conducted by Drs. Muir and Howard (Howard and Muir 2010; Howard and Muir 2006; Howard and Muir 2011). In their most recent work, 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 (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 3. Compounds with log octanol water partition coefficients greater than 8 were reviewed individually; those with high molecular weights were not considered bioaccumulative. In general, bioaccumulation tends to decrease in compounds with log octanol water partition coefficients great than 6 (Howard and Muir, 2010).

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 these chemicals into the top ten brominated, chlorinated, fluorinated, silicone and other class. Table 4 summarizes these results and indicates chemicals that the RMP should consider for future study.

Table 4. Top candidates for monitoring according to Howard and Muir (2010).

|  |  |  |  |
| --- | --- | --- | --- |
| **Chemical** | **Use** | **Method exists?** | **RMP Study Proposed?** |
| **Top Ten Brominated** |  |  |  |
| Tetrabromobisphenol A (TBBPA) | Largest flame retardant in used today. Used in epoxy resins (additive and reactive) and raw material to manufacture other FR. Applications to electronics. | Method available. Has been monitored by other programs. No Bay data. | No. Likely degrades in biota to BPA. |
| 1,2,3,4,5-Pentabromo-6-chlorocyclohexane (PBCC) | Flame retardant in polystrene | 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 and possible phase out of use. |
| 1,2-Dibromo-4-(1,2-Dibromoethyl)-Cyclohexane (β-TBECH) | Flame retardant | Method exist. Detect in Beluga whale blubber. | Yes |
| [bis(2-ethylhexyl) tetrabromophthalate (TBPH)](javascript:showMsgDetail('ProductSynonyms.aspx?CBNumber=CB4899202&postData3=EN&SYMBOL_Type=A');) | Flame retardant (Firemaster 550). Substitute for Penta BDE | Method exist. 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 Penta and Deca BDE. | Detected in Bay sediments but not in Bay biota. | Yes |
| [1,1'-(Ethane-1,2-diyl)bis(pentabromobenzene) (DBDPE)](javascript:showMsgDetail('ProductSynonyms.aspx?CBNumber=CB3740945&postData3=EN&SYMBOL_Type=A');) | Flame retardant. Substitute for Deca BDE | Not detected in Bay sediments; compromised results for Bay biota. | Yes |
| [Octabromo-1,3,3-trimethyl-3-phenylindan](javascript:showMsgDetail('ProductSynonyms.aspx?CBNumber=CB3182644&postData3=EN&SYMBOL_Type=A');) | Flame retardant. Substitute for Deca BDE | No environmental data. | Yes? |
| Ethylene bis(tetrabromophthalimide)(EBTBPI) | HPV Flame retardant for high impact polystyrenes, thermoplastic polyesters, polycarbonates. Possible Deca replacement | Possible method. | Yes |

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| --- | --- | --- | --- |
| **Chemical** | **Use** | **Method exists?** | **RMP Study Proposed?** |
| **Top Ten Fluorinated** |  |  |  |
| 4-Chloro-3-nitrobenzotrifluoride | Crop protection | Possible method. | Consider evaluating as part of pesticide studies? |
| 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-Chloro2,6-dinitro-4-(trifluoromethyl)benzene. | Crop protection and intermediate for 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. |  |

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| **Chemical** | **Use** | **Method exists?** | **RMP Study Proposed?** |
| **Top Ten Other** |  |  |  |
| 2,4,6-Tri-tert-butylphenol | Used as an intermediate in the manufacture of antioxidants for rubber. Toxic to fish and algae. | Possible method. |  |
| Triphenyl borane | Intermediate in formation of triphenylborane amine compounds that are catalysts for polymerization of acryclic esters. | Possible method. |  |
| Galoxolide | Popular fragrance used in soaps and detergents | Yes. | Consider evaluating fragrances in 2015 |
| 1,1-Bis(3,4-dimethylphenyl)ethane | Howard and Muir: Used in electronics/ electrical industry? | Possible method. |  |
| Musk dimethyl Indane | Musk fragrance | Yes. Detected in Great Lakes | Consider evaluating fragrances in 2015 |
| 2-(2H-Benzotriazol-2-yl)-4,6-ditertpentylphenol | Used as UV stabilizer in films, outdoor furniture and clear coat for automobiles. | Possible method. |  |
| Traseolide. Musk methyl ketone | Popular fragrance used in soaps and detergents. | Yes. Detected in Great Lakes | Consider evaluating fragrances in 2015 |
| 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. |  |

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

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| --- | --- | --- | --- |
| **Chemical** | **Use** | **Method exists?** | **RMP Study Proposed?** |
| **Top Ten Chlorinated** |  |  |  |
| 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 | HPV chemicals that is used to manufacture plastics; also used as an intermediate in pharmaceutical production | Yes. Detected in Great Lake bird eggs. Tentatively identified in Bay Area seals | Yes. One of 8 compounds identified in nontargetted RMP study of seals. |
| Triclocarban |  | Yes. Widely detected in environment. Never monitored in the Bay |  |
| Pentachlorothiophenol | Peptizing agent (reduce viscosity) for rubber | Possible method. |  |
| 3,5-dichloro -2,4,6 trifluoropyridine | Chemical intermediate for pesticides | Possible method. | Consider evaluating as part of pesticide studies? |
| Dibutyl chlorendate | Dibutyl chlorendate is used as reactive flame retardants in plastics. | ? Possible method ? | Not for 2014. |
| Dechlorane Plus | Flame retardant. | Yes. Measured in SF Bay at low levels. | No |
| Heptachlorocylcopentene | Intermediate for hexachlorocyclopentadiene, pesticide. | Yes. |  |
| Heptachlorocylcopentane | Howard and Muir: Use? | Possible method. |  |
| 2-chloropyridine | Howard and Muir: Pesticide intermediate? | Possible method. | Consider evaluating as part of pesticide studies? |

* 1. 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 southern 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 of 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, all of the above nine CECs were recommended for monitoring in treated municipal wastewater effluent and at locations currently receiving stormwater runoff. For Bay sediments, the screening suggested prioritizing flame retardants (BDE-47, BDE-99) and two pyrethroids (bifenthrin, permethrin). In biological tissues, the group is prioritizing monitoring of polybrominated diphenyl ethers (PBDEs) and perfluorinated chemicals (e.g., PFOS). SCCWRP is currently working with the State Water Board to develop a statewide monitoring effort, incorporating regional monitoring performed (e.g., as part of the Southern California Bight Survey and the RMP) to implement these recommendations.

*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, 14 polycyclic aromatic hydrocarbons, 5 inorganic and organic metals, and 6 perfluorinated surfactants (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 use, release, and exposures in the state, Washington’s Department of Ecology established a PBT Rule in 2006 (Washington 2006). The Rule defines specific PBT criteria 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 the chemicals, 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.

*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 the risks of CECs 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 the effects side of the issue. 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. It is augmented through use of the Adverse Outcome Pathway concept, a 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.

* 1. 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 found 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 (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.

1. 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 magnitude 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 the use of 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.

* 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 preliminary list of CECs newly identified in Bay seal blubber, and awaiting further verification and quantification is presented in Table 5. The results from this study, including concentrations of each of the compounds identified in both seal and mussel samples, are expected in 2013. Upon confirmation of these compounds, a study proposal will be developed. It is noted that the RMP already monitors for bifenthrin. 4,4’ – dichlorophenyl sulfone is also listed on the Howard and Muir list of CECs. It may be prudent to consider revisiting using this technique as chemical use changes over time and our analytical abilities improve.

**Table 5. Preliminarily identified compounds using Broadscan Analyses (to be confirmed).**

|  |  |  |  |
| --- | --- | --- | --- |
| **Name** | **CAS** | **Use** | **In Production?** |
| 4,4' - dichlorodiphenyl sulfone | 80-07-9 | Used in high temperature plastics (engineering plastics) and an intermediate in pharmaceutical synthesis (Dapsone-antibacterial) | Yes |
| 4,4' difluorobenzophenone | 345-92-6 | Used in the synthesis of high performance polymers (PEEK) and as a pharmaceutical intermediate | Yes |
| Chloropropylate | 5836-10-2 | Pesticide for use against ticks and mites that is no longer in production (related to DDT) | No |
| Dicofol | 115-32-2 | Agricultural pesticide for ticks and mites that is still applied in CA | Yes |
| 2,2'-dichlorobenzil | 21854-95-5 | ? | ? |
| 9,10-dichloroanthracene | 605-48-1 | Chlorinated PAH formed during combusion | Yes |
| 4,4-difluorodiphenylmethane | 457-68-1 | High performance polymer made for engineering plastics. Used in producing benzophenone (a UV blocker.) | Yes |
| Bayer 28,589 (also known as 2,6-di-tert-butyl-4-nitrophenol (DBNP)) | 728-40-5 | Develped as a miticide; used in lubricating oils and hydraulic fluids in submarines; | No |
| Bifenthrin | 83657-04-3 | Pyrethroid pesticide | Yes |

* 1. 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 a bioanalytical tool 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 study will be conducted by researchers at University of Florida and SCCWRP. The work will use silversides, a model estuarine fish (*Menidia beryllina*), 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-nonylphenol (NP), 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. This tool may prove particularly relevant to identifying potential harm caused to organisms living near outfalls and therefore likely to be exposed to a variety of estrogenic chemicals at concentrations relatively higher than found in the greater Bay. Successful application of this bioassay tool may also result in identification of specific estrogenic contaminants that merit chemical-specific monitoring studies. Long-term plans for use of this tool will be established once it has been shown to be an effective means of detecting estrogenicity.

1. 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; Pesticides (TBD) |  | PBDEs |  |  |
| Sediment |  | PFASs (sources); Fipronil; PBDEs; Pyrethroids;  Alternative flame retardants |  | PBDEs |  |
| Stormwater & Effluent |  | PFASs; Pyrethroids (stormwater) |  |  |  |
| Bivalves |  | PBDEs; Alt. flame retardants |  |  | PBDEs |
| Sport Fish |  | PBDEs |  |  | PBDEs |
| Bird Eggs |  |  | PBDEs |  |  |
| Seals |  | Alt. flame retardants | PBDEs |  |  |
| CECs Identified through Review of Literature & Other CEC Monitoring Programs (Section 4.0) | | | | | |
| New info tracking | Alternative flame retardants | Ongoing | Design study on PPCPs not yet examined in the Bay | ongoing | ongoing |
| Non-targeted Approaches to CEC Identification (Section 5.0) | | | | | |
| NIST screening | Identify chemicals | Follow-up monitoring study TBD |  |  |  |
| Bioanalytical tools | E1, BPA, NP, HHCB | Water, effluent testing | Follow-up monitoring study TBD |  |  |
| Supporting RMP Activities | | | | | |
| Special Studies | CEC Synthesis & Strategy;  PBDE Synthesis;  Pesticide Workgroup Meeting | |  |  |  |

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