Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations

2018 Update

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About the Update

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has been investigating contaminants of emerging concern (CECs) since 2001. 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 RMP Emerging Contaminants Workgroup (ECWG), established in 2006, includes representatives from RMP stakeholder groups, regional scientists, and an advisory panel of expert researchers that work together to address the workgroup's guiding management questions (MQs). The ECWG's guiding management questions are:
- MQ1: Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?
- MQ2: What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?
- MQ3: What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?
- MQ4: Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?
- MQ5: Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?
- MQ6: What are the effects of management actions?

The overarching goal of the ECWG is to develop cost-effective strategies to identify and monitor CECs to minimize impacts to the Bay.

To this end, the RMP first published a CEC Strategy document in 2013 (Sutton et al., 2013); a significant revision of the CEC Strategy was completed in 2017 (Sutton et al., 2017). The strategy is a living document that guides RMP special studies on CECs, assuring continued focus on the issues of highest priority to the health of the Bay. A key focus of the strategy is a tiered risk and management action framework that guides future monitoring proposals. The strategy also features a multi-year plan indicating potential future research priorities.

This 2018 CEC Strategy Update is a brief summary document that features revised tier designations for perfluoroalkyl and polyfluoroalkyl substances and the addition of recently monitored CECs to the tiered risk and management action framework. Reviews of findings relevant to San Francisco Bay are provided.

The 2018 Update also outlines the RMP's strategy for monitoring CECs in stormwater and wastewater pathways into the Bay, relevant to answering MQ2. The strategy prioritizes special studies based on available Bay monitoring data, chemical properties, and understanding of CEC uses in urban and industrial activity surrounding the Bay. A summary of contaminants and contaminant pathways prioritized for study are provided.

This Update introduces two models that were developed for traditional pollutants and can be leveraged to support the RMP's CEC strategy: 1) a watershed model that can be used to estimate CEC loads into the Bay from stormwater; and 2) a hydrodynamic model that simulates ambient concentrations in Bay

subembayments based on CEC loads from wastewater and stormwater pathways and assuming conservative behavior (no degradation, volatilization, or partitioning).

The Update concludes with a revised multi-year plan for RMP Special Studies on CECs. According to this multi-year plan, a full revision of the CEC Strategy is anticipated in 2021.

The RMP's Tiered Prioritization Framework: 2018

The RMP assigns CECs monitored in Bay water, sediment, and wildlife to tiers in the program's risk and management action framework (framework in Table 1; CEC tier assignments in Table 2). The degree of concern associated with a particular chemical or chemical class guides both RMP monitoring activities and external management actions, as outlined in Table 1. The criteria listed below were used for placement in each tier (Sutton et al., 2017).

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}[1]).

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 $PNEC$[2] or $NOEC$[3] but less than the EC_{10} or another low level effects threshold).

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

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

The RMP review of a CEC may also indicate whether monitoring suggests levels are declining or increasing over time, via ▼ and ▲ symbols, respectively. Modified symbols ▽ and △ are used when contaminants are expected to be declining or increasing over time based on information other than monitoring data.

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[1] EC_{10}, effect concentration where 10% of the population exhibits a response
[2] PNEC, predicted no effect concentration
[3] NOEC, no observed effect concentration

Table 1. The RMP Conceptual Tiered Risk and Management Action Framework for San Francisco Bay. See Sutton et al. 2017 for more information.

	Risk Level Description	Monitoring Strategy	Water Quality Management Actions
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.
Moderate Concern	Bay occurrence data suggest a high probability of a low level effect on Bay wildlife.	Consider including in Status and Trends monitoring. Special studies of fate, effects, sources, pathways, and loadings.	Action plan/strategy. Aggressive pollution prevention. Low-cost control/treatment actions.
Low Concern	Bay occurrence data suggest a high probability of no effect on Bay wildlife.	Discontinue or conduct periodic screening level monitoring in water, sediment, or biota. For CECs previously considered moderate concern, maintain Status and Trends monitoring for at least two cycles. Periodic screening level monitoring for chemical(s) detected in wastewater or stormwater to track trends.	Low-cost source identification and control. Low-level pollution prevention. Track product use and market trends.
Possible Concern	Potential for concerns or uncertainty in measured Bay concentrations or toxicity thresholds suggest uncertainty in the level of effect on Bay wildlife.	Screening level monitoring to determine presence in water, sediment, or biota. Screening level monitoring for presence in wastewater or stormwater.	Maintain (ongoing/periodic) effort to identify and prioritize emerging contaminants of potential concern. Track international and national efforts to identify high priority CECs. Develop biological screening methods and identify available analytical methods.

RMP CEC Tier Assignments: Recent Findings

Summarized below are recent findings relating to contaminants assigned to the RMP's tiered risk and management action framework for CECs. These include Moderate Concern contaminants PFOS, PFOA and long-chain carboxylates; as well as Possible Concern contaminants siloxanes, substituted diphenylamines (SDPAs), UV-benzotriazoles (UV-BZTs), and rare earth elements. These groups represent the only significant changes to the tiered framework since 2017.

The tier assignments for each CEC in this report were based on available information and will be updated annually as new information on the levels or potential risk of the CEC becomes available. The rationale behind the assignments of these CECs, as well as previously evaluated and assigned CECs, are provided in Table 2.

At this time, no CECs are considered to be a high concern for the Bay. For information on contaminants assigned to tiers but not discussed in this Update, see Sutton et al. (2017).

Table 2A. Current status of CECs in the tiered risk and management action framework for San Francisco Bay (Moderate and Low Concern).

	Contaminant Class	Trend	Current Bay Data
Moderate Concern	PFOS	▼	Bird egg concentrations have been greater than PNEC and are currently in the range of concentrations linked to reproductive effects in wild birds; possible risks to humans who frequently eat Bay sport fish; high concentrations in seal blood; high volume use of precursors; recent monitoring suggests declines in birds and seals.
	PFOA and Long-chain Perfluoro-carboxylates		Concentrations of PFOA and long-chain carboxylates do not exhibit significant declines in seals or bird eggs; concentrations in seal blood from South Bay are in the range of concentrations that have shown disruption to gene functions in Russian seals; additive effects expected.
	Fipronil	△	Sediment concentrations are in the range of toxicity thresholds for degradates; use has increased over the last several years and is high in urban areas; mitigation measures to reduce outdoor use in California were announced in 2017.
	Nonylphenols and Nonylphenol Ethoxylates		Ubiquitous in Bay water, sediment, bivalves, fish, bird eggs, with concentrations below most toxicity thresholds; possible impacts on larval barnacle settlement; possible synergistic effects with pyrethroids; estrogenic activity; previously high volume use in laundry detergent may be decreasing following phase-out.
Low Concern	PBDEs	▼	Concentrations in Bay wildlife and sediment have decreased over time, with detections now typically below thresholds of potential concern; tern egg concentrations are below reproductive toxicity threshold; sport fish concentrations are below protective human health thresholds for fish consumption; uncertainty regarding impacts on harbor seals; production and use phased out in US.
	PBDD/Fs	▽	Low concentrations; synthetic sources declining with PBDE phase out.
	HBCD	▽	Low concentrations measured in sediment, bird eggs, fish, harbor seals, bivalves; reduction in use anticipated worldwide.
	Pharmaceuticals (e.g., ibuprofen, sulfamethoxazole)	△	Concentrations below toxicity thresholds, toxicity to aquatic species sufficiently characterized; levels expected to increase with population.
	Personal Care and Cleaning Products (e.g., triclosan, galaxolide)	△	Concentrations below toxicity thresholds, toxicity to aquatic species sufficiently characterized; levels expected to increase with population.
	Pyrethroids		Detected infrequently and in low concentrations in Bay sediment; of High Concern in watersheds, as tributary sediment concentrations are comparable to or higher than toxicity thresholds; lower impact professional application methods have been prescribed via state regulations.

Table 2B. Current status of CECs in the tiered risk and management action framework for San Francisco Bay (Possible Concern).

	Contaminant Class	Current Bay Data
Possible Concern	Alternative Flame Retardants - Organophosphates including TPhP	Detection of several in water, sediment, and tissue; limited toxicity data for aquatic species; endocrine disrupting properties; additive/synergistic exposure effects unknown; high volume and potentially increasing use as PBDE replacements.
	Alternative Flame Retardants - Hydrophobic Brominated Compounds	Detection of several in sediment and tissue; limited toxicity data for aquatic species; additive/synergistic exposure effects unknown; high volume and potentially increasing use as PBDE replacements.
	Alternative Flame Retardants - Hydrophobic Chlorinated [Dechlorane] Compounds	Detection of Dechlorane Plus and a few related compounds in sediment and tissue; limited toxicity data for aquatic species; additive/synergistic exposure effects unknown; high volume use.
	Plastic Additives - Bisphenol A	Analyzed but not detected in surface waters (< 2,500 ng/L) or sediments (< 2,600 ng/g), PNEC=60 ng/L.
	Plastic Additives - Bis(2-ethylhexyl) Phthalate (BEHP or DEHP)	Sediment concentrations in the same range as low apparent effects threshold (but threshold not directly linked to DEHP).
	Plastic Additives - Butylbenzyl Phthalate (BBzP)	Sediment concentrations exceed low apparent effects threshold (threshold not directly linked to BBzP or effects in macrobenthos).
	Microplastic	Detected in Bay surface water; uncertainty in toxicity to Bay wildlife.
	Newly Identified Tissue Contaminants • 2,2'-dichlorobenzil • dichloroanthracenes • 4-tert-butylamphetamine • methyl triclosan	Detected in Bay wildlife tissue samples via non-targeted analysis; uncertainties in toxicity data.
	Other Pesticides	Concentrations below toxicity thresholds; uncertainty in toxicity to Bay wildlife.
	Other PFASs - Short-chain Perfluoroalkyl Substances, Polyfluoroalkyl Substances	Detection of several compounds in Bay matrices; indications of contamination with as-yet unidentified PFASs; potential for increased use as alternatives to PFOS and PFOA; toxicity to aquatic species not sufficiently characterized.

PCB 11	Ubiquitous contaminant and has been detected in Bay water, urban runoff, sediments, but not bioaccumulative like the more highly chlorinated PCB congeners (minor congener in small fish and bivalves); uncertainty in toxicity thresholds.
Polyhalogenated Carbazoles	Ubiquitous contaminants detected in Bay sediment, bivalves, fish, birds, and seals; uncertainty in toxicity thresholds.
Short-chain Chlorinated Paraffins	Concentrations below toxicity thresholds; uncertainties in toxicity data; high volume use.
Single-walled Carbon Nanotubes	Not detected; analytical limitations; toxicity information not available.
Siloxanes	Detected in bivalves; uncertainty in bioaccumulation potential; some sediment and water toxicity thresholds available.
SDPAs	Water and sediment concentrations below available toxicity thresholds; uncertainties in toxicity data.
BZT-UVs	Water and sediment concentrations below available toxicity thresholds; uncertainties in toxicity data.
Rare Earth Elements	Detected at low concentrations in ambient Bay sediment and water; concentrations below limited available toxicity thresholds.

PFOS (Moderate Concern), PFOA and long-chain carboxylates (Moderate Concern), and other PFASs (Possible Concern)

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are a broad class of fluorine-rich specialty chemicals. Some types of PFASs, and in particular the perfluoroalkyl forms, possess thermal stability, non-reactivity, and surfactant properties, making them useful for many different types of applications. More than 3,000 PFASs are used in consumer, commercial and industrial applications, including food packaging materials, waterproof textiles, stain-resistant carpets and furniture, fire-suppression foams, processing aids for the production of fluoropolymers like Teflon, mist suppressants in metal-plating, and hydraulic aviation fluids.

Perfluoroalkyl substances are fully fluorinated, meaning that no carbon-hydrogen bonds are present and only fluorine atoms are bonded to the carbon backbone of the molecule. In contrast, polyfluoroalkyl substances are not fully fluorinated, meaning that carbons may also have bonds to hydrogen, oxygen, or other atoms in addition to fluorine. Some polyfluoroalkyl substances can degrade to perfluoroalkyl substances; these compounds are referred to as "precursors" of perfluoroalkyl transformation products.

The carbon-fluorine bonds in PFASs are some of the strongest known to science, which means PFASs (or, in the case of precursors, their perfluoroalkyl transformation products) show extremely high persistence in the environment. Well-studied members of the perfluoroalkyl family, including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been shown to be highly toxic. Other perfluoroalkyl substances have received little to no testing; however, structural similarities suggest that they may pose similar concerns for human and ecological health.

At present, much of the regulatory focus has been on the long-chain perfluoroalkyl chemicals (generally containing at least seven to eight carbons) such as PFOS and PFOA, in part based on their extensive toxicity profiles, their multi-year half-lives in human blood, and past production volumes. The industry is shifting to alternatives that include the short-chain compounds containing four to six fluorinated carbons; however, there is very little toxicological information about these alternatives available, and there is concern that these short-chain compounds may be similarly problematic. While the short-chain PFASs have much shorter half-lives in human blood, they are more mobile in groundwater and less amenable to treatment via sorption technologies, which are typically employed to remove PFOS and PFOA from drinking water. Even less is known about the many members of the polyfluoroalkyl family, which have also seen increasing use as alternatives to PFOS and PFOA. For the polyfluoroalkyl substances, with the exception of a handful of compounds, we do not know which specific compounds are in use, making targeted analysis of environmental samples particularly challenging.

In the US, production of PFOS was phased out by 2002, and production of PFOA was phased out by 2015. This federal action was part of a broader international collaboration to reduce human and environmental risks associated with exposure to these compounds. In Europe, PFOS was restricted under the Stockholm Convention in 2009 as an Annex B chemical, allowing some specific exceptions to a total ban on PFOS. PFOA, a compound with 8 carbons (C8) and other PFAS compounds C9 through C14 are on the European Candidate List of High Concern compounds due to their persistence, ability to bioaccumulate and toxicity. The goal of the Candidate List is to restrict the use of these chemicals and encourage industry to move to safer alternatives. Although restricted in North America and Europe, PFOS and PFOA production continues in some countries, such as China and India. In addition, global production of related replacements, including the short-chain perfluoroalkyl substances and polyfluoroalkyl substances mentioned above, means continuing use of and exposure to compounds that may potentially pose similar risks.

The RMP has monitored PFASs in a variety of matrices for more than a decade. PFASs are widely detected in San Francisco Bay matrices including water and sediment. These contaminants are also ubiquitous in Bay biota including fish, bird eggs, and harbor seals. In particular, concentrations of PFOS in Bay harbor seals and bird eggs in 2004 and 2006 were some of the highest detected globally. Current PFOS concentrations in South Bay bird eggs may pose a risk to hatching success, according to available toxicity data. In addition, current sport fish PFOS concentrations may pose risks to humans eating high-fish diets, based on comparison to consumption guidelines from the State of Michigan. As a result, PFOS has been identified as Moderate Concern for San Francisco Bay.

Recent monitoring suggests decreases in PFOS concentrations in seals and cormorants, likely as a result of changing use patterns that include the nationwide phase-out in 2002. However, concentrations of other

members of the PFAS family, such as PFOA, have remained relatively constant, albeit it at substantially lower levels overall. Meanwhile, a number of "precursors" that degrade to the more persistent PFOS or PFOA have been detected in sediments.

Previously, all PFASs other than PFOS had been considered Possible Concerns for the Bay, a designation that indicates uncertainty and reflects the lack of clear toxicity thresholds. Based on an updated literature review and discussion with international PFAS experts (Sedlak et al., 2018), it is now considered appropriate to classify the long-chain carboxylate perfluorochemicals such as PFOA as Moderate Concerns for the Bay. The rationale for including long-chain carboxylates as Moderate Concern chemicals is based on the pervasive detection of these compounds in biota, the knowledge that these compounds do not degrade under environmental conditions, and the identification of adverse responses in mammalian systems at concentrations observed in Bay seals. This approach is consistent with management and regulatory approaches implemented by the European Union and US federal and state agencies. For example, as noted previously, the European Chemical Agency has listed PFOA and the C9 through C14 perfluorocarboxylates as substances of very high concern due to their persistence, bioaccumulation, and toxicity. Within the US, the USEPA has developed a chemical action plan for the long-chain perfluoroalkyl substances and a number of states have developed drinking water standards and advisories for several of the long-chain compounds. Several of the agencies are concerned about similar modes of actions and additive effects of these compounds.

For the remaining PFASs observed in San Francisco Bay, there is little available toxicity data. According to RMP studies, short-chain perfluoroalkyl substances are present at increasing levels in effluent, but appear to be less bioaccumulative, with no to low detections observed in bird eggs, seals, and fish. It is unclear whether these compounds are less toxic than PFOS and PFOA. Polyfluoroalkyl substances, including precursors that degrade to PFOS and PFOA, have been detected in sediment; tissue studies are not available. At the present time, insufficient toxicity information exists to evaluate whether these compounds pose a risk. Given this level of uncertainty, they must be considered Possible Concerns for the Bay.

More information on PFASs and their detection in the San Francisco Bay can be found in the RMP PFAS Synthesis and Strategy Report (Sedlak et al., 2018). Pathways monitoring data is summarized in the Strategy for Monitoring CECs in Pathways (page 23, Table 3).

Siloxanes (Possible Concern)

Volatile methyl siloxanes are organic compounds with backbones made up of silicon and oxygen (Si-O-Si). Due to their chemical, thermal, physical, and biological stability, smooth texture, and hydrophobic characteristics, siloxanes have been widely produced and used since the 1940s and have been classified as high production volume chemicals by the USEPA (Horii and Kannan, 2008; Jia et al., 2015; Surita and Tansel, 2014). The plethora of siloxane applications include personal care products (e.g., hair-care products, body wash, deodorants, skin lotion, toothpaste, cosmetics), pharmaceuticals, plastics, papers, building materials, fabrics, concrete, adhesives, rubber products (including pacifiers), cookware, household cleaning products and polishes, sealants, furniture, electronics, medical devices, cleaning

solvents (including dry cleaning), and industrial cleaning fluids (Fairbrother et al., 2015; Horii and Kannan, 2008; Jia et al., 2015; Surita and Tansel, 2014).

Siloxanes are suspected to enter the aquatic environment primarily through the use and down-the-drain disposal of personal care products. Due to their volatility, about 90% of siloxanes escape through evaporation, leaving about 10% of siloxanes discharged to wastewater treatment plants (Horii and Kannan, 2008; Mackay et al., 2015; Reiner et al., 2007). Siloxanes that are not removed through treatment and enter surface waters partition predominantly to the sediment, thereby exposing benthic species (Hughes et al., 2012). Decamethylcyclopentasiloxane, or D5, is the most abundantly manufactured and environmentally prevalent siloxane, and is typically discharged at sixteen times the amount of the next most common siloxane, octamethylcyclotetrasiloxane, or D4 (Surita and Tansel, 2014).

A *pro bono* analysis conducted by Environment and Climate Change Canada scientists for the RMP found detectable levels of linear and cyclic siloxanes in all San Francisco Bay bivalve tissue samples. Bivalves from 11 sites - ranging from the Lower South Bay to the confluence of the San Joaquin and Sacramento Rivers - were sampled in 2012 and analyzed for nine different siloxanes: four linear siloxanes (hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, and dodecamethylpentasiloxane, also known as L2, L3, L4, and L5, respectively), a branched compound (Tetrakis(trimethylsiloxy)silane, also known as M4Q), and four cyclic siloxanes (hexamethylcyclotrisiloxane, octamethylcyclotetra-siloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, known as D3 through D6).

The sum of all nine siloxanes was the highest at the Central Bay site near Treasure Island, with a cumulative concentration of 89 ng/g ww. D5 showed the strongest signals at all sites, with concentrations averaging 47 times that of the next most prevalent contaminant, D4. Concentrations of D5 ranged from 23 ng/g ww (near the west end of the Richmond Bridge) to 84 ng/g ww (near Treasure Island), with an average concentration of 43 ng/g ww across all 11 sites. The concentration of D5 in bivalves collected from the less impacted reference site near Bodega Bay was 1.0 ng/g ww; D3, D4, and D6 were also observed at concentrations of 0.03, 0.18, and 0.25 ng/g ww, respectively, in the sample from the reference site.

Several studies conducted on Atlantic cod and shorthorn sculpin in Norway (Warner et al., 2010), and predatory fish in Canada (McGoldrick et al., 2014), strengthen the hypothesis that higher concentrations of siloxanes in biota are found closer to anthropogenic sources. In addition, bivalves collected at a freshwater lake that occasionally receives untreated wastewater in Northern Norway showed D5 concentrations of 107±4.5 ng/g ww in the pea clam, *Pisidium* (Krogseth et al., 2017). This concentration is comparable to the concentration of 84 ng/g ww found in Central Bay bivalves. In contrast, a study conducted in remote marine waters off the island of Spitsbergen in Northern Norway did not detect siloxanes in three different bivalves (Campbell, 2010).

Relatively little is known about possible harmful effects of siloxanes in the environment, and limited environmental measurements have been taken. The most environmentally prevalent siloxane, D5, has hydrophobic properties that meet the ecological categorization criteria for persistence and bioaccumulation potential (Norwood et al., 2013). However, there are conflicting study results as to whether siloxanes bioaccumulate and biomagnify (Borgå et al., 2012; Gobas et al., 2015a; Jia et al., 2015;

Norwood et al., 2013; Wang et al., 2013), which prevent a determination as to whether D5 might potentially biomagnify in San Francisco Bay wildlife (Mackay, 2015).

The literature contains similarly conflicting reports on the potential for ecotoxicity of siloxanes. Some studies indicate that exposure to siloxanes leads to estrogen mimicry, connective tissue disorders, adverse immunologic responses, and fatal liver and lung damage in rodents (Granchi et al., 1995; Hayden and Barlow, 1972; He et al., 2003; Lieberman et al., 1999; Quinn et al., 2007; Wang et al., 2013). However, arguments have been made (Gobas et al., 2015b, 2015a) that these toxicological effects would require concentrations that exceed the solubility of siloxanes in water, or the sorption capacity of siloxanes in organisms.

The European Chemicals Agency (ECHA) lists the predicted no effect concentration (PNEC) of D5 in marine waters and marine sediment to be 0.12 µg/L and 1.1 mg/kg dw, respectively. Bay water and sediment have not been analyzed for siloxanes. ECHA has concluded that D4 and D5 are very persistent and very bioaccumulative. In the case of D5, Environment Canada (2012) concluded that it was not a danger to human health or the environment.

While D4 is not as predominant in aquatic environments as D5, there are more concerns about its toxicity. D4 is classified as a reproductive toxicant by the European Commission (EC, 2008). Environment and Climate Change Canada released a risk management strategy for D4 to encourage the lowest level of release of D4 that is technically and economically feasible. Industrial facilities that make or use D4 must development pollution prevention plans designed to limit concentrations to 2.3 µg/L for effluent released to surface water or to a wastewater system without treatment, and 17.3 µg/L for effluent entering wastewater systems with treatment (ECCC, 2017a). The USEPA is evaluating D4 and in 2014 entered into an agreement with five siloxane manufacturers for monitoring of wastewater treatment plant influent and effluent discharges, receiving waters, and environmental matrices (USEPA, 2014). The results of that effort are not yet available.

The limited amount of siloxane data in the Bay and the conflicting information regarding potential biomagnification and ecotoxicity of siloxanes has resulted in the designation of these contaminants as a Possible Concern for the Bay. Leveraging opportunities to gather data on levels of siloxanes in Bay water and/or sediment are recommended.

SDPAs (Possible Concern)

Substituted diphenylamines (SDPAs) are preservatives added in the manufacturing of products including industrial lubricants, plastics, polyurethane foam, and rubber to prevent oxidative degradation (Lu et al., 2016). Vehicle wear and leaks from products containing SDPAs, including rubber tires and vehicle lubricants, and roadside plastic litter, are some of the potential sources of SDPAs into the environment. SDPAs are used in the U.S. on the order of millions of kilograms a year (Lu et al., 2017b), and may be released into the environment during manufacture, application, and waste disposal of products containing these chemicals (Lu et al., 2017a).

A *pro bono* analysis of eight SDPA compounds conducted by Environment and Climate Change Canada scientists for the RMP found these compounds to be ubiquitously present in sediment and water collected from 12 ambient Bay sites in 2014 (De Silva and Muir, 2015). Median sediment concentration was 8.2 ng/g dw, with a maximum of 40 ng/g in Central Bay; median water concentration was 0.8 ng/L, with max concentration of 1.6 ng/L in Suisun Bay. For most of the Bay, the dominant congener in sediment samples was C8 (~75% of total SDPAs in eight of nine samples). However, the Lower South Bay site showed a different congener distribution, with both C8C8 and C8 congeners dominant.

Relatively few studies exist on SDPAs in the environment; recent publications include measurements in sediment, surface water, wastewater and biosolids, fish, and herring gull eggs in Canada (ECCC, 2017b; Lu et al., 2018). Sediment and water concentrations measured in SF Bay are in the same range of low ng/g dw and low ng/L levels as concentrations measured in Lake Ontario (ECCC, 2017b). SDPAs have not been studied in other matrices in the San Francisco Bay.

The Canadian studies indicate that densely populated urban sites are sources of SDPAs to the aquatic environment. A study of nine wastewater treatment plants in Canada showed over 90% removal of SDPAs in wastewater influent through biosolids separation. Median concentrations of total SDPAs in influent, effluent, and biosolids were 483 ng/L, 28.4 ng/L and 2,750 ng/g dw (Lu et al., 2017b). A follow-up study in a freshwater creek in southern Ontario within a watershed impacted by agriculture, manufacturing, and wastewater found higher concentration of SDPAs in sediment, crayfish, and fish downstream of an urban site compared to upstream (Lu et al., 2016). SDPA concentrations in crayfish were 1,000 ng/g lw, while those in pelagic fish were 30-50 ng/g lw, indicating sediment may be an important factor in exposure.

A recent study (Lu et al., 2018) of SDPAs in the lake trout food web in Lake Superior found patterns of SDPAs in herring gull eggs (maximum 7 ng/g ww) that suggested exposure from ingesting terrestrial sources of food and trash, while patterns in fish (maximum 0.46 ng/g ww) suggested exposure from high density urban river outflows. Aquatic organisms may also be exposed to SDPAs through ingesting trash and microplastics that are manufactured with SDPAs, or have sorbed SDPAs from the aquatic environment. Study findings suggested that SDPAs undergo trophic dilution.

There currently is little experimental toxicity information to evaluate potential concerns linked to measured environmental concentrations. Modeled toxicity values based on hydrophobicity have high uncertainty, but are in the microgram per liter range (ECCC, 2017b), which is orders of magnitude higher than ambient Bay concentrations, and in the range of wastewater effluent concentrations measured at Canadian facilities. SDPA toxicity is thought to be caused by an overall baseline narcotic effect (ECCC, 2017b), which is a non-specific mode of action characteristic of hydrophobic organic contaminants.

SDPAs are currently designed as a Possible Concern because there is insufficient toxicity data to evaluate whether Bay concentrations are at levels of concern.

UV-BZTs (Possible Concern)

Phenolic benzotriazoles (BZT-UVs) are another class of industrial preservative used as UV-stabilizers in plastic products to reduce degradation and discoloration (Nakata et al., 2009), and in consumer products, such as sunscreen and cosmetics, to prevent skin damage. For example UV-360, marketed as bisoctrizole, Tinosorb M, and Milestab 360, is an ingredient found in 100 sunscreen cosmetics at concentrations between 0.1-1.97% (NTP, 2011). While this compound is not yet approved as a sunscreen active ingredient in the U.S., it has been approved in Europe and other parts of the world. BZT-UVs are also applied to automobile components, paint, and plastic equipment (Nakata et al., 2009), and abrasion and litter of these products on the road may be a potential pathway into the environment. Over 10,000 tons per year of BZT-UVs are manufactured or imported into the U.S.; UV-328 and UV-234 congeners are manufactured and imported in the highest volumes, followed closely by UV-329 (octrizole) and UV-326 (Lu et al., 2017).

BZT-UVs have been widely detected in the environment, including indoor dust, wastewater influent and effluent, river water and sediment, and marine sediment (NTP, 2011). These compounds have also been measured in human breast milk (Lee et al., 2015), indicating human exposure and accumulation of these chemicals. Sediment is a sink for BZT-UVs in the environment because these compounds are hydrophobic and have low vapor pressure (Lu et al., 2016). Sediment is also expected to be the major exposure route for aquatic organisms, due to the compounds' persistence and bioaccumulation potential (Lu et al., 2016). While these compounds appear to have low acute toxicity for aquatic species, studies in fish and mammals have demonstrated specific BZT-UVs cause liver toxicities and endocrine disrupting effects (ECCC, 2016; NTP, 2011).

A pro bono analysis of five BZT-UV compounds (UV-234, UV-326, UV-327, UV-328, UV-329) conducted by Environment and Climate Change Canada scientists for the RMP in 2014 found these compounds to be ubiquitously present in sediment and water in the Bay. Concentrations of these compounds in the water ranged between <1 - 17 ng/L, with concentrations greater than 10 ng/L detected in Central Bay, South Bay, and San Pablo Bay. Sediment concentrations ranged between <1 - 9 ng/g dw in the sediment, with the two highest concentration detected in the Lower South Bay (De Silva and Muir, 2015). BZT-UVs have not been measured in other matrices in San Francisco Bay.

Water and sediment concentrations measured in a Canadian urban creek were in the ng/L and ng/g dw range, comparable to concentrations detected in the Bay (De Silva and Muir, 2015; Lu et al., 2016); even higher sediment concentrations, in the high ng/g dw range, were measured in suspended sediment in another heavily urbanized Canadian watershed (Parajulee et al., 2018). High concentrations of BZT-UVs in sediment have been measured in Oslofjord Norway (range 3.2-25.1 ng/g dw), and higher concentrations of BZT-UVs in water have been measured in Japan (Lu et al., 2017b).

Wastewater effluent is a known pathway for these compounds. A study of BZT-UVs at nine wastewater treatment plants in Canada demonstrated that wastewater treatment processes were effective in removing over 90% of BZT-UVs through sludge sorption and solids separation processes; average concentrations were 76.2 ng/L in influent, 4.84 ng/L in effluent, and 457 ng/g dw in biosolids. The size the population

served by each facility correlated with the concentration and loading of BZT-UVs in the wastewater influent (Lu et al., 2017b).

A recent study found that streams and stormwater runoff may be just as important as wastewater effluent as a pathway for BZT-UVs to enter the environment, and road sediment and plastic debris were indicated as sources of contamination. The amount of contamination may be linked to the intensity of use of specific BZT-UVs in consumer products for a particular region (Parajulee et al., 2018).

The congener detected at highest concentration in biota has been UV-328, and concentrations in the 50 ng/g ww have been measured in fish and porpoise blubber in the Ariake Sea, Japan (Nakata et al., 2009). In the Great Lakes, UV-328 was the only BZT-UV frequently measured in herring gull eggs, and was measured at concentrations up to 13 ng/g ww; in lake trout, UV-328 was detected at lower concentrations and frequencies, with maximum measurement of 6 ng/g ww (Lu et al., 2018). Concentrations of up to 800 ng/g of UV-P was measured in suspended sediment in urban watershed in Canada during a rainfall event; UV-P has higher water solubility compared to other commonly used BZT-UVs (Parajulee et al., 2018).

While toxicity data are scarce, lab-based exposures of aquatic organisms to individual BZT-UVs have indicated the potential for impacts. For example, measured BZT-UV endocrine disrupting effects include effects on thyroid hormone receptors and aryl hydrocarbon receptors in zebrafish (Fent et al., 2014; Liang et al., 2017) at the low and high µg/L level, respectively. In addition, UV-234 and UV-328 induced oxidative stress in algae (*C. reinhardtii*) at the molecular and cellular level (Giraudo et al., 2017) at concentrations of 10 µg/L. Simultaneous exposure to both substances indicated higher toxicity, suggesting synergistic effects and emphasizing the importance of complex-mixture toxicity dosing to mimic a natural exposure such as that found in the Bay. However, maximum Bay water concentrations for the measured five BZT-UV compounds have been detected at 17 ng/L, which is more than two orders of magnitude lower than the effect concentration for individual BZT-UVs.

Based on the limited data available, the European Chemical Agency (ECHA) has published a predicted no effect concentration (PNEC) for UV-328 of 1 ug/L in marine waters and 45 mg/kg dw in marine sediment. Bay water and sediment concentrations are significantly below these levels. Currently, the National Toxicology Program is testing the toxicity of several BZT-UVs, including all five of the congeners analyzed in Bay sediments (NTP, 2011). This class of compounds has been discussed by the Scientific Guidance Panel that advises California's Biomonitoring Program and will be the subject of further review (CA Biomonitoring, 2016).

At present, BZT-UVs are classified as a Possible Concern for San Francisco Bay because there is insufficient toxicity data to evaluate whether Bay concentrations are at levels of concern.

Rare Earth Elements (Possible Concern)

Rare earth elements include the 15 lanthanide elements (including lanthanum, cerium, and gadolinium), yttrium, and scandium. Rare earth elements are not actually rare; in 2008, 129,000 metric tons of rare earth oxides were used worldwide (Goonan, 2011). Gadolinium (Gd), used to enhance the contrast in medical magnetic resonance imaging (MRI), is tightly bound to an organic compound, which makes the

toxic metal ion safe for human consumption. However, this organic-bound Gd may degrade to more toxic Gd^{3+} ions in the environment. Gd is also used in variety of industrial and household applications, including nuclear energy, radar technologies, and microwaves. An estimate of 5% of Gd application worldwide is used for medical applications, and is discharged through the wastewater pathway (Rogowska et al., 2018). Lanthanum and cerium are commonly used as catalysts, and in glassmaking, lighting and metallurgy, and new markets are emerging for use of rare earth elements in ceramics, magnets, and battery alloys (Goonan, 2011).

In general, rare earth elements can be released to the environment through wastewater effluents from industrial and urban sources (Hatje et al., 2014, 2016). Additional natural sources of rare earth elements to the aquatic environment include natural geological and atmospheric deposition.

Environmental conditions determine aquatic concentrations and availability. Natural rare earth elements are particle-reactive and tend to be deposited to the sediment when passing from freshwater to saltwater in the low salinity regions of estuaries. In contrast, anthropogenic Gd, in the form of Gd-organic complexes, tend to be very stable and soluble and are not affected by natural removal processes (Kulaksız and Bau, 2007).

An analysis of eight ambient Bay water samples collected along a transect in 2013 showed that Gd concentrations ranged between 2-25 ng/L (14-171 pmol/kg), lanthanum (La) concentrations ranged between 6-27 ng/L (43-196 pmol/kg), and total rare earth element concentrations between 30-200 ng/L (181-1,246 pmol/kg). Lowest concentrations were measured in the Central Bay, while highest concentrations were detected in the Lower South Bay; and anthropogenic Gd accounted for up to 75% of total Gd in the South Bay. The plume of the San Francisco Bay waters entering the Pacific Ocean also displayed traces of anthropogenic Gd. Analysis of archived RMP water samples revealed that Gd concentrations in the Lower South Bay have increased by an order of magnitude in the last 20 years, from 4 ng/L (23.2 pmol/kg) in 1993 to 27 ng/L (171 pmol/kg) in 2013, which may be attributed to expanding use of MRI technology (Hatje et al., 2016).

Gd concentrations measured in the San Francisco Bay in 2013 were comparable to concentrations measured in 2005 in the Weser River (15-23 ng/L or 97-151 pM) and Weser Estuary (7-14 ng/L or 45-95 pM) (Kulaksız and Bau, 2007). The Weser River drains large urban areas of Germany, including major cities. Natural concentrations of rare earth elements are expected to be higher in the freshwater of rivers compared to the saltwater of estuaries, due to the salting out effect described earlier. The effluent from two wastewater treatment plants that discharge into the Weser River were a factor of two higher than river concentrations (Kulaksız and Bau, 2007). A review found one study indicating only 10% of Gd is removed through conventional wastewater treatment, but 100% removal is achieved through reverse osmosis treatment (Rogowska et al., 2018).

Much higher Gd concentrations, in the hundreds of ng/L, have been measured in the Rhine River (Kulaksız and Bau, 2011). In this study, La concentrations were an order of magnitude higher than Bay water concentrations, and were traced to wastewater discharged from a La production facility. Bay water concentrations were also lower than total rare earth element concentrations in temperate lakes in Canada (n=14) unaffected by mining, which were in the low hundred ng/L (low nM) range (Amyot et al., 2017).

In the Canadian lake food web, rare earth element concentrations were highest in non-predatory benthic invertebrates (400 ug/g or 0.1 nmol/g range) compared to those measured in whole fish (4 ug/g) and predatory invertebrates (100 ug/g), indicating rare earth elements were subject to trophic dilution in this temperate lake system. Further studies of rare earth element food web transfers are needed for marine and estuarine systems.

As novel uses of rare earth elements expand, there is growing concern about human and ecological exposure and risks. Rare earth element toxicity depends on its chemical form, bioavailability, and exposure route. Free Gd^{3+} ions are highly toxic because they can inhibit cell signaling via voltage-gated calcium channels. Gd-contrast agents are tightly bound to organic chelates to facilitate rapid excretion. MRI patients with kidney impairments have reported nephrogenic systemic fibrosis, and accumulation of Gd in bone, brain, and kidney tissue (Rogosnitzky and Branch, 2016). Animal studies have reported adverse effects from rare earth elements including inflammation, oxidative stress, and tissue damage (Pagano et al., 2015). It has also been demonstrated that despite Gd-complex stability, aquatic plants and animals can incorporate the complex in their tissues (Lingott et al., 2016).

A first attempt at measuring ecotoxicity of lanthanides yielded a predicted no effect concentration (PNEC) for cerium, gadolinium, and lutetium in the µM range, more than four orders of magnitude higher than measured rare earth element concentrations in the SF Bay. One of the challenges with evaluating rare earth element toxicity noted in this study was the formation of insoluble forms of rare earth elements in the test media, which can significantly reduce the actual exposure concentrations, leading to underestimation of the toxicity (Gonzalez et al., 2014). Toxicity studies of rare earth elements have mostly been limited to Ce, La, and Gd (Pagano et al., 2015).

There are significant knowledge gaps regarding the ecotoxicity and bioavailability of rare earth elements; as a result, these contaminants are classified as compounds of Possible Concern for San Francisco Bay. Because rare earth element concentrations are expected to increase with expanding use of MRI and other technologies, risks relating to these compounds should be reexamined as additional information on ecotoxicity, bioavailability, as well as biogeochemical and anthropogenic cycles becomes available.

Strategy for Monitoring CECs in Pathways

The Bay integrates inputs from a variety of pollution pathways, including atmospheric deposition and discharges of wastewater, stormwater, and flows from the Sacramento-San Joaquin Delta. Typically, the RMP evaluates the presence and levels of contaminants in Bay water, sediment, and/or biota first; when measurements suggest concern is warranted, the need for further work to characterize CECs in relevant pathways is evaluated to inform potential management actions to reduce contaminant loads into the Bay.

Outlined below is the RMP strategy for monitoring wastewater and stormwater pathways for CECs (Table 3), relevant to answering Management Question 2: What are the sources, pathways, and loadings leading to the presence of individual CECs in the Bay? Management Questions and guiding principles outlined in the Small Tributaries Loading Strategy (McKee et al., 2009; MYP2018) inform the stormwater pathway CEC monitoring recommendations. Other relevant factors considered in monitoring recommendations for both of these pathways include the chemical properties of the CECs, their sources, and available Bay Area monitoring data.

An additional contaminant pathway, atmospheric deposition, has not been rigorously examined previously as part of RMP work on CECs. For some CECs, characterization of this pathway may become priorities for the RMP.

Moderate Concern
Because significant management actions may be prudent for Moderate Concern contaminants, studies to inform these actions are given a high priority (Table 1). Currently, there are four CECs or CEC classes of Moderate Concern for San Francisco Bay: PFOS; PFOA and other perfluorinated long-chain carboxylates; fipronil and degradates; and nonylphenols and nonylphenol ethoxylates (Tables 2 and 3). In general, special studies are recommended for Moderate Concern emerging contaminants to better understand the relative roles of stormwater and wastewater loads entering the Bay (Table 1). Special studies may include pathways monitoring and/or development of conceptual, steady-state, or hydrodynamic models (see Modeling Tools for CECs in the Bay – page 30).

Stormwater and wastewater are recognized as significant pathways for PFASs to be introduced into the Bay. Based on the monitoring to date, stormwater and wastewater concentrations of PFOS and PFOA appear to be of similar magnitude, although the stormwater monitoring is somewhat dated and generally focused on relatively small urban watersheds. To date, a systematic characterization of the major tributaries has not been conducted. In addition, based on the limited sampling to date, no inferences can be made about trends and sources.

In contrast, monitoring of effluent from several of the largest wastewater dischargers suggests that concentrations of PFOS and PFOA are declining, being replaced by short-chain compounds such as PFHxS (a C6 compound) and PFBA (a C4 compound). In the case of both stormwater and wastewater, a significant portion of the discharge, in some instances over half the sample, is composed of unidentified precursors that can degrade to perfluorocarboxylates and sulfonates.

Lastly, it is widely recognized that PFASs are distributed throughout the planet, including remote areas such as the Arctic, in part because they are transported via the atmosphere and later deposited. To date, the RMP has not evaluated atmospheric deposition to assess whether this is a major pathway for these contaminants to the Bay.

The widely used urban pesticide fipronil was recently monitored in influent and effluent as part of an RMP Special Study (Sadaria et al., 2016). The pesticide and its degradates were detected in all samples collected, and concentrations in influent suggested spot-on flea control could be a major source of the down-the-drain discharges to wastewater treatment plants. While the RMP is not currently monitoring this contaminant in stormwater, monitoring is being conducted by local stormwater agencies; monitoring by agencies such as DPR and USGS may provide further information useful to RMP stakeholders.

Nonylphenols are derived from nonylphenol ethoxylates, industrial surfactants used in a broad array of products that may be sources of contamination to both wastewater (e.g., detergents and cleaning products) and stormwater (e.g., paints, pesticides, and car products). This class of contaminants has not been a focus of the RMP in recent years. Development of a monitoring strategy, informed by the state of the science on these contaminants as well as recent detections via both targeted monitoring of the South and Lower South Bay margins and non-targeted analysis of Bay water and effluent samples, is recommended. Such a strategy could include monitoring of pathways.

Low Concern
Low Concern contaminants may warrant low-cost control and pollution prevention efforts. Relative prioritization of monitoring in pathways is informed by expected trends in true sources of these contaminants. Polybrominated diphenyl ethers (PBDEs), polybrominated dioxins and furans (PBDD/Fs), and hexabromocyclododecane (HBCDs) concentrations are expected to decrease based on measured trends and/or management actions to phase out these chemicals. Pathways monitoring of these contaminants is therefore not a high priority for the RMP.

While both pharmaceuticals and personal care and cleaning product ingredients are currently considered Low Concern for the Bay, concentrations are expected to increase due to population growth and increasing use of these products. The RMP has monitored both of these contaminant classes in effluent in previous years, and is currently evaluating data collected voluntarily by seven Bay Area wastewater treatment plants as part of a 2018 RMP Special Study. Findings generated by this review of recent data, as well as product use and market trends, may suggest the need for a new study within Bay matrices. In general, the RMP has prioritized studies of pharmaceuticals in effluent, rather than stormwater, based on the assumption of down-the-drain disposal or elimination. In contrast, both effluent and stormwater may be relevant pathways for some of the contaminants within personal care and cleaning products.

While pyrethroids are a high concern in local tributaries, they are assigned a Low Concern for ambient Bay concentrations. Pathways monitoring in stormwater and wastewater effluent is not prioritized because water concentrations are generally expected to be low because of their low solubility in water. Therefore, monitoring pyrethroids in Bay sediment is recommended as a more suitable matrix.

Possible Concern

Possible Concern contaminants may be monitored periodically in pathways as part of screening studies, in particular through leveraging collaborations with academic and government partners to conduct analyses at reduced costs. Possible Concern contaminants have often been assigned to this category because there are insufficient toxicity studies to evaluate risk to Bay wildlife. Though lack of toxicity thresholds makes it difficult to interpret monitoring results, special studies can provide important information for water quality managers, including the presence or absence of CECs, and the relative importance of contributions from wastewater and stormwater pathways.

Alternative or non-PBDE flame retardants, considered Possible Concerns for the Bay, include organophosphate compounds, brominated compounds, and chlorinated (or Dechlorane-type) compounds. Among these three classes, the compounds of greatest potential concern in the San Francisco Bay are the organophosphates (Sutton et al., in prep). They are widely detected in Bay water, sediment, and tissue. Levels of one phosphate flame retardant, chlorinated Tris or TDCPP, in sediment and bivalves are comparable to levels of PBDEs, while levels in water (14-450 ng/L) regularly exceed a recently revised predicted no effects concentration (PNEC) for marine settings established by the European Chemicals Agency (20 ng/L). In addition, the maximum concentrations of triphenyl phosphate in ambient Bay waters are approaching the European Chemicals Agency marine PNEC of 370 ng/L.

The RMP screened three wastewater effluent grab samples, as well as stormwater grab samples collected during two storms at two different sites, and detected many organophosphate flame retardants in both pathways (Sutton et al., in prep). It is unknown whether the levels detected in these pathway samples are representative of the Bay Area. A simple modeling effort is recommended to inform future monitoring and management activities. Based on the chemical properties of the class, including their water solubility, partitioning to sediment, and volatility, a simple, multi-matrix model that includes wastewater and stormwater discharges and assumes steady-state conditions among Bay water, sediment, and air compartments would be informative. In particular, the air deposition of organophosphates is a data gap for the region; its relative importance could be explored via this multi-matrix modeling effort (e.g., Rodgers et al., in prep).

Microplastic particles are another Possible Concern for the Bay. A screening study detected microparticles in treated wastewater from eight Bay facilities; however, limitations of the analytical method suggest some of these particles may not have been plastic. A comprehensive study of microplastics in the Bay is now underway, funded primarily by the Gordon and Betty Moore Foundation, with matching funds from the RMP and others. Wastewater and stormwater samples have been collected and will be analyzed using novel methods; results will inform an associated modeling effort as well as management actions. Of note, characterization of the air deposition pathway is not included as part of this ongoing study; recent studies of Paris suggests this may be a pathway of interest (Dris et al., 2015, 2017).

Short-chain perfluoroalkyl substances and polyfluoroalkyl substances are classified as Possible Concerns for the Bay due to insufficient toxicity data. RMP and independent studies indicate both wastewater and stormwater are significant pathways for these contaminants. Levels of the short-chain perfluoroalkyl substances may be increasing in wastewater, due to increased use as alternatives to the phased-out long-chain compounds. In contrast, stormwater has not been analyzed with frequency; the most recent data

available are from samples collected in the winter of 2010/2011. Monitoring to estimate loads contributed by major tributaries is recommended. As with the long-chain perfluorinated compounds, the RMP has not evaluated air deposition as a possible pathway.

In the past, the RMP has not placed as much emphasis on monitoring CEC inputs from the stormwater pathway, relative to wastewater. Preliminary results of a recent effort to identify unexpected contaminants via non-targeted analysis found considerable evidence of contamination at a site in San Leandro Bay influenced by stormwater (Sun et al., 2017), indicating that stormwater is an important pathway for some CECs to the Bay. An example of a contaminant identified with high confidence was 1,3-diphenylguanidine (DPG), a rubber vulcanization agent likely derived from vehicle tires. The European Chemicals Agency has established a predicted no effect concentration (PNEC) of 3 μg/L in marine waters.

Meanwhile, an independent effort to develop a list of target emerging contaminant analytes specific to the stormwater pathway is underway, motivated by concerns relating to Coho salmon populations in the Puget Sound area (Du et al., 2017). This list is expected to include contaminants derived from vehicle tire wear such as DPG, urban use pesticides, and other CECs commonly detected in stormwater, such as bisphenol A. A screening study to determine the presence of these stormwater CECs in Bay tributaries is recommended.

Stakeholder Engagement
Monitoring of pathways requires high levels of engagement with stakeholders representing wastewater and stormwater discharges during proposal development and study design, sample collection, analysis and reporting, and follow-up that informs relevant management actions. In addition to stakeholder engagement within the ECWG, CECs scientists engage with the RMP's Small Tributaries Loading Strategy (STLS) team and the Bay Area Pollution Prevention Group (BAPPG) of the Bay Area Clean Water Agencies (BACWA) to identify information needs and communicate findings. CECs scientists also work with members of state and federal agencies, including California's Department of Pesticide Regulation, Department of Toxic Substances Control, and Water Resources Control Board, as well as the United States Geological Survey and Environmental Protection Agency.

Table 3a. Pathways Monitoring Strategy Matrix for Moderate Concern Contaminants in San Francisco Bay. Pathways: Atmospheric Deposition (Atmos. Depos.), Stormwater from Urban Areas, particularly Residential (SW Urban/Residential), Stormwater from Industrial Land Uses (SW Industrial), Urban Wastewater (Urban WW), Industrial Wastewater (Industrial WW). Pathways are marked as "Significant" only if RMP or independent local monitoring data exist; where local data are unavailable, a pathway may be "anticipated to be significant."

	Contaminant Class	Chemical Properties	Sources	Atmos. Depos.	SW Urban/ Residential	SW Industrial	Urban WW	Industria l WW
Moderate Concern	PFOS	Bioaccumulates; highly persistent; water-soluble; also binds to sediment	Fire-fighting foams, carpet treatments, water-resistant coatings for clothing, grease and water-proof coatings for paper products, and electroplating mist suppressant; phased out of use in the U.S. in 2002; may be present in imported products	Unknown	Significant; previous monitoring (2009-2011); monitoring to estimate loads recommended.		Significant; multiple studies (2009, 2012, 2014); fire-fighting foams are a source for some facilities; levels may be declining.	
	PFOA and Long-chain Perfluoro-carboxylates	Bioaccumulates; highly persistent; water-soluble; also bind to sediment	Fluorine-rich compounds with many industrial and consumer uses that can lead to contamination of both wastewater and stormwater, including production of Teflon, fire-fighting foams, self-shine floor polishes, metal cleaners, varnishes, and paper, leather, and textile treatments; phased out of use in the U.S. in 2015; may be present in imported products	Unknown for Bay Area; precursors can be transported long distances	Significant; previous monitoring (2009-2011); monitoring to estimate loads recommended.		Significant pathway for PFOA according to multiple studies (2009, 2012, 2014); other long-chain perfluorocarboxylates detected at lower levels or not at all; levels of PFOA may be declining.	
	Fipronil	Water-soluble; also binds to sediment; low volatility; degrades to compounds also toxic to invertebrates	Urban insecticide with indoor and outdoor uses including pet flea control spot-on products and ant and termite control; new requirements for professional applicators may reduce amounts used around buildings	Negligible	Significant; monitoring by stormwater agencies, DPR and USGS can inform the RMP.		Significant; spot-on flea control source identified.	Unknown
	Nonylphenols and Nonylphenol Ethoxylates	Bioaccumulates; water-soluble; also binds to sediment; nonylphenol ethoxylates degrade to more persistent nonylphenol	Surfactant with wide use in consumer and industrial products that can lead to contamination of both wastewater and stormwater, including detergents, cleaning products, cosmetics, paints, paper, textiles, plastics, lubricant oils, construction materials, rubber; high volume use	Limited, localized transport expected.	Anticipated to be a significant pathway; NPEs detected via non-targeted analysis at stormwater-influenced site.		Anticipated to be a significant pathway; NPEs detected via non-targeted analysis in wastewater.	

Table 3b. Pathways Monitoring Strategy Matrix for Low Concern Contaminants in San Francisco Bay.

	Contaminant Class	Chemical Properties	Sources	Pathways				
				Atmos. Depos.	SW Urban/ Residential	SW Industrial	Urban WW	Industr. WW
Low Concern	PBDEs	Bioaccumulate; persistent; low water solubility; bind to sediment	Flame retardant used in foam furniture, electronics, textiles and other consumer products; phased out of production and use in U.S.	Long-range transport expected.	Significant pathway		Significant pathway	
	PBDD/Fs	Low water solubility; bind to sediment; bioaccumulate	PBDE byproducts, combustion products, and natural sources					
	HBCD	Low water solubility; binds to sediment; bioaccumulates	Flame retardant used in building insulation, textiles, and other consumer goods; phased out of many uses via Stockholm Convention	Long-range transport expected	Some detections in recent RMP screening study.		No detections in recent RMP screening study.	
	Pharmaceuticals (e.g., ibuprofen, sulfamethoxazole)	Wide range	Prescription and over-the-counter medications; down-the-drain disposal dominates	Possible	Anticipated to be a less important pathway.		Significant pathway; data from BACWA facilities under RMP review.	Unknown
	Personal Care and Cleaning Products (e.g., triclosan, galaxolide)	Wide range	Consumer body care and cosmetic products and consumer and industrial cleaning products are likely to be disposed of down-the-drain; some products may also be used outdoors or volatilize from the indoor environment, leading to potential for stormwater contamination	Possible	Limited data; triclosan not detected in four stormwater samples (unpublished data).		Limited data; triclosan detected in wastewater from two facilities in previous studies.	
	Pyrethroids	Low water solubility; low volatility; bind to sediment; persistent	Insecticide commonly used in urban and agricultural settings; High Concern in Bay Area streams	Limited	Significant pathway; monitoring by stormwater agencies, DPR and USGS		Known pathway based on data from a California survey of wastewater facilities.	Unknown

Table 3c. Pathways Monitoring Strategy Matrix for Possible Concern Contaminants in San Francisco Bay.

	Contaminant Class	Chemical properties	Sources	Atmos. Deposition	SW Urban/ Residential	SW Industrial	Urban WW	Industrial WW
Possible Concern	Alternative Flame Retardants - Organophosphates including TPhP	Water-soluble; bind to sediment; semi-volatile; metabolized by organisms	Flame retardants used in consumer and industrial products including upholstered furniture, building insulation, electronics, engine oils; other uses include plastic, floor polish; used indoors and outdoors; volatilization may lead to deposition in local urban water bodies	Anticipated to be significant	Known pathways based on limited data, detected in RMP screening study; a modeling effort is recommended to ascertain whether existing data are sufficient to inform management actions.			
	Alternative Flame Retardants - Hydrophobic Brominated Compounds	Low water solubility; bind to sediment; bioaccumulate	Flame retardants used in consumer and industrial products including upholstered furniture, electronics	Possible	Known pathway, detection of several compounds in recent RMP screening study.		Known pathway, detection of EH-TBB and BEHTBP in RMP screening study.	
	Alternative Flame Retardants - Hydrophobic Chlorinated [Dechlorane-type] Compounds	Low water solubility; bind to sediment; bioaccumulate	Flame retardants used in consumer and industrial products including electronics and wiring, roofing materials	Anticipated to be limited	Detection of Syn-DP, Anti-DP, and several related compounds in RMP screening study.		Single detection of Anti-DP at the method limit of detection in RMP screening study.	
	Plastic Additives - Bisphenol A	Water soluble; low volatility; binds to sediment; metabolized by organisms	Used in polycarbonate plastics, epoxy resins, thermal paper, food can linings	Negligible	Limited data; detected in three of four stormwater samples; based on detections in other regions, a screening study recommended.		Known, based on limited data from single facility; recent voluntary testing by seven BACWA facilities.	
	Plastic Additives - Bis(2-ethylhexyl) Phthalate (BEHP or DEHP)	Water soluble; semi-volatile; binds to sediment; metabolized by organisms	Used in plastics, construction materials, fragrances in personal care and cleaning products	Anticipated to be significant	Unknown		Limited data; detected in wastewater from one facility in independent study.	

	Contaminant Class	Chemical properties	Sources	Atmos. Deposition	SW Urban/ Residential	SW Industrial	Urban WW	Industrial WW
Possible Concern	Plastic Additives - Butylbenzyl Phthalate (BBzP)	Water soluble; semi-volatile; binds to sediment; metabolized by organisms	Used in PVC plastics, adhesives	Anticipated to be significant	Unknown		Limited data; detected in wastewater from one facility in independent study.	
	Microplastic	Wide range	Microbeads in personal care products and fibers derived from washing synthetic clothing and textiles are washed down the drain; fragments of plastic litter, paint, and rubber tires, can be washed into streams	Possible	Known pathway; initial characterization is underway.		Known pathway. Study underway.	
	Newly Identified Tissue Contaminants 2,2'-dichlorobenzil, dichloroanthracenes, 4-tert-butylamphetamine, methyl triclosan	Bioaccumulate	Diverse sources: pharmaceuticals, personal care and cleaning products, plastics, coatings and dyes, combustion products					
	Other Pesticides	Wide range	Indoor and outdoor pesticide applications by professionals and consumers, antimicrobial cleaning products	Possible	Significant pathway; monitoring by stormwater agencies, DPR and USGS can inform the RMP.		Potential pathway for indoor pesticides	
	Other PFASs - Short-chain Perfluoroalkyl Substances, Polyfluoroalkyl Substances	May not bioaccumulate	Wide range of industrial and consumer products; expected increase in use	Unknown	Significant pathway; monitoring to estimate loads contributed by major tributaries is recommended.		Significant pathway	
	PCB 11	Does not bioaccumulate	Impurity in pigments used for inks, dyes, paints, textiles; found in printed newspaper, magazines, cardboard, plastic bags, cereal boxes	Anticipated to be significant	Known pathways based on RMP studies.			

	Contaminant Class	Chemical properties	Sources	Atmos. Depos.	SW Urban/ Residential	SW Industrial	Urban WW	Industrial WW
Possible Concern	Polyhalogenated Carbazoles	Bind to sediment; persistent; bioaccumulate	Information on potential sources is limited; anthropogenic sources may include indigo dyes and polymer production in electronics; natural sources may include production by marine fungus					
	Short-chain Chlorinated Paraffins	Bind to sediment; persistent; bioaccumulate	Industrial use as lubricants and coolants					
	Single-walled Carbon Nanotubes	Persistent	Nanoparticles used in electronics and energy applications, drug delivery, composite plastic polymers	Analytical limitations				
	Siloxanes	Bind to sediment; volatile; persistent; may bioaccumulate	Numerous consumer and industrial uses incl. pharmaceuticals, personal care products, plastics, paper, building materials, fabrics, adhesives, cookware, cleaning products, sealants, furniture, electronics; high volume use	Anticipated to be significant	Anticipated to be significant; volatilization may lead to deposition in local urban water bodies		Anticipated to be significant pathway	
	SDPAs	Bind to sediment; bioaccumulate	Preservatives used in industrial and consumer products incl. plastics, polyurethane foam, vehicular rubber tires, lubricants, and fuel	Anticipated to be low	Anticipated to be significant pathway based on Canadian stormwater studies; screening study recommended.		Anticipated to be significant pathway	
	BZT-UVs	Bind to sediment; bioaccumulate	UV filters used in industrial and consumer products including personal care products, and plastic products incl. building material, automobile components, paint, sports equipment; high volume use	Anticipated to be low	Anticipated to be an significant pathway based on Canadian stormwater studies; screening study recommended.		Anticipated to be significant pathway	
	Rare Earth Elements	Water soluble, particularly in organic complexes; bind to sediment	Natural geologic and atmospheric deposition; medical magnetic resonance imaging, catalysts in high-tech industries	Known pathway for natural sources	Anticipated to be potential pathway for natural sources		Anticipated to be significant pathway	

Modeling Tools for CECs in the Bay

The ECWG has recommended expanding the use of modeling to interpret and predict CEC fate and transport in the Bay, determine the relative importance of different contamination pathways, and evaluate responses to management actions. Such tools can include qualitative, conceptual models; steady-state, fugacity models; hydrological models of urban runoff; and hydrodynamic models of contaminants in the Bay.

An earlier RMP application of modeling techniques led to development of steady-state, fugacity model that was used to calculate a mass balance for PBDEs in the Bay and predict recovery under different source reduction scenarios (Oram et al. 2008). This model treated the Bay as a single, well-mixed volume with two compartments representing the water column and the bed (surface) sediments. Atmospheric exchange was incorporated. Conceptually, the model assumed that exchange between water, sediment, and air was more important than exchange between the various geographic subregions of the Bay.

A similar approach is proposed to explore the fate of organophosphate flame retardants in the Bay. The high concentrations of organophosphates in water, sediment, and air indicate the need for a multi-media model that can accommodate partitioning among all three matrices. The model can be used to evaluate the sensitivity associated with different variables and assess whether all significant pathways have been incorporated.

Meanwhile, in 2017, available hydrological and hydrodynamic models were modified to allow for initial use by the CECs team. These models focus on providing spatial and temporal outputs, rather than steady-state partitioning among matrices. Trial use was incorporated into the PFAS Synthesis and Strategy Report (Sedlak et al., 2018). Descriptions of these models are provided below.

Bay Area Hydrological Model

The Bay Area Hydrological Model (BAHM) is a continuous simulation model that was developed to estimate flow and pollutant loads from Bay Area watersheds. The model is built upon HSPF (Hydrological Simulation Program--Fortran), a comprehensive package for simulation of watershed hydrology and water quality for both conventional and toxic organic pollutants. The model uses continuous rainfall and other meteorologic records to compute streamflow hydrographs and pollutographs across multiple pollutant sources, spatial scales, and time steps. Currently, the BAHM divides the entire Bay Area into 63 individual watersheds. The model simulation period is from 1999 to 2016.

The BAHM can be used to estimate stormwater CEC loads from individual watersheds in the region in two ways. One is to simply multiply modeled flow by existing estimates of stormwater CEC concentrations. Another more sophisticated approach is to use the BAHM to directly simulate the fate and transport of CECs in stormwater. Since this is a continuous simulation model, the results of this

simulation are time histories of runoff flow rate and CEC concentrations, making it possible to detect interannual variability of CEC loads and how they change over time (trend). More importantly, the results can be fed into the Bay Hydrodynamic Model to simulate the spatial and temporal distributions of CEC concentrations in the Bay. Based on the load estimates, the watersheds that contribute disproportionately high CEC loads can be targeted for monitoring for further investigation. The data gaps identified during model development and implementation can also be used to guide future monitoring efforts. More detailed information about the BAHM is available from Dr. Jing Wu (jingw@sfei.org).

Bay Hydrodynamic Model

A three-dimensional hydrodynamic model of the Bay has been developed to support studies of the fate and transport of nutrients, CECs, and other pollutants. This physics-based model incorporates data for tides, Delta outflow, stormwater flows (derived from the BAHM described above), local winds, and regional wastewater and refinery discharges. Further details on the configuration and the water year 2013 validation of the model are available in the Interim Model Validation Report (Holleman et al., 2017).

The goal of the transport model is to relate concentrations in water entering the Bay, whether from stormwater, wastewater or refinery discharges, to estimated ambient concentrations of contaminants in the major subembayments of the Bay. BAHM-derived stormwater input is currently limited to a single contaminant concentration; regional variation in stormwater contamination can be added to future iterations of the model. In addition, 42 discharges are individually represented, 37 from wastewater treatment plants and five from refineries.

For the present CEC applications, the transport model was run from October 2012 to September 2013. During this period, numerical "dyes" were added to each discharge mentioned above, and the model predicted concentrations of these dyes throughout the Bay. The model results were condensed into a series of spreadsheets that summarize the relationship between concentrations in load streams (i.e., concentration in stormwater and in individual wastewater or refinery discharges) and ambient concentrations in the Bay for each subembayment. Using this spreadsheet requires specifying concentrations for each of the 42 discharges and a representative concentration for stormwater. The spreadsheet then calculates, for each region of the Bay, the sum of contributions from all sources, providing a baseline estimate for ambient CEC concentrations. The regions follow RMP subembayment delineations: Lower South Bay, South Bay, Central Bay, San Pablo Bay, and Suisun Bay.

For CECs that are persistent and water-soluble, the spreadsheet provides a reasonable estimate of ambient concentrations. Degradation over time, sorption to sediment, and exchange with the atmosphere are not currently included in the model. These estimates can be used to design sampling strategies by identifying likely hot spots, and aid in analytical method selection by predicting whether ambient levels will be within detection limits. When combined with measured ambient concentrations, the model results can reinforce certainty of the measurements, point to the role of missing processes, or offer hints on under-constrained pathway concentrations.

RMP CEC Multi-Year Plan

Assembled below are recommended studies that have grown out of the RMP's CEC Strategy, structured as a multi-year plan (Table 4). The multi-year plan focuses on RMP Special Studies, but also provides information on Status and Trends and other RMP monitoring efforts relevant to CECs, along with external, pro bono collaborations.

Special Studies are primarily designed in response to the RMP priority questions for emerging contaminants:

- MQ1: Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?
- MQ2: What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?
- MQ3: What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?
- MQ4: Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?
- MQ5: Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?
- MQ6: What are the effects of management actions?

The purpose of this multi-year plan is to guide program management. These recommendations will be revisited and revised each year as part of the RMP budget planning process. The plan will be adapted to reflect advances in science and changes in policy needs.

MULTI-YEAR PLAN FOR EMERGING CONTAMINANTS

Emerging contaminant studies and monitoring in the RMP from 2013 to 2021. Numbers indicate budget allocations in $1000s. Budgets in parentheses represent funding or in-kind services from external partners. Budgets that are starred represent funding that has been allocated for the given study within other workgroups.

Element	Study	Funder	Questions addressed	2013	2014	2015	2016	2017	2018	2019	2020	2021
CEC Strategy				20	20	20	48	50	65	70	65	80
MODERATE CONCERN CECs												
PFOS/PFASs	Perfluorinated Compounds in Harbor Seals	RMP	1,4,6		26							
	Sediment, Effluent Precursor Monitoring	AXYS	1,2		(30)							
	CECs in Municipal Wastewater[1]	RMP	1,2,4			27.5						
	Effluent TOF analysis	DTSC	1,2,4,6		(50)							
	Perfluorinated and Polyfluorinated Compounds in San Francisco Bay: Synthesis and Strategy	RMP	1-6					56				
	Margin Sediment Archiving	RMP	1						2.5			
	Stormwater PFASs[2]	RMP	1,2							147.5		
	Sediment and Seal PFASs	RMP	1,2,4,6								80	
	Air Deposition PFASs		1,2									100
	RMP Status and Trends[3]	RMP S&T	1,4		F		E		E	F		E
NP/NPEs	Margin Sediment Archiving, Analysis	RMP	1,4						2.5		50	
	Archived Tissue	RMP	1,4									100
Fipronil	CECs in Municipal Wastewater[1]	RMP	1,2,3			27.5						
	Fipronil, Fipronil Degradates, and Imidacloprid in Municipal Wastewater	RMP	1,2,3				30					
	Fipronil, Fipronil Degradates, and Imidacloprid in Biosolids	ASU	1,2,3				(8)					
	Sport and Prey Fish Food Web	RMP	1							78.5		
	RMP Status and Trends[3,4]	RMP	1,3,4		S				S			
LOW or POSSIBLE CONCERN CECs												
PBDEs	PBDE Summary Report	RMP	1-6	36								
	RMP Status and Trends[3]	RMP S&T	1,3,4		S, B, F		B, E		S, E	F		E
Alt. Flame Retardants	Monitoring Alternative Flame Retardants in SF Bay Water, Effluent, Stormwater,	RMP	1,2,4		104							

Element	Study	Funder	Questions addressed	2013	2014	2015	2016	2017	2018	2019	2020	2021
	Sediment and Biota											
	Phosphate Flame Retardants in Ambient Bay Water	RMP / ECCC	1,4		(2)			47				60
	Conceptual and Steady-State Model[6]	RMP	1,2,3,6							46.9		
Pharmaceut-icals	Pharmaceuticals in Wastewater	RMP / POTWs	1,2,4				(68)		30			
	Pharmaceuticals in Water & (Archived) Sediment – coordinated with EEWG glucocorticoid bioanalytical tools	RMP	1,2,4								180	
	Antibiotics in Sediment Cores	U Minn	1,3,4						(8)			
Plastic Additives	Bisphenol Compounds in Ambient Bay Water	RMP / SIU	1			(25)		50				
	Bisphenol Compounds in Archived Sediment	RMP	1								50	
	Phthalates in Bay Matrices		1,4									70
Personal Care/Cleaning	Triclosan in Small Fish	RMP	1					41				
	Musks in Water & Sediment[5]	RMP	1						64.5			
	Sunscreen Chemicals in Water & Fish	RMP	1							116.8		
	Quats in (Archived) Sediment	RMP	1								50	
	Siloxanes in Bivalves	ECCC	1		(5)							
Pesticides	Current Use Pesticides in Ambient Bay Water	RMP	1,2	15								
	Imidacloprid, Imidacloprid Degradates and other Neonicotinoids in Ambient Bay Water	RMP	1					40				
	DPR Priorities in Water & Sediment[5]	RMP / USGS	1,2,3						64.5 (6.8)			
	Agricultural Pesticides in Water & Sediment – coordinated with North Bay Margins	RMP	1,2								100	
SDPAs/BZTs	Water, Sediment	ECCC	1		(3)							
OH-BDEs / Triclosan	Water, Sediment Cores	U Minn	1,3,4		(125)							
PHCZs	Sediment, Tissue	SIU	1			(15)	(20)	(40)				
Brominated Azo Dyes	Archived Sediment, Tissue	RMP	1								60	

NON-TARGETED & OTHER STUDIES												
Non-targeted	Non-targeted Analysis of Water-soluble CECs	RMP / Duke / AXYS	1,2					52 (10) (6)				
	Non-targeted Analysis of Sediment	RMP	1,2						101			
	Follow-up Targeted Study[2]	RMP	1,2							105		
	Tissue (Polar and Nonpolar Compounds)	RMP / Sea Grant	1							75 (250)		
	Follow-up Targeted Study (2019 results)	RMP	1									100
	Trash Hot Spots Study	RMP	1									120
RELEVANT STUDIES IN OTHER WORKGROUPS												
Bioassay (EEWG)	Linkage of In Vitro Estrogenic Assays with In Vivo End Points	RMP / SCCWRP / UF	1,2	70	56 (125)			45				
	Development of Glucocorticoid Bioanalytical Screens	RMP / SCCWRP / UF	1							25 (50)	75 (100)	50 (50)
RMP-funded Special Studies Subtotal - ECWG				71	150	75	130	284	330	639.7	635	630
RMP-funded Special Studies Subtotal – Other Workgroups				70	56	0	0	45	0	25	75	50
Pro-Bono & Externally Funded Studies Subtotal				0	165	90	112	40	14.8	300+	100+	50+
OVERALL TOTAL				141	371	165	242	369	344.8	630+	880+	730+

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

2 – The proposed 2019 stormwater studies include $55k in estimated field work costs; the budget for this field work is split between the two proposed studies.

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

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

5 – The 2018 CECs in Municipal Wastewater study was a $129k study that included analyses of pesticides and fragrance ingredients; in this table the budget for this study has been split between these two contaminant groups.

6 – The Alternative Flame Retardants Conceptual Model will be co-funded by ECWG and STLS, with each group allocating $46.9k toward the study.

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