RMP Emerging Contaminants Workgroup Meeting

April 11-12, 2019
10:00 AM – 4:00 PM

REMOTE ACCESS
Audio by Phone: (415) 594-5500, Access Code 943-326-397#
Slides: https://join.me/sfei-conf-cw1

DAY 1 AGENDA - April 11th

1.	**Introductions and Goals for This Meeting** The goals for this meeting: ● Provide updates on recent and ongoing ECWG activities (today) ● Gain feedback on CEC Strategy 2019 Memo, including discussion of monitoring priorities for Low and Possible Concern contaminants and the multi-year plan (today) ● Discuss potential modeling strategy, and develop a consensus for next steps (tomorrow) ● Discuss potential changes to Status and Trends monitoring (tomorrow) ● Recommend which special study proposals should be funded in 2020 and provide advice to enhance those proposals (tomorrow) Meeting materials: 2018 ECWG Minutes (pg. 6 - 20)	10:00 Melissa Foley
2.	**Discussion: CEC Strategy Update** (Attachment) ● Review of recent RMP activities (30 min) ● Discuss recommended monitoring priorities for Low and Possible Concern contaminants; discuss proposed educational webinar on predictive toxicology (30 min) ● Review the multi-year plan, including criteria for prioritizing future studies; discuss future direction of the focus area (45 min) Desired Outcome: Feedback on the CEC Strategy 2019 Memo Deadline: April 30, 2019 Meeting materials: CEC Strategy 2019 Memo	10:15 Rebecca Sutton
	Lunch (provided)	12:00
3.	**Information: Bisphenols (BPs) and Organophosphate Esters (OPEs; Flame Retardants) in Bay Water** (Attachment)	12:40 Ila Shimabuku

	BPA, BPS, and a slough of OPEs were detected throughout San Francisco Bay, mostly in the dissolved phase, with elevated levels common in the Lower South Bay. Limited toxicity information exists for these classes of compounds; however, levels of BPA and TDCPP were comparable to or exceeded protective ecotoxicity thresholds. Cumulative impacts of these endocrine-disrupting compounds are poorly understood. Moderate Concern classification within the Tiered Risk Framework is recommended for both BPs and OPEs. Desired outcome: Consensus on classification within the Tiered Risk Framework Meeting materials: Flame Retardants and Plastic Additives in San Francisco Bay: Targeted Monitoring of Organophosphate Esters and Bisphenols (draft report)	
4.	**Information: Neonicotinoids and Degradates in Bay Water** (Attachment) Imidacloprid was detected in open Bay and margins water samples in the Lower South and Extreme Lower South Bay at levels comparable to or exceeding toxicity thresholds. No other neonicotinoid or degradate was detected. Conservative tracer modeling suggests wet season sampling may reveal higher concentrations. Moderate Concern classification within the Tiered Risk Framework is recommended for imidacloprid, Possible Concern for others. Desired Outcome: Consensus on classification within the Tiered Risk Framework Meeting materials: Neonicotinoids and Degradates in San Francisco Bay Water (draft report)	1:20 Nina Buzby
5.	**Information: Quaternary Ammonium Compounds and Antibiotics in Bay Sediment** Dr. Arnold's team developed an extraction and analytical procedure for the quantification of quaternary ammonium compounds (QACs) in water and sediment samples. Using this method, as well as one previously developed for antibiotics, they saw sporadic, quantifiable levels (ng/L) of antibiotics and QACs in open Bay sediments. The most frequently detected QACs have 16 or 18 unit carbon chains. Desired outcome: Informed Workgroup	1:50 Bill Arnold (UMinn)
	Short Break	2:20
6.	**Information: Triclosan and Methyl Triclosan in Prey Fish** Triclosan and methyl triclosan were detected in all prey fish samples collected in the Lower South and Extreme Lower Bay using a novel method developed by SGS AXYS. Concentrations in prey fish tissue indicated triclosan and methyl triclosan may bioaccumulate in the food web. Tissue concentrations of fish very near wastewater treatment plant discharges indicate potential cause for concern. Fish samples were collected in the summer of 2017 during the phase-out of triclosan from household soaps; therefore it is unclear whether concentrations of triclosan and methyl triclosan in the Bay will decrease as expected due to these management actions. Desired outcome: Informed Workgroup	2:30 Diana Lin

7.	**Information: Preliminary Results of Non-targeted Analysis of North Bay Fire-impacted Stormwater** In fall of 2017, wildfires devastated northern California communities in Napa, Sonoma, and Santa Rosa. To complement the Regional Water Boards' conventional contaminant analyses of stormwater runoff from wildfire-impacted regions and to provide a more comprehensive picture of contamination concerns, the RMP funded a study to identify unknown or unexpected contaminants of emerging concern in stormwater using non-targeted methods. The preliminary analysis has detected hundreds of unique contaminant signals and has specifically identified several unusual contaminants that may be associated with wildfires and may be of concern. Desired outcome: Informed Workgroup	3:00 Eunha Hoh (SDSU), June-Soo Park (DTSC)
	Adjourn	4:00

DAY 2 AGENDA - April 12th

1.	**Summary of Yesterday and Goals for Today** The goals for today's meeting: ● Brief recap of yesterday's discussions and outcomes ● Discuss potential modeling strategy, and develop a consensus for next steps ● Discuss potential changes to Status and Trends monitoring ● Recommend which special study proposals should be funded in 2020 and provide advice to enhance those proposals	10:00 Melissa Foley
2.	**Discussion: CEC Modeling Strategy** (Attachment) A proposed goal and vision for an emerging contaminants-focused modeling strategy is presented in the CEC Strategy 2019 Memo. Potential next steps will be discussed. Desired Outcome: Consensus on goal and next steps Meeting materials: CEC Strategy 2019 Memo	10:10 Rebecca Sutton, Diana Lin
3.	**Discussion: Status and Trends Monitoring Recommendations** Following on yesterday's discussion of contaminants that may merit Moderate Concern classification, discuss recommendations for Status and Trends monitoring of the Bay. Desired Outcome: Status and Trends monitoring recommendations	10:40 Rebecca Sutton

<table>
<tr><td>4.</td><td>Information: Ongoing CEC Trend Monitoring by POTWs (Attachment)

In response to the State Water Board's interest in ongoing CECs monitoring by POTWs, BACWA has been working to develop a proposal to monitor CEC trends at representative POTWs. Through this effort, BACWA will:
1. Develop a database of POTW characteristics that can be used to identify representative POTWs for specific effluent CEC monitoring studies; and
2. Develop a proposal for ongoing POTW monitoring to capture trends in CECs of highest concern.

Desired Outcome: Input on relevant POTW characteristics; ranking of contaminants or contaminant classes for ongoing monitoring

Meeting materials: TBD - Provided by BACWA</td><td>11:00
Lorien Fono (BACWA)</td></tr>
<tr><td>5.</td><td>Summary of Proposed ECWG Studies for 2020

The Principal Investigators will present the proposed special studies. Clarifying questions may be posed, however, the workgroup is encouraged to hold substantive comments for the next agenda item.

2020 Special Study Proposals include:

● Emerging Contaminants Strategy
● CECs in Stormwater (part 2 of 3)
● Pharmaceuticals in Lower South Bay Water and Archived Sediment
● Bisphenols in Bay Sport Fish
● Sunscreens in Effluent

Meeting materials: ECWG 2020 Special Studies Proposals (pg. 21)</td><td>11:15
Rebecca Sutton, Diana Lin, Ila Shimabuku</td></tr>
<tr><td>6.</td><td>Information: Characterizing the Mechanism of Toxicity of the Sunscreen Oxybenzone to Sea Anemones

Dr. Mitch will describe the current state of research on the metabolism of the sunscreen oxybenzone and whether its metabolites are phototoxic. Sea anemones are models for coral, organisms that are particularly sensitive to oxybenzone. Like coral, sea anemones are symbionts (animal/algae), but are easier to work with since they breed more often. They are also more relevant to the Bay ecosystem than coral.

Desired outcome: Informed Workgroup</td><td>12:15
Bill Mitch (Stanford)</td></tr>
<tr><td></td><td>Lunch (provided)</td><td>12:30</td></tr>
<tr><td>7.</td><td>Discussion of Recommended Studies for 2020 - General Q&A

The workgroup will discuss and ask questions about the proposals presented. The goal is to gather feedback on the merits of each proposal and how they can be improved.</td><td>1:00
Melissa Foley</td></tr>
<tr><td>8.</td><td>Discussion of Recommended Studies for 2020 - Prioritization</td><td>2:00
Melissa Foley</td></tr>
</table>

	The workgroup will consider the studies as a group, ask questions of the Principal Investigators, and begin the process of prioritization.	
9.	**Closed Session - Decision: Recommendations for 2020 Special Studies Funding** RMP Special Studies are identified and funded through a three-step process. Workgroups recommend studies for funding to the Technical Review Committee (TRC). The TRC weighs input from all the workgroups and then recommends a slate of studies to the Steering Committee (SC). The SC makes the final funding decision. For this agenda item, the ECWG is expected to decide (by consensus) on a prioritized list of which studies to recommend to the TRC. To avoid an actual or perceived conflict of interest, the Principal Investigators for proposed special studies are expected to leave the room during this agenda item. Desired Outcome: Recommendations from the ECWG to the TRC regarding which special studies should be funded in 2020 and their order of priority.	3:00 Karin North
10.	**Report out on Recommendations**	3:20 Karin North
	Adjourn	3:30

RMP Emerging Contaminants Workgroup Meeting

April 12-13, 2018
San Francisco Estuary Institute
4911 Central Avenue, Richmond, CA

Meeting Summary

Attendees

Science Advisor	Affiliation	Present
Lee Ferguson	Duke University	Yes
Kelly Moran	TDC Environmental	Yes
Derek Muir	Environment and Climate Change Canada	Yes
Heather Stapleton	Duke University	Yes
Bill Arnold	University of Minnesota	Yes
Miriam Diamond	University of Toronto	Yes

Others Present

Michael Fry (USFWS; EEWG Science Advisor)
Dan Schlenk (UC Riverside; EEWG Science Advisor)
Steve Weisberg (SCCWRP; EEWG Science Advisor)
Ed Kolodziej (University of Washington)
Dimitri Panagopoulos (EPA)
Bill Mitch (Stanford)
Eunha Ho (San Diego State University)
Tom Mumley (SFB Regional Water Board)
Ian Wren (Baykeeper)
Karin North (City of Palo Alto)
Luisa Valiela (EPA)
Daniel Oros (EPA)
Robert Wilson (City of Petaluma, BAPPG)
Doug Dattawalker (Union Sanitary District - chair of BAPPG)
Reid Bogert (C/CAG for San Mateo County)
Autumn Cleave (SFPUC pollution prevention)
Heather Peterson (SFPUC)
Eric Dunlavey (City of San Jose)
Simret Yigzaw (City of San Jose)
Ryan Mayfield (City of San Jose)
Mike Connor (EBDA)
Lorien Fono (BACWA)
Eva Agus (EBMUD)
Jen Jackson (City of San Francisco)
Tessa Fojut (State Water Board, CEC lead for Division of Water Quality)
Dawit Tadesse (State Water Board)
Jennifer Teerlink (DPR)
Anne Cooper Doherty (DTSC)
Daphne Molin (DTSC)
June-Soo Park (DTSC)
Shoba Iyer (OEHHA)
Holly Weir (Ocean Protection Council)
Rebecca Sutton (SFEI)
Meg Sedlak (SFEI)
Diana Lin (SFEI)
Jennifer Sun (SFEI)
Ila Shimabuku (SFEI)
Phil Trowbridge (SFEI)

Jay Davis (SFEI)
Carolynn Box (5 Gyres)
Bowen Du (SCCWRP)
Lark Starkey (State Water Board Sea Grant Fellow)
Terry Grimm (Cambridge Isotopes)
Helen Yu (San Diego Water Board Region 9 - CEC lead)
Greg LeFevre (University of Iowa)

The last page of this document has information about the RMP and the purpose of this document.

DAY ONE - April 12

1. Introductions and Review of the Agenda

No changes were made to the agenda.

2. Discussion: CEC Strategy Update

Rebecca Sutton presented an overview of the CEC program and elements of the CEC Strategy that were updated in 2018 via the Draft CEC Strategy Update. Five new compound classes were classified: PFOA and long-chain carboxylates were classified as Moderate Concern compounds, and siloxanes, substituted diphenylamines, UV-benzotriazoles, and rare earth elements such as gadolinium were classified as Possible Concerns due to uncertainty in ecotoxicity risks (lack of available toxicity thresholds). The workgroup discussed needs for refining the tiered risk classification framework, as well as specific recommendations for compounds to add to or move within the risk framework. A summary of this discussion is presented below.

Tiered Risk Classification Framework

- **Low Concern risk tier:** Tom Mumley suggested that the “Low Concern” risk tier be further differentiated between compounds that (1) are expected to remain a low concern, and (2) have data suggesting that risks could potentially be changing.
- **Possible Concern risk tier:** Tom Mumley suggested further differentiation of this risk tier, based on the reason compounds are classified in this category -- lack of toxicity data, uncertainty in available data.
- **Grouping by chemical function:** Miriam Diamond suggested that chemicals could be categorized by function, to identify those that can be addressed using similar management actions. Tom Mumley warned against grouping compounds broadly if there is insufficient evidence to group the whole compound class within a risk tier, but suggested that a separate table could be used to categorize compounds by function.

Classification Recommendations

- **Non-chemical pollutants:** Steve Weisberg suggested that the workgroup consider whether or not it will evaluate non-chemical pollutants, such as pathogens and antibiotic resistance, as emerging contaminants. SCCWRP is currently considering these groups as emerging contaminants.

- SCCWRP is also currently conducting an antibiotic resistance study, involving monitoring of genes, and could incorporate the RMP if desired. Antibiotic resistance itself is considered a public health issue; there is a public perception that wastewater discharge near beaches is a major source, with little evidence.
- Bill Arnold is currently working on a project to link antibiotic resistance genes with antibiotic levels in the environment, and creating a map of these linkages for Minnesota. This project also seeks to understand whether genes act more like microbes or chemicals in the environment.

- **Rare earth elements and other metals:** Consider high-tech sources for these compounds. Future studies of rare earth elements and other metals should take into account speciation and organic complexing of these compounds. Platinum, palladium, tellurium, and other catalysts have been poorly studied but are likely increasing in use via high-tech manufacturing, and should be considered for further study.
- **Personal care products:** Anne Cooper Doherty noted that the messaging of placing this entire class in the “Low Concern” tier, labeled as having “no impact,” is problematic, given ongoing efforts to manage these compounds. The “no impact” label in particular is an overly strong statement. Jen Jackson suggested revising this to state “minimal impact.” It should also be carefully noted and qualified that the compounds currently listed in this group only include a relatively narrow list of compounds (compared to the universe of personal care product ingredients) that have been monitored in the Bay by the RMP.
- **Precautionary approach for persistent contaminants:** Miriam Diamond suggested that risk be classified using a precautionary approach - compounds that are highly persistent, and for which production is increasing and/or greater than degradation, might be considered significant concerns even if toxicity is not well understood.
- **All PFASs could be assigned Moderate Concern:** Bill Arnold and Miriam Diamond supported classifying PFOS/PFOA precursors (currently Possible Concerns) with PFOS and PFOA as Moderate Concerns. Kelly Moran and Anne Cooper Doherty also noted that DTSC’s classification of PFASs as a class adds motivation for a similar classification for the RMP, which could provide similar messaging for management efforts. Others noted that the short-chain PFASs (currently Possible Concerns) are problematic because they are less degradable, more easily taken up into plants, and harder to treat with conventional methods such as granular activated carbon.

3. Information: Summary of Exposure and Effects Workgroup Meeting

Phil Trowbridge and the EEWG science advisors presented a summary of the previous day’s EEWG meeting. At this meeting, Nancy Denslow presented results from the third phase of the estrogenicity assay development study, which included a screening of water and sediment in Lower South Bay. No quantifiable estrogenic activity was detected, but some questions remain around extraction efficiency, dilution, and very low detections near the method detection limit.

The EEWG and ECWG science advisors cautioned against interpreting the results to indicate a lack of estrogenicity in Lower South Bay. Steve Weisberg suggested further application of the assay in other areas of the Bay in order to make a general assessment of the Bay using this tool; Lee Ferguson suggested using the assay alongside non-target POCIS sampling to make sure the assay is not missing pulses of estrogenic compounds.

Additionally, the EEWG recommended funding for the first year of a three year study that would link responses to a glucocorticoid assay to whole organism (*Menidia*) responses. Dan Schlenk indicated that the glucocorticoid assay has shown more activity in environmental samples than the estrogenic assay in early tests, and that the responses often cannot be fully explained by targeted analyses of known, glucocorticoid-active compounds such as specific pharmaceuticals.

Discussion

Tom Mumley expressed increasing support for including the use of bioanalytical tools in the CEC Strategy. These assays could be used to help spatially focus non-targeted chemical analyses as well as targeted monitoring. Kelly expressed a preference for supporting toxicity studies rather than bioassay development, as the lack of available toxicity data prevents evaluating the risk of many chemical groups, and would more directly affect management decisions relevant to the Bay. The group agreed that further integration of the EEWG and ECWG groups would help develop a strategy for using and addressing these tools and needs.

4. Information: Interaction of Alkylphenols and Alkylphenol Ethoxylates on Endocrine Responses to Pesticides in Fish

Dan Schlenk presented a summary of alkylphenol and alkylphenol ethoxylate (APE) impacts on aquatic biota, including several studies showing synergistic impacts of nonylphenol and pesticide compounds in fish. These studies show that different modes of action can combine to create synergistic *in vivo* impacts, which may not be detectable in *in vitro* studies. APEs can have a number of other impacts beyond estrogenicity, so estrogenicity assays are not sufficient to assess APE toxicity risks.

Dan highlighted that the majority of 4-nonylphenols in industrial mixtures are in the ortho-position, although most research is conducted on the para-position nonylphenol, and emphasized the need to use CAS numbers when addressing specific compounds. Dan recommended monitoring the short-chain ethoxylates if a narrower focus is necessary, given their higher toxicity. Hindered phenols (banned in Canada based on a modeling-only exercise) and halogenated nonylphenols should also be considered for monitoring. 2,4-di-tert butylphenols, tris(nonylphenyl) phosphite, and HDPEs (all plastics) are all major sources of APEs entering the environment.

Jay Davis suggested conducting *in vivo* testing in addition to bioassays, given the potential for indirect synergistic impacts. Lee Ferguson suggested caged fish studies. Dan emphasized the importance of doing the chemistry as well as the bioassays.

5. Discussion & Decision: Potential Monitoring Strategy for Nonylphenols and Nonylphenol Ethoxylates

Rebecca Sutton presented different strategies for monitoring nonylphenols and nonylphenol ethoxylates, the only compound class in the Moderate Concern risk tier that has not been recently monitored (most recent monitoring conducted in 2010). Suggested monitoring included targeted chemistry in ambient water, archived margins sediment, water and sediment in San Leandro Bay, and bioassays in effluent- and stormwater-influenced ambient water and sediment samples. The goal of this monitoring would be to assess whether these compounds should stay in the Moderate Concern category, using some metric such as bioassays or toxicity thresholds.

Anne Cooper Doherty indicated that NPE data in wastewater effluent would be particularly valuable for DTSC, which is assessing PFASs (recently listed in a priority product) and NPEs (currently being assessed primarily in cleaning products) out of the three Moderate Concern compound groups. Evidence of exposure in the aquatic environment is a key consideration for DTSC action, and can include wastewater effluent data and/or ambient Bay samples, even if a toxicity threshold is not available. Wastewater effluent data are sufficient to demonstrate a steady source to the aquatic environment. Data showing linkages between the ambient environment and sources is helpful, but not required for DTSC action.

Tom Mumley recommended that all compounds within the Moderate Concern category have their own strategy, including both a monitoring strategy and assessment of potential management actions that can be taken, the latter informed by further monitoring.

Monitoring recommendations are summarized below:

- Target Analytes
    - Expand monitoring to include long-chained nonylphenol and octylphenol ethoxylates (NPEs and OPEs, or alkylphenol ethoxylates [APEs])
    - Lee suggested expanding the list to include alcohol ethoxylates. These, along with the long-chained NPEs and OPEs, were present at very high quantities in the stormwater-influenced Bay non-target analysis samples, and are also toxic.
- Targeted Analysis methods
    - Both water and sediment sampling are necessary. Short-chain ethoxymers tend to partition to sediment, while more diverse mixtures are found in water.
    - Grab samples are needed -- passive sampling does not provide representative samples due to the chemical properties of these compounds.
- Bioassay methods
    - Bioassay methods have improved over the past 12 years and now may be able to detect effects.
    - *In vitro* assays could miss classes of compounds (i.e., long-chain ethoxylates) that are first metabolically activated before binding to estrogen (or other bioassay) receptors.

- Estrogenicity assays targeting areas like San Leandro Bay would not target only APEs; they would also be affected by the lighter PCBs that are estrogenic.
- Lee recommended targeted analysis of the long-chain ethoxylates first. Bioassays would need to be conducted alongside targeted analyses of other estrogenic compounds as well, such as estrogenic PCBs.

- Locations / Sources
  - The Port of Oakland could be a source of APEs from the shipping industry. While ballast water is not released into the environment, APEs from ship coatings could be a significant.

6. Information & Discussion: CECs Model Development

Rebecca Sutton and Jing Wu presented recent progress towards the development of a suite of modeling tools for CECs -- including steady-state one-box models, the Bay Area Hydrologic Model for stormwater (Jing Wu), a hydrodynamic model (Rusty Holleman), and a biogeochemical model under development (Zhenlin Zhang).

Miriam Diamond recommended developing a strategy for utilizing the models, or a simple "conceptual model of the models." She suggested that the models be loosely coupled in order to allow them to be used in sequence, and to provide a framework for utilizing different aspects of the modeling package for various purposes and compounds. Bill Arnold noted that coupling the BAHM would require significant spatial precision. Miriam also strongly advocated for including the atmospheric pathway in models, and noted that biota could be included in sequence after these models (i.e., bioaccumulation and food web monitoring suggested by Derek Muir), but in some cases may need to be included within mass-balance equations as organisms can be a contaminant reservoir.

Kelly Moran and Tom Mumley strongly supported focusing largely on conceptual models and other simple modeling before diving into the more complex options presented, particular in data poor environments. Kelly highlighted the need to simply focus on the relative importance of stormwater vs. wastewater pathways, and develop tools to further link wastewater pathways to sources.

Jennifer Teerlink was supportive of developing a modeling approach for fipronil, to understand the relative contribution of stormwater and wastewater pathways, as well as other potential pathways. Heather Stapleton cautioned that PFAS precursor data needs to be included in any PFAS bioaccumulation model.

7. Information: Identification, Sources, and Risks of Novel and Emerging Contaminants in Urban Stormwater

Ed Kolodziej presented results from a series of studies conducted to understand the potential CEC causes of acute Coho salmon mortality following urban storms in Washington. Pathogens, metals, pesticides, PAHs, ammonia, and basic water quality parameters have been tested and do not appear to be the sources of mortality, which can occur after 2-3 hours of exposure. Ed Kolodziej's group conducted cluster analyses on a series of non-targeted analyses conducted in stormwater runoff and various impacted fish tissues, utilizing this method of "biologically relevant suspect screening" to identify those compounds that are co-occurring in all these samples. Several key compounds identified included contaminants associated with roadways, including acetanilide (tire rubbers), 1,3-dicyclohexylurea, and diphenylguanidine (tire vulcanization). A GIS/landscape modeling study showed a higher level of mortality in areas with higher impervious surface area.

A follow up study was conducted to identify potential sources, which included conducting non-targeted analyses in leachates and dilutions of various roadway-related products, including vehicle fluids and tire leachate. The top 10 compounds detected in all samples with acute mortality were also found in tire rubber leachate, although little information is available about these compounds in the literature. Notably, contaminants in tire dust were more closely clustered with contaminant stream water than highway runoff. Field samples show no visual evidence of microparticles from tirewear, but Ed is exploring having samples analyzed for particles. Lee Ferguson suggested than benzotriazoles be included in Ed's follow-up LC/MS/MS targeted analyses. TIE follow-up tests are being considered but not currently planned, given the high probability of many negative results.

Of note, chum salmon do not succumb to the same toxicity as Coho salmon; hemoglobin on Coho salmon is more sensitive to oxidation, and juvenile Coho spend more time in freshwater than other species. Ed also noted that acute toxicity to smaller fish could be possible, but small fish carcasses are very rapidly preyed upon and therefore may not be easily observable. Anecdotally, Ed has heard of similar issues in Northern California; Luisa Valiela suggested a similar issue could be causing the leopard shark die-offs in South Bay, and Jen Jackson offered to ask creek groups if any similar evidence of acute toxicity has been observed locally.

8. Information: Pharmaceuticals in Bay Area Wastewater

Diana Lin presented preliminary data from the voluntary BACWA study on pharmaceuticals in wastewater. Because this was a voluntary study, different study designs were used at each location, and the participating facilities may not be representative of the entire Bay Area. Tom Mumley cautioned against making broad statements based on this limited dataset.

Kelly Moran supported the investment of time to calculate per capita influent loads, even based on grab samples. Bill Arnold noted that the same suite of antibiotics detected in the Bay have been detected in Minnesota, and the negative removal efficiencies observed were not unusual, as these compounds can become conjugated and deconjugated during treatment. Miriam Diamond noted that she has conducted some modeling of pharmaceuticals, and could potentially inform efforts by the RMP to model the dilution of observed effluent concentrations in the ambient Bay. Lorien Fono noted that the State Water Board is just as interested in effluent data as ambient Bay data, highlighting the value of this study even without further modeling.

9. Information: Preliminary Data on CECs in San Francisco Bay

Rebecca Sutton and Jennifer Sun presented preliminary data on wastewater indicator and pesticide compounds in margins sediment and water. No new red flags were raised; galaxolide fell below state monitoring trigger levels, which would allow it to be classified within the personal care products group as a Low Concern. Pyrethroid and fipronil / fipronil degradate data support current classifications as Low Concern and Moderate Concern, respectively. Imidacloprid data could potentially warrant classification as a Moderate Concern. Carbendazim was detected at all sites but only at one site above the available EPA aquatic life benchmark, and is not yet a major concern. Heather Stapleton asked about the strobilurin fungicide pesticide class, which were monitored; only azoxystrobin was detected, in water at several sites.

Kelly Moran noted that urban runoff is low during the time of sample collection, so detections may be more likely tied to wastewater sources, even if sources and product applications that would likely lead to stormwater pathways may be common for the detected compounds. Mike Connor suggested monitoring contaminant classes in harbor seal blubber sample in Lower South Bay to further focus on compounds with a greater likelihood of potential ecological effects.

10. Information: Partitioning and Persistence of Volatile Methylsiloxanes in Aquatic Environments: A Case Study for the Bay

Dimitri Panagopoulos presented a summary of available information on the physical-chemical characteristics and volatile methylsiloxanes (VMS), as well as a proposal to conduct *pro bono* analyses of VMS in the Bay. Published log Koc and enthalpy values are conflicting and may not be highly reliable, and result in substantial differences in estimates of environmental fate and residence times of these compounds. The proposed study would involve measurement of VMS in sediments and near wastewater effluent outfalls to empirically calculate residence times to compare with the modeled estimates. Science advisors cautioned that back-calculating log Kocs from the empirical measurements may not be reliable.

Jennifer Jackson noted that the Air Resources Board has banned perchloroethylene in dry cleaning by 2023, and since siloxanes are a potential alternative, data on the exposures and potential toxicity of these compounds would be useful to have soon. Mike Connor noted that the Water Environment Research Federation is currently working to understand the fate of siloxanes in wastewater treatment plants.

Mike Connor also suggested a more robust evaluation of physical-chemical parameters for CECs considered by the RMP, to inform the categorization of compounds within the tiered risk framework.

<u>Day 2 - April 13</u>

1. Summary of Yesterday and Goals for Today

2. Discussion: CEC Pathways Monitoring Strategy

Rebecca Sutton presented an overview of the pathways monitoring strategy that was added to the draft 2018 CEC Strategy Update. Pathways monitoring provides a stronger link to potential management activities, and presents an opportunity to identify early indicators of trends before significant concentrations are detected in the environment, given the higher concentration of contaminants in pathways. Major topics of discussion are summarized below.

Screening vs. Loading studies
Rebecca clarified that loadings studies will only be developed for chemicals of significant concern. Kelly Moran strongly support additional pathways monitoring, given the higher concentrations of contaminants in pathways and the linkages to sources, and cautioned against moving too quickly into loadings studies, which can be costly and drain resources from valuable screening level studies. Reid Bogart supported the primary focus on screening level studies. Mike Connor argued that the monitoring needs to be quantitative to be useful.

Atmospheric Pathway
Miriam Diamond highlighted that the atmospheric pathway includes not only wet deposition measured in stormwater, but also direct deposition to the Bay, which includes compounds that are not degraded before reaching the Bay. Kelly Moran noted that the atmospheric pathway modeling was included in the Copper and Brake Pad Partnership effort, but that the modeling was mainly relevant to stormwater. Tom Mumley argued that this pathway should be a lower priority: while direct deposition may be an issue, the major sources of direct atmospheric deposition are global, given that the prevailing winds move east. This looser link to potential local management action and the higher cost of addressing this new pathway should make it a lower priority.

Additional comments on details in the strategy are summarized below:

- Kelly Moran argued against developing a menu of monitoring options for different types of CEC compounds, which would be too generic to be useful for any one compound group.
- Kelly Moran suggested that the pathway categories include agricultural runoff.
- Tom Mumley noted that while there can be a framework for pathway categories to be addressed for all contaminants, they do not need to be addressed with equal effort (i.e., industrial sources for fipronil are unknown, but likely do not need to pursued with great effort).
- Karin North suggested monitoring upstream and downstream of low impact development (LID) projects to determine their effectiveness. Miriam Diamond supported this proposal, particularly as LID elements are in the process of being implemented; Kelly Moran expressed skepticism, given the often small size of the watersheds targeted and low overall concentrations detected in such studies.

- Jennifer Teerlink highlighted that the USEPA has now approved a label change for outdoor application products containing fipronil, which DPR believes should begin a downward trend in fipronil concentrations in surface water.
- Bill Arnold suggested that there may be certain industry-specific pathways, such as ports and marinas for APEs (i.e., boat paints and coatings). Lee Ferguson noted that epoxy coatings are also very common in concretes used indoors.

A larger subgroup will be convened to further develop the pathways monitoring strategy over the course of the year, including a specific strategy for wastewater treatment plants (not discussed at the meeting). Participants will include representatives from BASMAA/stormwater agencies (Reid Bogert), the City of San Jose, the City of Palo Alto, BAPPG/BACWA, and DPR. Miriam Diamond and Kelly Moran will provide review of the strategy.

Action Item
- Establish pathways monitoring strategy subgroup and schedule future meetings

3-5. Summary and Discussion of Recommended Studies for 2019

Rebecca Sutton, Meg Sedlak, Diana Lin, and Jennifer Sun presented 2019 Special Study Proposals on the following subjects:
- Emerging Contaminants Strategy
- Stormwater Loading Strategy for CECs
- Roadway Contaminants in Stormwater
- Alternative Organophosphate Flame Retardants Conceptual and Steady-State Model
- Fipronil and Fipronil Degradates in the Bay Food Web
- Sunscreens in Water and Fish
- Non-targeted Analysis of Sport Fish, Cormorant Eggs, Harbor Seals (matching funds for Cal Sea Grant proposal)

Following extensive discussion, studies were prioritized via a closed door session. Studies are listed in order of priority; major topics of discussion for each are summarized below.

Recommended for RMP Special Studies Funding

<u>Priority 1: CEC Strategy</u>
Tom Mumley requested that future proposals include a greater detail on the aspects of the strategy that will be developed each year. Candidates for addition to the current strategy proposal include expanding the strategies for monitoring effects, pathways, and modeling. Karin North reiterated to Becky that, should she need more funding for the emerging contaminants strategy, she should request funds from the Steering Committee.

<u>Priority 2: Non-Targeted Analyses</u>

No clarifying questions were asked. Funding was recommended for this study given the low cost relative to the total project cost leveraged.

Priority 3: Stormwater Screening Study (REVISED)
Multiple science advisors and stakeholders expressed a strong interest in leveraging the proposed Roadway Contaminants study to conduct a screening of other priority compounds, focusing on contaminant screening over loadings studies. Water Board and stormwater agency representatives noted that true monitoring for contaminant loads, as is done for PCBs, requires millions of dollars of investment, and at this stage additional screening-level data for compounds like PFASs can already significantly increase the accuracy of estimated loadings, which can then be used to justify the need for more robust loads monitoring, where appropriate. Tom and Karin both expressed an interested in optimally leveraging the proposed stormwater study to comprehensively evaluate contaminants in runoff. Miriam, Lee, and Kelly expressed support, as did Bill, who suggested including compounds with a range of physical-chemical properties. Mike Connor suggested including a broad array of contaminants, including some non-CEC contaminants such as PCB 153, which could be used within a cluster analysis as a reference to understand which contaminants tend to co-occur.

Compound classes recommended for studying included:

- PFASs - Eurofins has a new list of ~40 compounds for approximately $400/sample that North Carolina has used, and may cover the most important compounds for much cheaper that Chris Higgin's method. Total extractable organic fluorine should also be included to capture potential precursors. Erika Houtz's TOP method may provide a similar result to the total extractable organic fluorine method.
- Organophosphate esters, including those primarily used in plasticizers and those newly identified as flame retardants in Heather's recent studies
- Ethoxylated surfactants (see proposed study above)

Tom and Karin expressed strong support for this study, indicating that the Steering Committee could potentially provide additional funds to assist with study design and coordination costs, as well as support leveraging non-RMP staff resources to conduct this study.

Priority 4: Ethoxylated Surfactants Study (NEW)
Motivation

- Lee suggested monitoring APEs and alcohol ethoxylates in 2019. There may be mechanisms for effects other than estrogenicity, including for the long-chain ethoxylates, which have been shown to cause adipogenesis. Heather, and Anne Cooper (DTSC) supported this proposal.
- Anne Cooper indicated that DTSC is finding Bay NPE data old and limited. Additional margins data near pathways would be useful for DTSC to begin understanding sources. Data could be used to inform alternatives analyses as well. No thresholds are available to understand potential adverse impacts from levels currently detected in organisms, but this study may not be able to address this issue.

- Jennifer Teerlink indicated that these are not DPR priorities, but they are common ingredients in pesticide formulations and recent updates in DPR modeling tools (through Pesticide Use Reporting data) could be used to inform the monitoring

Straw-Man Proposal

- Ambient Bay water
- Stormwater - add to proposed stormwater CECs screening study (Roadway Contaminants)
- Margins sediment (archived from 2018)
- Wastewater effluent (small number of samples [~8] would be adequate for DTSC needs)
- Lee Ferguson can conduct analyses
    - Approximately $500/sample for octylphenols, nonylphenols, and several alcohol ethoxylates
    - Isotope-labeled standards are not available and would be difficult to synthesize. Unlabeled standards could be used, but results could be off by a factor of 2. The group agreed that this level of accuracy would be sufficient for such a screening study.

<u>Priority 5: Sunscreens Study</u>

Given the initial screening level of this study, Bill Mitch suggested revising the design to focus first just on sunscreen compounds in wastewater rather than in the ambient Bay and food web. Karin North and Lorien Fono agreed to provide wastewater effluent for such a study. In addition to butylparaben, methyl- and ethylparaben were recommended for monitoring, as they may be more common in sunscreen products. Fish collected in 2019 could potentially be archived for future monitoring.

Not recommended for RMP Special Studies funding

<u>Priority 6: Alternative Organophosphate Flame Retardants</u>

Tom Mumley indicated that this study could not be used to meet the stormwater municipalities' permit requirement. Tom and Kelly expressed concern that this modeling effort was premature for a Possible Concern compound with limited pathways data.

Heather Stapleton recommended that this compound group be expanded to include a broader range of organophosphate esters, including alkylated aryl phosphates. Many of these compounds are also or mostly used as plasticizers, and those sources should be considered in any related studies; other flame retardant alternatives also seem to be missing.

Miriam Diamond indicated that air concentrations in Toronto, likely from indoor ventilation, were high enough to cause washout into rivers at microgram per liter levels; available management interventions are chemical bans rather than actions that can be taken by the Water Board. For this study, air data is needed separate from stormwater data to inform the modeling, and there is a time limit to leverage graduate student labor costs to complete this work. To reduce costs, the modeling could be conducted using placeholder air data from Toronto, and filled in with monitoring data collected later from the Bay Area.

<u>Priority 7: Fipronil in the Bay Food Web</u>
Tom Mumley highlighted that this study would be a fate study, without wildlife and human health effects indicators. Derek Muir suggested monitoring these compounds alongside bioaccumulation benchmarks like PCB 153, which is known to bioaccumulate. Stable isotope data would be needed to calculate trophic levels for a true biomagnification study.

Jennifer Teerlink expressed interest in the study but noted that the results would not affect any DPR actions. Kelly Moran noted that these data could generate interesting information to compare against results from the SCCWRP study, which has led manufacturers to try to argue instead that fipronil does not bioaccumulate. However, the group agreed this study was a lower priority; fish should be archived below -20 C, a temperature at which lipids degrade.

Jay Davis recommended that fipronil be analyzed as an add-on to Status and Trends sport fish monitoring. Tom Mumley noted that the fipronil add-on could be a good candidate to receive funds for a small Supplemental Environmental Project (~$15,000).

<u>Not Prioritized: Stormwater Loadings</u>
The stormwater loading strategy study was recommended to be deferred to 2020, or following the stormwater screening study. Tom Mumley and other stakeholders expressed interest in the value of this study, but concern that a true loading strategy would be a bigger undertaking than the proposed study. Initial evaluation of the need for loadings study should fit into the larger CEC strategy (i.e., strategies for addressing Moderate Concern compounds, strategies for employing different types of studies and monitoring of different matrices, the pathways monitoring strategy, etc.).

Luisa Valiela noted that the EPA has some atmospheric monitoring equipment that could be utilized if needed. Kelly noted that air monitoring conducted by the Air Board is mostly designed for assessing long-range transport rather than local sources, which would be needed for RMP studies.

Additional Discussion - Effects vs. Chemical Monitoring Strategy

The group discussed several topics related to the integration of effects and chemical monitoring of CECs, including addressing: (1) mixture effects, (2) endpoints and indirect modes of action detected by whole organism vs. *in vitro* testing, and (3) dose levels and detection limits in effects-based testing. Kelly Moran suggested inviting additional experts to advise the group on these issues, such as from EPA’s ToxCAST group or NIEHS’s National Toxicology Program. Karin and Tom agreed that these issues would be discussed with the RMP Steering Committee and should be addressed in the CEC strategy.

Lee Ferguson relayed information from Nancy Denslow indicating that high throughput screens like ToxCAST and Tox21 are 1 or 2 orders of magnitude less sensitive than more targeted screenings like the estrogenicity assay, which may be detecting low levels that would be missed by these broader screens. Heather Stapleton suggested conducting effects-directed and chemical monitoring in parallel, as mixture effects cannot be predicted by ToxCAST. Derek Muir noted that the EPA has developed a priority compound list based on pure chemical tests, which at a coarse level could be compared to the RMP's monitoring priorities.

Action Items

- Develop new ethoxylated surfactants study
- Revise stormwater screening, CEC strategy, and sunscreens proposals

6-7. Decision: Recommendations for 2019 Special Studies Funding

Study Name	Modified Budget	Priority	Comments
Emerging Contaminants Strategy	$70,000	1	For next year, provide high level summary of networking and leveraging that have benefited the program and how much effort is associated with strategy improvements.
Non-targeted Analysis of Fish and Wildlife	$25,000	2	Need $25k each yr for 3 yrs or $75k total
Stormwater Screening Study	$300,000	3	Goal is quantifying presence/rough loads. Add PFASs (n=40, goldilocks level) and TOP fluorine (Colorado School of Mines?). Add organophosphate esters. Add ethoxylated surfactants. Comprehensive cluster analysis. Design needs to be improved (e.g., no Lagunitas). Develop proposal. Need a RMP technical report. Could spread cost over 2 years (planning/sampling in year 1, data mgmt/analysis and reporting in year 2).
Ethoxylated Surfactants Study	$50,000	4	Effluent, bay water, archived sediment. Develop proposal. DTSC has need for effluent data.
Sunscreens in Water and Fish	$50,000	5	Revise proposal to effluent testing only. Potentially use RMP archives of fish later.
Alternative Organophosphate Flame Retardant Conceptual and Steady-State Model		6	
Fipronil and Fipronil Degradates in the Bay Food Web		7	Will not affect DPR decisions now. Consider adding as a parameter to a few S&T sport fish samples.
Stormwater Loading Strategy for CECs	$0		Defer to later years after screening study
Total	**$495,000**		

2020 Emerging Contaminants Special Studies Proposals Abstracts

Study Name	Budget	Summary	RMP Tier	Critical Drivers	Deliverables (includes data management)	Page No.
Emerging Contaminants Strategy	$65k	Increasing interest in emerging contaminants issues by the San Francisco Bay Regional Water Board, RMP stakeholders, and the general public is reflected in headline news, as well as policy actions at local, state, and federal levels. Core deliverables include tracking new information regarding contaminant occurrence and toxicity and updating the RMP's Tiered Risk and Management Action Framework; responding to requests for information and assisting the Water Board with emerging contaminants action plans; and coordination of pro bono analyses by partners.		Essential to coordinate studies relevant to management actions. Inform policy actions at local, state, federal levels.	Technical assistance to stakeholders; Update and share CEC Strategy.	22-26
CECs in Urban Stormwater	$168k	Monitoring during the first, pilot year of a multi-year study on CECs in stormwater is being completed now. The study is designed to provide critical stormwater data needs for four contaminant classes: 1) a new, targeted list of CECs specific to stormwater; 2) per- and polyfluoroalkyl substances (PFAS); 3) phosphate flame retardants; and 4) ethoxylated surfactants. Year 2 activities include site selection, sample collection, and analysis for a greater number of samples for this Bay Area-wide screening study. Preliminary review of data will inform the third year of site selection and sample collection; final deliverables at the conclusion of the study will include scientific manuscripts and a summary of results to inform water quality managers. This multi-year study is proposed to provide an intensive and pioneering examination of CECs in urban stormwater.	Moderate, Possible, New CECs (not previously monitored)	Screen Bay stormwater for presence of stormwater-derived contaminants associated with ecotoxicity concerns; Initial data on CECs specifically related to stormwater is expected to inform monitoring or management actions; Identified true sources, such as vehicle tires, could be the subject of green chemistry focus; Multi-year effort that leverages other RMP sample collection activities.	Scientific manuscripts; Technical summary for managers; Data uploaded to CEDEN.	27-35
Characterization of Pharmaceutical Contamination in Lower South Bay Water, Margin Sediment, and Wastewater	$123.5k (optional $43k add-on)	Pharmaceutical contamination is widely detected in the Bay, and the most recent Bay study indicates key pharmaceutical contaminants may approach levels of concern for wildlife. This study will monitor Lower South Bay water (and optionally, margin sediment) for pharmaceutical contamination, providing data essential to a current evaluation of the potential risks of approximately 150 pharmaceutical contaminants to inform the RMP's Tiered CEC Risk and Management Framework.	Low, New CECs (not previously monitored)	Follow-up to recent RMP study in wastewater effluent indicating potential cause for concern for 17 specific pharmaceuticals	Technical report; Data uploaded to CEDEN.	36-47
Bisphenols in Bay Sport Fish	$54k	Bisphenols are a class of widely used, synthetic, endocrine-disrupting compounds, commonly found in polycarbonate plastics and epoxy resins, and frequently detected in many environmental matrices. Bay water samples collected in 2017 revealed detections of both BPA and bisphenol S (BPS) at levels in the range of a protective toxicity threshold for BPA (60 ng/L). This class of contaminants may merit a Moderate Concern classification in the RMP tiered framework. While other bisphenols were not detected in Bay waters, some of these compounds have chemical properties that suggest they are more likely to be found in the tissues of organisms than in water. We propose leveraging Status and Trends sport fish monitoring to obtain sport fish composite samples for bisphenols analysis. By analyzing this class of contaminants in fish tissue, we can develop a more complete picture of which bisphenols are in the Bay environment and determine whether fish consumption is a relevant pathway for human exposure.	Possible (Moderate classification possible)	Screen sport fish for wide range of bisphenols and evaluate potential for human and wildlife exposures; Results can inform DTSC's green chemistry priorities; Fish sampling will take advantage of 2019 RMP Status and Trends sport fish monitoring effort.	Technical report; Data uploaded to CEDEN.	48-56
Sunscreens in Bay Area Wastewater Effluent	$55k	Ultraviolet (UV) radiation filters such as oxybenzone and octinoxate are widely used as active ingredients in sunscreen lotions and in other products, such as cosmetics, paints, and plastics. For aquatic organisms, the main exposure route is through direct wash-off into surface waters during recreational activities, and indirect discharge of these chemicals from wastewater treatment facilities to surface waters. Several sunscreen active ingredients have been shown to cause adverse effects, such as endocrine disruption in fish and bleaching on coral reefs. The City of San Francisco is considering a resolution to examine the occurrence and potential impacts of some of these compounds. This study will quantify levels of sunscreens in Bay Area effluents to assess whether they may be a potential concern for the Bay.	New CECs (not previously monitored)	Respond to data needs identified by City of San Francisco Supervisors; Results can inform DTSC's green chemistry priorities.	Technical report; Data will **not** be uploaded to CEDEN.	57-62

Special Study Proposal:
Emerging Contaminants Strategy

Summary: Increasing interest in emerging contaminants issues by the San Francisco Bay Regional Water Board, RMP stakeholders, and the general public is reflected in headline news, as well as policy actions at local, state, and federal levels. The amount of effort needed to manage the RMP Emerging Contaminants Strategy has increased significantly in recent years. Core deliverables include tracking new information regarding contaminant occurrence and toxicity and updating the RMP's Tiered Risk and Management Action Framework; responding to requests for information and assisting the Water Board with emerging contaminants action plans; and coordination of *pro bono* analyses by partners. To accomplish these tasks, $65,000 is requested.

Estimated Cost: $65,000
Oversight Group: ECWG
Proposed by: Rebecca Sutton (SFEI)
Time Sensitive: Yes; essential annual strategy funding

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Information gathering from a variety of sources throughout the year, including presentations at scientific conferences, to inform Task 4	Year-round
Task 2. Assist Water Board and other RMP stakeholders with science summaries relating to policy including emerging contaminants action plans and comment letters regarding proposed actions of other agencies	Year-round
Task 3. Coordinate *pro bono* studies conducted in collaboration with RMP Status and Trends monitoring activities	Year-round
Task 4. Update the RMP CEC Strategy document with revised tiered framework tables (integrating new data and external information) and multi-year plan, discussion of new RMP data and information gathered (Task 1); present at spring ECWG meeting	Spring 2021
Task 5. Present an update of RMP CEC Strategy, ongoing or completed special and *pro bono* studies, and new studies to the Steering Committee	Summer 2021

Background

The science and management of contaminants of emerging concern (CECs) is an area of dynamic recent development. The RMP, a global leader on CECs, stays ahead of the curve by identifying problem pollutants *before* they can harm aquatic life.

In 2017, the RMP completed the first major revision of its CEC Strategy document, which outlines a comprehensive, forward-looking approach to addressing CECs in San Francisco Bay (Sutton et al. 2017). The RMP's CECs Strategy consists of three major elements. First, for contaminants known to occur in the Bay, the RMP evaluates relative risk using a Tiered

Risk and Management Action Framework. This risk-based framework guides future monitoring proposals for each of these contaminants. The second element of the strategy involves review of scientific literature and other aquatic monitoring programs to identify new contaminants for which no Bay data yet exist. Finally, the third element of the strategy consists of non-targeted monitoring, including broadscan analyses and bioanalytical tool development and use. In 2018, a strategy for monitoring CECs in pathways was introduced via a CEC Strategy Update (Lin et al. 2018).

For the RMP CEC Strategy to remain relevant and timely, it needs to be updated annually with new information on analytical methods and study findings from the RMP and others. Funds are needed to review new results, track research conducted elsewhere, and keep stakeholders apprised of findings. Coordination of *pro bono* analyses is another rapidly expanding component of the strategy fund.

Funds are also required to synthesize available ecotoxicity data, an essential component of classifying CECs within the Tiered Risk and Management Action Framework. This includes developing expertise in gleaning insights provided by new tools in the field of predictive toxicology. Likewise, it is important for RMP scientists to provide relevant, objective science to inform the growing number of policy actions concerning emerging contaminants, an increasing demand on staff time.

Beginning in 2017, the RMP directed significantly increased resources for monitoring and special studies relating to emerging contaminants, the result of an optional reduced monitoring schedule for municipal wastewater discharges to the Bay in exchange for increased payments to the RMP. By necessity, the level of funding directed towards emerging contaminants strategy also increased. For 2020, $65,000 is requested, similar to recent years.

Study Objectives and Applicable RMP Management Questions

Table 1: Study objectives and questions relevant to RMP ECWG management questions

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Compare existing occurrence data with new toxicity information reported in the scientific literature. Evaluate future monitoring needs and toxicity data gaps.	Does the latest science suggest a reprioritization of chemicals as we learn more about them? Which newly identified contaminants merit further monitoring? Which Possible Concern contaminants could be the subject of RMP-funded ecotoxicity studies?

2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Evaluate new knowledge regarding sources, pathways, and loadings for CECs in the context of a comprehensive conceptual model to allow prioritization of data gaps the RMP can fill.	What are the key sources or pathways that impact concentrations and potential risk of emerging contaminants?
3) 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?	Compare levels of parent CECs to degradates in light of processes expected to be active and influential in the Bay. Compare model predictions to monitoring results; assess potential reasons for differences between predicted and measured values. Does new research in other regions provide insight as to key processes that affect the fate of emerging contaminants?	Are relative levels of contaminants and degradates in different matrices or subembayments consistent with our expectations for various contaminant processes?
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	Compare Bay CECs levels measured over time. Do trend data from other regions suggest likely trends in the Bay?	Have specific CECs declined over time? Have functional replacements for these CECs increased?
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	Evaluate data on production, use, and source trends in the scientific and trade literature as a means of prioritizing potential risk of Bay contaminants in the future, and corresponding monitoring recommendations. Evaluate the expected impacts of changes to population, climate, affluence, and other factors.	Do production, use, and source trends suggest likely changes in the relative risk of specific emerging contaminants? What are the possible effects of changes to population, climate, and affluence on concentrations of CECs and associated risk?
6) What are the effects of management actions?	Evaluate the likely impacts of new management actions on contaminant levels. Which actions may have unintended consequences?	Are additional or different actions needed to reduce levels below aquatic toxicity thresholds?

Emerging contaminants strategy work most directly addresses questions 1, 2, 3, 5, and 6, by assuring all manner of relevant new information is brought to bear in evaluating the relative risk of emerging contaminants to Bay wildlife. For example, a new study identifying a lower toxicity threshold for a particular contaminant might suggest that the risk tier in which that contaminant had been placed should be revised.

Approach

The emerging contaminants strategy funding supports the review of key information sources throughout the year. These sources include:

- Abstracts and newly published articles in key peer-reviewed journals (e.g., Environmental Science and Technology, Environmental Toxicology and Chemistry, Environment International)
- Documents produced by other programs (e.g., USEPA, Environment and Climate Change Canada, European Chemicals Agency, Great Lakes CEC Program)
- Abstracts and proceedings from relevant conferences (e.g., Society of Environmental Toxicology and Chemistry, International Symposium on Brominated Flame Retardants)

In addition, strategy funding allows staff to provide additional services, such as:

- Numerous presentations, briefings, and stakeholder interactions
- Scientific assistance to the Water Board as the agency prepares emerging contaminant action plans
- Scientific assistance to stakeholders engaged in emerging contaminants policy
- Coordination of *pro bono* analyses

Starting in 2019, we will develop an approach for using predictive toxicology to review Possible Concern contaminants and prioritize special studies for those that have the highest potential to pose risks based on available data. New insights may highlight the need for the RMP to fund targeted toxicological studies to develop ecotoxicity thresholds that might allow for a more definitive classification in the High, Moderate, or Low Concern tiers.

The proposed deliverables table on the first page of this proposal lists the specific tasks to be completed and their due dates.

Budget

Table 2. 2020 Emerging Contaminants Strategy budget

Deliverables	**Budget**
Tasks 1-5: Information gathering from a variety of sources throughout the year, including presentations at scientific conferences, to inform Task 4; Assist Water Board and other RMP stakeholders with science summaries relating to policy including emerging contaminants action plans and comment letters regarding proposed actions of other agencies; Coordinate *pro bono* studies conducted in	$65,000

collaboration with RMP Status and Trends monitoring activities; Update the RMP CEC Strategy document with revised tiered framework tables (integrating new data and external infornation) and multi-year plan, discussion of new RMP data and information gathered (Task 1), present at spring ECWG meeting; Present an update of RMP CEC Strategy, ongoing or completed special and *pro bono* studies, and new studies to the Steering Committee.	

Budget Justification

Significant increases in RMP resources dedicated to CEC special studies, beginning in 2017 and expected to continue in 2020, require greater levels of engagement, outreach, coordination, and integration to assure strategic use of available funds. Funding for this task will allow for strategic thinking using the latest science, so that the RMP can continue to generate the information water managers need to effectively address emerging contaminants in the Bay.

Reporting

RMP CEC Strategy presentations (Emerging Contaminants Workgroup meeting and follow-up teleconference [as needed], Steering Committee, and Annual Meeting) provide opportunities to report on this work. A brief update to the RMP CEC Strategy, including revised tiered framework tables and multi-year plan, represents another key reporting mechanism.

References

Lin D, Sutton R, Shimabuku I, Sedlak M, Wu J, Holleman R. 2018. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2018 Update. SFEI Contribution 873. San Francisco Estuary Institute, Richmond, CA. https://www.sfei.org/documents/contaminants-emerging-concern-san-francisco-bay-strategy-future-investigations-2018-update

Sutton R, Sedlak M, Sun J, Lin D. 2017. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2017 Revision. SFEI Contribution 815. San Francisco Estuary Institute, Richmond, CA. https://www.sfei.org/documents/contaminants-emerging-concern-san-francisco-bay-strategy-future-investigations-2017

Special Study Proposal:
Contaminants of Emerging Concern (CECs) in Urban Stormwater

Summary: Monitoring during the first, pilot year of a multi-year study on CECs in stormwater is being completed now. The study is designed to provide critical stormwater data needs for four contaminant classes: 1) a new, targeted list of CECs specific to stormwater; 2) per- and polyfluoroalkyl substances (PFASs); 3) phosphate flame retardants; and 4) ethoxylated surfactants. Year 2 activities include site selection, sample collection, and analysis for a greater number of samples for this Bay Area-wide screening study. Preliminary review of data will inform the third year of site selection and sample collection; final deliverables at the conclusion of the study will include scientific manuscripts and a summary of results to inform water quality managers. This multi-year study is proposed to provide an intensive and pioneering examination of CECs in urban stormwater.

Estimated Cost: $168,000 for Year 2
(Year 1 $132,000; Year 3 est. $156,000)

Oversight Group: ECWG and SPLWG

Proposed by: Rebecca Sutton (SFEI), Ed Kolodziej (University of Washington), Chris Higgins (Colorado School of Mines), Da Chen (Jinan University), Lee Ferguson (Duke University)

Time Sensitive: Yes (multi-year study already undereway)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable (Year 2)	Due Date
Task 1. Site selection and reconnaissance, in coordination with SFEI stormwater and STLS teams; refinement of pilot sampling protocol	Summer 2019
Task 2. Field collection of stormwater samples	Fall 2019 – Spring 2020
Task 3. Laboratory analysis of samples	Spring – Summer 2020
Task 4. Preliminary review and analysis of data to inform Year 3 sample collection	Summer – Fall 2020

Background

An important element of the RMP's CEC Strategy is the application of non-targeted methods to identify unexpected contaminants that merit further monitoring (Sutton et al. 2017). In 2016, the RMP funded a special study to use a type of non-targeted analysis to examine Bay water samples collected from three sites influenced by three different pathways: effluent, stormwater, and agricultural runoff.

Findings from this study indicate that water samples from the stormwater-influenced site, San Leandro Bay, contained a broad array of unique contaminants with strong signals suggesting higher concentrations (Ferguson et al. in prep; Sun et al. in prep). One example of a contaminant identified with high confidence is 1,3-diphenylguanidine (DPG), a rubber vulcanization agent derived from vehicle tires. The European Chemicals Agency has established predicted no effect concentrations (PNEC) for DPG of 30 μg/L in freshwater and 3 μg/L in marine waters (ECHA 2018). While the non-targeted analysis provides only qualitative data, the high relative strength of the DPG signal suggests that this contaminant has the potential to be present at concentrations similar to these PNECs.

These findings indicate that stormwater is a pathway by which unique contaminants from vehicles and roadways make their way to tributaries and near-shore Bay environments. An additional factor contributing to a special interest in emerging contaminants from stormwater is that, unlike wastewater, this pathway generally receives no treatment. As a result, limited degradation or trapping of contaminants occurs prior to their discharge to the Bay. Furthermore, CEC investigations to date in the RMP and elsewhere have focused primarily on wastewater, and CECs in stormwater have received relatively little attention.

Stormwater-derived contaminants have been an especially high concern and research focus in the Puget Sound region, where adult coho salmon (*Oncorhynchus kisutch*) in Puget Sound streams experience acute toxicity and pre-spawn mortality following exposure to urban runoff (Du et al. 2017). This response is not correlated with conventional water chemistry parameters, including temperature, dissolved oxygen, and suspended solids; disease; spawner conditions; or exposure to monitored pesticides, metals, or polycyclic aromatic hydrocarbons (Scholz et al. 2011).

In an effort to identify the potential cause of this acute toxicity in the Puget Sound area, non-targeted analysis of stormwater and tissues from runoff-exposed fish were conducted and resulted in the identification of a number of unique contaminants with sources specific to vehicle traffic. One example is hexa(methoxymethyl)melamine (HMMM), a component of tire resin, which can occur in highway runoff at concentrations exceeding 10 μg/L (Kolodziej, unpublished data). More recent research indicates that aqueous leachates from automobile tires can induce acute toxicity in coho salmon, leading to a focus on understanding the risks of this pollutant source to salmonids and other aquatic organisms. In addition to the acute effects, related ecotoxicology research suggests that stormwater exposure can induce altered growth, decreased immune function, impaired lateral line development, and cardiotoxicity in salmonids (McIntyre et al. 2016; Young et al. 2018), suggesting that a suite of adverse sublethal impacts derived from stormwater exposures are important aspects of water quality in urbanized areas.

A direct outcome from these non-targeted analytical efforts in Puget Sound was the development, by Dr. Kolodziej, of a list of target analytes to assess the stormwater pathway as major contaminant inputs. While there are a number of targeted CEC lists designed around the influence of wastewater (e.g., focused on pharmaceuticals and other compounds typically disposed of down the drain), this is the first major effort to develop a CEC list targeting the influence of urban runoff in aquatic habitats with a concerted analytical effort. While the endangered coho salmon, the focus of the Puget Sound research effort, are now absent from tributaries discharging to the Bay, steelhead (*Oncorhynchus mykiss*), a threatened species, are observed in some Bay streams (e.g., Guadalupe River, Alameda Creek) and may also be susceptible to these contaminants.

In addition to this newly developed list of urban stormwater CECs, three other classes of emerging contaminants have been identified in recent RMP studies and ECWG discussions as critical data gaps for stormwater, and are included as part of this pioneering exploration of CECs in stormwater.

Per- and polyfluoroalkyl substances (PFAS) – PFOS, PFOA, and other long-chain perfluorocarboxylates are classified as Moderate Concerns for the Bay, while other PFAS are considered Possible Concerns. A conceptual model of sources of PFAS to stormwater includes outdoor textiles, plastic items, paints, and urban litter (e.g., food packaging), as well as industrial products such as fire-fighting foams. Atmospheric deposition is also possible. The RMP's draft PFAS Synthesis and Strategy (Sedlak et al. 2017) reviewed two studies of stormwater that have been conducted in the Bay Area: a seven site study conducted in water year 2010 (October 2009 through September 2010), and a 10 site study conducted in water year 2011. A relatively small number of PFAS were monitored; in addition, the watersheds monitored were not specifically selected to provide representative data for these contaminants in the Bay Area. The PFAS Synthesis and Strategy recommends stormwater monitoring as an RMP priority for future work.

Phosphate flame retardants – At present, alternative flame retardants are generally considered Possible Concerns for San Francisco Bay. A conceptual model of sources of these contaminants to stormwater includes outdoor products such as construction and building materials, as well as volatilization from a far broader assortment of consumer goods to the air followed by deposition to urban streams. Samples collected during two storms (water year 2014) at two Bay Area stormwater sites indicate the presence of phosphate flame retardants at concentrations generally comparable to those found in wastewater (Sutton et al. in prep). A draft RMP report that reviews available data for this class of CECs recommends stormwater monitoring as a priority for the RMP (Lin and Sutton 2018).

Ethoxylated surfactants – Ethoxylated surfactants include alkylphenol ethoxylates (classified as Moderate Concerns for the Bay), as well as alcohol ethoxylates and others. A conceptual model of sources of ethoxylated surfactants to stormwater includes outdoor use and automotive cleaners, lubricants and other fluids, as well as pesticides, plastics, paints, and many other products. The non-targeted analysis of San Francisco Bay sites described previously also identified a number of ethoxylated surfactants with strong signals in the stormwater-influenced site, San Leandro Bay (Ferguson et al. in prep; Sun et al. in prep). The RMP has funded a 2019 special study to screen Bay water, sediment, and wastewater for ethoxylated surfactants; results from the two studies will be complementary.

Study Objectives and Applicable RMP Management Questions

Table 1. Study objectives and questions relevant to RMP ECWG management questions

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Compare new occurrence data for stormwater CECs with toxicity information reported in the scientific literature. Evaluate future monitoring needs and toxicity data gaps.	Do any stormwater CECs merit additional monitoring in the Bay or a specific classification in the tiered risk framework? What are the potential risks of these CECs? Is a need for management actions indicated?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Compare concentrations observed at different sites in the Bay Area to glean possible insights regarding the influence of sources or land use types. Compare Bay Area concentrations to other measurements of other urban areas.	What are the key sources or land uses that are associated with individual CECs or CEC classes in stormwater?
3) 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?	N/A	
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	Compare concentrations with previous monitoring data for a limited number of analytes.	The data from this study can establish baseline data for stormwater CECs in the Bay Area. Instructive comparisons are possible for a subset of analytes previously examined in Bay Area stormwater, though robust trends cannot be inferred due to data limitations.
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	N/A	
6) What are the effects of management actions?	N/A	

Approach

<u>Stormwater Sample Collection</u>

Site selection will occur prior to sample collection, in consultation with the stormwater team at SFEI and the RMP's Small Tributaries Loading Strategy (STLS) team. Lessons learned from the pilot sample collection and analysis will inform site selection. Sites will be selected based on multiple factors including: 1) greater relative urban land use in the watershed, with an emphasis on proximity to roadways; 2) unique land uses associated with potential contaminant sources, such as airports; and 3) reduced sample collection costs due to existing sample collection underway as part of other studies. Site selection will be informed by the conceptual models of potential sources of the CECs to stormwater, with sites located in proximity to these sources being of particular interest.

Up to 20 samples (including field blank and duplicate samples) will be collected as part of Year 2 sample collection. Samples will consist of grabs or composites. Composites collected using an ISCO pump are preferred for the new stormwater CECs analyte list developed by Dr. Kolodziej. For the other types of contaminants, the ISCO pump may lead to procedural contamination. For these contaminants, one or more grab samples will be collected at each site, and may be combined in the field or in the analytical laboratory to produce a composite.

Particular focus will be placed on capturing the first fall flush at one or more sites of interest, using STLS storm size criteria. At least one site will be revisited during a later storm as an initial means of assessing variability. QA/QC samples collected will include at least one field duplicate and two field blanks.

<u>Chemical Analysis</u>

Up to 20 stormwater samples (including field duplicates and field blanks) will be characterized by four different academic laboratories with specialized expertise.

Stormwater CECs: Unfiltered samples will be analyzed by the Kolodziej Laboratory (University of Washington) with a newly developed, targeted analytical method using multi-residue solid phase extraction (SPE) and liquid chromatography with tandem mass spectroscopy (LC-MS/MS). Approximately 35 compounds will be monitored, including pharmaceuticals, pesticides, and several vehicle-specific analytes such as DPG and HMMM. A description of the analytes is provided as a separate attachment. This suite of representative tracers for urban runoff includes a broad range of contaminants with different physical-chemical parameters (e.g., various chemical functionalities, wide range of polarities and biodegradation potential). The compounds were selected to represent three primary urban sources: residential use, roadways, and wastewater.

PFASs: Unfiltered samples will be analyzed by the Higgins Laboratory (Colorado School of Mines) using quadrupole time-of-flight mass spectrometry (LC-Q-ToF-MS). The samples will be extracted and cleaned up using established protocols for the analysis of PFASs in soils and sediments (McGuire et al. 2014; Barzen-Hanson et al. 2017). Each sample will be split, with one aliquot being subjected to the TOP assay (oxidation followed by LC-QToF-MS; Houtz and Sedlak, 2012) and the other aliquot being directly analyzed by LC-QToF-MS. The stormwater extracts will be injected and separated on a C18 column prior to analysis by both ESI+ and ESI- LC-QToF-MS. Quantitative analysis will be performed on 45 PFASs, including different long- and short-chain perfluoroalkanoic acids, perfluoroalkane sulfonates, perfluoroalkane sulfonamides, fluorotelomer sulfonates, and fluorotelomer alkanoic acids. This list includes PFASs on the UCMR3 list along with many others.

Phosphate Flame Retardants: Both dissolved and particulate phase samples will be analyzed by the Chen Laboratory (Jinan University). Samples will be extracted in the U.S. by a partner laboratory, then shipped to China where Dr. Chen will characterize contaminants within the aqueous and solid phases using highly sensitive liquid chromatography–triple quadrupole mass spectrometry (LC-QQQ-MS/MS) based analysis methods (Chen et al. 2012; Chu et al. 2011). Limits of detection are typically in the range of 0.1 ppb. Dr. Chen has agreed to undertake method development to add recently identified phosphate flame retardants, including isopropylated and tert-butylated triarylphosphate esters (ITPs and TBPPs; Phillips et al. 2017) to his extensive list of target analytes.

Ethoxylated Surfactants: Stormwater samples will be analyzed for ethoxylated surfactants by the Ferguson Laboratory (Duke University), using a method to be developed. The matrix is likely to be total water, and the analyte list is expected to include the following surfactant families: nonylphenol ethoxylates, octylphenol ethoxylates, and C12, C14, and C16 alcohol ethoxylates. Analytes for each family will include compounds with a broad range of ethoxylate chains. Isotopically labeled standards are only available for a few of these analytes; however, the uncertainty associated with quantitation was deemed acceptable by the ECWG for screening purposes.

<u>Data Interpretation</u>
We anticipate that most of these contaminants will be widely observed in urban areas but have lower concentrations in non-urban areas. Therefore, screening data will be evaluated based on land-use type. Specific indicators of source types, such as road density, will be used for an initial investigation into key sources or land uses associated with these CECs.

In some cases, results can be compared with prior studies. For example, comparison to previous studies of PFAS in stormwater (Houtz and Sedlake 2012) may suggest increased prevalence of short-chain relative to long-chain (phased-out) PFAS, a potential result of shifting manufacturing practices. Results for the Bay Area will also be compared to levels observed in other urban regions.

Levels in Bay Area stormwater will also be compared to available toxicity thresholds. Findings may highlight concerns, data gaps, and the need for further research.

Budget

<u>Budget Justification</u>
The budget provided is specific to Year 2 of a multi-year study design and budget. The Year 2 budget emphasizes sample collection and analysis, with limited funds for data management and reporting. The majority of data review and reporting will occur during Year 3.

Planning and Stakeholder Engagement Costs
In consultation with RMP and STLS stormwater experts, we will establish a Year 2 study design that specifies site selection. Study design discussions and preliminary data reports will require regular participation in monthly calls with the STLS team.

Table 2. 2020 CECs in Stormwater budget (Year 2 only)

Expense	Estimated Hours	Estimated Cost
Labor - Year 2		
Study Design, Stakeholder Engagement	70	10000
Stormwater Sample Collection	500	70000
Data Technical Services		12000
Analysis and Reporting	130	18000
Subcontracts - Year 2		
Stormwater CECs: Kolodziej, U. Washington		10000
PFASs: Higgins, Colorado School of Mines		12000
Phosphate Flame Retardants: Chen, Jinan U.		14000
Ethoxylated Surfactants: Ferguson, Duke U.		11000
Direct Costs - Year 2		
Equipment		2500
Travel		2000
Shipping		6500
Grand Total		168000

Field Costs
The Year 2 budget includes $70,000 devoted to stormwater sample collection. Every effort will be made to minimize field costs through leveraging existing stormwater monitoring activities of the RMP. Based on the pilot year sampling experience, we anticipate that two-thirds of the sites visited in Year 2 will leverage RMP monitoring of legacy contaminants, while one-third of the sites will be specific to CECs.

Data Management Costs
Data services will include quality assurance review and upload to CEDEN during Year 3. Preliminary data management activities will occur during Year 2 and be supported by the Year 2 budget, including field collection data entry and communications with laboratories.

Analysis and Reporting Costs
Preliminary results will be reported to and reviewed by ECWG, STLS, and SPLWG. This activity would be supported by the Year 2 budget.

Preparation of draft manuscripts for publication in a peer-reviewed journal (stormwater-themed special issue) would occur following Year 3 sampling and analysis, and generally be led by the analytical partners. RMP scientists may be lead authors of one of the manuscripts, and coauthors of others. After the manuscripts are complete, RMP staff will produce a summary document for stakeholders, which describes the results and their implications for water quality management. Funding for this reporting would be part of the Year 3 budget.

Laboratory Costs
Each laboratory is receiving a budget sufficient to analyze up to 20 samples. Laboratory QA/QC samples will be analyzed at no charge, while field blanks and field duplicates will be considered part of the 20 samples charged to the RMP.

Reporting

Deliverables will include: a) draft manuscripts[1] that serve as RMP technical reports, due spring 2022; b) a summary for managers describing the results and their implications, due spring 2022; and c) additions to other RMP publications such as the Pulse.

References

Barzen-Hanson KA, Davis SE, Kleber M, Field JA. 2017. Sorption of fluorotelomer sulfonates, fluorotelomer sulfonamido betaines, and a fluorotelomer sulfonamido amine in National Foam Aqueous Film-Forming Foam to soil. Environ Sci Technol 51(21):12394-12404.

Chen D, Letcher RJ, Chu S. 2012. Determination of non-halogenated, chlorinated and brominated organophosphate flame retardants in herring gull eggs based on liquid chromatography – tandem quadrupole mass spectrometry. J Chromatogr A 1220: 169-174.

Chu S, Chen D, Letcher RJ. 2011. Dicationic ion-pairing of phosphoric acid diesters post-liquid chromatography and subsequent determination by electrospray positive ionization-tandem mass spectrometry. J Chromatogr A 1218(44): 8083-8088.

Du B, Lofton JM, Peter KT, Gipe AD, James CA, McIntyre JK, Scholz NL, Baker JE, Kolodziej EP. 2017. Development of suspect and non-target screening methods for detection of organic contaminants in highway runoff and fish tissue with high-resolution time-of-flight mass spectrometry. Environ Sci Process Impacts 19(9):1185-1196.

ECHA (European Chemicals Agency). 2018. Brief Profile: 1,3-diphenylguanidine. https://echa.europa.eu/brief-profile/-/briefprofile/100.002.730

Ferguson PL, Overdahl KE, DeStefano N, Sun J, Sutton R. in prep. Non-targeted Analysis of Polar Organic Contaminants in Ambient Bay Water and Wastewater to Identify Emerging

[1] The draft manuscript will be distributed to RMP stakeholders for review by email, not published on the website, so as to not jeopardize publication of the manuscript in a peer-reviewed journal.

Contaminants. Draft Report prepared for the Regional Monitoring Program for Water Quality in San Francisco Bay. Richmond, CA.

Houtz E, Sedlak D. 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. Environ Sci Technol 46(17):9342-9349.

Lin D, Sutton R. 2018. Alternative Flame Retardants in San Francisco Bay: Synthesis and Strategy. Draft Report. San Francisco Estuary Institute, Richmond, CA.

McGuire ME, Schaefer C, Richards T, Backe WJ, Field JA, Houtz E, Sedlak DL, Guelfo JL, Wunsch A, Higgins CP. 2014. Evidence of remediation-induced alteration of subsurface poly- and perfluoroalkyl substance distribution at a former firefighter training area. Environ Sci Technol 48(12):6644-6652.

McIntyre J.K., Edmunds R.C., Redig M.G., Murdock E.M., Davis J.W., Incardona J.P., Stark J.D., Scholz, N.L. 2016. Confirmation of Stormwater Bioretention Treatment Effectiveness Using Molecular Indicators of Cardiovascular Toxicity in Developing Fish. Environ Sci Technol 50(3):1561-1569.

Phillips, A.L., Hammel, S.C., Konstantinov, A., Stapleton, H.M. 2017. Characterization of individual isopropylated and tert-butylated triarylphosphate (ITP and TBPP) isomers in several commercial flame retardant mixtures and house dust standard reference material SRM 2585. Environ Sci Technol 51(22):13443-13449.

Scholz NL, Myers MS, McCarthy SG, Labenia JS, McIntyre JK, et al. 2011. Recurrent Die-Offs of Adult Coho Salmon Returning to Spawn in Puget Sound Lowland Urban Streams. PLoS ONE 6(12): e28013. doi:10.1371/journal.pone.0028013

Sedlak M, Sutton R, Wong A, Lin D. 2017. Per and Polyfluoroalkyl Substances (PFASs) in San Francisco Bay: Synthesis and Strategy. Draft Report. San Francisco Estuary Institute, Richmond, CA.

Sun J, Sutton R, Ferguson L, Overdahl K. in prep. New San Francisco Bay Contaminants Emerge. Draft Fact Sheet prepared for the Regional Monitoring Program for Water Quality in San Francisco Bay. Richmond, CA.

Sutton R, Sedlak M, Sun J, Lin D. 2017. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2017 Revision. SFEI Contribution 815. San Francisco Estuary Institute, Richmond, CA.

Sutton R, Chen D, Sun J, Greig D, Wu Y. 2019. Characterization of Brominated, Chlorinated, and Phosphate Flame Retardants in an Urban Estuary. Sci Total Environ 652: 212-223.

Young A, Kochenkov V, Mcintyre JK, Stark JD, Coffin AB. 2018. Urban stormwater runoff negatively impacts lateral line development in larval zebrafish and salmon embryos. Sci Rep 8, Article number: 2830.

Special Study Proposal: Characterization of Pharmaceutical Contamination in Lower South Bay Water, Margin Sediment, and Wastewater

Summary: Pharmaceutical contamination is widely detected in the Bay, and the most recent Bay study indicates key pharmaceutical contaminants may approach levels of concern for wildlife. This study will monitor Lower South Bay water (and optionally, margin sediment) for pharmaceutical contamination, providing data essential to a current evaluation of the potential risks of approximately 150 pharmaceutical contaminants to inform the RMP's Tiered CEC Risk and Management Framework.

Estimated Cost: $123,476 (option of adding sediment for $42,990)
Oversight Group: ECWG
Proposed by: Diana Lin and Rebecca Sutton (SFEI)
Time Sensitive: Yes (leverage monitoring priorities from previous effluent evaluation)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	*Due Date*
Task 1. Project Management (write and manage sub-contracts, track budgets)	January 2020
Task 2. Develop sampling plan with collaborators (MPSL-MLML and wastewater treatment facilities)	May 2020
Task 3. Field Sampling	August 2020
Task 4. Lab analysis	December 2020
Task 5. QA/QC and data management	February 2021
Task 6. Presentation at ECWG	April 2021
Task 7. Draft report	June 2021
Task 8. Final report	August 2021

Background

Pharmaceuticals are detected frequently in U.S. waterways, creating concern for their potential to impact aquatic life. Laboratory studies indicate fish exposed to antidepressant medications at environmentally relevant doses exhibit behavioral changes that affect survival and reproduction (e.g., Brodin et al., 2013; Weinberger and Klaper, 2014, Simmons et al., 2017). Antibiotic medications, designed specifically to kill organisms, may disrupt bacterial communities and essential ecosystem services provided by these microorganisms (e.g., Näslund et al., 2008), impart broader antibiotic resistance (e.g., Rizzo et al., 2013), and are often toxic to algal species (e.g., Ferrari et al., 2004). Other pharmaceutical compounds have significant endocrine disrupting effects on aquatic species (e.g., Niemuth and Klaper, 2015).

Pharmaceuticals can enter the environment through waste streams from human uses in households, hospitals, and nursing homes; manufacturing losses; or animal uses in veterinary clinics and industrial animal farming operations. Pharmaceuticals from human consumer use can enter the wastewater pathway through ingestion and subsequent excretion of unmetabolized medication, or disposing of unused medication down the drain. Wastewater effluent is expected to be the primary pathway for pharmaceutical contamination to enter the Bay. The Bay Area population is projected to increase and age in the coming decades, which will likely lead to increased use of pharmaceuticals and loadings via wastewater to the Bay. Therefore, periodic and vigilant monitoring of pharmaceuticals in the Bay is warranted.

In 2018, California passed the first legislation requiring a state-wide take-back program for pharmaceuticals and sharps used in households. California Senate Bill SB 212 (Jackson) was motivated by concerns about human health (e.g., antibiotic resistance in infectious bacteria, drug abuse, and accidental poisoning), rising drug expenditures, and environmental contamination (Wagoner, 2018). Given this growing policy focus on pharmaceuticals, it would be appropriate at this time for the RMP to gather new data to evaluate the level of concern that should be associated with the presence of these contaminants in the Bay.

The RMP has assessed pharmaceutical pollution in the Bay in two previous special studies in 2006 (Harrold et al., 2009) and 2009-2010 (Klosterhaus et al., 2013a). In another special study, the RMP evaluated results of pharmaceutical analysis in wastewater effluent from participating Bay wastewater treatment facilities (Lin et al., 2018). This most recent RMP study identified 17 pharmaceuticals in wastewater effluent that merit further monitoring in Bay waters. These pharmaceuticals are: the antibiotics azithromycin, ciprofloxacin, clarithromycin, erythromycin, ofloxacin, and sulfamethoxazole; the antidepressants amitriptyline, fluoxetine, and sertraline; the anti-convulsant carbamazepine; the painkillers codeine, oxycodone, and ibuprofen; the antihistamine diphenhydramine; the antidiabetic drug metformin; and high blood pressure medications metoprolol and propanolol.

Previous work indicated dilution of effluent may not be sufficient to reduce effluent-derived surface water concentrations below ecotoxicity thresholds, particularly in the Lower South Bay. Further monitoring for pharmaceuticals in the Bay was recommended. Of the 17 pharmaceuticals identified in wastewater in Lin et al. (2018), nine have not been targeted for analysis in Bay matrices or were below detection limits in previous studies; the remaining eight pharmaceuticals have been detected in open waters by previous studies (Klosterhaus et al., 2013, Nödler et al., 2014).

Study Objectives and Applicable RMP Management Questions

This study will provide data essential to determining the level of concern associated with pharmaceutical contamination in the Bay. The most recent evaluation of pharmaceuticals in wastewater effluent identified 17 pharmaceuticals that warrant further monitoring, which include antibiotics, antidepressants, painkillers, an antihistamine and anti-convulsant and antidiabetic, and high blood pressure medication. Should new monitoring show Bay levels of these pharmaceuticals frequently exceed toxicity thresholds, reclassification as moderate concern contaminants in the RMP tiered framework may be appropriate.
Laboratory analysis targeting only the 17 pharmaceuticals is not possible because the pharmaceuticals come from separate lists that require different extraction procedures and different runs on the LC-MS/MS instrument (SGS AXYS analytical method MLA-075,

Table 2). MLA-075 (Lists 1, 3, 4, and 5) was used most recently to screen 104 pharmaceuticals in wastewater effluent (Lin et al., 2018; Table 2), and the method can also be used to analyze surface water and sediment. Therefore, additional pharmaceuticals will be analyzed as part of the same analytical method for the 17 prioritized pharmaceuticals.

Additionally, List 6 from MLA-075 and MLA-104 List SA (SGS AXYS) include an additional 38 drugs of interest (23 [Table 2] and 15 [Table 3], respectively) that have not been targeted by the RMP for analysis in the Bay previously. MLA-075 List 6 includes pharmaceuticals that have been observed to cause impacts to biota in laboratory studies at low exposure levels, such as oxazepam (e.g., Brodin et al., 2013). MLA-104 includes diclofenac, a nonsteroidal anti-inflammatory drug (NSAID) that has been detected in effluent-dominated Los Angeles and San Gabriel Rivers above a risk-based state threshold for monitoring (Tadesse, 2016). The RMP has not analyzed for diclofenac in the Bay, although another group did not detect diclofenac in margin waters in the Bay in 2010 (n = 20, Nödler et al., 2014).

This study will evaluate concentrations of pharmaceuticals in Lower South Bay because surface water and sediment in this region are likely to have the highest concentrations of pharmaceuticals due to low dilution and flushing. Concentrations of pharmaceuticals in surface water and sediment can be compared to published ecotoxicity thresholds to evaluate risks to aquatic life.

While most ecotoxicity thresholds are based on water exposure concentrations, sediment exposure may be more appropriate for some pharmaceuticals. For example, ciprofloxacin, an antibiotic, has been detected in Bay sediment (Klosterhaus et al., 2013) at concentrations that exceed both a lowest observable effect concentration, or LOEC, for effects on bacterial community structure (100 ng/g dry weight) and a half maximal effective concentration, or EC_{50}, for pyrene degradation (400 ng/g dry weight; Näslund et al., 2008). This contamination level may be a concern for both bacterial diversity and essential ecosystem functions that bacteria perform in Bay sediment.

This proposal is for evaluation of pharmaceuticals in Bay water, and includes the option of analyzing archived sediment. Comparison of pharmaceutical concentrations in surface water and sediment with varying degrees of wastewater influence can provide preliminary information as to pharmaceutical fate in the Bay. Data may suggest that specific compounds are especially persistent in the environment and may require special attention, perhaps in the form of additional, targeted monitoring and management actions.

Table 2. Pharmaceutical analytes in MLA-075 Lists 1-6 (SGS AXYS). Superscripts indicate analytes for which only estimates of concentration are available.

List 1 - Acid Extraction in Positive Ionization

Acetaminophen
Azithromycin
Caffeine
Carbadox
Carbamazapine
Cefotaxime
Ciprofloxacin
Clarithromycin
Clinafloxacin
Cloxacillin [1]
Dehydronifedipine
Digoxigenin
Digoxin
Diltiazem
1,7-Dimethylxanthine
Diphenhydramine
Enrofloxacin
Erythromycin-H20
Flumequine
Fluoxetine
Lincomycin
Lomefloxacin
Miconazole
Norfloxacin
Norgestimate
Ofloxacin
Ormetoprim
Oxacillin [1]
Oxolinic acid
Penicillin G [1]
Penicillin V
Roxithromycin
Sarafloxacin
Sulfachloropyridazine
Sulfadiazine
Sulfadimethoxine
Sulfamerazine
Sulfamethazine
Sulfamethizole
Sulfamethoxazole
Sulfanilamide
Sulfathiazole
Thiabendazole
Trimethoprim
Tylosin
Virginiamycin

List 2 - Tetracyclines in Positive Ionization

Anhydrochlortetracycline
Anhydrotetracycline
Chlortetracycline
Demeclocycline
Doxycycline
4-Epianhydrochlortetracycline
4-Epianhydrotetracycline
4-Epichlortetracycline
4-Epioxytetracycline
4-Epitetracycline
Isochlortetracycline [2]
Minocycline
Oxytetracycline
Tetracycline

List 3 - Acid Extraction in Negative Ionization

Bisphenol A
Furosemide
Gemfibrozil
Glipizide
Glyburide
Hydroclorothiazide
2-hydroxy-ibuprofen
Ibuprofen
Naproxen
Triclocarban
Triclosan
Warfarin

List 4 - Basic Extraction in Positive Ionization

Albuterol
Amphetamine
Atenolol
Atorvastatin
Cimetidine
Clonidine
Codeine
Cotinine
Enalapril
Hydrocodone
Metformin
Oxycodone
Ranitidine
Triamterene

List 5 - Acid Extraction in Positive Ionization

Alprazolam
Amitriptyline
Amlodipine
Benzoylecgonine
Benztropine
Betamethasone
Cocaine
DEET
Desmethyldiltiazem
Diazepam
Fluocinonide
Fluticasone propionate
Hydrocortisone
10-hydroxy-amitriptyline
Meprobamate
Methylprednisolone
Metoprolol
Norfluoxetine
Norverapamil
Paroxetine
Prednisolone
Prednisone
Promethazine
Propoxyphene
Propranolol
Sertraline
Simvastatin
Theophylline
Trenbolone
Trenbolone acetate
Valsartan
Verapamil

List 6 - Acid Extraction in Positive Ionization

Amsacrine
Azathioprine
Busulfan
Citalopram
Clotrimazole
Colchicine
Cyclophosphamide
Daunorubicin
Diatrizoic acid
Doxorubicin
Drospirenone
Etoposide
Iopamidol
Medroxyprogesterone acetate
Melphalan
Metronidazole
Moxifloxacin [3]
Oxazepam
Rosuvastatin
Tamoxifen
Teniposide
Venlafaxine
Zidovudine

Table 3. Pharmaceutical analytes in MLA-104 SA (SGS AXYS Analytical).

Clopidogrel
Diclofenac
Eprosartan
Fenofibrate
Irbesartan
Lamotrigine
m-Chlorophenylpiperazin
Melengestrol acetate
Mycophenolate mofetil
Norquetiapine
Quetiapine
Ramipril
Tilmicosin
Topiramate
Trazadone

Management questions to be addressed by monitoring pharmaceuticals in Bay water, sediment, and wastewater effluent are shown in Table 3.

Table 3: Study objectives and information relevant to RMP management questions

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Monitor 156 pharmaceuticals in Bay water, sediment, and effluent. Compare measured concentrations to toxicity thresholds to determine levels of concern associated with each according to the Tiered CEC Risk Framework.	Do target pharmaceuticals have the potential to cause impacts to Bay aquatic life? Do data indicate a need for management actions?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Compare effluent pathway loads to concentrations in the water and sediment in the open Bay and margins.	Do pharmaceutical loads from effluent explain loads observed in Bay water and sediment?
3) 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?	Obtain information on pharmaceutical contamination in ambient Bay water, sediment, and wastewater.	Are relative distributions of pharmaceutical contaminants in effluents versus Bay water and sediment consistent with our expectations for various contaminant processes?

4) Have the concentrations of individual CECs or groups of CECs increased or decreased?	Review new results alongside available data from previous RMP studies for indications of trends in pharmaceutical contamination over time.	Are pharmaceuticals for which we have previous measurements found at increasing or decreasing levels in Bay media?
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?		
6) What are the effects of management actions?		

Approach

This study will focus on analyzing pharmaceuticals in water samples from Lower South Bay. There is also an option to add analysis of archived margin sediment samples from Lower South Bay. Evaluation of sediment samples will complement water measurements by providing additional data regarding persistence of pharmaceuticals in sediment and exposure to benthic organisms. A limited set of effluent samples will be collected to evaluate potential loadings in wastewater effluent and compare to effluent measurements from previous years.

<u>Lower South Bay Water Sampling</u>

Water samples will be collected in Lower South Bay in the summer of 2020 by the Marine Pollution Studies Laboratory at Moss Landing Marine Labs (MPSL-MLML). Grab samples of ambient water will be collected at fifteen Bay sites, in addition to two field duplicates and one field blank (18 total samples). Each sample will consist of up to 4 x 500 mL of water (2 x 500 mL required for analysis; an additional 2 x 500 mL may be collected as backup) collected in pre-cleaned HDPE containers provided by the analytical laboratory (SGS AXYS). MPSL-MLML will collect water samples, freeze them, and ship samples to SGS AXYS overnight.

Sampling sites will be selected randomly to capture an accurate representation of surface water concentrations in the Lower South Bay; additional sites may be targeted to evaluate wastewater influence. Sampling times will be scheduled when practical, particularly for margin sites that need to be sampled during high tide for access. Tide schedule is not expected to significantly influence sampled concentrations because of long water residence times in the Lower South Bay.

<u>Effluent Sampling</u>

Effluent samples provide essential information on the major pathway for pharmaceutical contaminants to enter the Bay. The state guidance on CEC monitoring generally directs agencies to include sampling WWTP effluent when screening for emerging contaminants (Dodder et al., 2015).

Two effluent sample from two wastewater treatment facilities discharging to the Lower South Bay will be collected. Twenty four-hour composite samples are preferred to better represent wastewater discharge and loading into the Bay. Sample volumes for effluent samples are the same as surface water samples (4 x 500 mL). Wastewater treatment facilities will be consulted on the best method for sample collection. Samples will be frozen and shipped overnight to SGS AXYS.

Bay Margin Sediment Sampling (optional add-on)

Margin sediment samples were collected from the RMP margin sediment sampling cruise in Upper South, Lower South, and Extreme Lower South Bays in the summer of 2017. Samples were collected using a Van Veen sediment grab. Several samples were archived using clean protocols for future analysis. Ten sites will be selected for analysis; sites will be selected based on geographic distribution and co-located surface water sampling sites.

Analytical Methods

Samples will be analyzed by SGS AXYS (Sidney, BC, Canada) for pharmaceuticals using SGS AXYS MLA-075 Lists 1, 3-6 and SGS AXYS MLA 104 List SA (Tables 2 and 3) using liquid chromatography tandem mass spectrometry (LC-MS/MS). SGS AXYS was selected to provide analytical services for this study because they have unique qualifications for analyzing pharmaceuticals in environmental media. They analyzed pharmaceutical compounds for the 2018 RMP Special study on pharmaceuticals in wastewater using the same methods.

Previous studies in the Bay have utilized Lists 1, 3, 4, and 5 only.

Budget

The following budget represents estimated costs for this proposed special study of water and effluent (Table 4). Efforts and costs can be scaled up or down by changing the types of analyses (e.g., MLA-104) and the number and type of samples.

Table 4. Proposed Budget.

Expense	Estimated Hours	Estimated Cost
Labor (SFEI)		
Project Management	25	3,700
Sample Collection	100	14,000
Data Management		10,000
Analysis and Reporting	220	32,100
Subcontracts		
Moss Landing (sample collection)		15,000
SGS AXYS (n=20 samples)		47,476
Direct Costs (SFEI)		
Equipment, Travel, Shipping		1,200
Grand Total		**$123,476**

Budget Justification

Project Management
Labor hours are estimated for SFEI staff to develop contracts with subcontractors and manage budgets.

Sample Collection
Sample collection costs includes a subcontract with MPSL-MLML for the collection of surface water samples (described and estimated separately below). Labor hours are estimated for SFEI staff to develop the sampling plan with MPSL-MLML for surface water samples and to collect two effluent samples from two wastewater treatment facilities (assumes wastewater facilities will provide assistance in collecting samples). Labor hours are also estimated to ship effluent samples from SFEI to SGS AXYS for analysis.

Data Management Costs
Data Services will include standard RMP QA/QC review and upload to CEDEN.

Analysis and Reporting Cost
The analysis and reporting task includes labor hours estimated for SFEI staff to conduct literature review, analyze data, prepare presentation for ECWG, and write a technical report. The cost for this task is in proportion with the large number of analytes to be evaluated.

Sample Collection (MPSL-MLML)
The subcontract cost (total $15,000) with MPSL-MLML for the collection of surface water samples includes task for sample collection ($11,800), shipping samples overnight to SGS AXYS Canada ($1,300), data management ($400), preparing CEDEN reporting template to SFEI), and project management ($1,500).

Laboratory Costs (SGS AXYS)
Analytical costs per sample for pharmaceuticals (MLA-075 List 1,3,4,5,6 and MLA-104 List SA) are expected to be $2,158 per sample. The estimated budget includes 18 ambient water samples (15 sites + 2 duplicates + 1 blank), and 4 effluent samples.

Optional Add-on
Cost to add analysis of ten archived sediment samples to this study is $42,990.
This includes laboratory costs (SGS AXYS) of $22,830 (ten samples x $2,283/sediment sample for MLA-075 List 1,3-6 and MLA-104 List SA); data management cost of $9,000; direct cost $1,000 (supplies, shipping, travel); and labor cost of $10,160 (includes additional 80 hours of labor to select sites; retrieve, process, and ship archived samples; and additional literature review, data analysis, and reporting).

Reporting

Data will be reported via RMP web tools (e.g., CEDEN). Participating wastewater facilities will determine how effluent data are published. Results will be reported to the RMP committees in the form of a presentation at the ECWG meeting and a final report by August 2021.

References

Brodin T, Fick J, Jonsson M, Klaminder J. 2013. Dilute concentrations of a psychiatric drug alter behavior of fish from natural populations. Science 339:814-815.

Dodder NG, Mehinto AC, Maruya KM. 2015. Monitoring of Constituents of Emerging Concern (CECs) in Aquatic Ecosystems – Pilot Study Guidance and QA/QC Guidance. SCCWRP Technical Report 854. Southern California Coastal Water Research Project, Costa Mesa, CA. http://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/854_CaliforniaCEC_PilotStudy_040315.pdf

Ferrari B, Mons R, Vollat B, Fraysse B, Paxeus N, Lo Giudice R, et al. 2004. Environmental risk assessment of six human pharmaceuticals: Are the current environmental risk assessment procedures sufficient for the protection of the aquatic environment? Environmental Toxicology and Chemistry 23:1344-1354.

Harrold KH, Yee D, Sedlak M, Klosterhaus S, Davis JA, Woudneh M, Riley P. 2009. Pharmaceuticals and Personal Care Products in Wastewater Treatment Plant Influent and Effluent and Surface Waters of Lower South San Francisco Bay. SFEI Contribution 549. San Francisco Estuary Institute, Oakland, CA. http://www.sfei.org/documents/2918

Klosterhaus SL, Grace R, Hamilton MC, Yee D. 2013a. Method validation and reconnaissance of pharmaceuticals, personal care products, and alkylphenols in surface waters, sediments, and mussels in an urban estuary. Environment International 54, 92–9.

Klosterhaus S, Yee D, Sedlak M, Wong A, Sutton R. 2013. Contaminants of Emerging Concern in San Francisco Bay: A Summary of Occurrence Data and Identification of Data Gaps. RMP Contribution 698. San Francisco Estuary Institute, Richmond, CA. http://www.sfei.org/documents/cec-synthesis

Lin, D., Sutton, R., Sun, J., Ross, J. 2018. Screening of Pharmaceuticals in San Francisco Bay Wastewater. SFEI Contribution No. 910. San Francisco Estuary Institute, Richmond, CA.

Näslund J, Hedman JE, Agestrand C. 2008. Effects of the antibiotic ciprofloxacin on the bacterial community structure and degradation of pyrene in marine sediment. Aquatic Toxicology 90:223-227.

Niemuth, N.J., Klaper, R.D., 2015. Emerging wastewater contaminant metformin causes intersex and reduced fecundity in fish. Chemosphere 135, 38–45. https://doi.org/10.1016/j.chemosphere.2015.03.060

Nödler, K., Voutsa, D., Licha, T., 2014. Polar organic micropollutants in the coastal environment of different marine systems. Marine Pollution Bulletin 85, 50–59. https://doi.org/10.1016/j.marpolbul.2014.06.024

Rizzo L, Manaia C, Merlin C, Schwartz T, Dagot C, Ploy MC, et al. 2013. Urban wastewater treatment plants as hotspots for antibiotic resistant bacteria and genes spread into the environment: A review. The Science of the Total Environment 447:345-360.

Simmons, D.B.D., McCallum, E.S., Balshine, S., Chandramouli, B., Cosgrove, J., Sherry, J.P., 2017. Reduced anxiety is associated with the accumulation of six serotonin reuptake inhibitors in wastewater treatment effluent exposed goldfish Carassius auratus. Scientific Reports 7, 17001. https://doi.org/10.1038/s41598-017-15989-z

Tadesse, D., 2016. Constituents of Emerging Concern (CECs) Statewide Pilot Study Monitoring Plan. California Water Board.

Weinberger J, Klaper R. 2014. Environmental concentrations of the selective serotonin reuptake inhibitor fluoxetine impact specific behaviors involved in reproduction, feeding and predator avoidance in the fish *Pimephales promelas* (fathead minnow). Aquatic Toxicology 151:77-83.

Wagoner, R., 2018. Senate Committee on Environmental Quality Analysis of SB 212 (Jackson): Solid Waste: Pharmaceutical and Sharps Waste Stewardship.

Special Study Proposal: Bisphenols in Bay Sport Fish

Summary: Bisphenols are a class of widely used, synthetic, endocrine-disrupting compounds, commonly found in polycarbonate plastics and epoxy resins, and frequently detected in many environmental matrices. Bisphenol A (BPA) is a high-production volume compound, and use volumes of several BPA analogues have increased in recent years. Bay water samples collected in 2017 revealed detections of both BPA and bisphenol S (BPS) at levels in the range of a protective toxicity threshold for BPA (60 ng/L). This class of contaminants may merit a Moderate Concern classification in the RMP tiered framework.

While other bisphenols were not detected in Bay waters, some of these compounds have chemical properties that suggest they are more likely to be found in the tissues of organisms than in water. These potentially bioaccumulative bisphenols have been observed in aquatic organisms in Lake Taihu, China, despite being present at far lower levels in water. We propose leveraging Status and Trends sport fish monitoring to obtain sport fish composite samples for bisphenols analysis. By analyzing this class of contaminants in fish tissue, we can develop a more complete picture of which bisphenols are in the Bay environment and determine whether fish consumption is a relevant pathway for human exposure. The results of this screening will further inform the classification of bisphenols within the RMP's tiered framework.

Estimated Cost: $54,000
Oversight Group: ECWG
Proposed by: Ila Shimabuku and Rebecca Sutton (SFEI)
Time Sensitive: No

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	***Due Date***
Task 1. Field collection of sport fish (Status and Trends monitoring)	Summer 2019
Task 4. Laboratory analysis of samples	Winter 2019-2020
Task 5. QA/QC and data management	Spring 2020
Task 6. Draft technical report	November 2020
Task 7. Final technical report	February 2021

Background

Bisphenols (BPs) are a class of high production volume, endocrine-disrupting chemicals that are used in the manufacturing of polycarbonate plastics and epoxy resins, as well as various other products. Bisphenol A (BPA), the most widely used and studied bisphenol, is one of the highest production volume chemicals in the world (estimated at 8 million tons per year), and can be found in products ranging from automotive and electrical equipment, polycarbonate plastic products, linings for food containers and drinking water pipes, and thermal paper receipts such as those used at ATMs, gas stations, restaurants, and grocery stores (MRC, 2014; EPA Action Plan, 2010).

Leading up to the California state and federal bans on BPA in certain feeding containers for children and babies in the early 2010s, several major manufacturers began replacing BPA in their products with alternative compounds—most commonly bisphenol S (BPS) and bisphenol F (BPF). Measured concentrations of BPS and BPF in human urine in the United States correspond to the increased use of these alternative bisphenol compounds in recent years (Ye et al., 2015).

At the same time, concentrations of BPA in other materials remain high. Recent studies have found high concentrations of both BPA and BPS (for example, 14 mg of BPA on a 3.125 x 12 in receipt) on thermal receipt papers, on which these compounds are used as developers (Apfelbacher, 2014). Bisphenols applied to the surface of the receipt paper are not bound to a polymer, and thus are readily transferrable both to humans and the environment. Studies have shown that concentrations of BPA can be up to 10 times higher in the urine of humans who have handled BPA-coated receipt paper for just four minutes (Hehn, 2015), and determined daily intake of BPA could be as high as 218 μg/d (Björnsdotter et al., 2017).

These compounds have been linked to a variety of potential negative health impacts in humans and wildlife, including estrogenic and genotoxic effects (Rosenmai et al., 2011; OEHHA, 2012; Lee et al. 2013). The European Union's marine predicted no effect concentration (PNEC) for BPA is 150 ng/L (Bakker et al. 2016), but is thought by some to be too high due to omission of a more sensitive species during derivation. In 2011, a new assessment established a PNEC for BPA of 60 ng/L, based on an assessment of 61 studies evaluating the ecotoxicological endpoints of survival, growth, development, and reproduction in 24 freshwater and marine organisms (Wright-Walters et al., 2011).

In 2012, the State Water Resources Control Board's CEC Science Advisory Panel published a CEC monitoring guidance document that recommended monitoring BPA in wastewater effluent, stormwater, and ambient embayment waters (Anderson et al., 2012). This recommendation was based on the PNEC calculated by Wright-Walters et al. (60 ng/L), as well as high environmental concentrations previously measured in California. The maximum concentrations measured in each matrix, as reported by the Advisory Panel, were 1,600 ng/L in ocean outfall wastewater effluent; 14,357 ng/L in stormwater runoff; and 500 ng/L in rainwater.

Empirical data on the toxicity and environmental fate of most alternative bisphenol compounds are scarce. A review conducted by Biomonitoring California (a joint program of the California Department of Public Health, Department of Toxic Substances Control, and Office of Environmental Health Hazard Assessment) in 2012 predicted that many of the alternatives such as bisphenol AF (BPAF), bisphenol AP (BPAP), bisphenol B (BPB), bisphenol C (BPC), bisphenol F (BPF), and bisphenol PH (BPPH) were likely to be toxic or very toxic to aquatic organisms, according to US EPA criteria (OEHHA, 2012). BPA is also listed on California's Prop 65 List for developmental and female reproductive toxicity.

Although BPA and several of its alternatives photo- and biodegrade relatively quickly under aerobic conditions, degradation for BPA, BPE, BPB, and BPS has been shown to be slow under anaerobic conditions, such as in anoxic estuarine sediments (Voordeckers et al., 2002; Ike et al., 2006). Biodegradation of BPS, in particular, has also been shown to be slow in marine environments (Danzl et al., 2009). Furthermore, regardless of degradation potential, the high production volume of these compounds suggests a constant source entering the environment, which may render even those compounds that degrade quickly a potential exposure concern for aquatic life.

The RMP previously analyzed open Bay water for BPA and 15 analogues in samples collected in 2017 (Shimabuku et al., in prep). BPA and BPS were detected in many samples with total water concentrations ranging from 1.5-35 ng/L and <1-120 ng/L, respectively.

Similar BPA concentrations (2.8-4.3 ng/L; n=3) were reported in the Puget Sound, a comparably urbanized estuarine system. BPA was also observed in fish within the Sound, at concentrations of up to 41 ng/g (wet weight) in salmon and 4.5 ng/g in sculpin that use the estuary (Meador et al., 2015). These results suggest it is possible that BPA might be present in Bay fish as well.

Most other bisphenol analogues were not detected in Bay water in the previous study (below method detection limits of 0.7-2.7 ng/L; Shimabuku et al., in prep). Some of these analogues are more hydrophobic and likely to be more bioaccumulative (log K_{OW}s range from 1.2 (BPS) to 7.2 (BPPH); OEHHA 2012). For these analogues, it may be more appropriate to examine tissue to assess presence in the Bay.

A study of a large lake with heavy industry influence in China, Lake Taihu, revealed significant detections of bisphenol analogues, both in water samples and in aquatic life (Wang et al. 2017). While some analogues appeared at higher concentrations in water than in organism tissues (e.g., BPS), others were detected at much higher levels in tissue. For example, BPC was responsible for <1% of ∑BPs in water, but comprised 33% of ∑BPs in tissue samples (or up to 15 ng/g ww; Figure 1). The bioaccumulation potential of bisphenols appeared to be significantly correlated with logK_{OW}; however, the six bisphenols with highest logK_{OW} were not included in the study (Wang et al. 2017). These findings provide further indication that water monitoring alone may not provide a comprehensive screening for the presence of various bisphenols in an ecosystem.

This proposal outlines a study to monitor BPA and 15 alternative bisphenol compounds in Bay sport fish. The results from this study will be used to inform the placement of bisphenols in the RMP's tiered risk framework. Findings may suggest the need to assess potential risks to aquatic life due to bioaccumulation in the food web, fish consumption as a pathway for human exposure to bisphenols, and may indicate the need for additional ecotoxicity or human health thresholds.

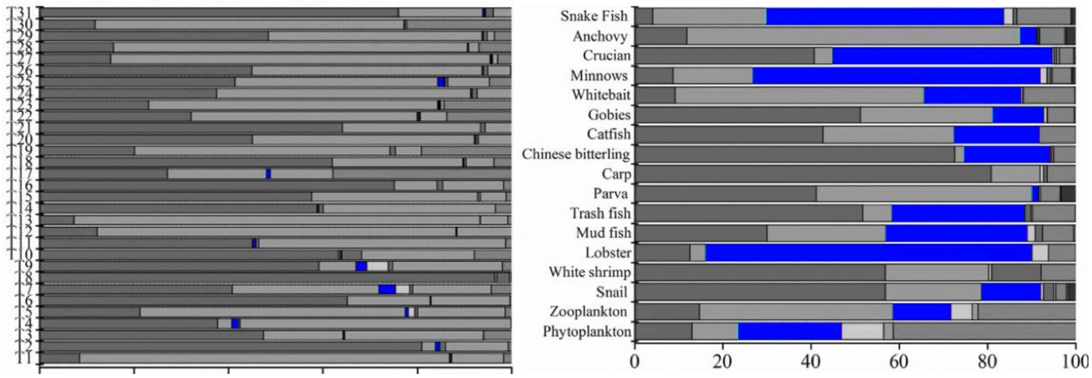

Figure 1. Modified from Wang et al., 2017. Water samples shown on the left, tissues on the right. BPC is represented in blue. Both x-axes represent 0-100% of the bisphenol profile.

Study Objectives and Applicable RMP Management Questions

This study will provide data to inform the placement of bisphenols in the RMP's tiered risk framework, which guides monitoring and management actions on emerging contaminants in San Francisco Bay (Sutton et al. 2013; Sutton and Sedlak 2015).

Table 1. Study objectives and questions relevant to CEC management questions.

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Characterize levels of bisphenols in Bay sport fish tissues.	Are detections observed previously in Bay water (BPA, BPS) capturing all bisphenols in the Bay environment? Is bioaccumulation in the food web a pathway for exposure and risk for aquatic life? Is fish consumption a pathway for human exposure to bisphenols? Is there a need to develop ecotoxicity or human health toxicity thresholds for bisphenols other than BPA?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?		

3) 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?	Compare relative concentrations of bisphenols in tissues to chemical characteristics such as log Kow to gain insights regarding potential for bioaccumulation.	Are bisphenols with higher hydrophobicity, which were not present at levels greater than detection limits in water samples,bioaccumulating in tissue?
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?		
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?		
6) What are the effects of management actions?		

Approach

Sport Fish Sample Collection

Bay sport fish sample collection will take place in the summer of 2019 as part of the RMP's regular Status and Trends sport fish monitoring effort. BP sampling will primarily focus on the southern portion of the Bay (e.g., Alviso Slough and Lower South Bay) due to the limited circulation and the tendency to observe higher concentrations of anthropogenic contaminants in fish from this area. We will also choose one site in Central Bay.

The RMP targets approximately 12 species of sport fish. We propose to focus monitoring on shiner surfperch and carp, as these are the species that accumulate the highest concentrations of PCBs and other high log K_{OW} chemicals (Sun et al. 2017). As part of Status and Trends, we will be collecting shiner surfperch at nine locations in the Bay. We will also collect carp at Artesian Slough, near the San José-Santa Clara wastewater treatment facility outfall. We will analyze approximately 20 sport fish composites, two each from the ten sites included in Status and Trends monitoring.

In addition, two composites will be provided in duplicate for quality assurance purposes. Minimum sample size is 10 g.

Analytical Methods

Samples will be analyzed by members of Dr. Da Chen's laboratory at Jinan University, the laboratory that previously analyzed Bay water samples collected in 2017. Scientists will conduct the analysis in the U.S. while occupying guest positions within the laboratory of Dr. Rob Hale at the Virginia Institute of Marine Science. The opportunity to analyze samples in the U.S. minimizes customs problems that can arise with international shipping of biological tissues.

Dr. Da Chen's team will modify their existing, highly sensitive water method, which uses liquid chromatography-electrospray ionization(-)-triple quadrupole mass spectrometry (LC-

ESI(-)-QQQ-MS/MS) for tissue samples. This method will include analysis of bisphenol A, as well as a suite of bisphenol analogues, including bisphenols B, C, AF, AP, BP, M, E, P, F, PH, Z, G, TMC, and C-dichloride. Estimated method detection limits: 0.05-0.15 ng/g ww.

Budget

The following budget represents estimated costs for this proposed special study (Table 2). If necessary, efforts and costs can be scaled back by reducing the number of samples.

Table 2. Proposed Budget

Expense	Estimated Hours	Estimated Cost
Labor		
Project Staff	145	20000
Data Technical Services		13000
Subcontracts		
Da Chen, Jinan University		20000
Direct Costs		
Equipment		300
Travel		200
Shipping		500
Grand Total		
		54000

Budget Justification

Labor: Field Costs
Field costs are minimized through sample collection during the RMP's 2019 Status and Trends sport fish monitoring efforts.

Labor: Data Technical Services Costs
To minimize data management costs, data will undergo RMP QA/QC and be formatted for CEDEN, but not uploaded. Data management costs are estimated at $13,000.

Subcontracts: Laboratory Costs
Analytical costs per sample are estimated to be $800. For 20 samples, including two field replicates and three additional QA/QC samples, the total analytical costs will be $20,000.

Reporting

Results will be provided to the RMP committees in a technical report. A draft of the report will be provided for review in November 2020. Comments will be incorporated into the final report by February 2021.

References

Apfelbacher, M., Cioci, M., and Strong, P. 2014. BPA and BPS in Thermal Paper: Results of Testing in Minnesota Hospitality Industry. Minnesota Pollution Control Agency. Available at: https://www.pca.state.mn.us/sites/default/files/p-p2s10-13.pdf

Anderson, P.D., Denslow, N.D., Drewes, J.E., Olivieri, A.W., Schlenk, D., Scott, G.I., Snyder, S.A. 2012. Monitoring Strategies for Chemicals of Emerging Concern (CECs) in California's Aquatic Ecosystems. Southern California Coastal Water Research Project: Technical Report 692. Available at: http://www.waterboards.ca.gov/water_issues/programs/swamp/cec_aquatic/docs/cec_ecosystems_rpt.pdf

Bakker, J., Hakkert, B.C., Hessel, E.V.S., Luit, R.J., Piersma, A.H., Sijm, D.T.H.M., Rietveld, A.G., van Broekhuizen, F.A., van Loveren, H., Verhoeven, J.K., 2016. Bisphenol A (No. 2015– 0192), Part 2. Recommendations for risk management. National Institute for Public Health and the Environment: Ministry of Health, Welfare and Support.

Björnsdotter, M. K., Boer, J. de, Ballesteros-Gómez, A. 2017. Bisphenol A and Replacements in Thermal Paper: A Review. Chemosphere. 182: 691–706.

Danzl, E., Sei, D., Soda, S., Ike, M., and Fujita, M. 2009. Biodegradation of Bisphenol A, Bisphenol F and Bisphenol S in Seawater. Int. J. Environ. Res. Public Health. 6(4): 1472-1484.

Hehn, R.S. 2015. NHANES Data Support Link between Handling of Thermal Paper Receipts and Increased Urinary Bisphenol A Excretion. Environ. Sci. Technol. 50(397-404).

Ike, M. Chen, M.Y, Danzl, E., Sei, K., and Fujita, M. 2006. Biodegradation of a variety of bisphenols under aerobic and anaerobic conditions. Water Sci Technol. 53(6): 153-9. http://wst.iwaponline.com/content/ppiwawst/53/6/153.full.pdf

Lee, S., Liu, X., Takeda, S., and Choi. K. 2013. Genotoxic potentials and related mechanisms of bisphenol A and other bisphenol compounds: A comparison study employing chicken DT40 cells. Chemosphere. 93: 434-440. https://www.researchgate.net/profile/Kyungho_Choi/publication/241691440_Genotoxic_potentials_and_related_mechanisms_of_bisphenol_A_and_other_bisphenol_compounds_A_comparison_study_employing_chicken_DT40_cells/links/53dd25670cf2a76fb667c749.pdf

Meador, J.P., Yeh, A., Young, G., Gallagher, E.P. 2016. Contaminants of emerging concern in a large temperate estuary. Environmental Pollution. 213:254-267.

Merchant Research & Consulting (MRC). 2014. http://www.prweb.com/releases/2014/04/prweb11761146.htm

Office of Environmental Health Hazard Assessment (OEHHA). 2012a. Preliminary Screen for Possible Future Consideration as Potential Designated Chemicals for Biomonitoring California. Some Bisphenol A Substitutes and Structurally Related Compounds. Materials for March 16, 2012 Meeting Scientific Guidance Panel (SGP). Available at: http://www.oehha.ca.gov/multimedia/biomon/pdf/031612PrelimScreen2.pdf

Rosenmai, A.K., Dybdahl, M., Pederson, M., Medea, B., van Vugt-Lussenburg, A., Wedebye, E.B., Taxvig, C., and Vinggaard, A.M. 2014. Are Structural Analogues to Bisphenol A Safe Alternatives? Toxicological Sciences.

Shi, J., Liu, X., Chen, Q., and Zhang, H. 2014. Spatial and seasonal distribution of estrogens and bisphenol A in the Yangtze River Estuary and the adjacent East China Sea. Chemosphere. 111: 336-343.

Shimabuku, I., Sutton, R., Chen, D., Wu, Y., Sun, J. 2019. Flame retardants and plastic additives in San Francisco Bay: a targeted monitoring of organophosphate esters and bisphenols. (in progress)

Sun, J.; Davis, J. A.; Bezalel, S. N.; Ross, J. R. M.; Wong, A.; Fairey, R.; Bonnema, A.; Crane, D. B.; Grace, R.; Mayfield, R. 2017. Contaminant Concentrations in Sport Fish from San Francisco Bay, 2014. SFEI Contribution No. 806.

Sutton R, Sedlak M, Davis J. 2013. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. SFEI Contribution 700. San Francisco Estuary Institute, Richmond, CA. http://www.sfei.org/documents/contaminants-emerging-concern-san-francisco-bay-strategy-future-investigations

Sutton, R., Sedlak, M., 2015. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2015 Update. SFEI Contribution No. 761. Regional Monitoring Program for Water Quality in San Francisco Bay, San Francisco Estuary Institute, Richmond, CA.

US Environmental Protection Agency. 2010. Bisphenol A Action Plan. Available at: https://www.epa.gov/sites/production/files/2015-09/documents/bpa_action_plan.pdf

Voordeckers, J.W., Fennell, D.E., Jones, K., and Haggblom, M.M. 2002. Anaerobic Biotransformation of Tetrabromobisphenol A, Tetrachlorobisphenol A, and Bisphenol A in Estuarine Sediments. Environ Sci. Technol. 35(4) 696-701.

Wang, Q., Chen, M., Shan, G., Chen, P., Cui, S., Yi, S., Zhu, L. 2017. Bioaccumulation and Biomagnification of Emerging Bisphenol Analogues in Aquatic Organisms from Taihu Lake, China. Sci. Total Environ. 598:814–820.

Wright-Walters, M., C. Volz, E. Talbott, and D. Davis. 2011. An updated weight of evidence approach to the aquatic hazard assessment of Bisphenol A and the derivation of a new predicted no effect concentration (PNEC) using a non-parametric methodology. Sci. Total Environ. 409: 676-685.

Ye, X., Wong, LY, Kramer, J., Zhou, X., Jia, T., and Calafat, A.M. 2015. Urinary Concentrations of Bisphenol A and Three Other Bisphenols in Convenience Samples of U.S. Adults during 2000-2014. Environ. Sci. Technol. 49, 11834-11839.

Special Study Proposal: Sunscreens in Bay Area Wastewater Effluent

Summary: Ultraviolet (UV) radiation filters such as oxybenzone and octinoxate are widely used as active ingredients in sunscreen lotions and in other products, such as cosmetics, paints, and plastics. Many of these sunscreen chemicals are quickly absorbed through human skin and circulated throughout the body. For aquatic organisms, the main exposure route is through direct wash-off into surface waters during recreational activities, and indirect discharge of these chemicals from wastewater treatment facilities to surface waters. Several sunscreen active ingredients have been shown to cause adverse effects, such as endocrine disruption in fish and bleaching on coral reefs. As a result, the State of Hawaiʻi and the city of Key West, FL, recently banned the sale of sunscreens containing oxybenzone and octinoxate. The City of San Francisco is considering a resolution to examine the occurrence and potential impacts of some of these compounds. Meanwhile, proposed sunscreen regulations released earlier this year by the US Food and Drug Administration (FDA) indicate that the agency now considers the safety information on oxybenzone and several other ingredients to be insufficient. Recent non-targeted analysis in SF Bay indicates the presence of oxybenzone in Bay water and effluent; this is a qualitative rather than quantitative method so concentrations are unknown. This study will quantify levels of sunscreens in Bay Area effluents to assess whether they may be a potential concern for the Bay.

Estimated Cost:	$55,000
Oversight Group:	Emerging Contaminants Workgroup (ECWG)
Proposed by:	William Mitch and Djordje Vuckovic (Stanford University); Meg Sedlak and Diana Lin (SFEI)
Time Sensitive:	No

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	***Due Date***
Task 1. Field collection of effluent samples	Summer/Winter 2020
Task 2. Laboratory analysis of samples	Fall/Winter 2020
Task 3. Review of data	Spring 2021
Task 4. Draft technical report	June 2021
Task 5. Final technical report	September 2021

Background

Ultraviolet (UV) radiation filters (sunscreens) are chemicals designed to absorb or reflect harmful solar radiation, and are used in products as diverse as personal care products (e.g., sunscreens, lotions, and cosmetics) and industrial products (e.g., insecticides, plastics, and paints) to mitigate deleterious effects of sunlight and extend product life.

At present, the FDA has approved 16 chemicals for sunscreen protection. These “active ingredients” in over-the-counter sunscreen products are frequently combined to increase the efficacy of the product. UV filter sunscreens are also additives to plastic. These chemicals are widely detected in the environment, and some may biomagnify (Gago-Ferrero et al. 2018).

These chemicals are also potential endocrine disruptors (Balazs et al. 2016), and there is increasing concern about their ecotoxicity (Kunz et al. 2006; Balmer et al. 2005; Downs et al. 2016).

Oxybenzone (also known as benzophenone-3 or BP-3) is of high concern due to its wide use in the U.S., detection in the environment, and its potential for endocrine disruption. In a recent study of personal care products, oxybenzone was detected in over 80 percent of the products analyzed (Liao and Kannan 2014). Oxybenzone is a High Production Volume chemical that is manufactured or imported into the U.S. in amounts greater than one million pounds per year. Oxybenzone has been detected in surface water, treated wastewater, invertebrates, fish, bird eggs, and coral tissue (Liao and Kannan 2014; Mao et al. 2018; Fent et al. 2010; Kim et al. 2014). It has been identified as an endocrine disruptor in fish, causing vitellogenin induction in male fish, among other effects (Coronado et al. 2008; Kunz et al. 2006; Kim et al. 2014). In a laboratory study of zebrafish, a significant skewing of the sex ratio towards females and effects on gonad maturation were observed (Kinnberg et al. 2015). Exposure to oxybenzone in another laboratory study of zebrafish caused mortality, unsuccessful hatching, and structural malformations such as deformed tails, impaired development of the jaw, and lack of swim bladder inflation (Balazs et al. 2016).

Due in part to the potential for endocrine disruption and other deleterious effects in fish, and the potential for these compounds to cause coral bleaching, there is currently regulatory interest in restricting their use. The State of Hawaiʻi and the City of Key West, FL, recently banned the sale of sunscreens containing oxybenzone and octinoxate due to exceedances of an ecological toxicity threshold for coral in water. The City of San Francisco is considering a resolution stating concerns about sunscreen chemicals oxybenzone, octinoxate, and butylparaben (a preservative) that are implicated in potential endocrine disruption of fish. City officials are interested in knowing whether these chemicals are detected in the Bay. Meanwhile, newly proposed sunscreen regulations from the FDA indicate there is insufficient safety information for the agency to determine whether oxybenzone, octinoxate, and ten other active ingredients are "generally recognized as safe and effective." Just two active ingredients, zinc oxide and titanium dioxide, were determined by FDA to be safe and effective; these mineral ingredients are not the subject of this study. This project will provide information on an important pathway by which sunscreens may be introduced into the Bay.

Study Objectives and Applicable RMP Management Questions

Table 1. Study objectives and information relevant to CEC management questions

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Quantify sunscreen chemicals that are detected in Bay effluent.	Identifying the presence of sunscreen chemicals in Bay Area effluent will be important for determining whether there is a potential problem for the Bay.

2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	This study will assess whether discharge of effluent is a possible source of sunscreen chemicals to the Bay.	The study will provide information to help assess the need for pollution prevention activities, and whether wastewater is an important pathway.
3) 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?		
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?		This study will provide baseline information that can be used to evaluate loading trends.
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?		
6) What are the effects of management actions?		

Approach

Sample Collection: Wastewater
We propose to collect effluent from eight wastewater treatment facilities that are of different sizes, treatment type (e.g., secondary vs. tertiary), and sewersheds. Based on a literature review, it appears that the removal of oxybenzone from treatment plants varies widely, from 68 to 93 percent (Balmer et al. 2005). We will collect 24-hour composites of effluent into glass containers that we will transport to the laboratory. We will collect samples mid-week to avoid variations that may occur during the weekend.

We are also interested in evaluating whether there are seasonal differences. We will undertake two sampling events during the summer months. After reviewing these dry weather results, we will sample the four facilities with the highest concentrations of sunscreen chemicals twice during the winter months to assess seasonal differences.

Sample Analysis
Drs. William Mitch and Djordje Vuckovic of Stanford University, the analytical partners for this proposed study, have expertise in analyzing sunscreens in environmental samples. They are currently investigating the mechanisms by which sunscreens cause toxicity in anemones (which are closely related to corals).

The target analyte list will at a minimum include: oxybenzone, octinoxate, and butylparaben. At present, the laboratory is confirming the analyte list (Table 2). Oxybenzone is the priority analyte because it is one of the most widely used sunscreens and has significant ecotoxicity concerns.

Data Analysis
We will compare the effluent concentrations to literature values to determine whether the levels are of concern. Data will be reviewed by RMP data management and QA staff and will not be uploaded to CEDEN.

Table 2. Potential Target Analytes

Compound	Concerns
Oxybenzone (Benzophenone-3, BP-3)	Wide use; frequent detection; ecotoxicity concerns. ECHA classified as very toxic to aquatic life. Prioritized by City of San Francisco.
4-hydroxybenzophenone (4HB)	BP-3 metabolite.
Benzophenone-1 (BP-1)	BP-3 metabolite.
Benzophenone-2 (BP-2)	
Benzophenone-12 (BP-12)	
4-Methylbenzophenone	
Octinoxate (Ethylhexyl methoxycinnamate, EHMC)	Wide use; frequent detection; ecotoxicity concerns. Prioritized by City of San Francisco.
Butylparaben	Wide use. Prioritized by City of San Francisco.

Budget Justification

Table 3. Proposed Budget.

Personnel	SFEI	Stanford
Sample design and site visit coordination	$5,000	
Collection of effluent at 8 sites in summer (two events) and at 4 sites in the winter (two events)	$15,000	
Laboratory Analyses (Stanford)		$10,000
Reporting (literature and summary)	$15,000	$2,500
Data Technical Services	$5,500	
Direct costs (field supplies, travel)	$2,000	
Total	**$55,000**	

Field Costs
Field costs will consist of sampling eight facilities twice for effluent during the summer months, and sampling effluent from four facilities twice during the winter months. We will coordinate with other special study projects that are sampling effluent to optimize fieldwork.

Reporting Costs
Reporting will consist of a literature review to provide context and a short technical summary of results. It is possible that Stanford researchers will prepare a manuscript.

Laboratory Costs
The laboratory costs are a fixed budget for the analysis of 24 wastewater effluent samples as well as 8 QA/QC samples.

Data Management Costs
The data will be reviewed by RMP data management staff; however, it will not be uploaded to CEDEN.

Reporting

Deliverables will be a technical report.

References

Balazs A, Krifaton C, Orosz I, Szoboszlay S, Kovacs R, Csenki Z, Urbanyi B, Balazs K. 2016. Hormonal activity, cytotoxicity, and developmental toxicity of UV Filters. Ecotoxicology and Environmental Safety. 131 45-53.

Balmer M, Buser HR, Muller M, Poiger T. 2005. Occurrence of some organic UV filters in wastewater, surface waters, and in fish from Swiss Lakes. Environmental Science & Technology. 39:953-962.

Coronado M, Haro H, Deng X, Rempell M, Lavado R, Schlenk D. 2008. Estrogenic activity and reproductive effects of the UV-filter oxybenzone (2-hydroxy-4-methoxyphenyl-methanone) in fish. Aquatic Toxicology. 90. 182-187.

Downs C, Kramarksky-Winter E, Segal R, Fauth J, Knutson S, Bronstein O, Ciner F, Jeger R, Lichtenfeld Y, Woodley C, Pennington P, Cadenas K, Kushmaro A, Loya Y. 2016 Toxicopahtological effects of the sunscreen UV filter, Oxybenzone (Benzophenone-3) on coral planulae and cultured primary cells and its environmental contamination in Hawaii and the US Virgin Islands. Archives of Environmental Contamination and Toxicology. P 265-288.

Fent K, Zenker A, Rapp M. 2010. Widespread occurrence of estrogenic UV-filters in aquatic ecosystems in Switzerland. Environmental Pollution 158(5). 1817-24.

Gago-Ferrero P, Diaz-Cruz M, Barcelo D. 2015. UV filters bioaccumulation in fish from Iberian river basins. Science of the Total Environment. 518-525.

Kinnberg KL, Petersen GI, Albrektsen M, Minghlani M, Awad SM, Holbech BF, Green JW, Bjerregaard P, Holbech H. 2015. Endocrine-disrupting effect of the ultraviolet filter benzophenone-3 in zebrafish, *Danio rerio*. Environmental Toxicology & Chemistry. 34(12):2833-40.

Kim S, Jung D, Kho Y and K Choi. 2014. Effects of benzophenone-3 exposure on endocrine disruption and reproduction of Japanese medaka (Oryzias latipes)--a two generation exposure study. Aquatic Toxicology, 155:244-52.

Kunz P, Galicia H, Fent K. 2006. Comparison of in vitro and in vivo estrogenic activity of UV filters in fish. Toxicological Science. 90(2) p 349-361.

Lioa C and K Kannan. 2014. Widespread occurrence of benzophenone-type UV light filters in personal care products from China and the US: An assessment of human exposure. Environmental Science & Technology. 48. 4103-4109.

Mao F, You L, Reinhard M, He Y, Gin K. 2018. Occurrence and Fate of Benzophenone-Type UV Filters in a Tropical Urban Watershed. Environmental Science & Technology. 52. 3960-3967.

Molins-Delgado D, Manez M, Andreu A, Hiraldo, F, Eljarrat E, Barcel D and M Diaz-Cruz. 2017. A Potential New Threat to Wildlife: Presence of UV Filters in Bird Eggs from a Preserved Area. Environmental Science & Technology. 51 (19) pp. 10983-10990

Poiger T, Buser H, balmer M, Bergvist P, Muller M. 2004. Occurrence of UV filter compounds from sunscreens in surface aters: regional mass balance in two Swiss lakes. Chemosphere. 55 (7) 951-953.