REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN SAN FRANCISCO BAY

sfei.org/rmp

RMP Emerging Contaminants Workgroup Meeting

April 12-13, 2021
9:00 AM – 3:00 PM

REMOTE ACCESS
https://zoom.us/j/94945382876
Meeting ID: 949 4538 2876

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DAY 1 AGENDA - April 12th

1.	**Introductions and Goals for This Meeting** The goals for this meeting: ● Provide updates on recent and ongoing ECWG activities (today & tomorrow) ● Discuss program review of Status and Trends monitoring (today) ● Discuss approaches to synthesize data and guide monitoring activities using models (tomorrow) ● Discuss future direction of the program (tomorrow) ● Recommend which special study proposals should be funded in 2022 and provide advice to enhance those proposals (tomorrow) Meeting materials: 2020 ECWG Meeting Summary pages 7 - 18	9:00 Melissa Foley

<table>
<tr><td>2.</td><td>Discussion: CEC Strategy Update (Attachment)

This item includes the following topics:

● Review of current RMP activities
● Update on State Water Board CEC Initiative projects
● Confirm need for full CEC strategy revision in 2022

This brief update will be followed by a more in depth discussion of future directions for the ECWG on day 2 (Item 14).

Desired Outcome: Informed Workgroup; Feedback on timing of strategy revision
Deadline for comments: 4/30/21

Meeting materials: 2021 ECWG Multi-year Plan, pages 19 - 22</td><td>9:15
Rebecca Sutton</td></tr>
<tr><td>3.</td><td>Discussion: Tire Contaminants: Update from the Microplastic Workgroup

In 2019, the RMP funded development of a microplastics stormwater conceptual model via the Microplastic Workgroup. The first phase of this conceptual model focused on tires, the apparent source of almost half the microplastics in urban runoff. Our literature review identified a few data gaps important for monitoring data interpretation, future RMP monitoring project design, and potentially for agency management decisions. The recognition that tire particles convey and release chemicals into urban runoff, as exemplified by the identification of a tire-derived chemical that is present in urban runoff and is lethal to coho salmon, revises the approach to the conceptual model, and indicates the need for discussion with the ECWG.

Desired Outcome: Informed Workgroup; Feedback on conceptual model and RMP approach to tire contaminants</td><td>9:50
Kelly Moran</td></tr>
<tr><td>4.</td><td>Information: Ethoxylated Surfactants in Bay Water, Wastewater, and Stormwater

The workgroup will review results from a 2019 RMP special study to quantify ethoxylated surfactants in Bay water, wastewater, and stormwater. Chemical classes examined include nonylphenol and octylphenol ethoxylates, as well as various alcohol ethoxylates. An exploratory method and custom standards were developed to examine an unusually broad array of analytes based on varying ethoxylated chain length. Characterization of ethoxylated surfactants in margin sediment collected in South and Lower South Bay will be completed later this year. The completed study will inform a strategy for future monitoring of these compounds in Bay matrices.

Desired Outcome: Informed Workgroup</td><td>10:25
Analise Lindborg (Duke)</td></tr>
<tr><td></td><td>Short Break</td><td>10:50</td></tr>
</table>

5.	**Information: Preliminary Results of Non-targeted Analyses of South and Lower South Bay Sediment** In 2018, the RMP funded a study to use non-targeted techniques to identify unknown or unexpected contaminants of emerging concern in margin sediment collected in South and Lower South Bay. The preliminary analyses of both polar and nonpolar contaminants have uncovered hundreds of unique contaminant signals, some of which are associated with ecotoxicological concerns. Findings will inform future targeted CEC monitoring of Bay matrices. Desired Outcome: Informed Workgroup	11:00 Eunha Hoh (SDSU), Lee Ferguson (Duke)
	Lunch	12:00
6.	**Information: Bisphenols in Wastewater and Sediment** Preliminary results from a 2020 RMP special study to characterize bisphenols in Bay margin sediment and wastewater will be presented. Observations will be discussed relative to existing data for bisphenols in Bay water and stormwater. Desired Outcome: Informed Workgroup	12:30 Miguel Mendez
7.	**Information: Building a Statewide Wastewater Pesticide Monitoring Network** In 2018, the Department of Pesticide Regulation's Surface Water Protection Program was awarded permanent funding to support a wastewater program. The justification for the award was built around the concept that addressing contaminant issues through source control is more effective than through treatment and relied heavily on special studies done in collaboration with the ECWG. The program includes special studies to better understand pesticides sources and fate and a statewide monitoring effort to characterize spatial and temporal trends in influent, effluent, and biosolids. Desired outcome: Informed Workgroup	1:00 Jennifer Teerlink (DPR)
	Short Break	1:30
8.	**Information: PFAS in Wastewater Matrices (BACWA Study)** SFEI is coordinating a study of PFAS in Region 2 POTWs that is currently being implemented in parallel with the statewide investigation orders to analyze PFAS in wastewater. The current study is a screening study of PFAS in influent, effluent, biosolids, and reverse osmosis concentration, with samples collected from 16 participating facilities. Preliminary results will be shared. Results will be used to prioritize study questions for further investigation of PFAS in POTWs. Desired Outcome: Informed Workgroup; Feedback on interpretation of results and guidance for further investigation.	1:45 Lorien Fono (BACWA), Diana Lin

9.	**Information & Discussion: Status and Trends Monitoring Review** The RMP is reviewing its Status and Trends study design, in part motivated by the anticipation of increased prioritization of CECs monitoring as part of Status and Trends activities. An updated study design for monitoring Bay water will be reviewed. CEC-specific considerations to inform monitoring of sediment and biota are needed. Desired Outcome: Informed Workgroup; Feedback on sediment and biota Deadline for comments: 4/30/21 Meeting materials: Slides	2:15 Melissa Foley
10.	**Information: Setting the Stage for Day 2** The workgroup will briefly review goals for tomorrow.	2:55 Rebecca Sutton
	Adjourn	

DAY 2 AGENDA - April 13th

11.	**Summary of Yesterday and Goals for Today** The goals for today's meeting: ● Brief recap of yesterday's discussions and outcomes ● Discuss approaches to synthesize data and guide monitoring activities using models ● Review progress on toxicology strategy ● Discuss future direction of the program ● Recommend which special study proposals should be funded in 2022 and provide advice to enhance those proposals	9:00 Melissa Foley
12.	**Discussion: Synthesizing Data to Guide Monitoring via Models** The RMP funded a project to build an integrated watershed modeling and monitoring implementation strategy to lay out the information needs and associated monitoring and modeling processes to address management questions for contaminants of interest. The integrated modeling and monitoring framework is proposed to support CECs study with both the power of monitoring and modeling. The framework will include elements of a road map to support monitoring design and model structure for emerging contaminants. Desired Outcome: Feedback on the integrated roadmap combining monitoring and modeling to solve ECWG management questions.	9:10 Tan Zi, Kelly Moran

<table>
<tr><td>13.</td><td>Information: Toxicology Strategy Update

In 2021, the RMP funded a study to synthesize and assess the quality of available thresholds for CECs detected in the Bay in the past ten years. Thresholds for data-poor contaminants could be calculated or estimated using EU guidance and predictive toxicology methods. The results of this study will inform risk screening for CECs in the Bay using a risk characterization ratio approach, and may support recategorization of some contaminants currently classified as Possible Concern due to insufficient toxicity data. The quality assessment approach will be shared with the workgroup.

Desired Outcome: Informed Workgroup</td><td>9:50
Ezra Miller</td></tr>
<tr><td></td><td>Short Break</td><td>10:10</td></tr>
<tr><td>14.</td><td>Discussion: ECWG Multi-year Plan and Future Work

The workgroup will review the multi-year plan and discuss the future direction of the focus area, identifying information needs for stakeholders.

Desired Outcome: Feedback on the 2021 ECWG Multi-year Plan
Deadline for comments: 4/30/21

Meeting materials: 2021 ECWG Multi-year Plan, pages 19-22</td><td>10:20
Rebecca Sutton</td></tr>
<tr><td>15.</td><td>Summary of Proposed ECWG Studies for 2022

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.

2022 RMP ECWG Special Study Proposals include:

● Stormwater monitoring strategy for CECs
● CECs in stormwater (year 4 of 4)
● Ethoxylated surfactants in wastewater and stormwater
● Non-targeted analysis of Bay water (wet season)
● Tire-related contaminants in Bay water (wet season)

Lower priority proposals that could be candidates for SEP funding include:

● PFAS in sediment (lower priority)
● Brominated flame retardants in sediment (lower priority)
● Chlorinated paraffins in sediment (lower priority)

2022 RMP Special Study Proposals for the Microplastic Workgroup that have relevance to ECWG include:

● Tires strategy
● Tire particle/contaminant fate and transport

Meeting materials: 2022 Special Studies Proposals, pages 23 - 69</td><td>11:10
Rebecca Sutton, Miguel Mendez, Ezra Miller, Diana Lin, Kelly Moran</td></tr>
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	LUNCH	12:00
16.	**Discussion of Recommended Studies for 2022 - General Q&A, Prioritization** 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. The workgroup will then consider the studies as a group, ask questions of the Principal Investigators, and begin the process of prioritization by stakeholders.	12:40 Melissa Foley
17.	**Closed Session - Decision: Recommendations for 2022 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 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 meeting during this agenda item. Desired Outcome: Recommendations from the ECWG to the TRC regarding which special studies should be funded in 2022 and their order of priority.	2:00 Karin North
18.	**Report out on Recommendations**	2:50 Karin North
	Adjourn	3:00

RMP Emerging Contaminants Workgroup Meeting

April 23-24, 2020
San Francisco Estuary Institute

Meeting Summary

Science Advisors	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
Dan Villeneuve	U.S. Environmental Protection Agency	Yes

Attendees

Abigail Noble (DTSC)
Alicia Gilbreath (SFEI)
Alicia Gilbreath (SFEI)
Alvina Mehinto (SCCWRP)
Andria Ventura (Clean Water Action)
Anne Balis (City of San Jose)
Anne Cooper Doherty (DTSC)
Autumn Cleave (SFPUC)
Bridgette DeShields (Integral Consulting)
Bryan Frueh (City of San Jose)
Charles Wong (SCCWRP)
Claire Waggoner (SWRCB)
Coreen Hamilton (SGS AXYS)
Da Chen (Jinan University)
Dawit Tadesse (SWRCB)
Diana Lin (SFEI)
Don Yee (SFEI)
Ed Kolodziej (UW)
Eric Dunlavey (City of San Jose)
Erica Kalve (SWRCB)
Ezra Miller (SFEI)
Frances Bothfeld (WA Dept of Ecology)
Gaurav Mittal (SFBRWQCB)
Gregory LeFevre (U of Iowa)
Heather Bischel (UC Davis)
Heather Peterson (SFPUC)
Holly Wyer (OPC)
Jay Davis (SFEI)
Jaylyn Babitch (City of San Jose)
Jen Jackson (City of SF)
Jennifer Teerlink (CDPR)
Jesselle Legaspi (DTSC)
June-Soo Park (DTSC)
Karin North (City of Palo Alto)
Laura McLellan (SWRCB)
Lester McKee (SFEI)
Lorien Fono (BACWA)
Luisa Valiela (EPA Region 9)
Maggie Monahan (SFRWQCB)
Mary Lou Esparza (CCCSD)
Mateo Stormwater Program)
Melissa Foley (SFEI)
Michael Fry (USFWS)
Miguel Mendez (SFEI)
Nina Buzby (SFEI)
Rebecca Sutton (SFEI)
Reid Bogert (BASMAA/San
Richard Grace (SGS AXYS)
Robert Wilson (City of Petaluma)

Roman Berenshteyn (BPC)
Sara Huber (SWRCB)
Scott Coffin (SWRCB)
Shoba Iyer (OEHHA)
Simona Balan (DTSC)
Simret Yigzaw (City of San Jose)
Steve Weisberg (SCCWRP)
Terry Grim (Cambridge Isotope Labs)
Tessa Fojut (SWRCB)
Thomas Mumley (SFBRWQCB)
Tony Luz (Integral Consulting)

DAY ONE - April 22

1. Introductions and Goals

Melissa Foley began the meeting by going over Zoom platform logistics and introducing the Workgroup advisors. Melissa also briefly introduced the various groups present with individual participants raising their virtual hands via Zoom.

Melissa then gave an overview of the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP), which outlined the program's goals, history, management questions, and monitoring structure. Additionally, Melissa summarized the goals of the meeting and noted a focus on the science in updates and special study proposals to gain input from the advisors and ensure alignment with stakeholder needs. Melissa ended by giving an overview of the Emerging Contaminant Workgroup (ECWG) daily agendas.

2. Discussion: CEC Strategy Update

Rebecca Sutton gave an update on contaminants of emerging concern (CEC) efforts and strategy, including an overview of current activities and the potential use of persistence as a secondary factor in classification of CECs within the RMP tiered risk-based framework. It was also noted that the Workgroup's Multi-Year Plan discussion will be deferred to a possible ECWG fall meeting.

Rebecca's outline of current CEC activities categorized efforts into three strategic elements: (1) targeted monitoring and risk evaluation, (2) learning from others/sharing expertise, and (3) non-targeted analysis (NTA). Multiple projects were noted for each element. The pending development of a monitoring strategy for CECs in stormwater was highlighted in the first strategic element. Rebecca also identified a few deliverables pending finalization, such as a draft manuscript on bisphenols and OPEs in Bay water. In addition, Rebecca discussed related efforts to reconvene the Ambient Ecosystems CEC Science Advisory Panel, and a current project with the State Water Board to analyze statewide CEC data using a tiered risk-based framework to guide recommendations for CEC monitoring and management priorities for the state.

Several attendees indicated the need to monitor quaternary ammonium compounds (QACs) in wastewater to determine the impact of the COVID-19 pandemic on their prevalence in the Bay. There was discussion of the urgency of sampling and opportunities to collaborate with studies collecting samples for detection of SARS-CoV-2. The EPA's list of approved substances to be used as antimicrobials during the pandemic includes QACs that should be targeted for analysis. Outdoor uses of QACs were also noted. Current challenges with laboratory access and personnel could lead to freezing and archiving samples for later analysis, though there are issues associated with freezing. Development of a sampling plan or special study for the duration of pandemic would be particularly useful. Tom Mumley acknowledged this would have to be a special effort due to the limited resource capabilities within the RMP and POTWs.

Rebecca then gave an overview on the possible inclusion of persistence in the environment as a secondary factor within the tiered risk-based framework. A conservative definition of persistence that is consistent with international standards was suggested as those chemicals with half-lives of 6 months or more within a matrix. Persistent chemicals are expected to accumulate in the environment with continued use. It is important to note a contaminant must also be bioavailable, meaning an exposure pathway to wildlife must be identified in order for persistence to be considered a risk. Consideration of persistence has direct implications for short-chain perfluoroalkyl and polyfluoroalkyl substances, known as "Other PFAS" in the risk-based framework, currently classified as Possible Concern. The previous review of the class found limited toxicity data relative to long-chain PFAS, though consideration of persistence as a secondary factor suggests reclassification as Moderate Concern is warranted.

Meeting participants were asked to respond to the suggestion of using persistence as a secondary factor and, if persistence were to be added as a factor, reclassification of "Other PFAS" to Moderate Concern. These recommendations were illustrated in the Draft CEC Strategy 2020 Update, circulated to the workgroup prior to the meeting; feedback is requested by May 29, 2020.

There was broad agreement among attendees to include persistence within the risk-based framework, and to elevate "Other PFAS" to the Moderate Concern tier. The group clarified that the type of persistence discussed relates to half-lives in abiotic matrices rather than within biota. Degradates must be evaluated for persistence as well. Several participants underscored the need to develop a strategy to manage the use of persistence as a secondary factor. Important concerns to consider within such a strategy include: (1) establishment of criteria for persistence, (2) burden of proof for persistence, (3) weighting multiple factors within the risk-based framework, (4) potential for different monitoring and management approaches for contaminants that are persistent compared to those that exceed toxicity thresholds, and (5) use of persistence as a characteristic to identify new candidates for monitoring. Eric Dunlavey also noted the importance of the tiered risk-based framework as a communication tool, which should be accounted for in further advancements of the framework. Care should be taken to not put everything in the Moderate Concern category, or the framework could lose some of its impact in communicating CEC priorities.

3. Discussion: CEC Toxicology Strategy

Ezra Miller presented a draft strategy to assess the potential toxicological risks of data-poor CECs, including usage of predictive toxicology tools. Ezra also introduced the new ECWG advisor, Dan Villeneuve, who is a research toxicologist at the US EPA's Office of Research and Development Center for Computational Toxicology and Exposure, Great Lakes Toxicology and Ecology Division.

Ezra outlined the framework for the proposed CEC toxicology strategy, highlighting use of predictive toxicology to inform prioritization for data poor-chemicals classified within the Possible Concern tier. Two classes of models, *in vitro* and *in silico,* are currently used within predictive toxicology to forecast chemical interactions within biological systems and resulting adverse effects. There are several available tools for both classes, such as ECOSAR (*in silico*) and EPA CompTox Chemistry Dashboard (*in vitro*), though use of these types of tools will vary based on the particular goals of the study. A "conceptual model" workflow was presented to the Workgroup to illustrate the approach to determine appropriate ecotoxicological thresholds for assessment within the tiered risk-based framework.

Ezra also provided details regarding proposed next steps including: (1) evaluation of the quality of available thresholds and use of predictive methods to calculate thresholds for contaminants without published thresholds, (2) screening studies to estimate the effects of unknowns and contaminant mixtures by assessment of biological activity of environmental samples using a battery of high-throughput bioassays, and (3) development of predictive toxicology tools specific to important Bay species.

Ezra then asked for comments from the workgroup members on the proposed strategy and recommended next steps. Participants were supportive, though several comments indicated the need to develop a conceptual model and decision-making framework for toxicology. In particular, Dan Villenueve suggested considering *in silico* methods as complementary to *in vitro* methods, and further development of the screening study to strategically identify use of assays to probe contaminants. Anne Cooper Doherty noted that the use of *in silico* tools requires caution and knowledge of what they are and are not capable of because of which compounds were used to develop them. Lee Ferguson suggested expanding this effort beyond toxicology to include exposure-relevant factors such as chemical use classification, production volume information, and number of patents for individual chemicals. Kelly Moran noted the need for Ezra's expertise to guide future monitoring priorities.

Miriam Diamond and Heather Stapleton suggested working towards a SF Bay-specific focus within the toxicology framework, and considering additional stressors such as climate change. Dan mentioned the possibility of providing exposure information, including existing data gaps, to other organizations/programs such as the US EPA that are looking for collaborations to help guide wider data collection and high-throughput analysis of chemicals efforts. He and Heather also indicated the need to have a clear plan for what to do with any information generated using *in vitro* methods; Dan encouraged development of clearly focused study questions and a plan for how to use different lines of evidence to classify CECs within the tiered risk-based framework. In particular, predictive tools may be useful in de-prioritizing contaminants from further study. Derek Muir noted that for contaminants with established toxicity thresholds, there is often disagreement among the agencies that calculate thresholds due to different approaches, and an assessment of these differences would be useful. He also asked whether it might be possible to address mixtures using the approach of summing toxic equivalents, which Dan suggested is reflected in the *in vitro* exposure activity tools. Tom Mumley and Karin North indicated strong support for this effort and the urgent need for effects-based information for stakeholders.

4. Discussion: Update on Monitoring of CECs in Urban Stormwater

Rebecca Sutton reviewed findings from the pilot year of monitoring CECs in urban stormwater, focusing primarily on preliminary results of per- and polyfluoroalkyl substances (PFAS), while also including partial results on bisphenols and organophosphate esters (OPEs). Rebecca explained to the workgroup that initial findings prompted changes to the PFAS sample collection methods.

While updating the workgroup on year 2 of the study, Rebecca noted that the expected intensive collection and analysis did not occur due to a drier winter and impacts from COVID-19. Rebecca outlined the potential to extend the study to a fourth year to obtain more results for analysis, noting time for further discussion the following day.

Related to the first year's PFAS TOP assay work, Rebecca informed the workgroup of issues related to replicate variability due to variation in sediment loads and field blank contamination. These results led to a suggested change in PFAS sampling design. Rebecca asked the participants for feedback on the revised sampling plan to focus on dissolved phase measurements and limit use of the TOP assay. There was agreement among the workgroup that the updated sampling design made sense.

Derek Muir suggested expansion of the current list of PFAS examined, noting in particular that trifluoroacetic acid would be an interesting analyte, though it does have multiple sources. Lee Ferguson and Bill Arnold advised a more thorough analysis of which PFAS to consider in each matrix. Tom Mumley wanted further clarification on sample site determination with a clear presentation within the proposals. Rebecca noted that proposed sites are reviewed each fall with the Small Tributaries Loading Strategy team to assure they are appropriate for the study. Andria Ventura mentioned a current State Water Board investigation of soils and groundwater around airports that could provide data.

Heather Stapleton commented on the results of OPEs data, noting the different OPEs present and suggesting to alter the analyte list and examine components of newly identified commercial mixtures. Derek noted the high proportion of OPEs associated with particles; Lester McKee reminded the group that suspended sediment in stormwater is likely not at equilibrium with the water, such that sediment-bound contaminants are derived from the landscape rather than partitioning from the water. Lee noted observation of OPEs derived from PVC plastic water pipes.

DAY TWO - April 23

1. Summary of Day 1 and Goals for Day 2

Melissa Foley reminded attendees of Zoom features and allowed time for an abbreviated roll call of the day's attendees. Melissa then reviewed the events of Day 1 of the meeting, noting interest from Jennifer Teerlink in having interested parties contact her regarding QACs monitoring and methods. Melissa also informed the meeting participants that the day's focus was on updates on the Status and Trends monitoring review as well as prioritization of special studies proposals.

2. Information: Status and Trends Monitoring Review

Melissa Foley began by outlining the motivations and objectives of the Status and Trends monitoring program review. Notably, CECs are partially driving this effort in order to develop an approach to incorporate CECs into Status and Trends monitoring. The goal for the revision is to develop a nimble sampling design that allows CECs to go in and out of the program as needed, likely at a higher frequency than legacy contaminants. Functional traits and pathways into the Bay, rather than specific contaminants, are critical factors to consider in determining the best monitoring methodology.

Melissa then went over the timeline of the redesign work, noting the kickoff meeting occurring the following week. Within the ECWG, Derek Muir is involved as a panel expert and the panel will likely reach out to the ECWG for input on the developing Status and Trends sampling plan. Tom Mumley is also actively involved, similarly noting a need for ECWG input, as this will ideally create more robust and agile programs for Status and Trends as well as ECWG. An update on the review will be provided at the 2021 ECWG meeting.

3. Summary of Proposed ECWG Studies for 2021

Rebecca Sutton gave an overview of all proposed special studies, highlighting the motivation and approach for each study, as well as associated budgets and deliverables. Meeting participants were allowed a few clarifying questions after the presentation of each proposal, though it was noted that more time would be available for discussion later in the meeting. The focus of discussion was on four high priority studies, with a more brief review of three lower priority proposals intended for inclusion on the Supplemental Environmental Projects (SEP) list.

The proposal for the third sampling year of the stormwater CECs screening study builds upon the work of the previous two years with the motivation to fill existing stormwater data gaps. The current approach targets sites with > 80% urban land use. Sampling also includes reference samples from less urban sites. There is a desire to also sample at sites with unique sources of contaminants such as airports. As prefaced the previous day, this work could be extended for another year to create a more robust data set, particularly given limited sampling in year 2. There are budget concerns to adding a fourth year, however, as there are fewer leveraging opportunities with other RMP projects compared to the first three years. Funds from reduced work in Year 2 will be applied to sampling in year 3, and year 4, if included. Initial discussion began on the potential extension of the study to a fourth year with questions on the budget and necessity of more data. In response to a question about adaptation of the analyte list, Ed Kolodziej clarified that his lab would soon update it with special attention to more causative agents.

Presentation of the study on PFAS in Bay water followed. The motivation for this study is to better understand risks in the Bay, updating a similar 2009 study with use of an embayment-wide approach and standardized methods including more analytes. This study would also review the toxicity of PFAS, including consultation with additional

PFAS experts. In response to a question on the connection to the model, Rebecca clarified it is used more as a tool to check if understanding of contaminants is correct, rather than driving design of the study. Derek Muir noted that the model predicted levels of PFOA and PFOS below method detection limits in some embayments. Rebecca noted that there are few differences between the lab for this study compared to the analytical partner for the stormwater study, which does not have capacity to analyze estuarine samples.Lee Ferguson expressed the value of sampling the same sites as the previous sampling effort, especially for those identified as significant sources.

A study comparing seasonal concentrations of bisphenols and OPEs in Bay water was introduced. This proposal would monitor sites during both wet and dry seasons to help understand the seasonal influence of stormwater and wastewater pathways, while also informing a potential Status and Trends study design. Sampling would occur once per month over three months of the wet and dry seasons. Samples would be analyzed by a different lab than the stormwater study in order to use standardized methods available in a commercial lab. The current analyte list for the commercial lab is more limited, though there may be opportunities to expand the list based on the results of the stormwater study. Rebecca clarified that the focus would be on sites in Lower South Bay, where higher levels were observed in previous work. Tom Mumley commented on the potential to cut back costs, particularly related to the large amount of QA samples.

The toxicological thresholds for emerging contaminants proposal was then presented, aiming to synthesize and assess the quality of available thresholds and calculate thresholds for data-poor contaminants that have been measured in the Bay. This project would also help establish a process that could be used to identify thresholds for future RMP studies and prioritize CECs within the tiered risk-based framework. A “living document” would be produced to continue to update these thresholds as new data emerges. Ezra also noted that the study will include all thresholds available, not limited in scope to the Bay, and would begin the task of addressing thresholds for stormwater contaminants. Miriam Diamond asked about the potential use of species sensitivity distributions in predicting PNECs, and Ezra responded that these would be used when possible, but many CECs have insufficient data for this approach.

The three SEP proposals were briefly outlined, noting that these studies are important to conduct in the Bay but are not currently suggested as top priorities for RMP funding. The study of PFAS in North Bay margins would look at archived sediment samples to better understand occurrence and risks in an area close to likely PFAS sources. Depending on the budget, the project could be expanded to include archived sediment samples from the South Bay margins (2017) and analysis using the TOP assay. A project on halogenated azo dyes in archived South Bay margins sediment followed, aiming to study the occurrence of these toxic CECs in the Bay for the first time. Hui Peng of the University of Toronto would be the analytical partner for this project, which could also include North Bay margins samples as an add-on option. Lee Ferguson suggested examining microplastics in addition to halogenated azo dyes because these contaminants may be riding on microfibers, which Miriam Diamond noted she is currently conducting, along with Hui Peng, and could provide complementary data. Bridgette DeShields asked if azo dyes could be compared to PCBs 11, 52 and 209, which were analyzed in South Bay Margin sediment samples. A non-targeted analysis of Bay harbor seal tissue was the final study presented, with a goal to determine if there are other contaminants of concern in the Bay. This would be a two-part study including screenings for both unexpected PFAS and lipophilic nonpolar contaminants.

3. Discussion of Recommended Studies for 2021 - General Q&A

Meeting attendees took the time to ask any remaining questions while proposal PIs were still in attendance. The discussion focused on the four high priority studies previously presented.

<u>Stormwater</u>

Discussion of the stormwater study noted general approval of planning for a fourth year, though the idea can be revisited after the third year of sampling. Kelly Moran suggested further description of the overlap between this effort and other monitoring efforts to inform recommendations for a third or fourth year of the study. Miriam Diamond suggested providing further information on the selection of sampling sites, especially for larger watersheds. Rebecca Sutton noted the study's focus on majority urban land use sites tends to exclude these larger watersheds, though there is a minimum watershed size requirement. Derek Muir expressed interest in the addition of sediment analysis to the study, though there were concerns about costs and analyte contamination. Bill Arnold suggested a fourth year could be scoped to include only those contaminants considered to be a higher priority. Related to leveraging other RMP efforts,Tom Mumley discussed the anticipated activities of the Small Tributaries and Loading Strategy team (STLS) and Sources Pathways and Loadings Workgroup (SPLWG). As the focus on legacy contaminants begins to fade, the possible opportunities for CEC work could increase, pointing to the need for a CEC monitoring strategy for stormwater. Tom also advised consideration of an interim report if four years of sampling are conducted to inform regional and statewide applications and give insight on continuing efforts with STLS.

<u>PFAS in Bay Water</u>

Derek Muir was concerned about the relatively high detection limits of the method and limited suite of analytes. Richard Grace, representing the study's analytical partner SGS

AXYS, noted lowering detection limits and expansion of the analyte list could be further explored. Tom Mumley thought there could be fewer sampling sites to enhance the number of analyses and save on costs. Additionally, Tom commented on the high reporting budget, though Rebecca Sutton highlighted new PFAS are likely to be identified and require more extensive toxicological review.

Bisphenols and OPEs

The discussion centered on the budget and scope of the project. Heather Stapleton suggested excluding bisphenols, though Miriam Diamond noted that previous study of bisphenols resulted in detections at levels in the range of PNEC values. Lee Ferguson expressed interest in expanding the analyte list to include the diol hydrolysis product of BADGE. Heather Stapleton advocated for changing the current OPEs list, which Richard Grace agreed to explore. Tom Mumley reiterated a need to lower costs, highlighting potentially fewer sites or QA samples. Rebecca Sutton noted a higher than average number of QA samples was included due to previous blank contamination and accurate comparison between wet and dry seasons.

Toxicology

When discussing the toxicology study, there were multiple comments on the scope of the project. Dan Villenueve underlined the necessity of a decision framework for a consistent approach to how we use threshold quality assessment within the tiered risk-based framework. Ezra Miller clarified that several factors are being considered to help rank compounds within the tiered risk-based framework, including bioaccumulation and the types of species affected. Miriam Diamond indicated that toxicity data and thresholds specific to sediment would be challenging. In response to a comment from Tom Mumley regarding the urgent need for information derived from this project, Melissa Foley noted the possibility to release funds earlier to help begin work to inform future multi-year planning.

General

There were also some comments on the general program as a whole. Kelly Moran brought up the decision to reduce strategy funds, which Rebeeca Sutton clarified was due to changes from last year where the budget was increased to account for added toxicology work. Kelly Moran also commented on the decision-making process regarding specific contaminants. Becky noted discussion with DTSC and potential synergy, as well as future plans to discuss building information on Moderate Concern contaminants. It was also noted that RMP modeling efforts are ongoing, though there are no CEC-specific modeling proposals at this time.

4. Closed Session - Decision: Recommendations for 2021 Special Studies Funding

Karin North led the closed door discussion. Following extensive discussion, studies were prioritized. A Zoom poll was conducted to help rank proposals. The resulting recommendations are shown in the following prioritization tables:

Study Name	Budget	Modified Budget	Priority	Comments
CECs in Stormwater (Year 3)	$148,000		1	Work with Tom to identify optimum sampling for year 3 with a contingency plan for year 4. Provide interim reporting at 2021 ECWG if proceed to year 4 (and/or to possibly help determine if proceed with year 4)
PFAS in Bay water	$66,000	*potentially lower*	3	Look into reducing number of QA samples and stations; lower budget could allow for QAC monitoring with extra funds
Seasonal Influence of Bisphenols and OPEs	$115,000	*$85,000 (loose estimate)*	4	Modify budget based on four stations (3 minimum); adjust analyte list based on in-Bay findings and WG expert recommendations
Toxicology Strategy (followup)	$60,000		2	New approach for the WG that could inform/incorporate stormwater efforts; hope to start in fall 2020 to advance timeline

SEP Project Ideas			
Study Name	Budget	Priority	Comments
PFAS in North Bay Margin Sediment	$40,000 - $125,000	3/4	Less potential for new information or important information for management
Azo dyes in South Bay Margin Sediment	$65,000 – $95,000	1	DTSC interested; important, new information; inform how much effort needed; consider including microplastics (fibers) in the study design
NTA for Perfluorinated and Nonpolar Contaminants in Seal Tissue	$75,000 – $250,000	3/4	Important to develop a comprehensive view of PFAS in the Bay including trends over time

COVID-19 Related QAC monitoring	*Discuss and develop with Bill Arnold and Jennifer Teerlink*	2	Should not miss this opportunity; DPR may not be able to solely cover this; develop a sampling plan or a contingency plan; San Jose and Palo Alto are able to collect samples

5. Report Out on Recommendations

After the closed door session, proposal authors were invited back to the meeting to hear the final prioritization decisions. Karin North summarized the discussed suggestions, highlighting possible reduction of costs and interest in developing a QAC proposal. Tom Mumley noted further discussion on the extension of the stormwater study is pending.

Adjourn

MULTI-YEAR PLAN FOR EMERGING CONTAMINANTS

Special studies and monitoring in the RMP from 2015 to 2024. Numbers indicate budget allocations in $1000s. Budgets in parentheses represent funding or in-kind services from external sources (e.g., SEP funds). Budgets that are starred represent funding that has been allocated for the given study within other workgroups. Bold boxes indicate multi-year studies. Items shaded in yellow are considered high priority for 2022 funding and beyond. Dollar signs indicate projected future priorities for RMP special studies funding. Budgets marked with ‡ have been designated as matching funds for non-RMP funded projects.

Element	Study	Funder	Questions addressed	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024
Strategy	CEC Strategy[1] (not a Special Study after 2020)	RMP	1-6	20	48	50	65	70	75	*60‡*	*80*	*60*	*60*
	Stormwater Monitoring Strategy	RMP	1,2								50	50	
MODERATE CONCERN CECs													
PFAS	CECs in Municipal Wastewater[2]	RMP	1,2,4	27.5									
	Effluent TOP Analysis	DTSC	1,2,4,6	(50)									
	PFAS: Synthesis and Strategy	RMP	1-6			56							
	Margin Sediment Archiving	RMP	1				2.5						
	PFOS/PFOA Bay Model	Interwaste	1,2,3,5				(7)						
	Stormwater PFAS[3]	RMP	1,2					33	40	29.6	25		
	North Bay Margin Sediment PFAS ($40-$125k)	SEP proposal	1,2,4,6										
	PFAS in Ambient Bay Water	RMP	1,4,6							50			
	PFAS in Influent, Effluent, Biosolids; Study TBD, est. value	BACWA	1,2,4,6							(365)			
	PFAS Wet Season Water Screen	RMP	1,2								40		
	Harbor Seal (PFAS and Nonpolar NTA; SEP proposal, ~$100k)[4]	SEP or RMP	1,4,6										100
	RMP Status and Trends[5]	RMP S&T	1,4		E 4*		E 4*	F 9*		E 4*			E, F 13*
Alkyl-phenols and Alkyl-phenol Ethoxylates	Margin Sediment Archiving	RMP	1,4				2.5						
	Stormwater Ethoxylated Surfactants[3]	RMP	1,2					33	40	29.6‡	25		
	Ethoxylated Surfactants in Water, Margin Sediment, and Wastewater	RMP	1,2,4					123					

Element	Study	Funder	Questions addressed	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024
	Trends Analysis (Sediment Core)	RMP	1,4								70		
Bisphenols	Bisphenols in Bay Water	RMP SIU	1	(25)		50							
	Bisphenols in Stormwater	RMP	1,2						21	29.6‡	25		
	Bisphenols in Wastewater, Sediment	RMP	1,2						72				
	Bisphenols in Sport Fish, Bivalves	RMP	1										80
	RMP Status and Trends[5]	RMP S&T	1,4							W 13*	wet 9*	W 13*	
Organo-phosphate Esters	Organophosphate Ester Flame Retardants in Ambient Bay Water	RMP ECCC	1,4			47							
	Stormwater Organophosphate Ester Flame Retardants[3]	RMP	1,2					33	40	29.6‡	25		
	OPE Air Monitoring	RMP	1,2,3,6									50	
	RMP Status and Trends[5]	RMP S&T	1,4							W 16*	wet 12*	W 16*	
Fipronil	CECs in Municipal Wastewater[2]	RMP	1,2,3	27.5									
	Fipronil, Degradates, Imidacloprid in Wastewater and Biosolids	RMP ASU	1,2,3		30 (8)								
	RMP Status and Trends[5]	RMP	1,3,4				S 12*						
Imida-cloprid	Imidacloprid, Degradates, and other Neonicotinoids in Bay Water	RMP	1			40							
LOW or POSSIBLE CONCERN CECs													
PBDEs	RMP Status and Trends[5]	RMP S&T	1,3,4		B, E 24*		S, E 42*	F 24*		E 18*	S 24*		F 24*
Alt. Flame Retardants	Brominated Flame Retardants in Bay Sediment and Tissue	RMP	1,4								80		
Pharma-ceuticals	Pharmaceuticals in Wastewater	RMP POTWs	1,2,4		(68)		30						
	Antibiotics and QACs in Surface Sediment and Cores	U Minn	1,3,4				(8)						
	Pharmaceuticals in Wastewater, Water & Archived Sediment	RMP	1,2,4									180	
Plastic Additives	Phthalates and Replacements in Archived Sediment	RMP	1,4										70

Element	Study	Funder	Questions addressed	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024
Personal Care/ Cleaning	Triclosan in Small Fish	RMP	1			41							
	Musks in Water & Sediment[6]	RMP	1				64.5						
	Siloxanes in Sediment and Effluent	SWEAM DTSC	1,2				(15)						
	Sunscreens in Wastewater	MMP	1,2						(36.5)				
	New Concerns in Bay Water, Wastewater[7]	RMP	1,2									30	
	QACs in Wastewater[7]	MMP	1,2,4							(58.2)		30	
Pesticides	DPR Priorities in Water & Sediment[6]	RMP USGS	1,2,3				64.5 (6.8)						
	Ag Pesticides in Water & Sediment of North Bay Margins (~$100k)	SEP proposal	1,2										
	Antimicrobials in Bay Water, Wastewater[7]	RMP	1,2									30	
PHCZs	Sediment, Tissue	SIU	1	(15)	(20)	(40)							
Brominated Azo Dyes	Archived Sediment (~$60k)	SEP proposal	1										
Building Materials	Isothiazolinone Biocides and Other Contaminants in Stormwater (~$50k)	U Iowa SEP Proposal	1,2					(2)					
	New concerns	RMP	1										50
Chlorinated Paraffins	Chlorinated Paraffins (medium-long) in Sediment (~$60k, 2022)	SEP proposal	1										
Vehicles, Roadways	Tire, Roadway Contaminants Follow-up from NTA, Stormwater[3]	RMP	1,2					33	40	29.6	25		
	Tire Contaminants Wet Season Water Screen	RMP	1,2								50		
NON-TARGETED & OTHER STUDIES													
Non-targeted	Non-targeted Analysis of Water-soluble CECs	RMP / Duke / AXYS	1,2		52 (10) (6)								
	Non-targeted Analysis of Sediment	RMP	1,2				101						
	Non-targeted Analysis of Runoff from North Bay Wildfires	RMP DTSC Water Brd	1,2				36 (20)						

Element	Study	Funder	Questions addressed	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024
		Duke					(27) (3)						
	Harbor Seal (PFAS and Nonpolar NTA; SEP proposal, ~$100k)[4]	SEP proposal	1,4,6										100
	Follow-up Targeted Study (2018 sediment results)	RMP	1									100	
	Microplastic Additives NTA Study[8]	RMP	1										50
Other	Toxicology	RMP	1					15		60	60	60	60
RELEVANT STUDIES IN OTHER WORKGROUPS													
Bioassay (EEWG)	Linkage of In Vitro Estrogenic Assays with In Vivo End Points	RMP SCCWRP UF	1,2			45							
Modeling (SPLWG)	Integrated Monitoring and Modeling Strategy - CEC Conceptual Model	RMP	1,2,4							50			
RMP-funded Special Studies Subtotal - ECWG				**75**	**130**	**284**	**366**	**325**	**328**	**258**	**475**	**530**	**510**
High Priority Special Studies for Future RMP Funding											**355**	**300**	**310**
RMP-funded CEC Strategy (not a Special Study after 2020)										**60**	**80**	**60**	**60**
RMP Status and Trends Analytical Costs for CECs				**0**	**28**	**0**	**58**	**33**	**0**	**51**	**45**	**29**	**37**
RMP-funded Special Studies Subtotal – Other Workgroups				**0**	**0**	**45**	**0**	**0**	**0**	**50**			
MMP & Supplemental Environmental Projects Subtotal				**0**	**0**	**0**	**0**	**0**	**36.5**	**58.2**			
Pro-Bono & Externally Funded Studies Subtotal				**90**	**112**	**90**	**37**	**2**	**0**	**365**			
OVERALL TOTAL				**165**	**270**	**419**	**461**	**360**	**514.5**	**842.2**	**600**	**619**	**607**

1 – The CEC Strategy funds preparation of RMP CEC Strategy Revisions, Updates, and Memos; it also funds literature review, scientific conference attendance, and responses to information requests from RMP stakeholders. A Revision to the CEC Strategy is planned for 2022, resulting in a higher funding request than in the prior years. While previously considered a Special Study, as of 2021 the CEC Strategy is considered part of program management.
2 – The 2015 CECs in Municipal Wastewater study ($55k) included analyses of PFAS and fipronil; the budget has been split between these two groups.
3 – The multi-year (2019-2022) stormwater study includes five groups of analytes: PFAS, ethoxylated surfactants, organophosphate esters, bisphenols (added year 2), and targeted stormwater analytes identified via non-targeted analysis. The total projected cost ($586k) is spread across five groups and three years.
4 – The proposed non-targeted analysis of harbor seal tissues includes investigations of PFAS ($100k) and nonpolar compounds ($100k).
5 – When a CEC may be included in the the RMP Status and Trends monitoring, there is a code in the cell denoting the matrix for which monitoring is proposed: W = water; S = sediment; B = bivalve; E = eggs; F = fish. Approximate analytical costs are provided to indicate CECs resources provided by Status and Trends monitoring. A new designation, “wet,” indicates trial wet season water monitoring, which may be funded in 2022.
6 – This 2018 special study ($129k) included analyses of pesticides and fragrance ingredients; the budget has been split between these two groups.
7 – A special study suggested for 2023 could analyze cleaning product ingredients including QACs and other antimicrobials; costs are split among these three groups.
8 – A suggested special study that uses non-targeted analysis to identify additives in microplastics is listed as potentially co-funded via both ECWG and MPWG.

Special Study Proposal: Stormwater Contaminants of Emerging Concern (CECs) Monitoring Strategy

Summary: Prior RMP projects – including a multi-year stormwater CECs monitoring project initiated in 2018 – identified the presence of CECs of moderate and potential concern in urban runoff. Available data from prior sampling are relatively limited, but nevertheless provide evidence that stormwater is a major pathway for CECs to enter San Francisco Bay. Due to high CECs monitoring costs and technical challenges, a well-thought out, carefully focused approach will be essential. The goals of this project are (1) to develop an approach for prioritizing CECs for stormwater monitoring, and (2) to develop an approach for sampling stormwater CECs in the context of the specific physico-chemical properties, sources, transport pathways, and fate of prioritized CECs. A stormwater CECs monitoring strategy is the first step in establishing a long-term stormwater CECs monitoring program and would form the basis for addressing both CECs and Sources, Pathways, and Loadings (SPL) management questions, such as estimating CECs loads discharged to the Bay.

Estimated Cost: $105,000 over 2 years ($50,000 for 2022; $55,000 for 2023)

Oversight Groups: ECWG & SPLWG

Proposed by: Kelly Moran, Rebecca Sutton, Lester McKee, Alicia Gilbreath, and Tan Zi (SFEI)

Time sensitive: No. However, this strategy will inform future monitoring, which could begin with piloting a few strategy elements as early as Water Year 2023 (October 2022 - September 2023) if this strategy is initiated in 2021.

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Development of draft stormwater CECs monitoring strategy	Fall 2021 – Spring 2023
Task 2. Present update to the SPLWG and ECWG	Spring 2022
Task 3. Presentation of draft strategy document to the SPLWG and ECWG	Spring 2023
Task 4. Final Strategy document	September 1, 2023

Background

CECs – a diverse group of substances with different sources, chemical properties, and fate – wash into stormwater from a variety of ongoing emissions sources. Prior RMP projects – including a multi-year stormwater CECs monitoring project initiated in 2018 – identified the presence of CECs of moderate and potential concern in urban runoff (Sutton et al. 2019a; Sutton et al. 2019b; Tian et al. 2020). Available data from this and other RMP CECs sampling are relatively limited, but provide a strong weight of evidence that stormwater is a major pathway for CECs to enter San Francisco Bay (e.g., Sedlak et al. 2018; Sutton et al. 2019a; Miller et al. 2020). Importantly, RMP CECs monitoring, which has focused on understanding the potential for CECs to occur in stormwater, has not been designed to address other management questions, such as estimating loads of CECs discharged to the Bay.

Due to the high cost, technical challenges, and practical challenges involved in stormwater CECs monitoring, there is a need for the RMP to develop a strategy to prioritize CECs for monitoring and to lay out an approach for developing CECs sampling plans that maximize the value of each sample and facilitates development of data and information to support management decisions.

The RMP has developed a Small Tributaries Loading Strategy (STL Strategy) and more recently, a STLS Trends Strategy for legacy contaminants (McKee et al. 2009; Wu et al. 2018). Due to their ongoing uses and diverse chemical properties, CECs do not have much in common with mercury and PCBs, the legacy pollutants that are the primary focus of the STL Strategy and the STLS Trends Strategy. Due to the focus on mercury and PCBs management questions defined by TMDLs (which remain important), the STL Strategy documents cannot be readily adapted to address CECs. The sampling designs for mercury and PCBs that flowed from the STL Strategy are built on the legacy and particle-associated nature of these pollutants and are not optimal for CECs.

Study Objectives and Applicable RMP Management Questions

The goal of this project is to develop a stormwater CECs monitoring strategy that would include two basic elements:

(1) an approach for prioritizing CECs for stormwater monitoring, and
(2) an approach for stormwater CECs sampling based on the physico-chemical properties, sources, transport pathways, and fate of prioritized CECs.

The near-term objectives of the sampling approach will be to (a) characterize the presence of the priority CECs in stormwater, and (b) develop data suitable for estimating loads of selected stormwater priority CECs to the Bay.

Table 1. Study objectives and questions relevant to RMP 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?	Develop an approach for prioritizing CECs for stormwater monitoring.	Using conceptual models to identify which CECs of potential or moderate concern for the Bay have sufficient outdoor exposure to occur in urban runoff. Using stormwater monitoring to identify CECs of potential concern for the Bay to inform future Bay monitoring design.
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Develop a CECs monitoring approach capable of generating data suitable for characterizing the presence of priority CECs in stormwater and estimating loads of selected stormwater priority CECs loads to the Bay.	Characterizing the presence of a CEC of potential or moderate concern in stormwater. Obtaining sufficient stormwater monitoring data to estimate loads of selected priority CECs to 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?	N/A	N/A
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?	N/A	N/A
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	Develop a CECs monitoring approach capable of generating data suitable for estimating stormwater priority CECs loads discharged to the Bay.	Predicting trends based on monitoring data and/or other factors (e.g., use trends, environmental and societal changes).
6) What are the effects of management actions?	Develop a CECs monitoring approach capable of generating data suitable for estimating stormwater priority CECs loads discharged to the Bay.	Predicting trends based on monitoring data and modeling of the effects of management actions. Providing data to support modeling to inform monitoring design refinements to most quickly and/or more cost-effectively measure reductions.

Table 2. Study objectives and questions relevant to RMP SPL management questions

Management Question	Study Objective	Example Information Application
1) What are the loads or concentrations of pollutants of concern from small tributaries to the Bay?	Develop a CECs monitoring approach capable of generating data suitable for characterizing the presence of priority CECs in stormwater and estimating stormwater priority CECs loads discharged to the Bay.	Characterizing the presence of a CEC of potential or moderate concern in stormwater. Obtaining sufficient stormwater monitoring data to estimate loadings of priority CECs to the Bay.
2) Which are the "high-leverage" small tributaries that contribute or potentially contribute most to Bay impairment by pollutants of concern	Develop a CECs monitoring approach capable of generating data suitable for estimating stormwater priority CECs loads discharged to the Bay.	Using stormwater monitoring data to estimate loadings of priority CECs to the Bay from individual watersheds.
3) How are loads or concentrations of pollutants of concern from small tributaries changing on a decadal scale?	Develop a CECs monitoring approach capable of generating data suitable for estimating stormwater priority CECs loads discharged to the Bay.	Predicting trends based on monitoring data and/or other factors (e.g., use trends, environmental and societal changes).
4) Which sources or watershed source areas provide the greatest opportunities for reductions of pollutants of concern in urban stormwater runoff?	Develop an approach for stormwater CECs sampling based on the sources, transport pathways, and fate of the CEC that characterizes the presence of the priority CECs in stormwater.	Using modeling (e.g., conceptual, statistical) to examine monitoring data correlations with watershed characteristics.
5) What are the measured and projected impacts of management action(s) on loads or concentrations of pollutants of concern from the small tributaries, and what management action(s) should be implemented in the region to have the greatest impact?	Develop a CECs monitoring approach capable of generating data suitable for estimating stormwater priority CECs loads discharged to the Bay.	Predicting reductions based on monitoring data and modeling the effects of management actions. Using modeling (e.g., conceptual, statistical) to examine monitoring data correlations with watershed/source characteristics.

Approach

We propose to develop a CECs monitoring strategy that would include two basic elements:

(1) an approach for prioritizing CECs for stormwater monitoring, and
(2) an approach for sampling stormwater CECs based on the physico-chemical properties, sources, transport pathways, and fate of the CEC.

1. Approach for prioritizing CECs for stormwater monitoring
Only a small subset of all CECs can feasibly be monitored by the RMP, making prioritization essential. The prioritization process would build on the RMP CEC Strategy, including the RMP tiered, risk-based framework (Miller et al. 2020). Additional stormwater specific considerations will be added. For example, the known linkage between tires and coho salmon toxicity drove the inclusion of multiple potentially toxic tire ingredients in the current stormwater CECs monitoring project (Tian et al. 2020). Available chemical use information (which is often limited) and tools like conceptual models may be used to evaluate the potential for a CEC to occur in stormwater.

We anticipate that this would be a flexible, weight-of-evidence-based prioritization process rather than a fixed, quantitative process due to the limited information available for CECs and the rapidly changing nature of available information. For CECs, information availability varies; key limitations include outdoor use information, physico-chemical property data, monitoring data from elsewhere, and aquatic toxicity data. Fast-moving scientific research and regulation outside of the San Francisco Bay Area and quickly advancing chemical analysis and predictive toxicology methods are expected to continue to provide a wealth of insights to support prioritization of CECs for stormwater monitoring.

Initial priorities will almost certainly include CECs of Moderate Concern for the Bay (based on the RMP tiered, risk-based prioritization framework), with the exception of pesticides or any other CEC addressed through existing, non-RMP monitoring. The monitoring strategy will also address identification of additional CECs of potential concern, based on growing scientific understanding of stormwater as a CEC conveyance and stormwater-specific potential CEC sources like tires, building materials, and clothing dryer emissions.

2. Approach for Stormwater CECs sampling design
The objectives of the sampling approach will be to (a) characterize the presence of the priority CECs in stormwater, and (b) develop data suitable for estimating loads of selected stormwater priority CECs to the Bay.

The strategy will address sampling location selection, sampling methods, and ancillary data needs to support modeling (e.g., flow gauge data). While there are generic considerations – such as design elements that best support modeling (e.g., alignment with Bay/margins sampling; use of fixed vs. rotating sampling locations, preference for composite samples due to high analytical costs) – a portion of the sampling approach will necessarily relate to the individual characteristics of each CEC monitoring candidate (e.g., ability to use automated samplers; need to sample sediment; priority sampling locations). This process will require us to consider the following elements for each CEC that is a candidate for stormwater monitoring:

- Physico-chemical properties (e.g., water solubility, partitioning to sediment, volatility)
- True sources, particularly as they relate to land use and directly connected impervious area
- Fate and transport processes occurring between true sources and stormwater (e.g., air pathway, relevance of transport via particles, relevance of out-of-watershed sources, degradation/transformation, phase transfer)

The Strategy will explore key issues for a CECs monitoring design, such as:

- What types of monitoring locations are appropriate for addressing the different RMP management questions (see Tables 1 and 2)? For example, anticipated "high source" sites may be suitable for reconnaissance monitoring to identify CECs with potential to adversely impact beneficial uses in San Francisco Bay, but fixed location "integrator" or "representative" sites may better support load modeling.
- What constitutes appropriate "reference" sites?
- What constitutes sufficient data for a first-order load estimate, and (later) a more refined load estimate?
- To what extent can CEC sampling designs leverage and/or partner with other ongoing Bay Area watershed sampling (e.g., monitoring conducted by the Surface Water Ambient Monitoring Program Stream Pollution Trends program, Department of Pesticide Regulation Surface Water Protection Program, or local agencies)?
- What types of monitoring data would be most helpful to agencies addressing CECs (e.g., California Department of Toxic Substances Control's Safer Consumer Products Program)?
- What watershed characteristics are anticipated to be needed to select sampling locations for CECs? Is information beyond what we currently have available likely to be needed?

The strategy will also integrate modeling. We will explore how modeling can inform our monitoring strategy as well as how our monitoring can be designed to support modeling to address RMP management questions (see Tables 1 & 2). Modeling data needs (e.g., for load estimation) will drive certain elements of monitoring design (e.g., use of some fixed location monitoring stations). Modeling will also inform monitoring design (e.g., to identify monitoring locations and/or prioritize pollutants for monitoring). While the Strategy will address how modeling integrates with CECs monitoring, it will not include any model development. It may identify potential future RMP modeling projects that would inform monitoring.

A monitoring strategy is not a sampling plan. The strategy will contain procedures and processes to form the basis of developing sampling plans for CECs monitoring projects. If work on the strategy can start soon enough, we hope to be able to pilot some elements of the strategy in CECs monitoring for the Water Year 2023 wet season.

Strategies are best treated as "living documents" intended to be revised/refined through experience and in response to near-term management priorities. This strategy will focus on the RMP planning horizon (up to 5 years), but will not omit important elements anticipated to be achieved after this planning horizon.

Budget

Table 3. Estimated costs for Stormwater CECs Monitoring Strategy.

Expense	Estimated Hours	Estimated Cost
Labor		
Project Staff (sum of below)	495	92000
Senior Management Review	24	5000
Creative Services		4000
Honoraria		
2 Expert advisors on CECs in stormwater/2 years		4000
Grand Total		**105,000**

<u>Budget Justification</u>

Labor Costs
Labor will primarily be spent on synthesizing the literature; exploring conceptual and numeric modeling approaches to inform monitoring location selection; examining monitoring approaches and locations to mesh with existing RMP and other monitoring programs; examining data requirements to support modeling of stormwater CECs loads; and consulting with relevant experts in the field. Senior managers will help guide the process and review interim products.

Project staff hours reflect the need for teamwork among RMP scientists with expertise in CECs, stormwater, and modeling. As we develop this strategy, we anticipate considerable engagement with the Small Tributaries Loading Strategy team, RMP stormwater and emerging contaminants stakeholders, and the Emerging Contaminants and Sources, Pathways, and Loadings Workgroups. We also anticipate the need to consult with additional external experts, and have allocated funds for honoraria to facilitate this consultation.

Early Funds Release Request
If this project is approved, we request early release of funds for use in 2021. We anticipate being able to pilot a few strategy elements as early as Water Year 2023 if this strategy is initiated in 2021.

Reporting

Deliverables will include a) a progress update presentation, to be presented to the SPLWG and ECWG in spring 2022; b) a Draft Strategy document, to be presented to the ECWG SPLWG and ECWG in spring 2023; and c) a Final Strategy document, to be completed September 1, 2023.

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

Summary: This study is designed to fill critical stormwater data needs for five contaminant classes: 1) a new, targeted list of CECs specific to stormwater; 2) per- and polyfluoroalkyl substances (PFAS); 3) organophosphate ester (OPE) plastic additives/flame retardants; 4) bisphenol plastic additives; and 5) ethoxylated surfactants. Year 1 of this multi-year study was focused on study design and pilot monitoring. Years 2 and 3 were intended to include a significant amount of monitoring and laboratory analysis, though this was constrained due to relatively dry weather and the Coronavirus. As a result, there is funding left in previous years' budgets, which will be directed towards initial monitoring and all laboratory analysis to occur in Year 4.

As scoped in the present proposal, Year 4 would be the final year of funding, and would support further site selection and sample collection for this Bay Area-wide screening study, as well as supplemental allocations for data management, preparation of scientific manuscripts, and preparation of a summary of results to inform waterquality managers.

Estimated Cost: $100,000 for Year 4
(Year 1 $132,000; Year 2 $181,000; Year 3 $148,000)

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 underway)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable (Year 4)	Due Date
Task 1. Site selection and reconnaissance, in coordination with SFEI stormwater and STLS teams	Summer 2021
Task 2. Field collection of stormwater samples	Fall 2021 – Spring 2022
Task 3. Laboratory analysis of samples	Spring – Summer 2022
Task 4. Data management and quality assurance	Fall – Winter 2022
Task 5. Draft manuscripts and management summary	Spring 2023
Task 6. Final manuscripts and management summary	September 2023

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 indicated that water samples from the stormwater-influenced site, San Leandro Bay, contained a broad array of unique contaminants with strong signals suggesting higher concentrations (Overdahl et al. 2021; Sun et al. 2020). 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 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 suggested 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 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 by the RMP and others have focused primarily on wastewater, and CECs in stormwater have received relatively little attention.

As a result, in Water Year 2019 the RMP began supporting a multi-year effort to screen Bay Area stormwater for CECs. A notable early outcome in this effort has been the retroactive characterization of Bay Area stormwater for a newly discovered toxicant, 6PPD-quinone, derived from a tire preservative. This toxicant has been established as the causal agent of the acute toxicity and pre-spawn mortality experienced by adult coho salmon (*Oncorhynchus kisutch*) in Puget Sound streams following exposure to urban runoff (Tian et al. 2021). Four of nine Bay Area stormwater samples contained levels of 6PPD-quinone that exceed the concentration at which half the coho salmon die after a few hours of exposure in laboratory experiments. 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 susceptibility to this contaminant has not yet been established.

In addition to vehicle and roadway CECs, four additional 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.

<u>Urban Runoff CECs</u> – A direct outcome of the effort to identify the cause of coho mortality in Puget Sound was the development of a list of target analytes consisting of contaminants of concern that are characteristic of urban stormwater. 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 CEC list targeting the influence of urban runoff in aquatic habitats.Unique contaminants with sources specific to vehicle traffic include the previously mentioned DPG and 6PPD-quinone, as well as hexa(methoxymethyl)melamine (HMMM), a component of tire resin, which can occur in highway runoff at concentrations approaching 10 μg/L (Peter et al. 2018).

Per- and polyfluoroalkyl substances (PFAS) – PFAS are classified as Moderate Concern for the Bay. A conceptual model of sources of PFAS tostormwater includes outdoor textiles, synthetic turf, construction materials, paints, plastic items, automotive fluids and waxes, 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 PFAS Synthesis and Strategy (Sedlak et al. 2018) reviewed two studies of stormwater thathave 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.

Organophosphate ester (OPE) plastic additives/flame retardants – OPEs were recently classified as Moderate Concern 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 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 indicated the presence of OPEs at concentrations generally comparable to those found in wastewater (Sutton et al. 2019). An RMP report that reviews available data for this class of CECs recommends stormwater monitoring as a priority for the RMP (Lin and Sutton 2018).

Bisphenol plastic additives – Bisphenols were recently classified as Moderate Concern for the Bay. A conceptual model of bisphenol sources to stormwater includes outdoor use plastics and coatings, as well as litter, including plastic items and thermal paper receipts. The RMP funded a 2020 special study to screen wastewater and archived samples of margin sediment for bisphenols; results from the two studies will be complementary.

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 stormwaterincludes outdoor use of automotive cleaners, lubricants and other fluids, as well as pesticides, plastics, paints, construction materials, 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 (Overdahl et al. 2021; Sun et al. 2020). The RMP funded a 2019 special study to screen Bay water, sediment, and wastewater for ethoxylated surfactants; results from the two studies will be complementary.

This proposal describes the final year in a multi-year monitoring effort. The current wet season, Year 3 in terms of funding, was intended to include a significant amount of monitoring and laboratory analysis, but this was constrained due to relatively dry weather and the COVID-19 outbreak, similar to Year 2. As a result, there is a significant level of unused funding in the Year 2 and 3 budgets, which will be carried forward towards monitoring in Year 4, as well as all associated laboratory analysis.

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-based 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 insights regarding the influence of sources or land use types. Compare concentrations to measurements of other urban areas.	This study will help identify if there are key sources or land uses or landscape attributes associated with individual CECs or CEC classes in stormwater, which can, in turn, focus management actions on those areas.
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 RMP stormwater team and the Small Tributaries Loading Strategy (STLS) team. 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 CECsto 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 4 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 composited in the field or laboratory.

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; Hou et al. 2019). Approximately 35 compounds will be monitored, including pharmaceuticals, pesticides, and several vehicle-specific analytes such as 6PPD-quinone, DPG, and HMMM. 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.

PFAS: Samples will be analyzed by the Higgins Laboratory (Colorado School of Mines) using quadrupole time-of-flight mass spectrometry (ESI+ and ESI- LC-Q-ToF-MS). The sampling design has been modified based on the Year 1 pilot monitoring results, which revealed greater variability in replicate analysis of total water samples relative to aqueous phase (filtered) samples, and significant uncertainty with respect to the total water TOP assay (oxidation followed by LC-QToF-MS; Houtz and Sedlak, 2012).

Based on our review of Year 1 data, the sampling design has been refined. Aqueous phase PFAS (filtered samples) will be characterized at all sites. At half the sites, particle-associated PFAS will be characterized; at one of these sites, an additional particulate sample will be collected for the TOP assay. The samples will be extracted and cleaned up using established protocols for the analysis of PFAS in soils and sediments (McGuire et al. 2014; Barzen-Hanson et al. 2017). Quantitative analysis will be performed on up to 45 PFAS, including different long- and short-chain perfluoroalkanoic acids, perfluoroalkane sulfonates, perfluoroalkane sulfonamides, fluorotelomer sulfonates, and fluorotelomer alkanoic acids. This list includes PFAS on the UCMR3 list along with many others.

Organophosphate ester (OPE) plastic additives/flame retardants: Both dissolved and particulate phase samples will be analyzed under supervision of the Chen Laboratory (Jinan University). Samples will be extracted in the U.S. by a partner laboratory, then Dr. Chen and his staff 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). Dr. Chen has agreed to undertake method development to add recently identified OPEs, including isopropylated and tert-butylated triarylphosphate esters (ITPs and TBPPs; Phillips et al. 2017) to his extensive list of target analytes.

Bisphenol plastic additives: Both dissolved and particulate phase samples will be analyzed by the Chen Laboratory (Jinan University) using a highly sensitive liquid chromatography–electrospray ionization(-)-triple quadrupole mass spectrometry (LC–ESI(-)-QQQ-MS/MS) based analysis method. This method will include analysis of bisphenol A, as well as suite of alternative bisphenol compounds, including bisphenols S, B, C, AF, AP, BP, M, E, P, F, PH, Z, G, TMC, and C-dichloride.

Ethoxylated surfactants: Stormwater samples will be analyzed for ethoxylated surfactants by the Ferguson Laboratory (Duke University), using a recently developed method. Stormwater samples will be filtered with a 0.45 micron filter, and the analyte list includes the following surfactant families: nonylphenol ethoxylates, octylphenol ethoxylates, and C12, C13, C14, and C16 alcohol ethoxylates. Analytes for each family will include compounds with a broad range of ethoxylate chains (ethoxymers 3-15). Isotopically labeled standards are generally not available for 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 Sedlak 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

Table 2. 2022 CECs in Stormwater budget (Year 4 only)

Expense	Estimated Hours	Estimated Cost
Labor - Year 4		
Study Design, Stakeholder Engagement	40	5500
Stormwater Sample Collection	350	50000
Data Technical Services		5000
Analysis and Reporting	45	6500
Subcontracts - Year 4		
Manuscript preparation: Kolodziej, U. Washington		20000
Direct Costs - Year 4		
Equipment		1000
Travel		2000
Shipping		10000
Grand Total		**100,000**

Budget Justification

As scoped in the present proposal, Year 4 is to be the final year of funding and monitoring. The Year 4 budget would support site selection and sample collection for this Bay Area-wide screening study, as well as an additional allocation of hours towards data management, preparation of scientific manuscripts, and preparation of a summary of results to inform water quality managers. Funding remaining in the Year 2 and 3 budgets due to the limited field season will be directed towards initial monitoring and cover all associated laboratory analysis in Year 4.

Planning and Stakeholder Engagement Costs
In consultation with RMP and STLS stormwater experts, we will establish a Year 4 study design that specifies site selection. Study design discussions and preliminary data reports will require participation in calls with the STLS team. Year 3 funds for coordination have not been depleted and will be carried over to Year 4.

Field Costs

The Year 4 budget includes $50,000 devoted to stormwater sample collection; the Year 2 and 3 budgets for this element of the study are not yet exhausted, and will supplement this allocation. Every effort will be made to minimize field costs by leveraging existing stormwater monitoring activities of the RMP. Based on the pilot year sampling experience, we anticipate that half of the sites visited in Year4 will leverage RMP monitoring of legacy contaminants, while half of the sites will be specificto CECs.

Data Management Costs

Preliminary data management activities have occurred during prior years; data services funding allocations for Years 2 and 3 have not yet been exhausted and will be carried over to Year 4, with a small supplement suggested in the Year 4 budget. Data services will include quality assurance review and CEDEN upload.

Analysis and Reporting Costs

Preparation of one or more draft manuscripts for publication in a peer-reviewed journal would occur following Year 4 sampling and analysis, with Dr. Kolodziej offering to lead a manuscript that includes multiple analyte classes, given his expertise in the stormwater matrix. Funding allocations to Dr. Kolodziej and RMP staff are indicated to support the development of manuscripts. The allocation of fundsto RMP staff is modest because the majority of funding from the Years 2 and 3 budgets that was intended to cover reporting activities ($36,000) remains available. The total budget for reporting will be $42,500.

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. Year 2 and 3 funds for analysis and reporting remain and will be carried over to Year 4 activities.

Laboratory Costs

Funds from prior year's budgets are sufficient to cover samples collected in Year 4.

Reporting

Deliverables will include: a) draft manuscript(s)[1] that serve as RMP technical reports, due September 2023; b) a summary for managers describing the results and their implications, due September 2023; and c) additions to other RMP publications such as the Pulse.

[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.

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Special Study Proposal: Tracking Ethoxylated Surfactants in Wastewater and Stormwater

Summary: Ethoxylated surfactants are nonionic surfactants that are widely used in industrial and household products. Preliminary results from a 2019 RMP special study of a broad suite of ethoxylated surfactantsin Bay water samples, effluent, and stormwater suggest variable concentrations in all matrices, particularly in effluent, in which concentrations varied by four orders of magnitude among facilities.

This proposed study will further investigate the temporal variation of ethoxylated surfactants in wastewater effluent and biosolids to understand whether changes may be linked to potential sources. This study focuses on quantifying nonylphenol, short-chain nonylphenol ethoxylates, and octylphenol, which were not quantified in the 2019 study, but are expected to be major degradation products and important contributors to the persistence and toxicity of this broad class of compounds.Additionally, this study includes analyzing these compounds in Bay urban stormwater runoff by leveraging the multi-year CEC stormwater study that is funded separately. The data will also guide development of a monitoring and management strategy for this class of contaminants that has been classified by the RMP as a moderate concern in the tiered, risk-based framework for CECs.

Estimated Cost: $83,415
Oversight Group: ECWG
Proposed by: Diana Lin, Miguel Mendez, Rebecca Sutton (SFEI)
Time Sensitive: No

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Complete stormwater sample collection	April 2022
Task 2. Coordinate sampling design and protocol with wastewater treatment facilities	April 2022
Task 3. Complete wastewater effluent sample collection	August 2022
Task 4. Complete laboratory analysis of samples	November 2022
Task 5. QA/QC and data management	February 2022
Task 6. Preliminary results presentation for ECWG meeting	April 2023
Task 7. Draft report	June 2023
Task 8. Final report	August 2023

Background

Ethoxylated surfactants are a broad class of nonionic surfactants used in a wide range of potential consumer and industrial applications as emulsifiers, wetting agents, dispersing agents, stabilizers, antioxidants, curing agents, and surface tension agents. A list of potential products containing ethoxylated surfactants is provided in Table 1. Use and manufacturing of these products can lead to the release of thesecompounds into residential, commercial, and industrial wastewater as well as urban stormwater runoff.

Table 1. Products that can contain ethoxylated surfactants (non-exhaustive list)

Products
Detergent
Industrial cleaning products
Household cleaning products
Degreasers
Fuel and lubricant oil additives
Car wash and car care products
Paints
Pesticide formulations
Textiles
Personal Care products (hair color, mousse, conditioner, cosmetics)
Adhesives
Varnishes
Polymers, plastics (e.g., PVC, styrene-butadiene for sealing membranes, polyvinyl acetate, acrylics, vinyl acrylic resins for roofing, façade, anticorrosion)
Phenolic resins for floor coating, coated steel reinforcement, coated metal surfaces, anti-corrosion paint for vehicles (undercoat)
Concrete
Tire rubber
Foam suppressant

Ethoxylated surfactants are manufactured by reacting alcohol or alkylphenol chains with ethylene oxide to form a neutrally charged molecule with both a hydrophobic alkyl chain and hydrophilic ethylene oxide chain (EO) of varying lengths. The ethoxylation process forms a complex mixture that includes linear and branched alkyl isomers with varying chain lengths.

Nonylphenol ethoxylates (NPEs or NPEOs) and octylphenol ethoxylates (OPEs or OPEO) are two of the most widely used and studied ethoxylates. NPEs represent up to 85% of alkylphenol ethoxylates used in the U.S., with production amounts measured in the hundreds of millions of pounds per year (EPA, 2010). NPEs incleaning products typically use NPEs with an ethoxylate chain length between 4 and 15 (DTSC, 2018). Long-chain NPEs can degrade to more toxic and hydrophobic products, such as, nonylphenol diethoxylates (4-NP2EO), nonylphenol monoethoxylates (4-NP1EO), and nonylphenol (NP). Nonylphenols are persistent in the aquatic environment, moderately bioaccumulative, and extremely toxic to aquatic organisms (USEPA 2010). The carboxylic forms of these compounds are also produced. Alcohol ethoxylates are often used as replacement products because they degrade faster and are expected to be less toxic (Soares et al., 2008).

Ethoxylated surfactants are challenging to analyze because they are complex mixtures that lack analytical standards for most compounds. The compounds also span a wide range in hydrophobicity, which require different analytical methods to extract and analyze. Most environmental studies only analyze a small subset of the compounds in this class, particularly the short-chain nonylphenol ethoxylates (which will be used in this proposal to include nonylphenol, NP1EO, and NP2EO).

The RMP funded special studies in 2019 to analyze a broad set of ethoxylated surfactants in ambient Bay water, margin sediment, wastewater, and stormwater using HPLC-MS/MS (Ferguson et al., 2000). Samples were analyzed for the ethoxylate series $C_{12\text{-}14}$EO, C_{16}EO, $C_{12(Br)}$EO, NPEs and OPEs. NPEs and OPEs were among the most important ethoxylate series in each matrix, though ethoxylate chain units of one and two were below reporting limits and nonylphenol and octylphenol were not analyzed. These short chain compounds are more toxic than the long chain parent compounds and are expected to represent a significant fraction of the total NPEs, particularly in wastewater effluent (Soares et al., 2008).

The wastewater investigation was designed as a screening study to analyze single 24-hour composites from eight participating POTWs representing diverse geographies, service industries, and treatment types. Concentrations of the dominant ethoxylate series were correlated, indicating that analyzing NPEs can be a good surrogate for evaluating trends in concentrations of the larger class of ethoxylatedsurfactants in wastewater. Wastewater effluent concentrations were significantly variable, ranging four orders of magnitude, with the maximum concentration of NPE ten times higher than the next highest concentration. Investigations of NPEs in wastewater facilities elsewhere have linked higher concentrations of NP/NPEs in wastewater from industrial or more urban areas (Soares et al. 2008). In stormwater, NPEs and OPEs were generally the dominant ethoxylate series at each site.

The short-chain NPEs, specifically 4-NP, 4-NP1EO, 4-NP2EO, have been analyzed in Bay surface water, sediments, bivalves, small fish, and aquatic bird eggs in a previous RMP study (Klosterhaus et al., 2013). Only 4-NP was detected in Bay water ranging from <10-73 ng/L, while concentrations of 4-NP1EO and 4-NP2EO were below detection limits (<10 ng/L). Sediment concentrations of 4-NP, 4-NP1EO, 4-NP2EO were detected at up to 86, 40, 19 ng/g dw, respectively. Based on this occurrence dataset and limited toxicity information, alkylphenol and alkylphenol ethoxylates are classified as Moderate Concern compounds in the Bay (Sutton et al., 2017).

This proposal will support the analysis of short-chain nonylphenol ethoxylates and octylphenol (specifically, 4-NP, 4-NP1EO, 4-NP2EO, and 4-n-OP) in wastewater and stormwater samples. These compounds were not included in the previous ethoxylates surfactant study. Of note, 4-NP and 4-tert-OP (but not the ethoxylates) are analyzed in the multi-year CEC stormwater study through urban runoff CECs analysis conducted by the Kolodziej Laboratory (Hou et al., 2019). This study will investigate the temporal patterns of nonylphenol in wastewater effluent to evaluate whether the range in concentrations measured in the previous screening study are representative of concentrations in Bay effluent, and shed light on possible sources of ethoxylated surfactants. Biosolids will also be analyzed because the predominant removal mechanism for these compounds from wastewater is through solids removal (Soares et al., 2008).

Additionally, this study will analyze these compounds in Bay Area urban stormwater runoff. Other studies have reported leaching of octylphenol from tires, and nonylphenol from construction materials (paints, concrete, plastics), as well as automotive fluids and parts (e.g., brake fluids) (Lamprea et al., 2018), and these products are potential sources to urban stormwater.

This follow-up study is important to round out the analysis of ethoxylated surfactants in wastewater and stormwater pathways, initiated by the prior studies, to support a more complete answer to the study questions listed in Table 2.

Moreover, the Department of Toxic Substance Control's (DTSC) Safer Consumer Products program is preparing a formal regulatory proposal to list NPEs in laundry detergent as a Priority Product under its Safer Consumer Products regulation, due to concerns for the contaminants' persistence and toxicity in the aquatic environment (DTSC 2018). Data from this study may provide useful insights regarding the dominant pathways and potential sources of ethoxylated surfactants to the Bay.

Study Objectives and Applicable RMP Management Questions

Table 2. 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 ethoxylated surfactant occurrence data with toxicity information reported in the scientific literature. Evaluate future monitoring needs and toxicity data gaps.	Do findings suggest ethoxylated surfactants should be classified as high, moderate, low, or possible concern within the RMP's tiered framework.
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 in wastewater and stormwater runoff. Investigate the temporal pattern in wastewater effluent and biosolids. Compare concentrations observed at different stormwater watersheds to glean insights regarding the influence of sources or land use types.	How do concentrations in wastewater compare with urban stormwater runoff, and what does that suggest about relative loads? Do discharge patterns indicate intermittent or continuous sources? Can discharge patterns be compared to expected industrial releases to wastewater?

	Compare concentrations to 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?	Evaluate the distribution of ethoxylate chain length in wastewater and stormwater. Compare concentrations of short-chain NPEs and OP in wastewater effluent with biosolids.	How do degradation of NPEs and OPs in the wastewater pathway compare with stormwater? What proportion of NPEs and OPs removed by wastewater treatment partition to biosolids?
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	N/A	N/A
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	Compare detected ethoxylated surfactant analytes in wastewater and stormwater to those subject to proposed management actions.	Will management actions targeting nonylphenol ethoxylates in wastewater have an effect on the main pathways entering the Bay?
6) What are the effects of management actions?	N/A	N/A

Approach

Sample Collection

Three POTWs will be targeted for this study to monitor the concentration of short chain alkylphenols in final effluent and biosolids. We propose sampling at Hayward, Vallejo, and EBMUD because these facilities had the highest concentrations of ethoxylated surfactants in effluent among eight facilities sampled in the previous study. Among the three facilities, Hayward has the largest proportion (20%) of influent flows coming from industrial customers instead of residential and commercial customers. Vallejo (97%) and EBMUD (94%) service mostly residential and commercial customers. All facilities service industries that are associated with use of ethoxylated surfactants, including paint production, automatic vehicle washing, electronic manufacturing, fabricated metal production, agriculture, industrial laundries.

Up to 27 effluent samples will be collected from the three facilities, including a field blank at each facility. Twenty-four-hour composites of final effluent will be collected using automated sampling equipment regularly in use at the facility. Field blanks will be collected by pouring reagent water into empty sample containers at the facility. This sample collection method is consistent with the approach in the 2019 study.

The effluent sampling design will be developed through discussion with participating facilities, who will have a better understanding of operations of their customers. A suggested sampling design is to collect replicates on four sample dates to assess variations in weekday/weekend flows, weekday flows during a different week, and weekday flows during a different season. The higher number of replicates and sampling will provide the opportunity to investigate temporal flow patterns that may be associated with changes in industrial, residential, and commercial discharge patterns. Up to eleven biosolid samples will be collected from the same three facilities; this includes a single biosolid sample collected during each of the four sample dates for effluent, plus a field duplicate at one facility, and field blanks at each facility.

Additionally, ten stormwater samples will be collected (eight samples, one field duplicate, and one field blank). Sampling will occur as part of Year 4 CEC stormwater sampling, with samples collected at the same locations sent to Duke University to analyze for the broader set of ethoxylated surfactants including long chain ethoxylates.

<u>Analysis</u>

SGS AXYS method MLA-004 --which will be used for the effluent and stormwater samples -- quantifies concentration of 4-n-octylphenol, 4-nonylphenol (10 isomers), 4-nonylphenol monoethoxylate (11 isomers) and 4-nonylphenol diethoxylate (11 isomers). The NP/NPE standards are from technical mixtures. Aqueous samples are extracted by aqueous acetylation and liquid-liquid extraction with hexane. Solid samples are extracted by base digestion and liquid-liquid extraction with hexane followed by non-aqueous acetylation. Analysis is performed on a Restek Rtx-5 capillary gas chromatography column coupled to a low-resolution mass spectrometer (LRMS). Typical sample size for aqueous samples are 1L and sediment/solid samples is 5 g. Method detection limits are 10 ng/L for 4-nonylphenol and 50 ng/L for NP1EO, NP2EO, and OP.

<u>Data Interpretation</u>

The study results will be synthesized with results from the prior ethoxylated surfactant study results to establish a baseline for ethoxylated surfactant concentrations in effluent and stormwater (covered by a separate ECWG study). This comparison will provide some insight as to whether management actions currently being implemented to address NPEs in wastewater will have a measurable effect on Bay loadings, or whether additional management actions should be considered.

Evaluation of temporal patterns in short-chain NPEs in wastewater will support understanding about the discharge patterns of this class of compounds, and results may be linked to potential industrial, residential, and commercial sources. For example, consistent flow patterns may indicate more diffuse residential and commercial sources, while variable concentrations may provide evidence for more dominant industrial sources. Additionally, data will be used to inform how best to monitor and assess representative concentrations in Bay effluent.

Stormwater data will be evaluated along with the broader set of ethoxylated surfactants and other prioritized CECs funded through a separate study. 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 compounds.

Understanding the sources and pathways of ethoxylated surfactants can inform what management decisions may be effective in reducing future concentrations. This evaluation will inform future study design to further identify major sources to the wastewater pathway. Results will be compared to other regions.

Budget

Table 3. Proposed Budget.

Expense	Estimated Hours	Estimated Cost
Labor		
Project Management	30	4,600
Study Design and Sample Collection	100	10,400
Analysis and Reporting	140	18,600
Data Technical Services		15,000
Subcontracts		
SGS AXYS		32,815
Direct Costs		
Shipping		2,000
Grand Total		**83,415**

Budget Justification

Project management
Project management costs include managing budgets, stakeholder engagement, and subcontract development and management.

Study design and sample collection
SFEI staff will develop a sampling design in consultation with participating POTWs. POTW staff will collect and ship samples to the analytical lab. Twenty staff hours are budgeted to supplement CEC stormwater sampling efforts to collect and ship an additional set of samples for analysis.

Data Management Costs
Data services will include QA/QC review and upload to CEDEN.

Analysis and Reporting
Preliminary results will be presented to ECWG in 2023. Results will be summarized in a technical report.

Laboratory Costs
Estimated costs include 27 effluent samples ($595/sample), 16 biosolid samples ($675/sample), and 10 stormwater samples ($595/sample). Analytical costs could be lowered by reducing the number of field samples.

Direct Costs
Direct costs will cover shipping costs for wastewater and stormwater samples, including incidental equipment and travel reimbursement.

The following budget represents estimated costs for this proposed special study (Table 3. Efforts and costs can be scaled back by reducing the number of sites sampled.

Reporting

Deliverables will include: a) preliminary results presentation during the ECWG spring 2023; b) a draft and final report describing the results and their implications, due summer 2023.

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Special Study Proposal: Wet Season Non-Targeted Analysis (NTA) of Bay Water and Stormwater

Summary: Non-targeted analysis, a key element of the RMP CEC Strategy and recent state CEC guidance, can help to provide a measure of assurance that the RMP is not missing unexpected yet potentially harmful contaminants simply because of failures to predict their occurrence based on use or exposure prioritization criteria. The RMP Status and Trends water monitoring design is being updated in 2022 to include wet season monitoring to measure the concentration of urban runoff-associated CECs in the Bay when the stormwater pathway is active. This new proposed study would leverage the pilot 2022 Status and Trends sampling effort to identify additional stormwater-associated contaminants in the Bay using two different non-targeted techniques, providing data on both polar and nonpolar compounds. This type of non-targeted study will lay the foundation for future targeted CEC monitoring by helping to identify new potential contaminants of concern without a priori knowledge of their occurrence.

Estimated Cost: $112,000
Oversight Group: ECWG
Proposed by: Ezra Miller, Rebecca Sutton (SFEI), Ed Kolodziej (University of Washington), Leah Chibwe (University of Toronto)
Time Sensitive: Yes, leverages Status and Trends 2022 wet season monitoring

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Example Due Date
Task 1. Develop detailed sampling plan	October 2021
Task 2. Field sampling – Bay water	Winter 2022
Task 3. Lab analysis	August 2022
Task 4. Contaminant risk review	November 2022
Task 5. Presentation at ECWG	April 2023
Task 6. Draft manuscript and fact sheet	June 2023
Task 7. Final manuscript and fact sheet	September 2023

Background

The RMP has developed a pro-active emerging contaminants program, and conducts policy-relevant monitoring via Special Studies to help identify and address problematic, unregulated contaminants before they cause significant harm to the Bay. The RMP has established a unified emerging contaminants strategy (Sutton et al., 2017) with three elements: 1) targeted chemical monitoring and relative risk evaluation using a tiered risk-based framework; 2) review of the scientific literature and other aquatic monitoring programs as a means of identifying new emerging contaminants for which no Bay occurrence data yet exist; and 3) non-targeted analysis to create inventories of unanticipated contaminants in tissues, sediment, or water that can be used to direct targeted chemical monitoring or toxicity identification evaluations.

State guidance on emerging contaminants in aquatic ecosystems echoes many aspects of the RMP strategy (Dodder et al., 2015). In particular, non-targeted analysis plays a key role in the comprehensive CEC management framework (see pg 40, Dodder et al., 2015). Non-targeted analysis is an essential means of assuring focus on the contaminants with greatest potential to impact an ecosystem, by seeking to remove a "knowledge bias" on previously identified problem chemicals.

One class of non-targeted methods highlighted by the state guidance includes those "designed to screen for new or unexpected contaminants; i.e., unknown CECs" (pg 29, Dodder et al., 2015). Recent RMP non-targeted analysis of Bay water and wastewater indicated that stormwater is an important and under-characterized emerging contaminant pathway (Overdahl et al., 2021; Sun et al., 2020). A number of contaminants, including many urban, industrial, and outdoor use chemicals, were detected in samples from San Leandro Bay, a site strongly influenced by urban stormwater runoff. Recent targeted screening of Bay water and stormwater also identified many road-associated contaminants, including a tire preservative responsible for coho salmon mortality in urban streams in the Puget Sound area (Tian et al., 2021).

Based on these findings, follow-up screening of Bay water and stormwater to identify other emerging contaminants of potential concern is now recommended. The current proposal is to use two different non-targeted analytical techniques (liquid and gas chromatographic methods of separation) to scan for a wide range of organic contaminants with various physico-chemical properties, including both polar, water soluble contaminants and non-polar contaminants that may associate with sediment particles. Sampling can occur in conjunction with a pilot wet season Status and Trends monitoring effort designed specifically to observe stormwater-related contaminants in Bay water, as current Status and Trends monitoring occurs in the summer, when this pathway is not active.

Should a non-targeted analysis of Bay water and stormwater runoff identify unexpected contaminants, the information could indicate a need for a follow-up RMP Special Study designed to specifically assess the new "candidate" CECs on a quantitative basis. It could also point to ecotoxicity data gaps or suggest new management priorities. Thus, positive identifications resulting from the proposed study would be potentially very high in impact.

In contrast, because of the comprehensive nature of the non-targeted methods proposed herein, should few unexpected contaminants be identified, the RMP would then have considerable evidence that existing CEC monitoring is already focusing on the highest priority contaminants for the Bay.

Study Objectives and Applicable RMP Management Questions

Traditional, targeted contaminant monitoring focuses on specific lists of chemicals already identified as potentially problematic through either expert judgement, anticipation of high toxicity, use-based prioritization, or other a priori methods. Through non-targeted monitoring, we can provide a measure of assurance that the RMP is not missing unexpected, potentially harmful contaminants in the Bay water simply because of failures to predict their occurrence based on use or exposure prioritization criteria. Chemicals identified with non-targeted analysis will be evaluated for potential toxicity concerns and prioritized for future targeted monitoring.

Table 1. 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?	Identify water contaminants not yet characterized by targeted monitoring efforts. Evaluate future monitoring needs and toxicity data gaps.	Identify additional contaminants that may merit further monitoring.
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Comparison of Bay water near stormwater inputs vs. ambient mid-Bay water with respect to non-targeted detections. Initial comparison of sites influenced by the stormwater pathway.	Compare the suite of contaminants detected in stormwater to those in ambient Bay water near stormwater inputs and mid-Bay post-storms. Identify regional or pathway-related differences in the presence of newly identified 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?	Investigate the influence of the stormwater pathway for water contaminants.	Identify differences in detection that may suggest persistence, degradation, or additional pathways for specific contaminants.
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?	N/A	
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

Bay Water Sampling

This project will leverage RMP Status and Trends 2022 pilot wet season water sampling efforts, as shown in Figure 1. As part of this effort, samples will be collected at two in-Bay stations near stormwater inputs shortly following two appropriately-sized storms. In coordination with existing RMP stormwater monitoring activities where possible, additional sample collection will occur at an upstream stormwater site that feeds into each location during the storm itself. Samples will also be collected at two ambient stations (one Central Bay, one South Bay or Lower South Bay) within three weeks of the same storm. During a single wet season, we anticipate collecting sixteen grab samples, not including field blanks and duplicates, across two storms (two grabs per site per storm) and two sites. At the ambient sites, we anticipate collecting four samples, not including field blanks and duplicates, after two storms (one grab per storm). At least one field blank and one duplicate will also be collected for each matrix, following the current RMP standard of at least one field blank and duplicate for every 20 samples.

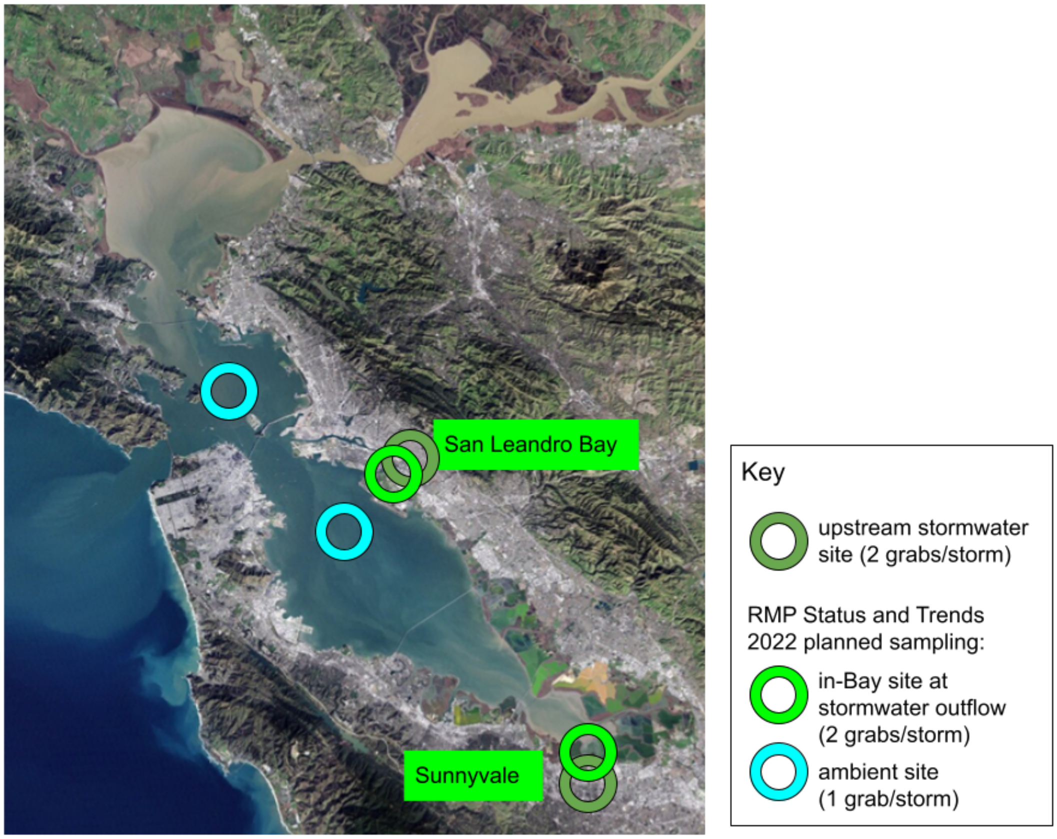

Figure 1. Proposed sampling locations, based on current Status and Trends 2022 pilot wet season sampling design planned at San Leandro Bay, Sunnyvale, and ambient sites.

<u>Analytical Methods</u>

Samples will be analyzed by the laboratory of Ed Kolodziej, University of Washington using liquid chromatography methods, and by Leah Chibwe, a member of the laboratory of Chelsea Rochman, University of Toronto using gas chromatography methods. Using these methods in tandem will allow potential observation of a wider range of polar and nonpolar compounds, and ensure the RMP has less of a chance of missing any stormwater contaminants of interest.

Samples will be extracted for liquid chromatography with tandem mass spectrometry (LC-MS/MS) with established methods (Du et al., 2017; Peter et al., 2018). Briefly, unfiltered samples will be extracted using multi-residue C18 solid phase extraction (SPE) with deionized water and methanol. For quality control, samples will be spiked with labelled standards both prior to extraction and analysis. Analysis will be conducted using an Agilent 1290 Infinity UHPLC for separation and an Agilent 6530 Quadrupole Time-of-Flight (QTOF) HRMS with electrospray Jet Stream Technology for detection, focusing on ESI+ detections.

Samples will be extracted for comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC/TOF-MS) using previously described methods

(Chang et al., in review). Briefly, vacuum-filtered storm water samples will be extracted using OASIS HLB SPE with acetone and dichloromethane. The samples will further be dried with sodium sulphate and concentrated to 400 uL prior to analysis. For quality control, samples will be spiked with labelled standards both prior to extraction and analysis. Data will be processed using the LECO ChromaTOF software and will include baseline correction, background subtraction and peak deconvolution. The Statistical Compare feature will additionally be used to align peak features across the samples based on 1st and 2nd retention times, and mass spectral similarity to assess similarities/differences between collected samples. Chemicals will predominantly be tentatively identified using the NIST EI mass spectral library. However, elution order profiles in the 2D chromatograms and retention indices will also be considered. Furthermore, any features not matched in the EI mass library, but showing high detection frequencies or peak intensities in the samples will be retained as unknowns for further scrutiny.

Previous USEPA work comparing the identification rate of 1269 substances by a liquid chromatography/quadrupole time-of-flight (LC/Q-TOF, +ESI and -ESI) and a GC×GC/TOF-MS method resulted in moderate overlap (40%) in the number of compounds detected by each method (Ulrich et al., 2019).

Budget

Table 2. Proposed Budget

Expense	Estimated Hours	Estimated Cost
Labor		
Study Design	16	2400
Sample Collection	32	3200
Analysis and Reporting	142	23400
Creative Services	24	4000
Subcontracts		
Univ. Washington		35000
Univ. Toronto		35000
Direct Costs		
Equipment		4000
Shipping		5000
Grand Total		**112,000**

Budget Justification

Field Costs
Field costs are minimized by leveraging the sample collection during the RMP's Status and Trends wet season monitoring and RMP stormwater monitoring, where possible. Only a small amount of planning hours are included in this budget.

Reporting Costs
Preparation of a draft manuscript for publication in a peer-reviewed journal would be the responsibility of the analytical partners and will require relatively little RMP staff time. After the manuscripts are complete, RMP staff will produce a 2-page fact sheet to describe the results and their implications for RMP stakeholders and the general public.

Laboratory Costs
Funds will cover lab supplies, staff time to analyze samples and interpret detections, and indirect costs.

Data Management Costs
No data management is needed for this proposed project, as it is not targeted, analyte-specific analysis.

Reporting

Deliverables will include: a) a draft manuscript that serves as an RMP technical report, due spring 2023; b) a plain language RMP fact sheet describing the results and their implications, due spring 2023; and c) additions to other RMP publications such as the Pulse.

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Special Study Proposal: Tire and Roadway Contaminants in Wet Season Bay Water

Summary: 6PPD-quinone and other toxicologically relevant contaminants derived from tires have been observed in Bay Area stormwater. These compounds have not yet been quantified in Bay receiving waters. As part of its Status and Trends (S&T) program, the RMP is expected to undertake a pilot monitoring effort to quantify a number of contaminants in Bay water samples collected following storm events to provide information on the impact of stormwater discharges on Bay contaminant concentrations. This proposed study would leverage the pilot S&T effort to evaluate the concentrations of tire and roadway contaminants in Bay water. Results will indicate whether these stormwater-derived contaminants reach concentrations of concern within receiving waters, filling a data gap relevant to the RMP tiered risk-based framework for emerging contaminants. Findings will also be used to evaluate whether wet season monitoring would be useful to incorporate into the Status and Trends monitoring design for Bay water.

Estimated Cost: $36,000
Oversight Group: ECWG
Proposed by: Rebecca Sutton (SFEI), Ed Kolodziej (University of Washington)
Time Sensitive: Yes, leverages pilot wet season water monitoring (S&T 2022 - fall 2021-spring 2022)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Develop sampling plan	August 2021
Task 2. Field sampling – Bay water	Fall 2021 – Spring 2022
Task 3. Lab analysis	Summer 2022
Task 4. QA/QC and data management	October 2022
Task 5. Presentation at ECWG	April 2023
Task 6. Incorporation of data into draft stormwater manuscript	June 2023
Task 7. Final stormwater manuscript	September 2023

Background

A number of potentially toxic tire-derived contaminants have been observed in Bay Area stormwater, including the newly discovered coho salmon toxicant, 6PPD-quinone, derived from a tire preservative (Tian et al. 2021). Four of nine Bay Area stormwater samples collected in WY2019 contained levels of 6PPD-quinone that exceeded the LC_{50}, the concentration at which half the coho salmon die after a few hours of exposure in laboratory experiments. While coho salmon are now absent from Bay tributaries, steelhead (*Oncorhynchus mykiss*), a threatened species, are observed in some streams (e.g., Guadalupe River, Alameda Creek), and their susceptibility to this contaminant has not yet been established. Another tire-derived contaminant, the rubber vulcanization agent 1,3-diphenylguanidine (DPG), was detected in stormwater at levels up to 1.8 µg/L (SFEI, unpublished data). The European Chemicals Agency established predicted no effect concentrations (PNEC) for DPG of 30 µg/L in freshwater and 3 µg/L in marine waters (ECHA 2018). Monitoring of 6PPD-quinone, DPG, and other tire-derived contaminants is possible through a recently developed method designed to evaluate emerging contaminants in stormwater (Hou et al. 2019).

These tire-derived contaminants have not yet been monitored in the Bay itself and, therefore, have not yet been classified within the tiered, risk-based framework for emerging contaminants in San Francisco Bay (Sutton et al. 2017). Overall, limited sampling has been conducted in the Bay during the wet season to evaluate the concentration of these and other emerging contaminants when the stormwater pathway is most active. Wet season water sampling has not been conducted by the RMP since 2010 and sites were restricted to deep channel stations far from stormwater inputs.

A proposal that has arisen from the ongoing review of the RMP Status and Trends study design is the addition of a pilot wet season water sampling effort to measure concentrations of contaminants for which stormwater is a major transport pathway. Stormwater monitoring conducted by the RMP and others has shown that stormwater is a major pathway for emerging contaminants of Moderate Concern for the Bay, including bisphenols, organophosphate esters (OPEs), and PFAS (Houtz and Sedlak 2012; Sutton et al. 2019; SFEI, unpublished data). Sampling for these contaminants in both wet and dry seasons is important for understanding how different pathways contribute to Bay concentrations throughout the year and how those concentrations, and potential risks to aquatic life, vary spatially and temporally based on the dominant pathway.

To build on previous RMP stormwater monitoring and address the Bay occurrence data gap for stormwater contaminants, we propose a study to leverage the first year of this pilot Status and Trends wet season monitoring effort to evaluate concentrations of tire-derived compounds in Bay water. Results will inform the classification of these contaminants within the tiered, risk-based framework and indicate whether further information is needed to assist water quality management decision-making.

Study Objectives and Applicable RMP Management Questions

The purpose of this study is to assess the concentrations of tire-derived contaminants in Bay waters to improve our understanding of risks to wildlife. These compounds may then be placed within a risk tier of the RMP tiered, risk-based framework. The framework provides guidance on the need for additional monitoring and science to inform management of individual emerging contaminants and contaminant classes.

Table 1. 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 tire-derived contaminants and other stormwater-associated CECs in Bay water.	Do these compounds have the potential to cause impacts to aquatic life? Which compounds are of greatest concern?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Evaluate concentrations in Bay water relative to RMP stormwater monitoring.	Are Bay water concentrations near stormwater and wastewater influenced sites consistent with the hypothesis that stormwater is the dominant 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?	Compare concentrations in near-field vs. mid-Bay sites.	Are these stormwater-derived contaminants rapidly removed from Bay water?
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?	N/A	
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

Bay Water Sampling

The RMP Status and Trends water monitoring design is expected to be updated in 2022 to include wet season monitoring to measure concentrations of urban run-off-associated CECs in the Bay when the stormwater pathway is active. Samples will be collected at two in-Bay stations near stormwater inputs plus one station near wastewater input (for contrast) shortly following two appropriately-sized storms, including the first flush if possible (Figure 1). For stormwater sampling in the watershed, SFEI uses 0.75 inches of rain in six hours as its sampling criterion. Sampling at targeted sites will be completed within two tidal cycles of the storm at locations meeting this criterion.

Samples will also be collected at six ambient stations (one Central Bay, one South Bay, and four Lower South Bay) within three weeks of the same storm. During a single wet season, we anticipate collecting ten samples from the near-field pathway sites, not including field blanks and duplicates, across two storms (two grabs per storm) and three sites. At the ambient sites, we anticipate collecting six samples, not including field blanks and duplicates, after a single storm.

Samples will be collected using an ISCO pump, consistent with monitoring of stormwater in Bay Area watersheds. QA/QC samples collected will include two field duplicates and two field blanks. Samples will be shipped overnight to Dr. Kolodziej at the University of Washington.

Analytical Methods

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 spectrometry (LC-MS/MS; Hou et al. 2019). Approximately 35 compounds will be monitored, including pharmaceuticals, pesticides, and several tire-derived analytes such as 6PPD-quinone and DPG. 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.

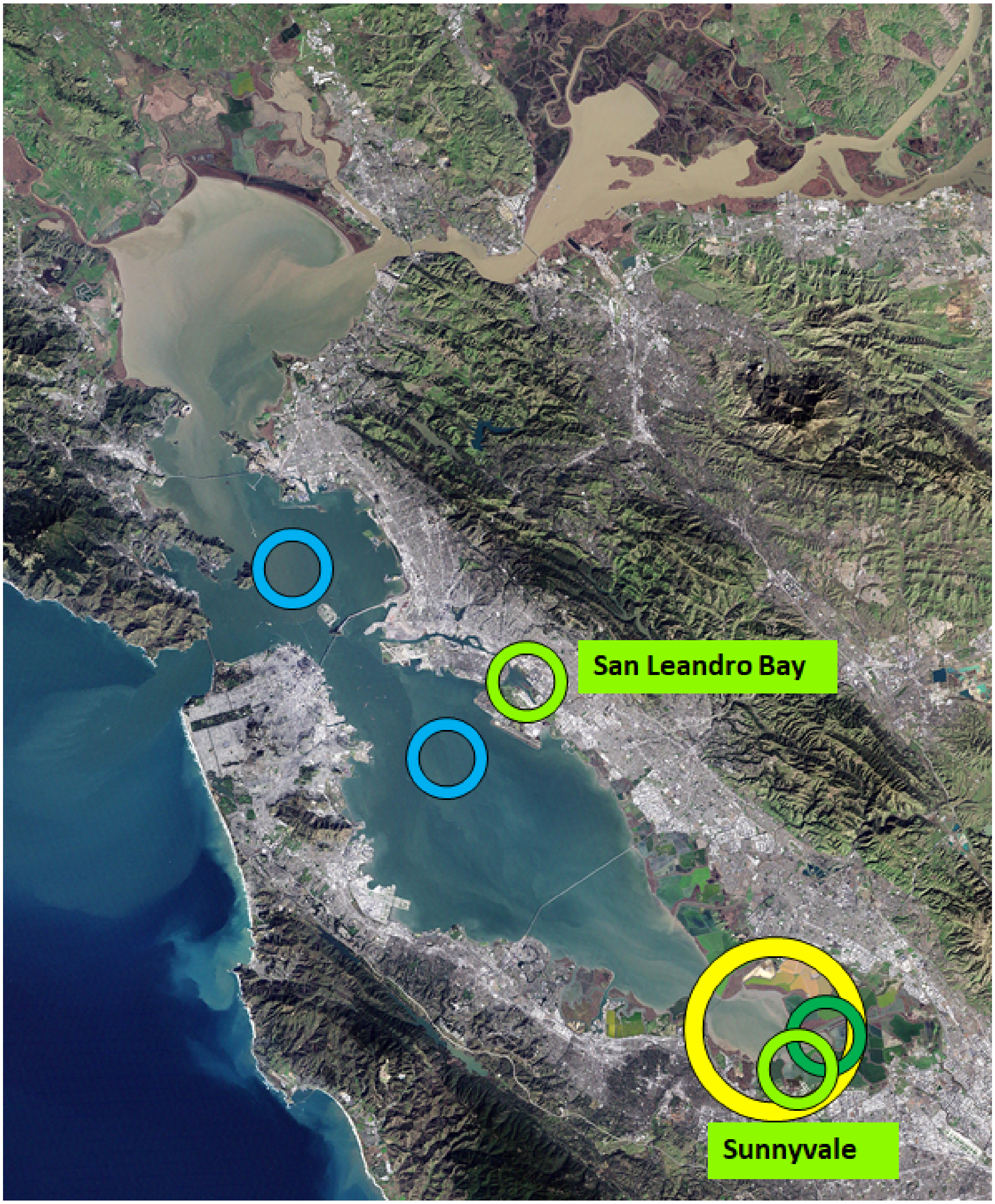

Figure 1. Proposed site selection for pilot wet season Status and Trends monitoring effort, WY 2022.

Budget

Table 2. Proposed Budget

Expense	Estimated Hours	Estimated Cost
Labor		
Study Design	16	2400
Sample Collection	32	3200
Data Technical Services		8500
Analysis and Reporting	48	8000
Subcontracts		
Univ. Washington		10,000
Direct Costs		
Equipment		700
Shipping		3200
Grand Total		**36,000**

Budget Justification

SFEI Labor
Labor hours are estimated for SFEI staff to manage the project, develop the study design, support sample collection, analyze data, present findings, and assist with manuscript preparation.

Data Technical Services
Standard RMP data management procedures will be used for this project. Data will be uploaded to CEDEN.

Sample Collection
Costs are minimized through leveraging sample collection during the RMP 2022 Status and Trends pilot wet season water monitoring effort.

Laboratory Costs (Ed Kolodziej, University of Washington)
Analysis of 23 samples, including two field blanks and two field duplicates, as well as assistance with interpretation, are included in a subcontract for $10,000.

Reporting

Results will be presented to the ECWG at the spring 2023 meeting; data will be incorporated into a stormwater manuscript funded primarily by the RMP multi-year stormwater screening project, and will be reviewed by the ECWG and TRC. Comments will be incorporated into the final manuscript, due 9/30/23.

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Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Bay Sediment

Study Budget, Total: $55,000 - $125,000

SFEI Contacts:

- Technical – Miguel Mendez, miguelm@sfei.org; Rebecca Sutton, rebeccas@sfei.org
- Financial – Jennifer Hunt, jhunt@sfei.org

Analytical Laboratory Partner: SGS AXYS

Study Description

Per- and polyfluoroalkyl substances (PFAS) are an extensive chemical class of fluorine-rich compounds. Their thermal and chemical stability have resulted in more than 4,700 PFAS to be used in consumer, commercial, and industrial applications. The widespread use of PFAS means they are largely ending up in waste streams directly linked to the environment. Their highly persistent and recalcitrant nature, combined with bioaccumulation risks, raise concerns regarding possible negative impacts on human and ecological health. Perfluorooctanoic sulfonate (PFOS) and perfluorooctanoic acid (PFOA), the best studied compounds within the class, have been identified as highly toxic with potential for multi-system and developmental effects. PFOS, PFOA, and other PFAS have been previously detected in San Francisco Bay biota, sediment, and water, and identified as Moderate Concern within the RMP tiered risk-based framework. Specifically, previous RMP studies have found detectable levels of several PFAS, including precursor compounds that degrade (oxidize) to persistent end members like PFOS and PFOA in sediments.

To improve our understanding of the occurrence and risks associated with PFAS in the Bay, this study aims to assess Bay sediment samples for PFAS. Through the current design of the RMP Status and Trends (S&T) program, ambient sediment samples would be collected from 27 sites in 2022. The S&T study design is undergoing active review, with possible changes to the timing and number of samples for ambient sediment, and the potential for collection of samples in more near-shore (e.g., margin) settings; depending on available resources, some or all of these sites could be included. Should ambient sampling be delayed significantly, archived samples collected in 2018 may be used for this analysis. Additionally, there is an opportunity to analyze PFAS via both targeted methods using tandem liquid chromatography/mass spectrometry (LC-MS/MS), and via the total oxidizable precursors (TOP) assay, which allows a characterization of the overall presence of precursors. Additional data generated by this proposed study can provide a preliminary indication of temporal trends of PFAS in sediment, including precursors, while identifying other potential PFAS targets not currently known. The data collected in this study could help identify areas where upstream source control efforts would be most beneficial to reducing PFAS concentrations in the Bay. Depending on available resources, deliverables can include preparation of a technical report or draft manuscript, as well as upload of data to CEDEN.

Brominated Flame Retardants in Bay Sediment

Study Budget, Total: $45,000 – $110,000

SFEI Contacts:
- Technical – Rebecca Sutton, rebeccas@sfei.org
- Financial – Jennifer Hunt, jhunt@sfei.org

Analytical Laboratory Partner: SGS AXYS

Study Description

Flame retardant chemical additives are incorporated into a wide range of consumer goods to meet regulatory or voluntary flammability standards. Following state bans and nationwide phase-outs of polybrominated diphenyl ethers (PBDEs), one of the most commonly used brominated flame retardants historically, alternative chemicals saw greater use. Among these are a diverse array of bromine-containing compounds for which there are considerable data gaps concerning production and use, environmental occurrence, and toxicity. Some of these chemicals have been in use for decades, while others are relatively new.

The RMP conducts regular monitoring of PBDEs in ambient Bay sediment, providing critical trends information indicating reduced contamination as a result of management actions (Sutton et al. 2015). In contrast, concentrations of several non-PBDE flame retardants in Bay sediment have only been evaluated twice, as part of RMP special studies (Klosterhaus et al. 2012; Sutton et al. 2019), with insufficient data to establish trends. Brominated flame retardants detected in Bay sediment include hexabromocyclododecane (HBCD), 2,4,6-tribromophenyl allyl ether (TBP-AE), bis(2,4,6 tribromophenoxy) ethane (BTBPE), BEH-TBP and EH-TBB (or TBPH and TBB, the brominated components of the PentaBDE replacement commercial mixture, Firemaster 550), hexabromobenzene (HBBZ), 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (DBE-DBCH, also known as TBECH). These earlier studies indicated detections at concentrations at least one order of magnitude lower than PBDEs.

The goal of this study is to assess ambient Bay sediment samples collected as part of Status and Trends monitoring for brominated flame retardants using high-resolution mass spectrometry. Under the current program, sediment samples would be collected from 27 sites in 2022. However, the design of the Status and Trends program is currently undergoing review; changes in the timing of ambient sediment sampling and the number of samples are possible. Should ambient sampling be delayed significantly, archived samples collected in 2018 may be used for this analysis. The potential for regular collection of samples in more near-shore (e.g., margin) settings is also under consideration; depending on available resources, some or all of these sites could be included. Concentrations in Bay sediment would be compared to available toxicity thresholds to inform placement within the RMP tiered risk-based framework for CECs and determine whether follow up study is needed. Comparison to measurements from prior studies can provide a preliminary indication of temporal trends. Depending on available resources, deliverables can include preparation of a technical report or draft manuscript, as well as upload of data to CEDEN.

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Chlorinated Paraffins in Bay Sediment

Study Budget, Total: $50,000 – $120,000

SFEI Contacts:
- Technical – Rebecca Sutton, rebeccas@sfei.org
- Financial – Jennifer Hunt, jhunt@sfei.org

Analytical Laboratory Partner: SGS AXYS

Study Description

Chlorinated paraffins (CPs) are chlorine-containing compounds related to paraffin wax that are primarily used as lubricants and coolants in the metal forming and cutting industries, and plasticizers and flame retardants in plastics. Minor uses include paints, rubber formulation, adhesives and sealants. They are commonly categorized as short-chain (SCCPs, C_{10-13}), medium-chain (MCCPs, C_{14-17}), and long-chain CPs (LCCPs, $C_{\geq 18}$).

Chlorinated paraffins are persistent, bioaccumulative, and toxic. Short-chain chlorinated paraffins are believed to be more toxic to aquatic organisms than MCCPs and LCCPs, though the compounds generally appear to share similar mechanisms of toxicity. Short-chain chlorinated paraffin production in the US stopped in 2012 as part of a settlement negotiated with USEPA (2012), and a significant new use rule now exists requiring potential manufacturers or processors of SCCPs to notify USEPA at least 90 days before the activity to provide an opportunity to evaluate and protect against potential unreasonable risks, if any (USEPA 2014). As global phase-out of SCCPs occurs, the use of MCCPsand LCCPs as alternatives is expected to increase.

SCCPs were characterized in Bay biota in 2006-2007 (Klosterhaus et al. 2013). Seal blubber contained the highest total SCCP concentrations (25-50 ng/g wet weight), followed by cormorant eggs (4-6 ng/g wet weight), and then sport fish (<1-1 ng/g wet weight). Medium- and long-chain chlorinated paraffins have not been the subject of RMP monitoring studies.

The goal of this study is to assess ambient Bay sediment samples collected as part of Status and Trends monitoring for short-, medium-, and long-chain chlorinated paraffins (individually and as sums) using a newly available Ultra-Performance Liquid Chromatography (UPLC) and tandem mass spectrometry (MS/MS) method developed by SGS AXYS, a commercial laboratory and frequent analytical partner. Under the current Status and Trends program, sediment samples would be collected from 27 sites in 2022. However, the design of the Status and Trends program is currently undergoing review; changes in the timing of ambient sediment sampling and the number of samples are possible. The potential for regular collection of samples in more near-shore (e.g., margin) settings is also under consideration; depending on available resources, some or all of these sites could be included. Concentrations in Bay sediment would be compared to available toxicity thresholds to inform placement within the RMP tiered risk-based framework for CECs and determine whether follow up study is needed. Depending on available resources, deliverables can include preparation of a technical report or draft manuscript, as well as upload of data to CEDEN.

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