



RMP Emerging Contaminants Workgroup Meeting

April 11-12, 2022
9:00 AM – 3:00 PM

REMOTE ACCESS

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DAY 1 AGENDA - April 11th

1.	<p>Introductions and Goals for This Meeting</p> <p>The goals for this meeting:</p> <ul style="list-style-type: none"> • Provide updates on recent and ongoing ECWG activities (today & tomorrow) • Review revised Status and Trends monitoring design (today) • Discuss modeling projects in other workgroups that include CECs (today) • Discuss CEC Strategy Revision and future direction of the program (tomorrow) • Recommend which special study proposals should be funded in 2023 and provide advice to enhance those proposals (tomorrow) <p>Meeting materials: 2021 ECWG Meeting Summary pages 8 - 26</p>	9:00 Melissa Foley
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2.	<p>Information: CEC Strategy Update</p> <p>This item includes the following topics:</p> <ul style="list-style-type: none"> • Review of current RMP activities • Update on State Water Board CEC Program projects <p>This brief update will be followed by a more in-depth discussion of the 2022 CEC Strategy Revision and future directions on day 2 (Item 12).</p> <p>Desired Outcome: Informed Workgroup</p>	9:15 Rebecca Sutton
3.	<p>Information: There's PFAS in the Bay: Where is it coming from?</p> <p>Past work reported elevated levels of PFAS, especially PFOS, in the Bay's seals and cormorants, as well as water and sediment. Levels were found to be particularly high in locations receiving inputs from wastewater treatment plants and stormwater. The question is, where are the PFAS coming that contribute to loadings? Studies that have reviewed the patents and reported on PFAS in specific products that have been tested, showing myriad real and potential sources from indoor and outdoor uses. However, the contributions from various sources to wastewater and stormwater are not clear. We will discuss confirmed uses of PFAS, particularly in outdoor building materials, that could be contributing to stormwater loadings.</p> <p>Desired Outcome: Informed Workgroup</p>	10:00 Miriam Diamond (University of Toronto)
	Short Break	10:30
4.	<p>Discussion: Stormwater CECs Monitoring Approach</p> <p>The workgroup will hear an update on the RMP sponsored 2-year effort to develop a CECs monitoring strategy for stormwater. The strategy will integrate modeling to cost-effectively address near-term priority RMP management questions for CECs in stormwater, including presence and loads relative to other pathways. The project will develop (1) an approach for prioritizing CECs for stormwater monitoring, and (2) a process for integrating modeling when developing CEC-specific stormwater monitoring study designs. The proposed <i>CECs in Stormwater: PFAS</i> project would pilot this approach while in parallel building resources to support all future stormwater CECs monitoring.</p> <p>Desired Outcome: Informed Workgroup; Feedback on considerations to include when prioritizing CECs for stormwater monitoring and on the preliminary approach for developing CECs study designs.</p>	10:40 Kelly Moran, Alicia Gilbreath
	Lunch	11:40
5.	<p>Information: Ethoxylated Surfactants in Bay Water, Wastewater, and Stormwater - Method Development Update</p>	12:20 Lee Ferguson (Duke)

	<p>The workgroup will hear an update on the progress achieved in expanding the ethoxylated surfactants analytical method to include short-chain alkylphenols and alkylphenol ethoxylates. This new analytical method will be the most comprehensive method available for this contaminant class. Method development was funded in 2022 as the first year of a two-year study (year two proposal to be discussed tomorrow), which would include reanalysis of existing samples and collection and analysis of additional wastewater samples to better assess concentrations in this pathway. The completed study will inform a strategy for future monitoring of these compounds in Bay matrices.</p> <p>Desired Outcome: Informed Workgroup</p>	
6.	<p>Information: Quaternary Ammonium Compounds (QACs) in Wastewater</p> <p>The workgroup will hear an update including some preliminary findings on QACs in wastewater. Last year, Dr. Arnold received significant additional funding from the National Science Foundation to study QACs in wastewater in Minnesota and the Bay Area, supplementing our existing study to permit quarterly monitoring through 2023. As a result, we recommend changing the deadline for the RMP project deliverable, a technical memo, from August 2022 to August 2024.</p> <p>Desired Outcome: Informed Workgroup; Feedback on refinement of RMP deliverable and deadline</p>	<p>12:40 Bill Arnold, Anna Mahony (UMinn)</p>
7.	<p>Information: Status and Trends Monitoring Review</p> <p>The RMP has reviewed its Status and Trends study design, in part motivated by the increased prioritization of CECs monitoring as part of Status and Trends activities. An updated study design for monitoring Bay matrices will be reviewed.</p> <p>Desired Outcome: Informed Workgroup</p>	<p>1:10 Melissa Foley</p>
	Short Break	2:00
8.	<p>Information: Strategy for Development of an In-Bay Fate Model to Support Contaminant and Sediment Management in San Francisco Bay</p> <p>The workgroup will learn about a strategy and multi-year workplan for modeling legacy contaminants (PCBs), CECs, and sediment in the Bay. A robust in-Bay fate model will be valuable in guiding S&T monitoring of CECs (e.g., placement of sampling stations and timing of sample collection) and in assessing the likely spatial distribution and temporal duration of potential water quality impacts.</p> <p>Desired Outcome: Informed Workgroup</p>	<p>2:10 Jay Davis</p>
9.	<p>Information: Integrated Watershed Bay Modeling Strategy and Pilot Study</p> <p>The workgroup will hear an update on the scope and progress of a CEC related modeling project, the Integrated Watershed-Bay Modeling Strategy and Pilot Study. This is a 3-year project to develop a modeling strategy to integrate watershed and Bay models to better support RMP management (1st year). The project also will demonstrate</p>	<p>2:30 Tan Zi</p>

	<p>the utility of the Integrated Watershed-Bay Modeling framework to support RMP management questions with a pilot study (2nd year).</p> <p>Desired Outcome: Informed Workgroup; Feedback on priority ECWG management questions that modeling could help answer</p>	
10.	<p>Information: Setting the Stage for Day 2</p> <p>The workgroup will briefly review goals for tomorrow.</p>	2:55 Rebecca Sutton
	Adjourn	

DAY 2 AGENDA - April 12th

11.	<p>Summary of Yesterday and Goals for Today</p> <p>The goals for today's meeting:</p> <ul style="list-style-type: none"> • Brief recap of yesterday's discussions and outcomes • Update on the tires strategy • Discuss CEC Strategy Revision and future direction of the program • Recommend which special study proposals should be funded in 2023 and provide advice to enhance those proposals 	9:00 Melissa Foley
12.	<p>Discussion: 2022 CEC Strategy Revision - Management Questions, Tiered Risk-based Framework, Future Priorities</p> <p>The workgroup will review and discuss the ECWG management questions, potential revisions to the tiered risk-based framework, and priorities for future special studies.</p> <ul style="list-style-type: none"> • Management questions (20 minutes) • Recommended revisions to the tiered risk-based framework (20 minutes) • Future special study priorities (20 minutes) <p>Desired Outcome: Feedback on the ECWG management questions and the suggested changes to the RMP's tiered risk-based framework. Comment deadline: June 30, 2022.</p> <p>Meeting materials: 2022 CEC Strategy Revision Memo; 2017 CEC Strategy Revision Management Questions</p>	9:10 Rebecca Sutton
	Short Break	10:10
13.	<p>Discussion: Tires Strategy Update</p> <p>In 2021, the RMP funded development of a cross-workgroup multi-year plan to address tire-related water pollution ("Tires Strategy"), focusing on contaminants. This 5-year plan builds from the Tires Conceptual Model project, which was funded in 2020 and is nearly complete. It identified key information gaps around the connections between tires and aquatic habitats. International scientific research into this high-interest, high-impact area is starting to clarify aquatic hazards posed by tire particles and some chemicals (e.g.,</p>	10:20 Kelly Moran, Ezra Miller, Alicia Gilbreath

	<p>6PPD-quinone) and starting to identify additional associated chemicals of ecological interest. Monitoring data and information about emission, fate, transport, and mitigation options remain relatively limited. Within this rapidly changing context, a short-term RMP multi-year plan is in development. Once the science has solidified (anticipated by the end of the plan's 5-year horizon), tire-related work would fold into the emerging contaminants and microplastics strategies. The plan is intended to be based on stakeholder needs and the special capabilities of the RMP.</p> <p>Desired Outcome: Informed Workgroup; Feedback on RMP approach to tire contaminants</p>	
14.	<p>Summary of Proposed ECWG Studies for 2023</p> <p>The ECWG science lead 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.</p> <p>2023 RMP ECWG Special Study Proposals include:</p> <ul style="list-style-type: none"> ● Stormwater CECs monitoring approach (year 2 of 2) ● CECs in stormwater: PFAS ● Ethoxylated surfactants in ambient water, margin sediment, wastewater, part 2 (year 2 of 2) ● PFAS and nontargeted analysis of marine mammal tissues (year 1 of 2) ● Mining nontargeted analysis data ● Tire and roadway contaminants in wet season Bay water, part 2 (year 1 of 2) ● PFAS in archived sport fish <p>Special Study Proposals for other workgroups that are relevant to ECWG include:</p> <ul style="list-style-type: none"> ● SPLWG strategy report & management questions update ● CECs stormwater modeling (SPLWG) ● Microplastics air monitoring (MPWG) ● In-Bay contaminant modeling (PCBWG) <p>Meeting materials: 2023 Special Studies Proposals, pages 27 - 84</p>	<p>11:10 Rebecca Sutton, Alicia Gilbreath, Diana Lin, Ezra Miller, Kelly Moran, Miguel Mendez</p>
	LUNCH	12:00
15.	<p>Discussion of Recommended Studies for 2023 - General Q&A, Prioritization</p> <p>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.</p> <p>The workgroup will then consider the studies as a group, ask questions of the Principal Investigators, and begin the process of prioritization by stakeholders.</p>	<p>12:40 Melissa Foley</p>
16.	<p>Closed Session - Decision: Recommendations for 2023 Special Studies Funding</p> <p>RMP Special Studies are identified and funded through a three-step process. Workgroups recommend studies for funding to the Technical Review Committee (TRC).</p>	<p>2:00 Karin North</p>

	<p>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.</p> <p>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.</p> <p>Desired Outcome: Recommendations from the ECWG to the TRC regarding which special studies should be funded in 2023 and their order of priority.</p>	
17.	Report Out on Recommendations	2:50 Karin North
	Adjourn	3:00



Bay RMP Stakeholder and Workgroup Meetings

Guidelines for Inclusive Conversations

This document is intended as a guideline for engagement at Bay RMP Technical Review Committee, Steering Committee, and Workgroup meetings. This is a living document. If you have input on what could be added, please email Melissa Foley (melissaf@sfei.org).

Zoom Etiquette

- Rename yourself - consider adding your name, organization, preferred pronouns and whose native land you are on.
- “Raise your hand” virtually if you wish to speak.
- In the case of a land acknowledgement, take the time to determine whose native land you are on at the time of your meeting (<https://native-land.ca/>). People may be invited to share the name in the chat.

Meeting Agreements¹

- TRY IT ON: Be willing to “try on” new ideas, or ways of doing things that might not be what you prefer or are familiar with.
- PRACTICE SELF FOCUS: Attend to and speak about your own experiences and responses. Do not speak for a whole group or express assumptions about the experience of others. Work on examining your default assumptions about another person's identity or lived experience.
- UNDERSTAND THE DIFFERENCE BETWEEN INTENT AND IMPACT: Try to understand and acknowledge impact. Denying the impact of something said by focusing on intent is often more destructive than the initial interaction.
- PRACTICE “BOTH / AND”: When speaking, substitute “and” for “but.” When used to connect two phrases in a sentence, the word “but” essentially dismisses the first phrase altogether. Using “and” acknowledges multiple realities and promotes inclusion.
- REFRAIN FROM BLAMING OR SHAMING SELF & OTHERS: Practice giving skillful feedback.
- MOVE UP / MOVE BACK: Encourage full participation by all present. Take note of who is speaking and who is not. If you tend to speak often, consider “moving back” and vice versa.
- PRACTICE MINDFUL LISTENING: Try to avoid planning what you’ll say as you listen to others. Be willing to be surprised, to learn something new. Listen with your whole self.
- RIGHT TO PASS: You can say “I pass” if you don’t wish to speak.
- AVOID JARGON: Try to avoid using jargon and/or acronyms.
- IT’S OK TO DISAGREE: Not everyone will be in agreement all of the time, and that’s ok!

¹ Adapted from Visions, Inc. Guidelines for Productive Work Sessions found at: https://www.emergingsf.org/wp-content/uploads/2017/08/EBMC_AgreemntsMulticulturalInteractions15.09.13-copy.pdf.



RMP Emerging Contaminants Workgroup Meeting

April 12-13, 2021
San Francisco Estuary Institute

Meeting Summary

Science Advisors	Affiliation	Present
Lee Ferguson	Duke University	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)	Coreen Hamilton (SGS AXYS)
Alicia Chakrabarti (EBMUD)	Denise Greig (Cal Academy of Sciences)
Alicia Taylor (DTSC)	Diana Lin (SFEI)
Amanda Roa (Delta Diablo)	Don Gray (EBMUD)
Analise Lindborg (Duke)	Don Yee (SFEI)
Andria Ventura (Clean Water Action)	Doug Dattawalker (USD)
Anne Balis (City of San Jose)	Ed Kolodziej (UW)
Anne-Cooper Doherty (DTSC)	Eric Dunlavey (City of San Jose)
Artem Dyachenko (EBMUD)	Erica Kalve (SWRCB)
Autumn Cleave (SFPUC)	Eunha Hoh (SDSU)
Blake Brown (CCCSD)	Ezra Miller (SFEI)
Bonnie de Berry (EOA/SCVURPPP/BASMAA)	Frances Bothfeld (WA Dept of Ecology)
Bryan Frueh (City of San Jose)	Gaurav Mittal (SFBRWQCB)
Charles Wong (SCCWRP)	Hallie McManus (UC Berkeley)
Chris Sommers (EOA/SCVURPPP/BASMAA)	Heather Lee (DTSC)

Heather Peterson (SFPUC)	Miguel Mendez (SFEI)
Jay Davis (SFEI)	Nina Buzby (SFEI)
Jaylyn Babitch (City of San Jose)	Paul DeLeo (Integral Consulting Inc.)
Jen Jackson (City of SF)	Rachel Scholes (UC Berkeley)
Jennifer Branyan (UC Davis)	Rebecca Sutton (SFEI)
Jennifer Christmann (Vista Analytical)	Reid Bogert (BASMAA/San Mateo CCAG)
John Coleman (Bay Planning Coalition)	Richard Looker (SFBRWQCB)
Jennifer Teerlink (CDPR)	Richard Grace (SGS AXYS)
June-Soo Park (DTSC)	Robert Wilson (City of Santa Rosa)
Karin North (City of Palo Alto)	Sam Good (SFBRWQCB)
Kelly Moran (SFEI)	Scott Coffin (SWRCB)
Kirsten Overdahl (Duke)	Shoba Iyer (OEHHA)
Kristian Fried (Integral Consulting Inc.)	Simona Balan (DTSC)
Lester McKee (SFEI)	Simret Yigzaw (City of San Jose)
Lilly Sabet (SDSU)	Stephanie Jarmul (OEHHA)
Lisa Austin (Geosyntec)	Steve Weisberg (SCCWRP)
Liz Falejczyk (Novato Sanitary District)	Tan Zi (SFEI)
Lorien Fono (BACWA)	Terry Grim (CIL)
Luisa Valiela (EPA)	Thomas Mumley (SFBRWQCB)
Maggie Monahan (SFBRWQCB)	Topher Buck (DTSC)
Mary Cousins (BACWA)	Wendy Linck (SWRCB)
Mary Lou Esparza (CCCSD)	Yun Shang (EBMUD)
Melissa Foley (SFEI)	

DAY ONE - April 12

1. Introductions and Goals for This Meeting

Melissa Foley began the meeting by highlighting remote meeting tips, reviewing the Zoom platform functionalities, and giving a land acknowledgment to the Native peoples of the San Francisco Bay Area. Melissa then introduced the Workgroup advisors and continued with a brief roll call for the various groups present to introduce themselves.

Melissa followed by reviewing the ECWG two-day agenda and giving an overview of the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP), including the program's goals, history, management questions, monitoring structure, and budget. Additionally, Melissa communicated the goals of the meeting, highlighting discussion on the science during updates on finished and ongoing projects, prioritization of special study proposals, and future directions.

2. Discussion: CEC Strategy Update

Rebecca Sutton updated the group on contaminants of emerging concern (CECs) efforts and strategy, including an overview of current activities and revision to the CEC strategy. She began by introducing the SFEI team, particularly noting the addition of Kelly Moran, a now former external advisor to the ECWG. 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). Related ongoing projects and activities were noted for each element. Rebecca gave a brief aside on Status and Trends monitoring of PFAS in sport fish, noting the larger analyte list, as well as the continued presence of significant levels of PFOS and PFOSA. She also mentioned the limited human health guidance available across the US, with none yet developed for consumption of fish in SF Bay.

Further, Rebecca identified a couple of forthcoming deliverables, including final manuscripts for triclosan in small fish and OPEs and bisphenols in Bay water (submitted in July and August, respectively). She continued with discussion of two projects connected to the State Water Board CEC Initiative. The first study involves synthesizing and analyzing state CECs data from various matrices in CA waters using a tiered risk-based framework similar to that of the Bay RMP to guide recommendations for monitoring and management priorities for the state. The second effort, also connected with the Ocean Protection Council (OPC), is the reconvening of the Ambient Ecosystems CEC Science Advisory Panel ("EcoPanel") to examine the current CEC monitoring and assessment framework.

Rebecca discussed the upcoming CEC strategy revision, noting its purpose to guide future monitoring efforts undertaken by the Bay RMP. SFEI staff recommended moving forward with the scheduled update in 2022, and noted it as a more significant effort than other smaller update efforts. Rebecca presented reasons in support of the revision, including that the last significant update was five years ago, and this provides the opportunity to update the tiered risk-based framework, standardize information on CEC classes, and incorporate strategy developments (i.e., persistence, toxicology). This revision would include an additional cost of \$30K.

Meeting participants were asked for their input on moving forward with the revision in 2022, with most in support of conducting the revision. Dr. Miriam Diamond commented on wanting further information on CECs management summaries with Rebecca Sutton clarifying there are more specific documents available on individual contaminant classes and the revision of the strategy would be to inform managers on potential next steps, especially on what monitoring would help answer important stakeholder questions. Others in the group inquired about the coordination of this revision to planned statewide work. Rebecca remarked that the statewide strategy would be ready by early next year, giving enough time to consider it as a part of the 2022 revision. Steve Weisberg agreed and noted Dr. Derek Muir, ECWG Advisor, is on the statewide panel and can help to ensure there is coordination between the RMP and statewide efforts. Tom Mumley agreed with a revision, though noted issues with the timing and level of effort required. Tom

noted the ongoing Status and Trends (S&T) redesign was focused on CECs, so the revision should correlate with updates to the S&T monitoring design. He also mentioned inclusion of necessary stakeholder participation and up-to-date CECs management strategy and needs within the update, with several participants in agreement. Though time was tight on the first day, Melissa Foley noted further discussion with stakeholders could occur during the prioritization of special studies on day two.

3. Discussion: Tire Contaminants: Update from the Microplastic Workgroup

Melissa Foley began the item by noting the motivation behind the tire contaminant work, where it is important to consider the occurrence and impacts of both particles and chemical contaminants. Melissa also noted the collaboration across workgroups (ECWG, MPWG, and SPLWG) for this project and introduced Kelly Moran to discuss the tire wear stormwater conceptual model funded by the RMP.

Kelly presented the current status of the conceptual model, an RMP special study in its second year. The focus of the conceptual model work has been on tire particles because they were the most common type of microplastic entering San Francisco Bay. Kelly highlighted the importance of viewing tire particles as both microplastics and chemical carriers, as illustrated by evidence implicating a tire-related toxicant in the pre-spawn mortality of coho salmon in the Pacific Northwest. She discussed the size distribution of tire wear particles, their large surface area for leaching contaminants, and their pathways of release into the environment. Kelly then presented the diagram of the conceptual model, walking through the various sources and pathways for tire wear particles to reach stormwater runoff, including the long-range transport via air and short-range transport to land surfaces. She continued by introducing the tire particle mitigation options diagram, emphasizing the variety of available mitigation measures that could be implemented by various key players, including tire and vehicle manufacturers, government entities, and the general population. She reviewed the many data gaps remaining, including management-relevant data gaps in the areas of environmental monitoring, fate and transport, and mitigation, a subset of which could be potential near-term priorities for the RMP.

Kelly asked the meeting participants some questions, particularly on their input for the conceptual models and data gap priorities. Several in the group discussed potential expansions of the study including examination of contaminants that remain (i.e., do not leach) on particles for potential source tracking, direct measurement of various matrices, chemical transformation as it relates to fate, bioavailability, and connection to air quality. Kelly noted existing knowledge gaps in these areas and the further studies that are needed before pursuing these project avenues. Miriam Diamond noted the potential to develop a framework of the most pressing needs to address toxicity of tire particles, including identifying the most mobile fraction, the pathway(s) to the Bay, and wildlife exposure within the Bay. Such a framework would need to incorporate consideration of regional differences between noted studies (i.e., with lower levels of rainfall in the Bay Area relative to the Pacific Northwest, washoff may be more limited and the

time for in-watershed processes longer). Additionally, Dr. Dan Villeneuve mentioned the difficulty in comparison of studies across a range of manufacturers and particle sizes, highlighting consideration of referring to current samples as “uncharacterized complex mixtures.” The chat also included lively discussion with participants digging deeper into topics such as tire wear source control and collection as well as development of standardized tire wear particles for testing. Reid Bogert indicated that stormwater stakeholders generally support science to inform tire particle/chemical source control.

4. Information: Ethoxylated Surfactants in Bay Water, Wastewater, and Stormwater

Analise Lindborg, a Masters student at Duke University, presented preliminary results of the 2019 RMP special study examining ethoxylated surfactants in San Francisco Bay water, wastewater, and stormwater. Ethoxylated surfactants are commonly detected in the aquatic environment, with a previous RMP study published in 2013 finding nonylphenol in Bay water and nonylphenol ethoxylates (NPEOs) in Bay sediment and mussel tissue. As Analise highlighted, this study builds on previous work to confirm the presence and quantify the concentration of ethoxylated surfactants in the Bay by looking at a broad range of analytes of varying ethoxylated chain lengths including NPEOs, octylphenol ethoxylates, and alcohol ethoxylates, as well as examining a variety of matrices to understand the pathways of contamination into the Bay.

For wastewater effluent, Analise noted the highest concentrations were detected for shorter ethoxymer chain lengths, with WWTPs performing secondary treatment showing an order of magnitude greater concentrations than detected in WWTPs with advanced secondary treatment. One site in particular showed significantly higher levels of these contaminants, likely due to industrial influence from a paint manufacturer. Analise continued with stormwater samples, which also featured various analytes at similar levels to wastewater, with higher concentrations at sites known to have greater industrial and transportation land-use influence. Compared to stormwater and wastewater, ambient Bay sites showed lower concentrations, with quantifiable detections at very few sites and different contaminant signatures relative to other matrices and across subembayments.

Analise closed by highlighting the relevance of the wastewater and stormwater pathways, while noting limitations due to blank detection issues and limited data availability. She also provided future directions for the study of ethoxylated surfactants, including analysis of margin sediment collected in South and Lower South Bays. Several meeting participants asked questions, beginning with Tom Mumley inquiring about the importance of vehicles in the stormwater pathway. Analise suggested potential explanations, including detection of compounds in tire leachate and their use in emulsifiers (such as in anti-freeze), though Dr. Lee Ferguson noted it is hard to establish a direct link to vehicles. Miriam Diamond wondered about the variability in results and if transformation between the point of release and actual mobilization could be a potential explanation. Analise noted the difficulty in addressing what is happening in the

intermittent stages, though examining influent concentrations could help address variability in wastewater. Lee reminded the group of the special challenges associated with this class of analytes, including widespread uses leading to field and lab blank contamination for some compounds, and the lack of well-characterized standards (including linear vs. branched molecules). His team created standards specifically for this project.

5. Information: Preliminary Results of Non-targeted Analyses of South and Lower South Bay Sediment

Dr. Eunha Hoh of San Diego State University and Dr. Lee Ferguson of Duke University both presented preliminary results on a 2018 RMP special study to use non-targeted analyses (NTA) to identify unknown CECs in margin sediments in South and Lower South Bays. Dr. Hoh first presented on non-polar contaminants, followed by Dr. Lee Ferguson discussing polar contaminants. Dr. Hoh gave an overview of the strategy for NTA of non-polar compounds, highlighting study goals to determine which compounds are only present, or present at significantly greater levels in margin sites compared to ambient ones, and prioritize these compounds for future environmental monitoring. She continued by discussing the unique analytical method using GCxGC/TOF-MS, the overall approach to non-target screening, and the framework for compound inclusion and identification. Preliminary results showed detection of 476 compounds and identification of 206 at ambient sites, compared to detection of 401 compounds and identification of 173 at margin sites. A total of 130 identified compounds were found in only margin samples or were significantly higher in absorbance there than in ambient sites. Of those 130 compounds, Dr. Hoh remarked that 54% are PAHs and 30% were detected at more than half of sites, though there was notably no relationship between frequency of detection and absorbance (a proxy for concentration). Using the Decision Analysis by Ranking Techniques (DART) software (which ranks chemicals by ubiquity, chemical properties, and toxicity), the 130 compounds were prioritized with 33 contaminants within the top four most concerning ranks including various PAHs, phthalates, and terpenes. Dr. Hoh also noted the interesting signature of legacy pollutant p,p'-DDE, suggesting continued sources, and the overall utility of NTA as a complementary effort to targeted monitoring.

Dr. Lee Ferguson followed by presenting on the polar compound analysis on a subset of the same samples used for non-polar analysis, particularly focusing on preliminary data from margin samples. He discussed the slight differences in prioritization strategy, which is still being developed, and the varying analytical approaches when compared to the non-polar analysis. Roughly, 300-400 compounds have been detected with 59-64 identified, though the identification process is ongoing. Preliminary identifications included antioxidants, quaternary ammonium compounds, and tricresyl phosphate. Also of note was detection of mystery brominated compounds in Lower South Bay, potentially a cyanobacterial toxin based on environmental factors, including proximity to local salt ponds. In addition, previously unreported azo dye compounds were detected in LSB sediments; roadway paint is one hypothetical source. Overall, most of the compounds detected were putative natural products, though these had low

structure annotation confidence scores, with nitrogen heterocycles being prominent contaminants at sites close to roadways.

Several meeting participants discussed the potential for future efforts to identify sources for PAHs and further explore natural products based on existing structural knowledge. Jay Davis commented that examination of the presence of legacy contaminants in South and Lower South Bays suggests the difference between margins and ambient sites may not be particularly significant due to mixing over time, and wondered if assessment is possible without bias towards any site type (ambient vs. margin). Dr. Hoh noted that it is possible though likely to expand the number of compounds examined.

6. Information: Bisphenols in Wastewater and Sediment

Miguel Mendez presented preliminary results on bisphenols in wastewater and archived sediment samples (2017) from a 2020 RMP special study. Bisphenols are high production volume chemicals that are used in a broad array of applications, and they are known endocrine disruptors, with some included on California's Prop 65 List. A previous 2017 RMP study found bisphenols A (BPA) and S (BPS) in ambient Bay waters at levels comparable to protective thresholds, motivating classification as moderate concern under the RMP-risk based tiered framework, and further study in other matrices and pathways. Overall, Miguel noted bisphenols A and F were predominantly detected in both sediment and effluent samples, though effluent samples showed three other bisphenol detections. Compared to other matrices, including data from a complementary study on stormwater and previous ambient water data, Miguel showed the median concentration in effluent for BPA, BPF, and BPS was higher than other bisphenols and close to their predicted no-effect concentrations (PNECs), with additional concern for potential additive or mixture effects. He suggested focusing on the three main bisphenols detected (BPA, BPF, BPS) and continued monitoring of bisphenols in ambient water via S&T efforts.

Miriam Diamond inquired about the bisphenols relative signatures across stormwater and wastewater, and Miguel responded that stormwater samples showed more BPA, though data is preliminary. A comparison of the two matrices is planned. Tom Mumley asked for further insights on future monitoring and Miguel responded that contamination issues with BPF in the previous ambient water study and potential changes over time warrant another look at three bisphenols in surface water. Derek Muir also wondered about why PNECs were chosen, with Ezra Miller commenting that the chosen PNECs include a broad array of species, are protective, and correlate with the thresholds used by the state's EcoPanel.

7. Information: Building a Statewide Wastewater Pesticide Monitoring Network

Dr. Jennifer Teerlink from the California Department of Pesticide Regulation (DPR) presented on DPR's efforts to establish a permanent wastewater monitoring system through its Surface Water Protection Program (SWPP). Dr. Teerlink began by giving an overview of the SWPP, noting the

various approaches taken to protect surface waters (i.e., prevention, regulation, assessment, modeling). She focused on prevention efforts, highlighting the use of a pesticide registration evaluation model to identify compounds that pose a risk through information from product labels, chemical data, and toxicity data. She continued by highlighting previous work with the RMP finding fipronil in wastewater and its minimal removal via wastewater treatment processes. Recent developments have allowed for funding of a wastewater program including special studies to understand pesticide sources and fate, as well as a statewide monitoring effort to characterize spatial and temporal trends in influent, effluent, and biosolids. Dr. Teerlink discussed preliminary results, which widely detected fipronil and its degradates, as well as imidacloprid and some pyrethroids. She also noted that influent and effluent showed different chemical signatures. A conceptual model was developed to help examine potential sources of pesticides to WWTPs and best target mitigation practices. Dr. Teerlink closed with discussion on next steps for the wastewater monitoring program, including establishment of analytical methods and long-term monitoring studies, while highlighting areas of collaboration with the RMP, such as inclusion of pesticides in the RMP's tiered risk-based framework, the QACs study, and investigations on "inert" ingredients within pesticide formulations that are not pesticide active ingredients (like PFAS) and antimicrobials (as DPR does not currently have access to a laboratory with analytical methods for antimicrobials).

Meeting participants discussed interest in various analytes including DEET, fungicides, carbamates, and legacy pesticides (e.g., lindane). Dr. Teerlink noted DEET and many fungicides were not prioritized for analysis due to high aquatic toxicity thresholds, while also commenting that she would look further into the presence of carbamates. She also remarked that legacy pesticides are not prioritized for DPR, though it may be a good idea to flag detections (e.g., via non-targeted analysis) for partner regulatory agencies. Building materials impregnated with pesticides were flagged by experts as an important indoor source of interest for future studies of wastewater.

8. Information: PFAS in Wastewater Matrices (BACWA Study)

Dr. Lorien Fono of the Bay Area Clean Water Agencies (BACWA) discussed the development of the PFAS study in Region 2 Publicly Owned Treatment Works (POTWs), which emerged as part of a statewide investigation order to analyze PFAS in wastewater in California. She noted the utility of working with the RMP to inform region-wide understanding, design an efficient study to inform management actions, and leverage the other work and resources of the RMP. Lorien also talked about the comparability of the Region 2 study to statewide efforts and highlighted the overall importance of this study to better understand the sources, transport, and fate of PFAS.

Diana Lin continued by giving an overview of the two-phase project: Phase 1 examined a representative subset of facilities in Region 2, while Phase 2 will tailor additional monitoring based on the results of Phase 1. She discussed the design of Phase 1 where influent, effluent, and biosolids were sampled at fifteen representative facilities selected using a diverse set of factors (such as discharge volume, service population, industrial discharges). Grab samples

were collected at most facilities, though, as a comparison of sample methods, a few collected both composite and grab samples. Diana noted that target analysis was done on all samples, while total oxidizable precursor (TOP) analysis, to indirectly quantify potential PFAS precursors, was only done on influent and biosolids. She continued by presenting preliminary results, mentioning minimal contamination of blank samples (possible contamination of 6:2 fluorotelomer sulfonate) and similar concentrations among grab and composite samples from select facilities. Across all matrices, 30 PFAS analytes were detected above the reporting limit, with most significant increases in short-chain carboxylates at municipal POTWs. Further, summed concentrations of PFAS measured using TOP analysis in influent were roughly double those detected using the target method, suggesting significant presence of precursors. Diana asked for input on potential next steps for Phase 2 including suspect screening analysis, total organofluorine analysis (TOF), and reverse osmosis concentrate monitoring of additional facilities.

Workgroup experts generally agreed on next steps, with Dr. Derek Muir particularly noting the benefit of TOF across matrices to understand the full view of potential PFAS contamination. Dr. Lee Ferguson agreed with the addition of TOF, and inquired about the confidence of TOP results, particularly in biosolids. Diana noted confidence in TOP results received so far, though biosolids TOP results have yet to be received due to method difficulties. Several workgroup members also mentioned potential additions to Phase 2 including Dr. Miriam Diamond on study of PFAS breakdown products and Dr. Heather Stapleton on broadening the target analyte list to include diPAPS and fluorotelomer alcohols, as a complement to suspect screening. Richard Grace of SGS AXYS gave a brief overview of the general analytical process and method availability related to extra analyte groups. Miriam Diamond anticipated difficulty in identifying unique PFAS signatures associated with specific sources due to the high production volumes of PFAS, consistent with widespread use in many types of products.

9. Information: Status and Trends Monitoring Review

Melissa Foley introduced the item by outlining the motivations and objectives of the Status and Trends monitoring program review. Notably, the sampling design will be tailored to efficiently incorporate CECs into S&T monitoring and ensure data are relevant to management needs. Melissa highlighted the variety of expert advisors and stakeholders involved to effectively redesign monitoring efforts towards CECs. Compared to current efforts, the revision would focus on CECs versus legacy contaminants, leading to differences in sample collection location and timing as well as allowing for fluid movement of CECs on and off S&T lists. Further, Melissa talked about the decision pathway used to determine how to best monitor specific CECs, based on particular factors, including the expected pathway, toxicity thresholds, chemical properties, and existing data in the Bay as well as a simple CEC conceptual model. She continued by reviewing the general sampling design aspects, particularly changes in analytes examined per matrix, varying site types with a Lower South Bay focus, and temporal features (i.e., seasonal, annual) to site selection. These features were spotlighted in the sampling design for the pilot S&T effort for CECs in water during the wet and dry seasons. Melissa discussed the timeline for

the effort, including finishing individual matrices (water, sediment, biota) by the end of the summer of 2021, presenting at the Multi-Year Planning Workshop in October, and final design presentation to the TRC in December 2021.

Melissa noted the important role of the ECWG to weigh in on priorities and approve special studies using S&T as a platform for additional work, concluding with a few questions asking for input on the S&T redesign. Several meeting participants discussed the use of non-target analysis and how to best employ the data to inform future monitoring efforts. Lee Ferguson inquired about the geochronology done in the SF Bay, noting it would be ideal to examine a site with high sediment deposition close to a potential source. Don Yee mentioned wetland edges tended to have appropriate geochronology compared to the open bay and also noted consideration of a passive sediment surface trap to collect recently mobilized sediment. A few participants also mentioned the benefits of continuing to monitor via bivalves as well as potential incorporation of spatial variability and effects-based monitoring. Dan Villeneuve suggested considering prey fish monitoring based on experience in the Great Lakes. Miriam Diamond mentioned consideration of how S&T data can inform source reduction as a part of strategy development. Tom Mumley highlighted the importance of the CEC strategy revision to optimize the S&T program design through a more integrated approach.

10. Information: Setting the Stage for Day 2

Rebecca Sutton thanked the group for their focused, productive discussion, and then reviewed the schedule and goals for the following day. She highlighted some potential points of discussion for the MYP and future directions items including: proactive pathways monitoring, biota monitoring priorities, and efforts dedicated to new CECs versus moderate concern contaminants. Rebecca also asked for input on discussion topics, highlighting some points brought up by participants, including future utilization of NTA and tying work to source reduction.

DAY TWO - April 13

11. Information: 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 as well as the agenda and goals for Day 2, with a particular focus on prioritization of special study proposals.

12. Information: Discussion: Integrated Watershed Modeling and Monitoring Strategy to Support CECs

Kelly Moran began by highlighting the objectives of the integrated watershed modeling and monitoring strategy, particularly to develop a road map to support monitoring design and model structure for CECs. She continued with discussion of maximizing effectiveness through efficient integration of watershed modeling and monitoring work, which is particularly important for CECs

as they have high analytical costs. Tan Zi then talked about the differences between monitoring and modeling, noting the complicated and iterative process of incorporating both together. He presented the draft diagram of the roadmap for the projects, where management questions are examined to identify data gaps. Then, linked monitoring and modeling are used to inform cost-effective study designs to fill data gaps. This process is iterative, building from simple conceptual models and limited monitoring data to obtain early answers to management questions and, in areas where more detail is needed, using initial data to build dynamic models (again a process integrated with monitoring design) to provide refined answers to management questions.

Kelly closed by reviewing the project timeline, with a draft report expected September 2021, and posing discussion questions, spotlighting input on roadmap development related to the project. Meeting participants discussed the current approach, with Lee Ferguson noting continued work about specific applications to CECs and potential for use of a pilot chemical like ethoxylated surfactants, for which degradation is a factor. Miriam Diamond also noted choosing candidate chemicals known to travel by different pathways, including air, as well as potential addition of a management question addressing control and mitigation. Don Yee mentioned that legacy contaminants could be useful as initial candidates to provide breadth of data along with calibration and validation of the data. Dan Villeneuve inquired about development of models, highlighting opportunities to leverage other efforts within the US. Tan noted a combination of new model development and partner collaborations are planned depending on project needs. Tom Mumley also noted the work will integrate with a variety of other projects under the purview of the RMP and continue to connect with similar projects on a regional and national scale. Chris Sommers noted an open question for CECs modeling regarding the levels of precision and accuracy needed.

13. Information: CEC Toxicology Strategy Update

Ezra Miller introduced the item by outlining the background and motivations for the CEC toxicology strategy update, a study to synthesize and assess the quality of available thresholds for CECs detected in the Bay, as well as calculate thresholds for data-poor CECs and establish a process for identifying thresholds for future CECs. Ze discussed the current project to compile ecotoxicological thresholds, noting the current approach to create a living document of important thresholds derived from an extensive literature review, and detected CEC concentrations from the past ten years of RMP-funded studies. Ezra reviewed the types of thresholds generally used, describing the development of ecosystem level thresholds (e.g., PNECs), while also spotlighting the wide variety of important CECs and sources of ecotoxicological thresholds to consider. Ze noted each threshold is given a quality indicator to identify transparency and uncertainty. These thresholds are then compared to available concentrations to examine risk characterization ratios and associated level of concern, with an additive mixture approach considered for appropriate classes. Ezra concluded by highlighting next steps using predictive toxicology methods to calculate thresholds, with the living document of thresholds

expected to be completed before the next ECWG meeting, along with an additional proposal on predictive toxicology.

Several meeting participants discussed potential future directions including a site-specific hazard index in the Bay, incorporating modes-of-action of chemicals (e.g., narcosis, which could be considered cumulative across chemicals/classes), and development of a collection of chemical properties of CECs to inform toxicological considerations. Miriam Diamond and Derek Muir noted further consideration of use trends as well as integration of bioaccumulation and persistence. Ezra noted these various factors are currently considered separately, so work still remains to develop a framework to combine and examine them together. Dan Villeneuve recommended greater transparency with respect to use of these secondary factors in the risk screening process.

14. Discussion: ECWG Multi-year Plan and Future Work

Rebecca Sutton discussed the current ECWG MYP and potential options for future work within the ECWG. She reviewed the MYP, highlighting the wide breadth of pending work from lower to top priority studies for strategy, CECs categorized in the RMP's tiered risk-based framework from possible to moderate concern, new CECs, NTA, and toxicology. Rebecca also noted several future directions for the focus area including: use of NTA results, role of the RMP in identifying CEC sources and pathways, proactive pathways monitoring including air pathway, monitoring to inform source reduction, deprioritizing work on key classes, balance of efforts on new CECs with those established as moderate concern, and determining priorities for biota monitoring.

Rebecca suggested a couple of areas of discussion, including incorporation of topics from yesterday like the use of NTA and source reduction. Several meeting participants discussed the best ways to use NTA and the resulting data, with most noting the need to develop a framework for utilization that includes further mining of available data for information, retrospective analysis, and also considers what is not detected (when conceptual models might suggest it should be present). Dan Villeneuve spotlighted the importance of NTA to develop a view of the contaminant landscape, and thinking about atmospheric deposition to understand the air pathway. Derek Muir and Miriam Diamond supported characterization of the air pathway (dry deposition), and also recommended a focus on high production volume chemicals. Tom Mumley inquired about the value of new NTA studies in marine mammals versus other wildlife and the potential to combine target (e.g., PFAS) and non-target analysis. The group agreed with the combination approach, especially harvesting NTA data for new CECs and leveraging targeted data to get estimates of NTA analytes. Derek Muir noted that seals (mammals) may not be the best species due to the low bioaccumulative value for many CECs, with Tom suggesting prey fish as potential biota to study. Miriam Diamond noted the possible use of passive sampling as a cost-effective alternative to biota, as there is less need to determine exact concentrations.

15. Summary of Proposed ECWG Studies for 2022

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 in the next agenda item. The focus of discussion was on five high-priority studies, with a more brief review of three lower-priority proposals intended for inclusion on the Supplemental Environmental Projects (SEP) list, and two special study proposals for the Microplastic Workgroup with relevance to ECWG.

The proposal for the fourth, and final, sampling year of the stormwater CECs screening study aims for intensive sample collection with the motivation to fill existing stormwater data gaps. The project would examine over 10 sites with a subset of sites sampled twice, focusing on sites with greater urban land use, unique sources or land uses, and opportunities to leverage monitoring with other RMP efforts. Remaining funds from reduced work in years 2 and 3 will be applied to sampling in year 4.

The stormwater monitoring strategy proposal was then presented, aiming to develop a novel, long-term stormwater monitoring approach to effectively address CECs. The strategy includes developing frameworks for prioritizing CECs for stormwater monitoring and tailoring the sampling design to CECs. Within the sampling design, there is flexibility to respond to stakeholder data needs as well as integrate modeling insights and needs to maximize cost-effectiveness. Chris Sommers highlighted the importance of engaging with stakeholders and continued discussion regarding future directions. Since this is a two-year study, Tom Mumley wondered whether the project could be completed in one year and noted interest in an interim product or at least interim use of the developing strategy to inform monitoring before the strategy is complete. .

Presentation of a followup study of ethoxylated surfactants in wastewater and stormwater followed. The motivation of this study is to fill existing data gaps on ethoxylated surfactants analysis and investigative potential sources in wastewater. This proposal would investigate temporal variation (including comparison of weekday and weekends, short-term, and seasonal variation) in wastewater effluent at three POTWs across four sampling dates with a focus on four specific analytes not included in the original analysis. In addition, biosolids would be sampled at POTWs and stormwater would be screened to leverage existing CECs efforts. Lee Ferguson and Richard Grace talked about analytical methods related to ethoxylated surfactants and options to capture those of concern. Tom Mumley and Chris Sommers discussed biosolids and whether this matrix falls within the scope of the RMP.

A study on tire contaminants in Bay water was introduced, which examines 6PPD-quinone and other tire contaminants observed in Bay Area stormwater to inform their classification within the

tiered risk-based framework. This study leverages the pilot S&T wet season monitoring to understand the impact and presence in the Bay while evaluating the pilot effort.

The final proposal discussed non-target analysis in Bay water, focusing on further characterization of stormwater as a CEC pathway, as well as screening Bay water influenced by stormwater for unexpected or new contaminants for follow-up special studies or monitoring. This project would also leverage the pilot S&T monitoring efforts as well as incorporate stormwater sites upstream from those known to already be stormwater influenced. Partnerships with two different labs will allow for analysis using two different methodologies.

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 first two studies assess PFAS and brominated flame retardants in sediment samples to better understand occurrence, risk, and temporal trends. The third study would examine chlorinated paraffins, a new contaminant class, to assess its occurrence and risk, especially as medium and long-chain paraffins have gained use as a regrettable substitution for short-chain paraffins. Two proposals for the MPWG were also quickly reviewed: the first an overall strategy for tire particles and ingredients to address existing information gaps in the Bay, while the second is an investigation of tire particle characteristics that impact the fate and transport of tire particles and associated contaminants.

16. Discussion of Recommended Studies for 2022 - General Q&A, Prioritization

Melissa Foley introduced the item by reviewing the process for prioritization and recommendation of special studies. She also noted the overall planning budget for the special studies to prioritize for the TRC and overall scope of the budget within the RMP. Meeting attendees asked any remaining questions while proposal PIs were still in attendance. The discussion focused on four of the high priority studies previously presented.

Stormwater CECs Monitoring Strategy

Tom Mumley discussed cutting the current scope of the project, potentially narrowing it to a single year effort. Kelly Moran and Rebecca Sutton noted the considerable value of taking a strategic approach and necessary time and resources to develop the best framework possible. Dan Villeneuve and Chris Sommers echoed these sentiments, highlighting the importance of an effective and flexible strategy. Miriam Diamond talked about potential control actions related to these contaminants and potential of an interim deliverable.

Ethoxylated Surfactants in Wastewater and Stormwater

There was discussion among meeting participants regarding the inclusion of biosolids, with Diana Lin noting the utility to compare to effluent samples, potential for mass balance calculation, and analysing temporal trends. Lee Ferguson highlighted that removal efficiency is affected significantly by treatment, stressing a need to adjust expectations and study questions

to the study design. Anne-Cooper Doherty remarked about the value of including both short-chain and long-chain analytes within the study, with Lee discussing the potential to reanalyze samples from a previous RMP study to have a complete data set. Diana Lin noted the proposal will be reviewed and edited to reflect the noted discussion (i.e., less focus on biosolids and inclusion of both short- and long-chain analytes).

NTA of Bay Water

Several meeting participants discussed the current approach and whether it best identifies potential target compounds, particularly as there are few sampling sites and not much expansion from what has already been done previously. Dan Villeneuve noted the potential to expand the scope of the NTA study to include different sites and scale sampling over a couple of years. Jay Davis noted the objective of this project is to understand what CECs are of concern in the Bay, potentially focusing on collection now and conducting chemical analyses over time. Tom Mumley mentioned greater site selection at stormwater sites as well as the potential to archive water samples. Rebecca Sutton noted doing all stormwater sites for this study is possible and would minimally change the budget; stormwater is a matrix that has not yet been characterized via NTA, unlike wastewater. Derek Muir asked about the comparability of NTA results to previous studies, with Lee Ferguson noting difficulty due to data incompatibility. Lee expressed interest in potential pro-bono work to analyze some of the samples using 2016 methods.

Tire-related Contaminants in Bay Water

Discussion centered around the design of the project, with several meeting participants noting analysis of dry season samples to understand if these contaminants may be airborne and leave a detectable deposition. Examination of dry weather would also help figure out persistence in the Bay as well as better understand temporal variation and peak concentrations. Anne-Cooper Doherty noted the importance of coordinating efforts with DTSC.

17. Closed Session - Decision: Recommendations for 2022 Special Studies Funding

Eric Dunlavey 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
Stormwater monitoring strategy for CECs	\$50,000	\$50,000	2	\$105,000 (\$50,000 for 2022; \$55,000 for 2023); with stakeholder clarifications in the proposal; reevaluate the scope of the strategy for Year 1 (and Year 2)

FINAL

CECs in stormwater (Year 4 of 4)	\$100,000	\$100,000	1	
Ethoxylated surfactants in wastewater and stormwater	\$83,415	\$60,000	4	\$12k for biosolids (don't include); reduce number of samples (6-7 per WWTP?; fewer stormwater sites?) or archive; find lab with method for short chain compounds or go back to original samples; add additional field blank(s)
Non-targeted analysis of Bay water (wet season)	\$112,000	\$95,000	5	Number of sites could be adjusted (focus on stormwater?) and/or phased over multiple years (save extraction and archive); also method used could be GC or LC only instead of both
Tire-related contaminants in Bay water (wet season)	\$36,000	\$50,000	3	add dry weather samples in LSB (summer 2021)

SEP Project Ideas			
Study Name	Budget	Yes/No	Comments
PFAS in Sediment	\$55,000 - \$125,000	Yes (2)	TOF should be included
Brominated flame retardants in sediment	\$45,000 - \$110,000	No	levels likely low, so less of a priority
Chlorinated paraffins in sediment	\$50,000 - \$120,000	Yes (1)	No data in the US; but likely present. Highest priority of these SEP proposals

Relevant Studies			
Study Name	Budget	Yes/No	Comments
Tires strategy	\$25,500	Yes	
Tire particle/contaminant fate and transport	\$110,000	Yes	

18. Report out on Recommendations

After the closed door session, proposal authors were invited back to the meeting to hear the final prioritization decisions. Eric Dunlavey summarized the discussed suggestions and recommendations.

Adjourn

About the RMP

RMP ORIGIN AND PURPOSE

In 1992 the San Francisco Bay Regional Water Board passed Resolution No. 92-043 directing the Executive Officer to send a letter to regulated dischargers requiring them to implement a regional multi-media pollutant monitoring program for water quality (RMP) in San Francisco Bay. The Water Board's regulatory authority to require such a program comes from California Water Code Sections 13267, 13383, 13268 and 13385. The Water Board offered to suspend some effluent and local receiving water monitoring requirements for individual discharges to provide cost savings to implement baseline portions of the RMP, although they recognized that additional resources would be necessary. The Resolution also included a provision that the requirement for a RMP be included in discharger permits. The RMP began in 1993, and over ensuing years has been a successful and effective partnership of regulatory agencies and the regulated community.

The goal of the RMP is to collect data and communicate information about water quality in San Francisco Bay in support of management decisions.

This goal is achieved through a cooperative effort of a wide range of regulators, dischargers, scientists, and environmental advocates. This collaboration has fostered the development of a multifaceted, sophisticated, and efficient program that has demonstrated the capacity for considerable adaptation in response to changing management priorities and advances in scientific understanding.

RMP PLANNING

This collaboration and adaptation is achieved through the participation of stakeholders and scientists in frequent committee and workgroup meetings (see Organizational Chart, next page).

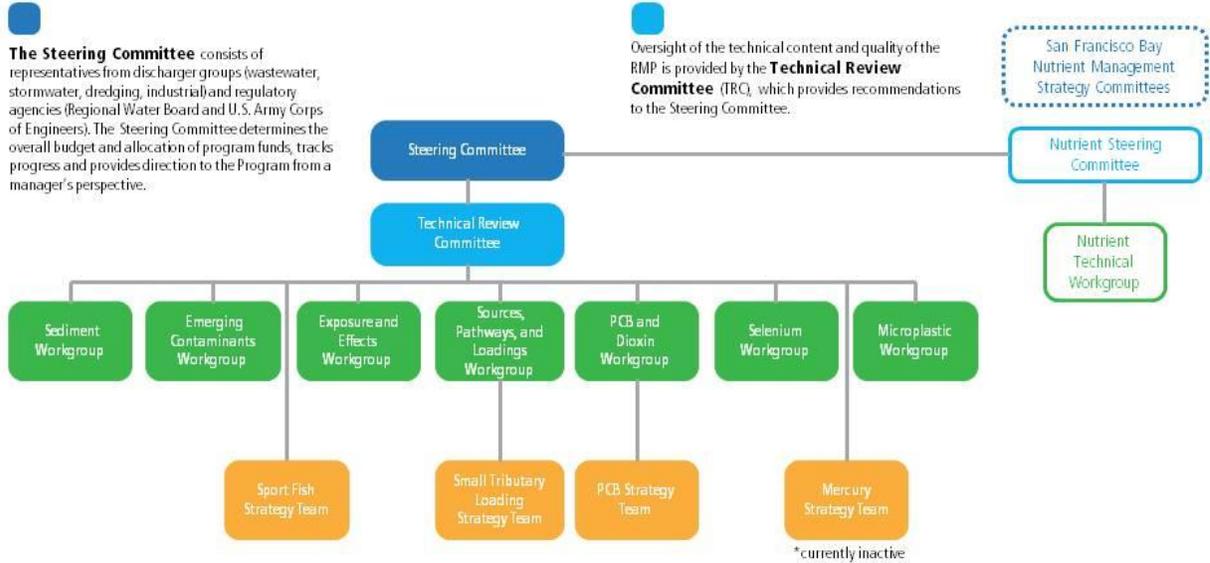
The annual planning cycle begins with a workshop in October in which the Steering Committee articulates general priorities among the information needs on water quality topics of concern. In the second quarter of the following year the workgroups and strategy teams forward recommendations for study plans to the Technical Review Committee (TRC). At their June meeting, the TRC combines all of this input into a study plan for the following year that is submitted to the Steering Committee. The Steering Committee then considers this recommendation and makes the final decision on the annual workplan.

In order to fulfill the overarching goal of the RMP, the Program has to be forward-thinking and anticipate what decisions are on the horizon, so that when their time comes, the scientific knowledge needed to inform the decisions is at hand. Consequently, each of the workgroups and teams develops five-year plans for studies to address the highest priority management questions for their subject area. Collectively, the efforts of all these groups represent a substantial body of deliberation and planning.

PURPOSE OF THIS DOCUMENT

The purpose of this document is to summarize the key discussion points and outcomes of a workgroup meeting.

Governance Structure for the Regional Monitoring Program for Water Quality in San Francisco Bay



The Steering Committee consists of representatives from discharger groups (wastewater, stormwater, dredging, industrial) and regulatory agencies (Regional Water Board and U.S. Army Corps of Engineers). The Steering Committee determines the overall budget and allocation of program funds, tracks progress and provides direction to the Program from a manager's perspective.

Oversight of the technical content and quality of the RMP is provided by the **Technical Review Committee (TRC)**, which provides recommendations to the Steering Committee.

Workgroups report to the TRC and address the main technical subject areas covered by the RMP. The Nutrient Technical Workgroup was established as part of the committee structure of a separate effort – the Nutrient Management Strategy – but makes recommendations to the RMP committees on the use of the RMP funds that support nutrient studies. The workgroups consist of regional scientists and regulators and invited scientists recognized as authorities in the field. The workgroups directly guide planning and implementation of special studies.

RMP strategy teams constitute one more layer of planning activity. These stakeholder groups meet as needed to develop long-term RMP study plans for addressing high priority topics.

Special Study Proposal: Stormwater Contaminants of Emerging Concern (CECs) Monitoring Strategy - Year 2

Summary: Prior RMP projects – including a multi-year stormwater CECs monitoring project initiated in 2018 – identified the presence of CECs of Moderate and Possible 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. This proposal is for the second year of this two-year project

Estimated Cost: \$55,000 for Year 2
(Year 1 \$50,000)

Oversight Groups: ECWG & SPLWG
Proposed by: Kelly Moran, Rebecca Sutton, Lester McKee, Alicia Gilbreath, and Tan Zi (SFEI)

Time sensitive: Yes (multi-year study already underway).

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 Possible Concern in urban runoff (Sutton et al. 2019a; Sutton et al. 2019b; Tian et al. 2021). 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.

This strategy builds off of the Integrated watershed modeling and monitoring implementation strategy (to be completed in 2022) and the CEC Stormwater Loads Modeling Exploration (to be completed in early 2023). It will feed into the updating of the Sources, Pathways, and Loadings Strategy, proposed for 2023. The second year of this project is designed to mesh with the first year of the CECs stormwater modeling project, also proposed for 2023. The CECs in Stormwater: PFAS project proposed to be initiated in fall 2022 (Year 2023 funds), pilots several elements of this strategy and is intended to mesh with the completion of the strategy in 2023. Finally, this strategy will also help to inform wet season CEC monitoring (types of CECs and locations) that is currently being piloted as part of the Status and Trends program.

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.

*Stormwater CECs Monitoring Strategy – ECWG 2022/SPLWG, 2022***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 Possible 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 Possible 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 Possible 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. 2021). 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 will 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 the consideration of 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:

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- 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 the monitoring design (e.g., use of some fixed location monitoring stations) and inform others (e.g., 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, some elements of the strategy in CECs monitoring could be piloted in the Water Year 2023 (October 2022 - September 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 (both years; \$50,000 of this was funded for calendar year 2022).

Expense	Estimated Hours	Estimated Cost
<i>Labor</i>		
Project Staff	495	92000
Senior Management Review	24	5000
Creative Services		4000
<i>Honoraria</i>		
2 Expert advisors on CECs in stormwater/2 years		4000
<i>Grand Total</i>		105,000

Budget Justification

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 2022 to allow coordination with other parallel projects and completion of the draft strategy in spring 2023.

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

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SPLWG and ECWG in spring 2023; and c) a Final Strategy document, to be completed in fall 2023.

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Special Study Proposal: CECs in Stormwater: PFAS

Summary: This study will pilot portions of the Stormwater CECs monitoring strategy that is in development and will develop a study design appropriate for estimating the annual load of PFAS entering the Bay via the stormwater pathway. While this study will include some stormwater monitoring, its primary focus is to complete the groundwork necessary to develop a robust, practical, and cost-effective study design for stormwater PFAS monitoring that could be implemented starting in Water Year (WY) 2024. Proposed project elements include: (1) developing a preliminary conceptual model for PFAS in urban runoff; (2) analyzing prior PFAS monitoring data to inform monitoring design; (3) filling out the SFEI stormwater sampling site database to include sites and site characteristics needed for PFAS monitoring site selection; (4) developing a limited study design to pilot PFAS remote sampling methods; (5) developing and piloting testing remote samplers for PFAS sample collection, including stormwater and blank sample collection; (6) PFAS chemical analysis, data management, QA review, and data interpretation; and (7) preparation of a PFAS monitoring study design, which would be ready for implementation in WY 2024.

Estimated Cost: \$180,000
Oversight Group: ECWG and SPLWG
Proposed by: Alicia Gilbreath, Kelly Moran, Rebecca Sutton
Time Sensitive: Yes, because it pairs with the second year of the Stormwater CECs Strategy project

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Data analysis to inform monitoring design and preliminary conceptual model development	Fall 2022-Summer 2023
Task 2. Sampling location data assembly & addition to database	Fall 2022-Summer 2023
Task 3. Remote sampler development and pilot testing including field collection of stormwater samples	Winter 2022-Spring 2023
Task 4. Laboratory analysis of pilot testing samples	Spring-Summer 2023
Task 5. Update presentations to ECWG and SPLWG	Spring 2023
Task 6. Data management and quality assurance	Summer 2023
Task 7. Data interpretation and development of study design	Spring-Fall 2023
Task 8. Draft Study Design Report	Fall 2023
Task 9. Final Study Design Report	December 2023

Background

The RMP funded the first year of a two-year study to develop a stormwater CECs monitoring approach (“Stormwater CECs Strategy”) during CY 2022 and 2023 (the RMP will consider funding the second year of that project in parallel with this project proposal). Due to high CECs monitoring costs and technical challenges, a well-thought out, carefully focused approach is essential and the first step in establishing a long-term stormwater CECs monitoring program that addresses both ECWG and Sources, Pathways, and Loadings (SPL) management questions, such as estimating CECs loads discharged to the Bay via urban stormwater runoff. The approach will contain procedures and processes to form the basis of developing sampling plans for CECs monitoring projects.

A cornerstone of the new stormwater CECs monitoring approach is the integration of modeling and monitoring designs to maximize the value of each sampling event. A second key element of the stormwater CECs monitoring approach is the use of remote samplers to reduce sample collection costs and to increase the number of samples that can be collected during each storm event. This project will pilot implementation of the new stormwater CECs monitoring approach and build out resources to support its implementation (e.g., remote samplers and a monitoring site selection database). The new stormwater CECs monitoring approach is chemical-specific, recognizing that each individual CEC or class has different sources, fate, transport, and sampling challenges. No single monitoring study design can provide a timely, cost-effective data set to support stormwater load estimates for all CECs. However, the process developed in this pilot will be used to develop monitoring designs for other CECs. PFAS were selected for this pilot project based on their status as a Moderate Concern CEC in the RMP tiered, risk-based framework for prioritizing CECs, high priority at the state level, stakeholder interest, and data availability from past and parallel projects.

PFOS, PFOA, and other PFAS have been previously detected in San Francisco Bay biota, sediment, and water, including wastewater and stormwater pathways. Surface water monitoring conducted in 2009 found detectable levels of various PFAS, especially in areas impacted by wastewater and stormwater.

The RMP’s PFAS Synthesis and Strategy (Sedlak et al. 2017, Sedlak et al. 2018) reviewed two studies of stormwater that have been conducted in the Bay Area: a seven site study conducted in water year 2010 (October 2009 through September 2010), and a 10 site study conducted in water year 2011. A relatively small number of PFAS were monitored; in addition, the watersheds monitored were not specifically selected to provide representative data for these contaminants in the Bay Area. The PFAS Synthesis and Strategy recommended stormwater monitoring as an RMP priority for future work. These studies, as well as the known toxicity and persistence of PFAS, led to classification of PFAS as Moderate Concern within the RMP tiered risk-based framework.

In Water Years 2019-2022, the RMP funded a multi-year effort to screen Bay Area stormwater for CECs, including PFAS. Thirty-one samples have been collected to date. Significant improvements in analytical methods now allow for a greater ability to characterize PFAS, including more short-chain PFAS. Data from the first year has been reported from the analytical lab to SFEI and

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could be used for study design development in this proposed project. The full dataset from this four-year study will be analyzed later this year.

Currently, as part of the Status and Trends (S&T) pilot wet season monitoring effort during the winter of 2021-2022, a study is in progress to assess PFAS in ambient Bay water samples. The wet season study design includes the collection of 10 samples (including two duplicates and field blanks) at six ambient sites in the Lower South Bay after one storm event. The sites were also characterized for PFAS in the summer of 2021, allowing a direct comparison of concentrations by season. Additionally, PFAS samples are being collected at the mouth of three creeks (one in each San Mateo, Santa Clara and Alameda Counties) directly after two storm events. These data will contribute to understanding the role of the stormwater pathway to the Bay.

Taken together, these past and parallel efforts form a strong context for a more intensive monitoring program for PFAS in stormwater. In addition to piloting the stormwater CECs monitoring approach, this study is designed to complete the groundwork necessary to develop a robust, practical, and cost-effective study design for stormwater PFAS monitoring to answer the near-term priority management question of whether the local watershed PFAS runoff load to San Francisco Bay is big or small as compared to loads from other pathways (e.g., municipal wastewater), as well as to develop a robust initial dataset for more intensive dynamic modeling and total mass load estimation to the Bay.

If this project is implemented, we intend to explore the potential for collaboration with three ongoing efforts. First, the State Water Board Surface Water Ambient Monitoring Program Stream Pollution Trends Program (SWAMP-SPoT) is piloting measurements of PFAS in bed sediment at the base of urban watersheds, including up to four sites in the San Francisco Bay area. These data could be leveraged to enhance our understanding of PFAS transport in urban watersheds, particularly for the long-chain PFAS. Second, the University of Toronto (Miriam Diamond), the Green Science Policy Institute (GSPI), and additional collaborators have a project underway examining PFAS in outdoor building materials, a likely (and perhaps major) source of PFAS in urban runoff. This project will inform the conceptual model and could influence the selection of sampling locations. Third, the USGS has started development of a second-generation low cost remote stormwater sampler based on a proven US EPA design (Kahl et al., 2014). We are currently exploring partnering with USGS to pilot this sampler in WY 2023.

Study Objectives and Applicable RMP Management Questions

Table 1. Study objectives and questions relevant to the 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?	N/A	
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Pilot portions of the Stormwater CECs Monitoring Strategy that is in development. Develop data to support estimating the annual load of PFAS entering the Bay via the stormwater pathway.	Determining whether stormwater pathway PFAS loads are large or small relative to other pathways for PFAS to reach the Bay will inform stakeholder prioritization of potential PFAS management strategies.
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?	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

The proposed project includes multiple elements, all of which are necessary to develop a robust, practical, and cost-effective PFAS-specific stormwater monitoring study design to answer the near-term priority management question of whether the local watershed PFAS runoff load to San Francisco Bay is big or small as compared to loads from other pathways.

One group of project elements implements a key part of the new stormwater CECs approach: integrating modeling into monitoring design. This is accomplished by (1) developing a preliminary conceptual model for PFAS in urban runoff; (2) evaluating the data needs for first-order loads estimation modeling via analysis of prior RMP PFAS monitoring data; (3) filling out the SFEI stormwater sampling site database to include sites and site characteristics needed for PFAS

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monitoring site selection based on the conceptual model; and (4) using watershed modeling data needs in combination with the conceptual model to select monitoring locations for the PFAS study design. The load modeling needs will flow from the watershed model selected for this purpose, which will be identified through the separate RMP CEC Stormwater Loads Modeling Exploration project (led by SPLWG), anticipated to be completed in 2022.

A second group of project elements is aimed at developing a practical, cost-effective method for remotely collecting stormwater samples. Remote sampler capabilities reduce collection costs and make it possible to obtain many more samples per storm event than is possible with current manual sampling techniques. Having this capacity will shorten the time frame necessary to address CECs management questions requiring stormwater monitoring data. These project elements include (1) developing a limited study design to pilot and evaluate remote samplers for usability for PFAS sampling; (2) selecting and piloting specific remote samplers and conducting QA/QC testing of the samplers to evaluate potential for sample contamination; and (3) completing associated PFAS chemical analysis, data interpretation, data management, and QA review.

Finally, the project will conclude with preparation of a report outlining a PFAS monitoring study design that could be implemented as soon as WY 2024.

Integrating modeling into monitoring design*Preliminary conceptual model*

The purpose of this task is to build a preliminary conceptual model that synthesizes and integrates our current understanding of PFAS sources and pathways to urban runoff to inform monitoring design. PFAS sources will be identified through a literature review and the possible collaboration with the University of Toronto/GSPI building materials project, with a focus on true sources, i.e., products or activities that provide a pathway for release of PFAS into the outdoor urban environment. The conceptual model will focus on probable major sources only. It will include limited consideration of fate and transport, drawing from prior published conceptual models (e.g., Prevedouros et al. 2006, De Silva et al. 2021). A conceptual model diagram will identify the pathways for PFAS to be transported from these sources, via urban runoff only, into San Francisco Bay, with the intent of providing information sufficient to inform the initial monitoring design. The diagram and brief description will be part of the study design report.

In the future, a more detailed conceptual model beyond the scope of the proposed effort could be developed to aid data interpretation or update the study design to address future management questions (e.g., linkages to specific PFAS sources or understanding how PFAS transformation affects transport or loads in stormwater entering the Bay).

Analysis of prior PFAS monitoring data to inform monitoring design

The PFAS monitoring data previously mentioned, coupled with geospatial data (e.g., land use, road map, imperviousness), provide an initial dataset for assessing sample variability. The data analysis will provide a general picture of existing monitoring data and a rough estimation of sources of variability in the monitoring data. By exploring the variability between samples collected at the same location and between samples collected at different locations, the data analysis can further guide monitoring approaches. For example, the analysis can help us answer the following questions: What

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is the variability between samples at the same location and at different locations? Are there any linkages between variability and geospatial features? Assessing monitoring data variability can address some key monitoring design questions, such as how many replicates are needed for a sampling site and how many sites are required for load estimation purposes. From a modeling point of view, which monitoring locations are suitable for load monitoring and which are suitable for identifying PFAS sources? These types of questions will be addressed in the study design report.

Sampling location database

Typically for past RMP stormwater monitoring, sites have been selected each year in collaboration with the Small Tributaries Loading Strategy (STLS) team, a subgroup to the Sources Pathways and Loadings Workgroup composed of RMP staff, Water Board staff, and Permittee representatives. Site selection priorities have focused on characterizing Hg and PCBs in stormwater runoff in the Bay Area, and identifying sites that may be higher-leverage watersheds for potential follow-up management actions.

A moderate effort is required each year to develop new potential sampling site lists and assess these sites for safety, feasibility, and land use characteristics. While the current process has been effective, it has not been structured and archived consistently from year to year, nor are sites that are relevant to characterizing and identifying high-leverage watersheds for Hg and PCB management action necessarily the same as those ideal for characterizing PFAS, or other CECs, in urban runoff.

To select sites for the most effective and efficient monitoring design for PFAS and CECs, both in the current proposal and future monitoring programs, we must develop an organized sampling location database that includes pertinent information that would be relevant to sampling various CECs. RMP staff have begun developing this sampling location database through funding from the Stormwater CECs Monitoring Strategy project, including gathering lists of sites sampled by the USGS, Water Board, municipalities, and SFEI. We have also solicited information on potential sampling locations from the Permittees. In this task, we propose to fill out the SFEI stormwater sampling site database to include sites and site characteristics needed for PFAS monitoring site selection based on the conceptual model. This will first focus on characterizing sites that have flow gauging (beneficial data for modeling purposes), and then look more broadly at sites that do not have flow gauging. The effort includes compiling the existing site lists; potentially developing new datasets on land use attributes that support site selection for PFAS monitoring; and conducting reconnaissance of these sites to assess sampling feasibility using a variety of sampling techniques.

Remote samplers - pilot stormwater sampling and evaluation*Remote sampler selection*

RMP scientists intend to pilot two very different remote stormwater samplers. The USEPA has developed an in-stream remote sampling device (Kahl et al., 2014) that collects whole water samples using a micropump. The EPA is collaborating with the USGS, which is starting the process of modifying the current sampler to include telemetry and stage-measurement capabilities. We are currently in discussion with the EPA and USGS and it is likely that we would be able to pilot these samplers in the Water Year 2023 wet season (begins October 2022).

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In addition to pilot testing the EPA/USGS samplers, we would also test traditional automated pumping samplers, specifically drawing upon samplers we already have in-house (ISCO, model 6712). These samplers are placed on the side of the channel with tubing extending into the channel. This traditional sampling approach is well-proven and may be needed if the EPA/USGS samplers do not prove workable for PFAS (e.g., if they have unacceptable levels of blank contamination). Deployment of the ISCO samplers is anticipated to be more labor-intensive (securing the conduit and tubing in the channel, housing the ISCO or leaving it outside a lock box, which leaves it vulnerable to vandalism) and overall more expensive (due to the cost of the sampler, tubing and cleaning costs for the tubing, as well as a more intensive effort to deploy) than the EPA/USGS samplers.

In both cases, several blank samples will be collected and analyzed to ensure the equipment does not influence the PFAS concentrations in the samples.

Pilot stormwater sampling

A limited pilot study design, including site selection, sample analysis methods, and finalization of field methods will be developed by RMP staff in consultation with ECWG and SPLWG advisors as well as reviewed by Dr. Erika Houtz, an expert in PFAS sampling and analysis.

Pilot site selection will occur in consultation with the RMP stormwater team and the STLS team. Sites will be selected from the compiled site location database. Pilot site selection will be informed by the parallel modeling efforts to the extent feasible.

Up to 20 pilot project samples (including several field blank and several field duplicate samples) will be collected. Sample collection will include limited field deployment (up to four sites) as the primary focus will be on method development and QA samples such as equipment blanks, field blanks, and field duplicates. Field samples will consist of flow-weighted composites collected using the two different remote samplers (previously described) deployed side-by-side. Other tasks required for stormwater sampling include: securing permits, training staff, pre-season and pre-storm preparation, the deployment and retrieval of samplers, shipping bottles to laboratories, and cleaning equipment.

Chemical analysis, data management and QA, and data interpretation

Up to 20 samples will be characterized by SGS AXYS Analytical Laboratories, Inc. for target PFAS, PFAS Total Oxidizable Precursors (TOP), and adsorbable organic fluorine (AOF). All analytical methods are also being applied to Bay Area wastewater samples through an ongoing BACWA study. The sample number includes collection at up to four sites around the Bay Area, equipment blank samples, field blank samples, and field duplicates.

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For target PFAS¹ analysis, after spiking with isotopically labeled surrogate standards, samples are extracted and cleaned up by Solid Phase Extraction (SPE). The extracts are then analyzed by liquid chromatography/mass spectrometry (LC-MS/MS). Final sample concentrations are determined by isotope dilution/internal standard quantification.

Analysis of Total Oxidizable Precursors (TOP) measures oxidizable polyfluoroalkyl substances (PFAS) converted into terminal perfluorinated carboxylic acids (PFCAs) through the use of persulfate oxidation and subsequent analysis of perfluorinated carboxylates (C4-C14) and sulfonates (C4-C10, C12). The increase in concentration of the terminal carboxylic acids following oxidation represents the precursor potential of the sample.

The determination of adsorbable organic fluorine (AOF) is applicable to aqueous samples including water, wastewater, and diluted products. This analysis is proposed here to evaluate it as a potential element of the stormwater PFAS study design and for comparison to similar measurements being conducted at Bay Area municipal wastewater treatment plants. The method targets compounds that are adsorbed onto activated carbon. After passing the sample through an activated carbon column, the carbon containing the adsorbed organic material is rinsed with neutral nitrate solution to remove inorganic fluorine salts and then subjected to the combustion process and ion chromatographic determination of the fluoride in the sample.

Data management and QA will include field collection data entry, communications with laboratories, quality assurance review and upload to CEDEN of target PFAS concentrations (as appropriate).

Data interpretation will include evaluating samplers for potential contamination and examining pilot data in the context of other PFAS work (including the similar measurements underway at Bay Area municipal wastewater treatment plants) to inform selection of monitoring methods for the study design. These tasks will be completed by RMP staff in consultation with Dr. Erika Houtz.

The overall experiences with the samplers and the chemical analysis data, particularly the blank samples, will be evaluated in the study design report as input to the selection of the sampling and chemical analysis approach in the stormwater PFAS study design.

Stormwater PFAS monitoring study design

A draft report presenting a study design for monitoring PFAS in stormwater will be prepared on the basis of the project elements above. Watershed modeling data needs in combination with the conceptual model will be used to select monitoring locations. The pilot sampler experience will determine the selection of the sampling methods and analytical techniques. The study design report will include the outcomes of each of the above project elements.

¹Anticipated analysis includes: perfluoroalkyl carboxylates (11 compounds including PFOA), perfluoroalkyl sulfonates (eight compounds including PFOS), fluorotelomer sulfonates (three compounds), fluorotelomer carboxylates (three compounds), perfluorooctane sulfonamides (three compounds), perfluorooctane sulfonamidoacetic acids (two compounds), perfluorooctane sulfonamidoethanols (two compounds), ether carboxylates (five compounds), and ether sulfonates (three compounds).

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During the study design development, we will also explore potential collaboration with SWAMP SPoT, which is planning sediment PFAS monitoring at four Bay Area creek locations, and collaboration with the University of Toronto/GSPI building materials PFAS project.

Budget

Table 2. Proposed Budget

Expense	Estimated Hours	Estimated Cost
<i>Labor</i>		
Conceptual Model, Analysis of Prior PFAS Monitoring Data to Inform Design, Sampling Location Database	366	61,000
Remote Sampler Development and Pilot Stormwater Sampling	296	45,000
Data Interpretation	30	7,000
Data Technical Services	76	12,000
Study Design Report	100	20,000
<i>Subcontracts</i>		
PFAS, TOP Assay, and AOF: SGS AXYS		22,000
Honorarium		2,000
<i>Direct Costs</i>		
Equipment		9,800
Travel		400
Shipping		800
<i>Grand Total</i>		180,000

Budget Justification

SFEI Labor

Labor hours are estimated for SFEI staff to complete all project elements: developing a preliminary conceptual model for PFAS in urban runoff; evaluating the data needs for first-order loads estimation via analysis of prior RMP PFAS monitoring data; filling out the SFEI stormwater sampling site database to include sites and site characteristics needed for PFAS monitoring site selection; developing and piloting remote samplers for CECs sample collection; developing a limited study design to pilot sampling methods; data interpretation; and preparation of the PFAS monitoring study design and report. SFEI will also work internally and with potential USGS collaborators to design remote samplers and then pilot test their deployment during storm events.

*CECs in Stormwater: PFAS – ECWG 2022**Laboratory Costs*

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

Data Technical Services

Data services will include field collection data entry, communications with laboratories, quality assurance review following standard RMP data management protocols and data upload of target PFAS concentrations to CEDEN.

Reporting

A presentation in Spring 2023 will update the ECWG and SPLWG. The primary focus of reporting will be on developing the draft study design by Fall 2023 (final study design report due December 2023), for potential use in WY2024.

References

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Special Study Proposal: Ethoxylated Surfactants in Ambient Water, Margin Sediment, Wastewater, Part 2, Year 2

Summary: Ethoxylated surfactants are nonionic surfactants that are widely used in industrial and household products. This contaminant class is currently classified as of Moderate Concern in the RMP tiered, risk-based framework for CECs. A 2019 RMP special study quantified a broad suite of ethoxylated surfactants in Bay water, effluent, and stormwater, including lauryl alcohol ethoxylates (C12-14EO), tridecyl alcohol ethoxylates (C16EO), nonylphenol ethoxylates, and octylphenol ethoxylates. Sum of ethoxylated surfactants concentrations ranged from 1-95 µg/L. A 2022 RMP special study supported Duke University to update analytical methods to include alkylphenols and short-chain alkylphenol ethoxylates. This new analytical method is the most comprehensive method available for this contaminant class, and few laboratories have the capabilities to perform this analysis.

This project is the second half of the full proposal presented as a 2022 ECWG special study, and will include collection of additional wastewater samples that will be analyzed using the updated analytical method. These wastewater samples are needed to refine estimates of concentrations of ethoxylated surfactants in wastewater effluent, due to the wide range observed in the initial 2019 screening study. These additional samples are important to further compare relative loads from wastewater versus stormwater runoff, a comparison which was initiated by prior studies. This project will supplement remaining funds from the 2019 and 2022 studies to complete project deliverables, including more comprehensive monitoring of ambient water and margin sediment samples. The full dataset will guide re-evaluation of this contaminant class in the tiered framework for CECs and inform development of a monitoring strategy.

Estimated Cost: \$30,000 (supplementing 2022 funding of \$30,000)
 Oversight Group: ECWG
 Proposed by: Diana Lin and Rebecca Sutton (SFEI) and Lee Ferguson (Duke)
 Time Sensitive: Yes; year 2 of a multi-year study

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Finalize sampling design and protocol with wastewater treatment facilities	April 2023
Task 2. Complete wastewater effluent sample collection	August 2023
Task 3. Complete laboratory analysis of samples	January 2024
Task 4. QA/QC and data management	April 2024
Task 6. Draft report	September 2024
Task 7. Final report	November 2024

Background

Ethoxylated surfactants are a broad class of nonionic surfactants used in a wide range of consumer and industrial applications as emulsifiers, wetting agents, dispersing agents, stabilizers, antioxidants, curing agents, and surface tension agents. Commonly used products that may contain ethoxylated surfactants include cleaning products, degreasers, fuel and lubricant fuel additives, paints, pesticide formulations, textiles, personal care products, adhesives, varnishes, plastic polymers, phenolic resins, concrete, tire rubber, and foam suppressant. Use and manufacturing of these products can lead to the release of these compounds into residential, commercial, and industrial wastewater as well as urban stormwater runoff.

Nonylphenol ethoxylates (NPEO or NP_nEO, where n = the ethoxylate chain length) and octylphenol ethoxylates (OPEO or OP_nEO) are two of the most widely used and studied ethoxylates, and are within the subclass of alkylphenol ethoxylates. NPEOs 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). Cleaning products typically use NPEO with an ethoxylate chain length between 4 and 15 (DTSC, 2018). Long-chain NPEO can degrade to more toxic and hydrophobic products, such as nonylphenol diethoxylates (NP2EO), nonylphenol monoethoxylates (NP1EO), and nonylphenols (NP). NP are persistent in the aquatic environment, moderately bioaccumulative, and extremely toxic to aquatic organisms (USEPA 2010). Alcohol ethoxylates are often used as replacement products because they degrade faster and are expected to be less toxic (Soares et al., 2008); however, alcohol ethoxylates have received very little scientific attention and there are toxicity concerns (Lara-Martin et al., 2012).

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, nonylphenol, and octylphenol.

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 C12-14EO, C16EO, C12(Br)EO, NPEO and OPEO. The wastewater investigation was designed as a screening study that evaluated ethoxylated surfactant concentrations from eight POTWs that represent diversity in geography, treatment technologies, as well as a focus on larger facilities that discharge a greater portion of wastewater flows to the Bay. Results from the wastewater analysis indicated surprising variation in the concentrations of ethoxylated surfactants from the eight facilities (Lindborg et al., in prep). Concentrations for each ethoxylate series ranged two to four orders of magnitude among facilities. The facility with the highest level of ethoxylated surfactants had a concentration that was at least an order of magnitude greater compared to that of the second highest facility. The facility with the highest measured concentration accounted for a majority of the estimated daily ethoxylated surfactant loads based on flows, despite not being among the largest facilities measured. However, this analysis is based on a single 24-hour composite sample from each facility.

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An important limitation in the analytical method used previously is that short-chain NPEO and short-chain OPEO (including octylphenol, OP1EO, and OP2EO) were either not analyzed or not quantified. This is particularly important for wastewater samples, where alkylphenol ethoxylates are known to degrade to short-chain ethoxylates during treatment. Therefore, last year, the RMP funded another special study to update the analytical method to capture the alkylphenols and short-chain alkylphenol ethoxylates and begin to re-analyze the wastewater, stormwater, and surface water samples analyzed from the 2019 study. The analyte list will include previously analyzed compounds (C12-14nEO_{n=3-15}, C16nEO_{n=3-15}, C12(Br)nEO_{n=3-15}, NPnEO_{n=3-15} and OPnEO_{n=3-15}) in addition to short-chain NPEO (nonylphenol, NP1EO, NP2EO) and short-chain OPEO (octylphenol, OP1EO, OP2EO).

This follow-up study supplements the previously funded study and includes collection of additional wastewater samples that will be analyzed using the updated analytical method. Additional wastewater samples are needed to refine measured concentrations of ethoxylated surfactants in wastewater effluent due to the significant range in the observed levels in the initial screening study. These additional samples are important to compare relative loads from wastewater versus stormwater runoff, which was initiated by prior studies. Additional stormwater samples are being collected and analyzed as part of the multi-year ECWG special study to screen CECs in stormwater.

Study Objectives and Applicable RMP Management Questions

Table 1. Study objectives and questions relevant to the 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?	<p>Compare ethoxylated surfactant occurrence data with toxicity information reported in the scientific literature.</p> <p>Evaluate future monitoring needs and toxicity data gaps.</p>	<p>What are the current concentrations of ethoxylated surfactants in Bay water and sediment?</p> <p>Which newly identified contaminants merit further monitoring?</p> <p>Do findings suggest ethoxylated surfactants should be classified as high, moderate, low, or possible concern within the RMP's tiered risk-based framework?</p>
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Investigate the influence of different pathways based on ethoxylated surfactant concentrations in wastewater effluent vs. stormwater, as well as patterns in ambient Bay sample locations (e.g., comparison of ambient water and sediment concentrations near stormwater vs. wastewater discharges).	How do concentrations in wastewater compare with urban stormwater runoff, and what does that suggest about relative loads?
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 ethoxylated surfactant profiles in pathways vs. ambient samples.	<p>Which ethoxylated surfactants appear persistent in the Bay?</p> <p>How do average ethoxymer chain lengths in ambient water compare with the wastewater and stormwater pathway?</p>
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	Compare ethoxylated surfactant concentrations with previous monitoring data for a limited number of analytes.	Have concentrations of nonylphenol and short-chain nonylphenol ethoxylates in the Bay increased or decreased from previous measurements?

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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

Additional wastewater samples (n = 13) will be collected and analyzed for ethoxylated surfactants to evaluate the representativeness of previously collected results. Previous wastewater samples from the 2019 special study included only one sample from eight participating facilities, and concentrations varied significantly. In this phase of the project, we propose collecting additional wastewater samples at Hayward, EBMUD, and EBDA. Data from the 2019 special study indicated the highest concentration of ethoxylated surfactants was from Hayward, which is hypothesized to be significantly influenced by a paint manufacturing facility within the sewershed. We suggest four additional effluent samples from Hayward to capture weekday variations. We also recommend collecting upstream influent discharged from the upstream paint manufacturer as well as combined influent at Hayward’s Wastewater Treatment Facility to evaluate the contribution of this specific source to Hayward’s wastewater influent. We also propose collecting two additional samples at EBMUD, which had the second highest level of ethoxylated surfactant. We propose two additional effluent samples from EBDA, which was not included in the 2019 special study and is the combined outfall for Hayward, Oro Loma Sanitary District, City of San Leandro, and Union Sanitary District, as well as the Livermore Amador Valley Water Management Agency.

All samples will be collected as 24-hour composites. Field blanks will be collected at each facility by pouring reagent water into empty sample containers. This sample collection method is consistent with the 2019 study.

Analysis

Wastewater samples will be analyzed using the recently updated method to capture the full suite of ethoxylated surfactants. The method uses a mixed-mode high performance liquid chromatography with electrospray mass spectrometry, modified from methods published previously (Ferguson et al., 2001) to include a broader range of ethoxylated surfactants in addition to the nonylphenol, octylphenol and the short-chain nonylphenol ethoxylates and octylphenol ethoxylates. Specifically, modifications to the method include changes to gradient conditions and mass spectrometer polarity switching in order to capture both ethoxylated surfactant adducts (positive mode) and alkylphenol compounds (negative ion), as well as optimization of mobile phase additives and ion source conditions to enable detection of the short-chain (1 & 2 EO) polyethoxymers. The required sample volume for final effluent is 1 L, while the required volume for an influent sample is 40 mL.

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The analyte list will include previously analyzed compounds (C12-14nEO_{n=3-15}, C16nEO_{n=3-15}, C12(Br)nEO_{n=3-15}, NPnEO_{n=3-15} and OPnEO_{n=3-15}) in addition to short-chain NPEO (nonylphenol, NP1EO, NP2EO) and short-chain OPEO (octylphenol, OP1EO, OP2EO). Analytes for each family will include compounds with a broad range of ethoxylate chains. Isotopically labeled standards are only available for a few of these analytes (i.e., short-chain NPEO); however, the uncertainty in precision associated with quantitation was deemed acceptable by the ECWG for screening purposes. The expected analytical method detection limits for analytes are expected to be at least in the 1-50 ng/L range for water. These detection limits are below reported effects concentration in water in the 1 µg/L range (Billinghurst et al., 1998). Water samples are analyzed as the dissolved fraction after filtration (0.45 µm GF/F).

Data Interpretation

The study results will provide additional data to understand the levels of ethoxylated surfactants in wastewater. Data from the initial screening study indicate that levels of ethoxylated surfactants in wastewater effluent are highly variable among facilities and may be strongly influenced by particular industries and/or treatment technology at the POTW.

Additional samples at Hayward and EBMUD will be used to refine estimates of concentrations in final effluent. Influent collected at Hayward's Wastewater Treatment Facility and directly from the paint manufacturer will be used to evaluate whether this operation contributes a significant amount of ethoxylated surfactants to Hayward's wastewater and the Bay.

All wastewater results will be used to compare relative loadings from the wastewater and stormwater pathways. This comparison will provide some insight as to whether management actions currently being implemented to address NPEOs in wastewater will have a measurable effect on Bay loadings, or whether additional management actions should be considered. Results will be compared to other regions.

Additionally, comparison of contaminant profiles in pathways versus ambient samples may indicate degradation or persistence of specific contaminants, particularly within an ethoxylate family. The full dataset will guide re-evaluation of this contaminant class, currently classified as Moderate Concern, and inform development of a monitoring strategy.

*Ethoxylated Surfactants in Wastewater, Part 2, Year 2 – ECWG 2022***Budget****Table 2.** Budget

Expense	Estimated Hours	Estimated Cost
<i>Labor</i>		
Project Management	15	2,000
Study Design and Sample Collection	45	6,000
Data Technical Services ¹	N/A	3,100
Analysis and Reporting ¹	45	6,000
<i>Subcontracts</i>		
Ferguson/Duke U.	N/A	11,200
<i>Direct Costs</i>		
Shipping		1,700
<i>Grand Total</i>		30,000

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. SFEI will provide sampling and shipping instructions.

Data Management Costs

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

This budget will supplement the data management budget allocated in the 2019 Ethoxylated Surfactants in Ambient Water, Margin Sediment, and Wastewater, and the 2022 Part 2 study. The additional budget will support managing data associated with additional wastewater samples.

¹This 2023 budget will supplement remaining Data Management and Analysis and Reporting budget allocated in the 2019 and 2022 special study proposal.

*Ethoxylated Surfactants in Wastewater, Part 2, Year 2 – ECWG 2022**Analysis and Reporting*

Results from the full dataset, including this proposal and the 2019 and 2022 special study projects, will be summarized in one draft and final technical report. Funds will also support other RMP publications as appropriate (e.g., CEC Strategy).

Subcontracts/Laboratory Costs

Estimated costs include an additional 17 effluent samples (\$600/sample, 13 field samples, 4 field blanks).

Direct Costs

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

Reporting

Deliverables will include: a) a draft and final report describing the results and their implications, due November 2024. This report would be combined with the reporting deliverable in the 2019 and 2022 ethoxylated surfactant special studies. Additional reporting may include other RMP publications such as the Pulse and CEC Strategy, as well as a draft manuscript led by Duke University.

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Special Study Proposal: PFAS and Nontargeted Analysis of Marine Mammal Tissues

Summary: A recent review of the RMP Status and Trends (S&T) study design led to the recommendation to explore the addition of Bay marine mammals like harbor seals to the species included in periodic S&T monitoring. To inform the potential inclusion of marine mammals to the S&T program, this two-year study proposal includes examination of PFAS in multiple tissues of two local species, harbor seals and harbor porpoises. Nontargeted analysis of PFAS and hydrophobic halogenated compounds is recommended to leverage the sample collection in this pilot study, providing a means to identify unanticipated contaminants that may merit follow-up targeted monitoring. Anticipated study outcomes would include recommendations for S&T monitoring of marine mammals, as well as priorities for future investigations of newly identified CECs observed in marine mammal tissues.

Estimated Cost: \$115,500 (year 1; \$126,500 year 2)
Oversight Group: ECWG
Proposed by: Ezra Miller and Rebecca Sutton (SFEI), Bernard Crimmins (AEACS, Clarkson University), Eunha Hoh (San Diego State University)
Time Sensitive: No

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Establish study design & sample collection protocol	January 2023
Task 2. Sample collection	2023-2024
Task 3. Target PFAS analysis	2023-2024
Task 4. Nontargeted analysis	2023-2024
Task 5. Draft manuscript(s), S&T study design recommendations (technical memo), presentation to TRC	June 2025
Task 6. Final manuscript(s)	September 2025

Background

Through special studies, the RMP has conducted periodic monitoring of CECs in Pacific harbor seals (*Phoca vitulina richardi*) in San Francisco Bay. These apex predators have relatively high site fidelity, such that contaminants observed in their tissues are likely derived from the local food web. Previous RMP investigations (Sedlak et al., 2007; Sedlak et al., 2017; Sedlak et al., 2018) have indicated that South Bay harbor seals are exposed to high levels of per- and polyfluorinated alkyl substances (PFAS), a broad class of fluorine-rich contaminants that are of elevated environmental concern because they are ubiquitous, extremely persistent, and several have been shown to be highly toxic and bioaccumulative. Temporal trends in harbor seal serum concentrations suggest declines in

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perfluorooctane sulfonate (PFOS) following phase-out in the US; however, perfluorooctanoic acid (PFOA) and other long-chain carboxylates have not shown similar declines (Sedlak et al., 2017).

The RMP recently convened a panel of stakeholders and experts to review the design of its Status and Trends (S&T) monitoring program. An outgrowth of this in-depth review was the suggestion to explore whether it would be appropriate to add harbor seals to the S&T study design, with PFAS monitoring of highest priority.

This proposal outlines a pilot study of marine mammal tissues that leverages existing recovery and sample collection efforts by the Marine Mammal Center (Sausalito, CA). To explore options and inform potential S&T monitoring design, we recommend pilot monitoring of two resident Bay species, Pacific harbor seals and harbor porpoises (*Phocoena phocoena*).

PFAS will be monitored in two tissues, serum and liver; improved analytical techniques will allow quantification of many more fluorinated compounds than previously available. Liver samples will also be examined for additional PFAS via nontargeted analysis; a recent study of marine mammal tissue collected across the northern hemisphere used nontargeted analysis to identify an additional 33 PFAS that have not been observed previously in marine mammals (Spaan et al., 2019).

In addition to PFAS, marine mammals tend to bioaccumulate hydrophobic and persistent chlorinated and brominated organic contaminants. The RMP funded a nontargeted analysis of San Francisco Bay seal blubber samples a decade ago, which identified chlorinated and brominated compounds including legacy pollutants and their metabolites and a few additional contaminants that had not been previously monitored (Sutton and Kucklick, 2015). Methods have improved significantly in recent years; an examination of additional blubber samples using improved methods is expected to reveal new insights. A recent nontargeted analysis of southern California marine mammal blubber samples identified several contaminants, including PCB metabolites, chlordane metabolites, and isomers of tris(4-chlorophenyl)methane, that would not have been observed by traditional targeted methods (Cossaboon et al., 2019).

Results may indicate the presence of PFAS and other contaminants accumulating in Bay wildlife that are not typically analyzed in targeted monitoring studies. Alternatively, should results reveal most compounds are already included in targeted monitoring studies, this will help confirm that current Bay monitoring sufficiently captures priority contaminants.

Study Objectives and Applicable RMP Management Questions

Table 1. Study objectives and questions relevant to the 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?	Evaluate target PFAS concentrations relative to tissue-specific ecotoxicity studies. Screen CECs identified via nontargeted analysis for potential toxicity concerns.	Are PFAS concentrations at or above levels associated with health impacts in mammals? Do any newly identified CECs merit follow-up targeted monitoring?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Evaluate chemical profiles for evidence of source types.	Do PFAS profiles suggest influence of any specific sources?
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?	Assess results of nontargeted analysis for the presence of unanticipated transformation products.	Do the results of nontargeted analysis indicate transformation of parent compounds into unanticipated contaminants with potential concerns for Bay wildlife?
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	Compare target PFAS concentrations in harbor seal serum to prior observations.	Do concentrations in harbor seal serum suggest temporal trends for any target PFAS relative to previous years' monitoring?
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	N/A	N/A
6) What are the effects of management actions?	N/A	N/A

Approach

Study Design

Tissues from ten harbor seals and ten harbor porpoises will be collected over approximately two years (2023-2024). Animals recovered from within San Francisco Bay will be the highest priority for analysis. However, to reach target sample size, we may also include animals found along the nearby coast (e.g., Half Moon Bay to Point Reyes).

This study will focus on harbor seal pups. The majority of the live harbor seals that the Marine Mammal Center receives for rehabilitation are pups, which arrive as early as February, with the peak usually in April. Until approximately mid-May, these animals are generally younger than weaning age. The pups will likely be too young to have eaten any prey items from San Francisco Bay, but will have bioaccumulated contaminants from their mother (although how much milk they received before rehabilitation cannot be determined). Previous studies on harbor seals showed higher concentrations of PFOS and perfluorodecanesulfonic acid (PFDS) in tissues of pups than (non-paired) adults, whereas concentrations of perfluorocarboxylic acids like PFOA were similar between pups and adults (Shaw et al., 2009), indicating fluorinated compounds are passed not just via milk but also via placental transfer. Pups that survive rehabilitation can be used for serum monitoring; pups that do not survive rehabilitation are suitable for monitoring of multiple tissues, including liver.

Porpoise samples will be obtained from stranded (recently deceased) animals recovered by the Marine Mammal Center all year round, with greatest numbers generally observed in the summer.

Liver samples will be collected for targeted and nontargeted PFAS analysis, serum samples will be collected for targeted PFAS analysis, and blubber samples will be collected for nontargeted analysis of hydrophobic halogenated contaminants. Results will be compared between tissues and species, and harbor seal serum results will be compared to prior RMP data to assess temporal trends. Contaminant profiles will also be compared to southern California pinniped and cetacean data to assess larger geographic trends. Nontargeted PFAS results will be used to determine if target PFAS analysis captures the majority of PFAS present.

Tissue Sampling

Studies of the tissue distribution of PFAS in harbor seals indicate the highest body burden in blood (38%) and liver (36%), with a relatively low burden (2%) in blubber (Ahrens et al., 2009). Similarly, harbor porpoise livers have the highest levels of PFAS compared with other tissues (Van de Vijver et al., 2007). To our knowledge, no literature exists comparing PFAS in blood serum vs. liver in porpoises.

Up to 60 g of liver and 40 g of blubber will each be sampled by the Marine Mammal Center from up to 10 harbor seals and 10 harbor porpoises. These tissues will be subsampled to send to multiple laboratories (see below). Blood samples will be collected from harbor seal pups while still alive, and from stranded (deceased) harbor porpoises; blood sample collection constraints reflect differences in

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biology and capture/rehabilitation limitations of the two species. Serum will be separated from whole blood by the Marine Mammal Center and used for analysis.

Serum from additional harbor seal pups (up to 10) who survive rehabilitation and were collected from within San Francisco Bay may also be collected and analyzed.

Analytical Methods

PFAS Targeted Analysis

For targeted quantification of PFAS (analytes listed in Table 2), liver tissue samples will be spiked with isotopically labeled surrogate standards, then extracted with methanolic potassium hydroxide solution, with acetonitrile, and finally with methanolic potassium hydroxide solution, each time collecting the supernatants. The supernatants are combined, treated with ultra pure carbon powder and evaporated to remove methanol. The resulting solution is diluted with water and cleaned up by solid phase extraction using weak anion exchange cartridges. The extracts will then be spiked with recovery standards, and analyzed by liquid chromatography/mass spectrometry (LC-MS/MS). Serum samples will be spiked with isotopically labeled surrogate standards and then extracted with 50% formic acid. The resulting solution will be cleaned up by solid phase extraction on a weak anion exchange sorbent. The eluent tubes will be spiked with recovery standards and then eluent collected and analyzed by LC-MS/MS.

Analysis of sample extracts will be performed on a UPLC-MS/MS (ultrahigh performance liquid chromatography) reversed phase C18 column using a solvent gradient. The column is coupled to a triple quadrupole mass spectrometer run at unit mass resolution in the Multiple Reaction Monitoring (MRM) mode, using negative electrospray ionization. Final sample concentrations are determined by isotope dilution/internal standard quantification. Each compound is determined as the total of linear and branched isomers where branched standards are available to confirm their retention time.

Table 2. Targeted PFAS analytes.

Perfluoroalkyl carboxylates	Perfluorobutanoic acid (PFBA) Perfluoropentanoic acid (PFPeA) Perfluorohexanoic acid (PFHxA) Perfluoroheptanoic acid (PFHpA) Perfluorooctanoic acid (PFOA) Perfluorononanoic acid (PFNA) Perfluorodecanoic acid (PFDA) Perfluoroundecanoic acid (PFUnA) Perfluorododecanoic acid (PFDoA) Perfluorotridecanoic acid (PFTrDA) Perfluorotetradecanoic acid (PFTeDA)
Perfluoroalkyl sulfonates	Perfluorobutanesulfonic acid (PFBS) Perfluoropentanesulfonic acid (PFPeS)

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	Perfluorohexanesulfonic acid (PFHxS) Perfluoroheptanesulfonic acid (PFHpS) Perfluorooctanesulfonic acid (PFOS) Perfluorononanesulfonic acid (PFNS) Perfluorodecanesulfonic acid (PFDS) Perfluorododecanesulfonic acid (PFDoS)
Fluorotelomer sulfonates	1H, 1H, 2H, 2H-perfluorohexane sulfonic acid (4:2 FTS) 1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (6:2 FTS) 1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2 FTS)
Fluorotelomer carboxylates	2H, 2H, 3H, 3H-perfluorohexanoic acid (3:3 FTCA) 2H, 2H, 3H, 3H-perfluorooctanoic acid (5:3 FTCA) 2H, 2H, 3H, 3H-perfluorodecanoic acid (7:3 FTCA)
Perfluorooctane sulfonamides	Perfluorooctanesulfonamide (PFOSA) N-Methylperfluorooctanesulfonamide (N-MeFOSA) N-Ethylperfluorooctanesulfonamide (N-EtFOSA)
Perfluorooctane sulfonamidoacetic acids	N-Methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA) N-Ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA)
Perfluorooctane sulfonamidoethanols	N-Methylperfluoro-1-octanesulfonamidoethanol (N-MeFOSE) N-Ethylperfluoro-1-octanesulfonamidoethanol (N-EtFOSE)
Ether carboxylates	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propionic acid (HFPO-DA) Decafluoro-3H-4,8-dioxanonoate (ADONA, DONA) Perfluoro-3,6-dioxaheptanoate (NFDHA) Perfluoro-3-methoxypropanoate (PFMPA) Perfluoro-4-methoxybutanoate (PFMBA)
Ether sulfonates	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (9Cl-PF3ONS) 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS) Perfluoro(2-ethoxyethane)sulfonic acid (PFEESA)

Nontargeted Analysis for Fluorinated Compounds

For nontargeted screening for PFAS (Crimmins lab; AEACS, Clarkson University) in liver homogenates will be processed in accordance with Crimmins et al. (2014) and Fakouri Baygi et al. (2021). Homogenates will be extracted using methods described in Point et al. (2019) and then analysed by ultra-high performance liquid chromatography-quadrupole time-of-flight mass spectrometry (UPLC-QToF) in electrospray ionization (ESI) mode. The instrument will be configured to operate in a data independent MS/MS mode, alternating between low and high energy channels to capture precursor and product ions for identification and confirmation of detected species. The data files will be analyzed using an algorithm developed in house to screen for halogenated acids including polyfluorinated acids (Fakouri Baygi et al., 2016; Fakouri Baygi et al.,

2021). The data reduction will consist of isolating species containing halogenated acid, ether, and sulfonate moieties.

Nontargeted Analysis for Non-Polar Compounds

Nontargeted screening for non-polar compounds will be performed on blubber by two laboratories. Cross-laboratory comparison of contaminant identifications using complementary methods and libraries of spectra will allow for broader determination of the presence of unanticipated, bioaccumulative contaminants in blubber samples.

In the Crimmins lab (AEACS, Clarkson University), DCM will be eluted through desiccated blubber homogenates followed by size exclusion chromatography for lipid removal (Fernando et al., 2018). Extracts will then be analyzed using a 2-dimensional gas chromatography equipped with a high-resolution time of flight mass spectrometer (GC×GC-HRT, LECO) in accordance with Fernando et al. (2018) and Renaguli et al. (2020). The GC×GC resolves the extract mixture into 1000's of individual components. The exact mass spectra of these components will be compared against a reference library containing over 500,000 chemicals to identify components in the tissues. Previously, this analysis has only been performed using electron impact ionization. The new system also has electron capture negative chemical ionization capabilities (ECNI). This mode selects for compounds that generate negative ions (halogenated components) and is traditionally used by low resolution instruments to quantify legacy halogenated chemicals (e.g., polybrominated diphenyl ethers). The new system is one of few available in the world that provides enhanced sensitivity of ECNI and 2-D chromatographic (GC×GC) and exact mass (30,000) resolution. The result will be a list of halogenated species for each tissue and concentration estimates using one or more representative reference standards. Compound identifications will be qualified by retention time, library matching, and spectral interpretation with exact mass accuracy (< 5 ppm).

In the Hoh lab (San Diego State University), blubber will be processed following protocols outlined by Cossaboon et al. (2019). Final extracts will be analyzed on a Pegasus 4D GC×GC/TOF-MS equipped with an Agilent 6890 gas chromatograph using instrument parameters optimized for marine mammal blubber by Hoh et al. (2012). Data will be processed using the LECO ChromaTOF mass spectrometer data system (version 4.51.6.0 optimized for Pegasus) and an automated data handling procedure. Briefly, custom data reduction software was developed based on the algorithm described by Pena-Abaurrea et al. (2014), which examined mass spectra for ion intensity ratios characteristic of halogenation. Additional rules and a cross-checking procedure are then applied to reduce the false positive rate. If the same mass spectrum is present in > 2 samples, the cross-checking procedure requires a manual search for the compound in the remaining samples.

The contaminant profiles for San Francisco Bay harbor seals and harbor porpoises will be compared to profiles acquired previously from southern California marine mammal blubber. All analyses were conducted with the same sample preparation and GC×GC/ TOF-MS methods. This includes the Shaul et al. (2014) and Mackintosh (2016) datasets consisting of 8 dead stranded common bottlenose dolphin (*Tursiops truncatus*) collected between 1995-2010 and the Cossaboon et al. (2019) dataset consisting of three cetacean species (n = 5 individuals each) and two pinniped species (n = 5

PEAS & NTA of Marine Mammal Tissues – ECWG 2022

individuals each) that were dead stranded or bycatch, collected between 1990-2014. The cetaceans were long-beaked common dolphin (*Delphinus delphis bairdii*), short-beaked common dolphin (*Delphinus delphis delphis*), and Risso's dolphin (*Grampus griseus*). The pinnipeds were California sea lion (*Zalophus californianus*) and Pacific harbor seal. Results from these three prior studies have been merged into a single dataset containing approximately 400 biomagnifying contaminants identified in the California marine environment.

Budget

Table 3. Budget

Expense	Estimated Hours	Estimated Total Cost	Year 1 Request
<i>Labor</i>			
Study Design	40	6,500	6,500
Sample Collection	48	7,400	4,000
Data Technical Services		14,000	4,000
Analysis and Reporting	180	30,000	10,000
<i>Subcontracts</i>			
AEACS, LLC		100,000	50,000
San Diego State University		50,000	25,000
SGS AXYS		22,080	11,000
<i>Direct Costs</i>			
Equipment		4,000	4,000
Travel		0	0
Shipping		8,020	5,000
<i>Grand Total</i>		242,000	115,500

Budget Justification

This proposal describes a two-year study with a total estimated budget of \$242,000. Options to significantly reduce the budget include eliminating all or some of the nontargeted analyses. Reducing the number of samples would result in only modest changes to the budget. Early release of funds would be beneficial to assure study design and sample collection protocols can be established prior to the arrival of the first pups at the Marine Mammal Center.

*PFAS & NTA of Marine Mammal Tissues – ECWG 2022**SFEI Labor*

Labor hours are estimated for SFEI staff to manage the project, develop the study design in collaboration with partners, support sample collection, analyze data, review toxicological risks, present findings, assist with manuscript development, and prepare a technical memo detailing study design recommendations for S&T monitoring.

Data Technical Services

Standard RMP data management procedures will be used for target PFAS data. These data will be uploaded to CEDEN.

Sample Collection

Costs are minimized by leveraging existing marine mammal recovery and sample collection activities of the Marine Mammal Center.

Laboratory Costs

For target PFAS analysis, SGS AXYS analytical costs are \$480 per sample. The analytical budget of \$22,080 includes analysis of blood and liver tissues from 20 specimens, one field duplicate for each species and tissue, and two standard reference tissues, for a total of 46 samples. If additional serum samples from live harbor seal pups are available during the sample period, an increase in this budget would be recommended.

The Crimmins Laboratory (AEACS, Clarkson University) can provide nontargeted analysis for PFAS on liver tissues and nonpolar halogenated compounds on blubber tissues for a total cost of \$100,000 (including 25% indirect rate). This budget includes both analysis and manuscript preparation.

The Hoh Laboratory (San Diego State University) can provide complementary nontargeted analysis of nonpolar halogenated compounds on blubber tissues for a total cost of \$50,000 (including 25% indirect rate). Liver tissues may also be analyzed, if appropriate. This budget includes both analysis and manuscript preparation.

Reporting

Deliverables will include: a) draft manuscript(s) that serve as RMP technical report(s) (draft for RMP review due June 2025, submission-ready draft¹ due September 2025); b) a technical memo describing S&T study design recommendations, due June 2025; and c) a presentation of study design recommendations to the TRC.

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

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Special Study Proposal: Mining Nontargeted Analysis Data for Additional Targets for Future Study

Summary: The RMP has invested resources in nontargeted analysis (NTA) of Bay matrices as a tool to inform follow-up targeted analysis and risk screening studies. At present, hundreds of contaminants have been tentatively identified in the Bay via NTA. Ongoing studies of tire-derived contaminants and ethoxylated surfactants are examples of RMP studies that are addressing the most readily identifiable and urgent science priorities arising from this analysis. However, the majority of the CECs observed via NTA have not been screened for information as to potential sources and/or ecological concerns. This proposal would fund a desktop exercise to compile data on sources and ecotoxicological information for a larger proportion of these contaminants, aiming to identify additional CECs that could be high priorities for further study in the Bay.

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Estimated Cost: \$45,000
 Oversight Group: ECWG
 Proposed by: Rebecca Sutton, Ezra Miller, Miguel Mendez (SFEI)
 Time Sensitive: No

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Develop spreadsheet structure, assemble available contaminant identifications, ancillary and metadata	May 2023
Task 2. Review available source and toxicity information	December 2023
Task 3. Presentation to ECWG on additional targets	April 2024
Task 4. Spreadsheet of compiled data mining results	July 2024

Background

Nontargeted analysis (NTA) is a powerful and rapidly evolving tool in environmental monitoring that allows scientists to screen samples for thousands of chemicals and identify new contaminants that would be missed by traditional targeted methods. Some of these unanticipated contaminants may merit follow-up targeted, quantitative analysis to inform evaluation of exposure and risk.

The RMP has invested in multiple studies using NTA to characterize Bay matrices, an important step to create an inventory of observed compounds (Sutton et al., 2017). A review of the contaminants tentatively identified in Bay water and wastewater via NTA (Overdahl et al., 2021) led to major follow-up studies to characterize ethoxylated surfactants in multiple matrices, and tire-derived contaminants in stormwater and Bay water.

While these efforts address the highest priority contaminants identified to date via NTA, hundreds more have been identified in the Bay but have not been screened to assess potential sources and ecological concerns. At the spring 2021 ECWG meeting, experts and stakeholders expressed a desire to explore existing contaminant identifications before conducting further exploratory NTA studies to maximize the utility of the information we have already obtained.

This proposal is a response to the ECWG request to more fully review available identifications of CECs with respect to potential sources and ecotoxicity concerns, in an effort to identify additional contaminants that may be appropriate for targeted, quantitative monitoring and evaluation via the RMP tiered risk-based framework.

Study Objectives and Applicable RMP Management Questions

Table 1. Study objectives and questions relevant to the 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?	Screen CECs identified in Bay matrices via nontargeted analysis for likely sources and potential toxicity concerns.	Are there additional CECs that merit follow-up targeted monitoring based on compiled information on sources and ecotoxicity concerns?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Screen CECs identified in pathways via nontargeted analysis for likely sources and potential toxicity concerns.	Are there additional CECs that merit follow-up targeted monitoring based on compiled information on sources and ecotoxicity concerns?
3) What are the physical, chemical, and biological	Assess results of nontargeted analysis for the presence of	Do the results of nontargeted analysis indicate

Data Mining – ECWG 2022

processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	unanticipated transformation products.	transformation of parent compounds into unanticipated contaminants with potential concerns for Bay wildlife?
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?	N/A	N/A
6) What are the effects of management actions?	N/A	N/A

ApproachAssembling Contaminant Spreadsheet

We will create a spreadsheet of CECs tentatively identified via NTA in samples of Bay water (at sites influenced by various pathways), wastewater (Overdahl et al., 2021), and South Bay ambient and margin sediment (studies ongoing). In collaboration with analytical partners, it may be possible to include limited pro bono stormwater NTA data (Ed Kolodziej, University of Washington), and identifications resulting from a preliminary retrospective NTA of previously analyzed Bay water and wastewater samples (Lee Ferguson, Duke University).

The spreadsheet will include relevant data concerning matrix type, sample location, and influential sources and pathways. These parameters and others can be used to sort and prioritize the CECs to be investigated.

Compiling Source and Ecotoxicity Information

The spreadsheet structure will include categories for recording source and ecotoxicity information and references. A variety of sources of information will be explored, depending on accessibility and efficiency. We will examine peer-reviewed literature, toxicity databases, government and NGO reports, and may also assess US patent information and publicly available industry publications. A minimum of 40 contaminants will be examined.

Budget

Table 2. Budget

Expense	Estimated Hours	Estimated Cost
<i>Labor</i>		
Study Design (spreadsheet structure)	40	6,500
Data Technical Services		0
Analysis and Reporting	260	38,500
<i>Subcontracts</i>		
None		0
<i>Direct Costs</i>		
Equipment		0
Travel		0
Shipping		0
<i>Grand Total</i>		45,000

Budget Justification

Labor

This is a desktop analysis, with funding intended to support SFEI staff conducting the literature review and spreadsheet development.

Reporting

Deliverables will include 1) a presentation to the ECWG, due April 2024, and 2) a spreadsheet of compiled information, due July 2024.

References

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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 and in wet season Bay water samples from 2021. As part of its Status and Trends (S&T) program, the RMP is undertaking 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 more fully the concentrations of tire and roadway contaminants in Bay water during the wet season. 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. Results will be shared with California Department of Toxic Substances Control's Safer Consumer Products Program, which seeks data to support its evaluation of tire chemical ingredients.

Estimated Cost: \$80,000 (\$40,000 Year 1; \$40,000 Year 2)
Oversight Group: ECWG
Proposed by: Kelly Moran and Rebecca Sutton (SFEI), Ed Kolodziej (University of Washington)
Time Sensitive: Yes, leverages S&T pilot wet season water monitoring (2023, 2024)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Update sampling plan	August – September 2022
Task 2. Field sampling – wet season Bay water samples	Fall 2022 – Spring 2024
Task 3. Lab analysis	Summer 2023-Summer 2024
Task 4. QA/QC, data management, and data upload	October 2024
Task 5. Presentation at ECWG	April 2025
Task 6. Draft short report	June 2025
Task 7. Final short report	September 2025

Background

A number of potentially toxic tire-derived contaminants have been observed in Bay Area stormwater, including the salmonid toxicant, 6PPD-quinone, derived from an ubiquitously used tire preservative chemical (Tian et al. 2021; Brinkmann et al. 2022). Four of nine Bay Area stormwater samples collected in WY2019 contained levels of 6PPD-quinone that exceeded the LC₅₀, 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,

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steelhead (*Oncorhynchus mykiss*), a threatened species, are observed in some streams (e.g., Guadalupe River, Alameda Creek), and are also similarly susceptible to toxic effects from this contaminant at concentrations somewhat higher than coho (Brinkmann et al. 2022). 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 (PNECs) 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 contaminants in stormwater (Hou et al. 2019).

To inform Status and Trends (S&T) sampling design, the RMP is piloting wet season water sampling to measure Bay 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 (as defined in the RMP tiered, risk-based framework for emerging contaminants) 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. Prior to 2021, wet season water sampling had not been conducted by the RMP since 2010 and sites were restricted to deep channel stations far from stormwater inputs.

Tire-derived contaminants have only been monitored in Bay water during fall 2021, in the first year of the pilot S&T wet season monitoring. These limited data, which have not been through quality assurance review, suggest that these contaminants appear in the Bay in the wet season and potentially persist for many days after a storm event. Dry season sampling (a single cruise) did not detect 6PPD-quinone and detected only traces (< 20 ng/L) of the other tire-derived contaminants. These chemicals have not yet been classified within the RMP tiered, risk-based framework for emerging contaminants (Sutton et al. 2017). To build on previous RMP stormwater monitoring and to more fully understand the occurrence of tire contaminants in the Bay, we propose a follow-up study to continue to leverage the second and third years of the pilot S&T wet season monitoring effort to evaluate concentrations of tire-derived compounds in Bay water. Due to the low concentrations measured in the 2021 dry season, this project would not include any additional dry season monitoring for tire-related contaminants.

Results will inform the classification of these contaminants within the tiered, risk-based framework, and will be shared with California Department of Toxic Substances Control's (DTSC) Safer Consumer Products Program, which seeks data to support its evaluation of tire chemical ingredients, and indicate whether further information is needed to assist water quality management decision-making. Should one or more of these contaminants be classified as Moderate Concern for the Bay, it may be appropriate to continue wet season monitoring via S&T activities. Because this project addresses a group of chemicals uniquely

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present in urban stormwater, these data will also inform RMP watershed-to-Bay modeling projects currently underway.

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 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 stormwater.	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?	Monitor tire-derived contaminants and other stormwater-associated CECs in Bay water.	Establish a baseline for future trend analysis.
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 S&T water monitoring design was updated in 2022 to include wet season monitoring to measure concentrations of urban runoff-associated CECs in the Bay when the stormwater pathway is active. This project will involve collection of additional water samples in conjunction with the planned S&T monitoring.

All samples will be whole, unfiltered water collected using a stainless steel bailer, consistent with the fall 2021 Bay wet season water sample collection effort.

Samples will be collected at three in-Bay stations near stormwater inputs (two storm events) plus one station near wastewater input (for contrast, one storm only) shortly following appropriately-sized storms, including the first flush if possible (Figure 1). In total, during each of the two wet seasons, we anticipate collecting a total of seven samples from the near-field pathway sites, not including field blanks and duplicates. 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 four or five ambient stations (one Central Bay, two South Bay, and one — or two if accessible — Lower South Bay) within three weeks of one of the same storms sampled at the near-field locations. In total, during each of the two wet seasons, we anticipate collecting a total of four or five samples from the ambient sites, not including field blanks and duplicates.

QA/QC samples collected will include at least two field duplicates and two field blanks. Samples will be shipped overnight to Dr. Kolodziej at the University of Washington for LC/MS/MS analysis.

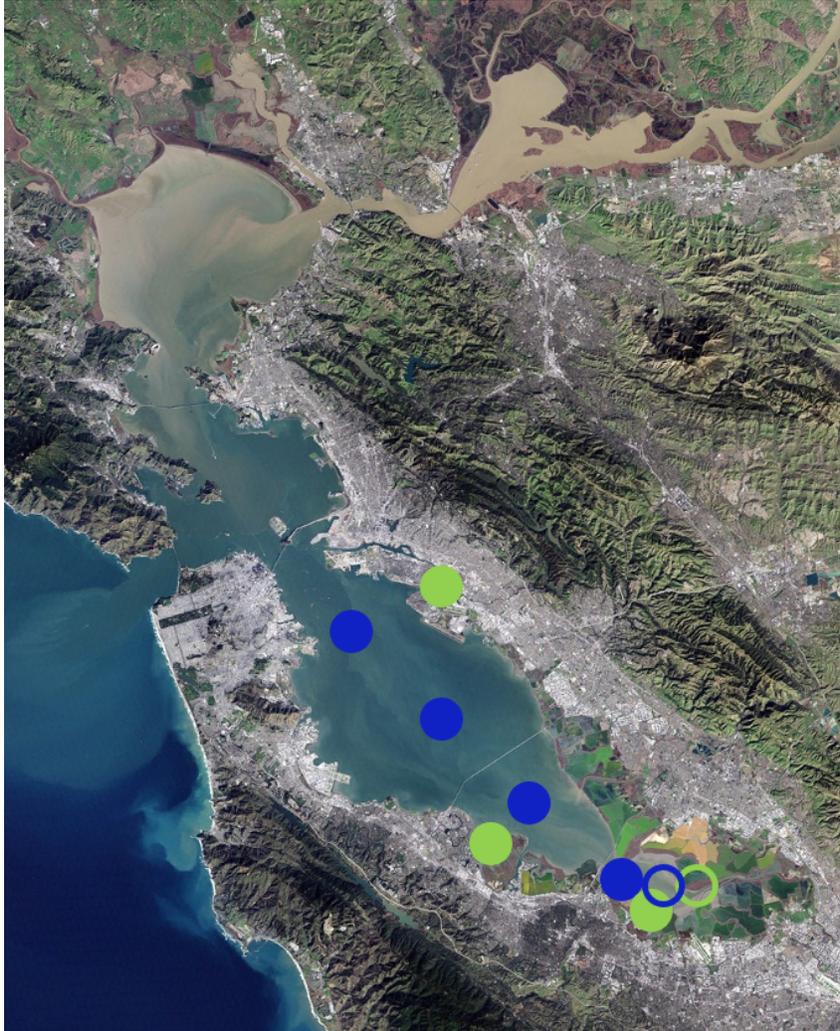
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Figure 1. Proposed site selection for pilot wet season Status and Trends monitoring effort, WY 2023 and 2024. Blue circles identify ambient Bay sites; green circles identify near-field sites (near San Leandro Creek, Redwood Creek, Stevens Creek, and Coyote Creek). Open circles indicate sites proposed for sampling that could not be sampled in fall 2021.

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.

Budget

Table 2. Proposed Budget

Expense	Estimated Hours	Estimated Cost
<i>Labor</i>		
Study Design and coordination (details for this project)	50	8,500
Sample Collection (additional costs for this project)	50	7,000
Data Technical Services	70	10,000
Analysis and Reporting	130	25,000
<i>Subcontracts</i>		
Univ. Washington		20,000
<i>Direct Costs</i>		
Equipment		2000
Shipping		7500
<i>Grand Total</i>		80,000

Alternatives

To best meet DTSC's needs, a stand-alone short report or manuscript is preferred. The budget above reflects the most expensive option, the stand-alone short report. The report would summarize the data, compare results to relevant toxicity thresholds, provide qualitative data interpretation, and make recommendations regarding future related monitoring. If the University of Washington obtains non-RMP funding for related projects (e.g., monitoring of these chemicals in other estuaries), it could combine the data from this study and its interpretation into a larger paper, which would result in a cost savings of about \$5,000.

Alternatively, the data interpretation could be combined into the biennial RMP CECs strategy update anticipated in 2025. This option would include more limited data analysis, focusing only on the placement of the monitored chemicals in the RMP's tiered, risk-based framework and recommendations regarding future related monitoring. This option would also result in a cost savings of about \$5,000 as compared to the proposed budget.

Budget Justification

SFEI Labor

Labor hours are estimated for SFEI staff to manage the project, develop the study design details, support sample collection including shipping and coordination with the laboratory, review relevant literature, analyze and interpret data, present findings, and prepare a short stand-alone report.

*Tire and Roadway CECs in Bay Water – ECWG 2022 Draft**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 S&T 2023 and 2024 pilot wet season Bay water monitoring efforts.

Laboratory Costs (Ed Kolodziej, University of Washington)

Analysis of samples and associated QA/QC as well as assistance with data interpretation are included in a subcontract for \$20,000.

Reporting

Results will be presented to the ECWG at the spring 2025 meeting; data will be incorporated into a short report summarizing the data, evaluating the placement of tire-related chemicals into the CECs tiered, risk-based framework, and providing recommendations regarding future monitoring of tire chemicals. The short report will be reviewed by the ECWG, TRC, and SC. Comments will be incorporated into the final short report, due 9/30/25.

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Special Study Proposal: PFAS in Archived Sport Fish

Summary: California state agencies are prioritizing efforts to characterize existing PFAS contamination in our state and the associated ecological and human health risks. Locally, a virtual forum on PFAS in San Francisco Bay fish in February drew over 250 participants into a discussion about the risks this contamination may pose to fishing communities, including tribal members and residents in disadvantaged African American neighborhoods like Bayview Hunters Point in San Francisco and Bayo Vista in Rodeo. While RMP monitoring has provided some of the only data on PFAS in sport fish in California, samples analyzed to date are insufficient to determine PFAS status and trends in different species in the Bay. We propose analyzing archived sport fish samples to fill data gaps and enhance the RMP Status and Trends (S&T) study design to support evaluation of temporal trends.

Estimated Cost: \$72,500
Oversight Group: ECWG, Sport Fish Strategy
Proposed by: Miguel Mendez, Ezra Miller, Martin Trinh, Jay Davis, Rebecca Sutton (SFEL)
Time Sensitive: No

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Study design	Jan 2023
Task 2. Ship archived samples to analytical laboratory	Feb 2023
Task 3. PFAS analysis	Spring 2023
Task 4. Data QA review	July 2023
Task 5. Draft report	Fall 2023
Task 6. Final report	Winter 2023

Background

Per- and polyfluoroalkyl substances (PFAS) have become a major priority for multiple California agencies, including the State and Regional Water Boards, the Department of Toxic Substances Control, and the Office of Environmental Health Hazard Assessment. This class of emerging contaminants is generally considered persistent and toxic, and many individual substances are also bioaccumulative.

Specific human health concerns relating to consumption of contaminated fish were discussed at a recent virtual forum organized by San Francisco Estuary Institute, Clean Water Action, and the California Indian Environmental Alliance.¹ Speakers and participants included tribal members and community leaders from disadvantaged African American communities around the Bay, alongside representatives from state agencies, scientific institutions, and stakeholder groups. The forum demonstrated the dietary, cultural, and spiritual significance of fish and fishing in the region, and the need for additional data on PFAS in sport fish from the Bay. A more comprehensive dataset would inform our understanding of risks to human health and would improve current and future assessments of geographic and temporal trends. For more information on the forum, visit: <https://www.sfei.org/projects/PFASBayFish>

The RMP has a robust sport fish status and trends monitoring program designed to assess levels of legacy contaminants, such as PCBs and mercury; a limited amount of PFAS analysis began in 2009. The most recent round of PFAS sampling occurred in 2019 at six sites across the Bay (Suisun Bay, Central Bay, Oakland Harbor, Redwood City Harbor, Coyote Creek, and Artesian Slough), and included samples of five species (largemouth bass, striped bass, shiner surfperch, white sturgeon, and white croaker; Buzby et al., 2021), but only 16 samples in total were analyzed (Figure 1). PFAS were observed in 14 of the 16 samples, with largemouth bass and striped bass showing the highest average concentrations of PFOS (9 and 7.5 ppb wet weight, respectively), followed by shiner surfperch (3.8 ppb wet weight). The few samples analyzed so far indicate higher levels in the South Bay, as observed in other biota (Sedlak et al., 2018). The long-term dataset is relatively limited, but suggests that PFAS are persisting in fish in the Bay. The RMP's next steps are expected to include expanded PFAS monitoring in the next scheduled round of sampling in 2024, involving monitoring of more species at more sites across the Bay, to create a dataset similar in scope to those for mercury and PCBs. The data from this proposed study will improve our understanding of PFAS occurrence in Bay sport fish and inform S&T study design for 2024 and beyond.

¹ Funding for the virtual forum was provided by the Gordon and Betty Moore Foundation, the Rose Foundation for Communities and the Environment, and the Satterberg Foundation; additional assistance was provided by the Green Science Policy Institute and the Water Foundation.

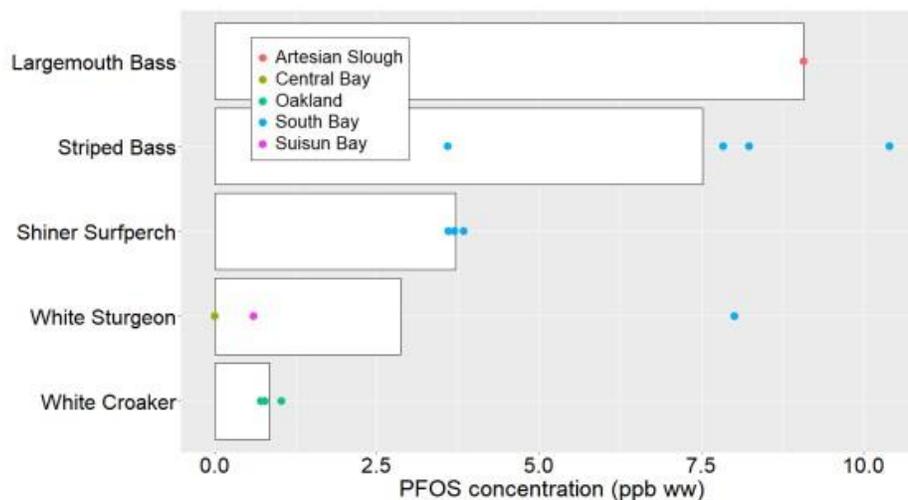


Figure 1. PFOS Concentrations (ppb ww) in San Francisco Bay, 2019. Bars indicate average concentrations. Points represent individual or composite samples. Points are colored by sampling location.

Study Objectives and Applicable RMP Management Questions

Table 1. Study objectives and questions relevant to the 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?	Evaluate PFAS concentrations relative to available fish consumption advisory tissue levels (e.g., from other states).	Are PFAS concentrations at or above levels potentially associated with increased human health risks for those who eat fish from the Bay?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Evaluate spatial patterns of PFAS contamination.	Spatial patterns may indicate areas, at a regional or local scale, that have elevated concentrations that relate to inputs 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 in the Bay?	Compare PFAS levels observed in 2014 and 2019 to begin to establish temporal trends.	Are available data suggestive of temporal trends for any PFAS?
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	N/A	N/A

6) What are the effects of management actions?	Evaluate PFAS concentrations observed in 2014 and 2019 in light of the phase-out of PFOS and long-chain carboxylates.	Do concentrations of PFAS phased out of production suggest declines from 2014 to 2019? Are there observations of any PFAS considered regrettable substitutions in fish tissue?
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Approach

Study Design

Archived tissue samples from fish with the highest concentrations of PFAS previously detected—largemouth bass, striped bass, and shiner surfperch—collected during the 2009, 2014, and 2019 S&T sport fish monitoring efforts will be used for analysis. Dissection and compositing of tissue samples for largemouth and striped bass were performed following method MP5L-105 with fish dissected with skin-off, and only the fillet muscle tissue used for analysis. Shiner surfperch are too small to be filleted; instead they were processed whole but with head, tail, and viscera removed. Fish samples were archived as either individuals (bass) or composites (surfperch). Composites were created by combining equally-weighted aliquots from each fish, typically from the same sampling location and size class, and homogenizing these aliquots into a single composite, using methods established during previous RMP fish sampling events (SFEI 2015; Davis et al. 1999).

Previous RMP studies have indicated elevated PFAS levels in the South Bay, which will be the primary focus of this study. Figure 2 shows the sport fish monitoring stations sampled in 2019. Artesian Slough is of particular interest as it is near a major wastewater outfall and has consistently shown the highest concentrations across the years of RMP study. Five samples (including two duplicates; 2019) of largemouth bass and three samples (2014) of striped bass from Artesian Slough will be analyzed via the targeted PFAS method. In addition, seven samples (3 from 2014, 4 from 2019 including a duplicate) of shiner surfperch from the South Bay (Redwood Creek) site will also be examined using the target method. Results will be added and compared to prior RMP data to elucidate any temporal trends for different species in the South Bay.

There is also an opportunity to further examine sport fish samples in Central and North Bay sites to more fully understand the prevalence of PFAS throughout the Bay. Though previous RMP monitoring has shown lower concentrations in these regions, there have been fewer samples examined overall when compared to South Bay. The recent virtual forum on PFAS in SF Bay Fish also highlighted the concern of local fishing communities, many in the Central and North Bay, and the risks of contamination to already disadvantaged communities. This study would examine 14 samples of striped bass from five Central and North Bay sites sampled in 2009 and/or 2014. Further, 26 samples of shiner surfperch from seven different sites (including three field duplicates) spanning 2014 and 2019 sampling efforts will be examined to better understand and identify the spatial extent of potential PFAS concerns. Overall, this project will help us add significantly to the current available sport fish data and better understand the presence of PFAS throughout the Bay.

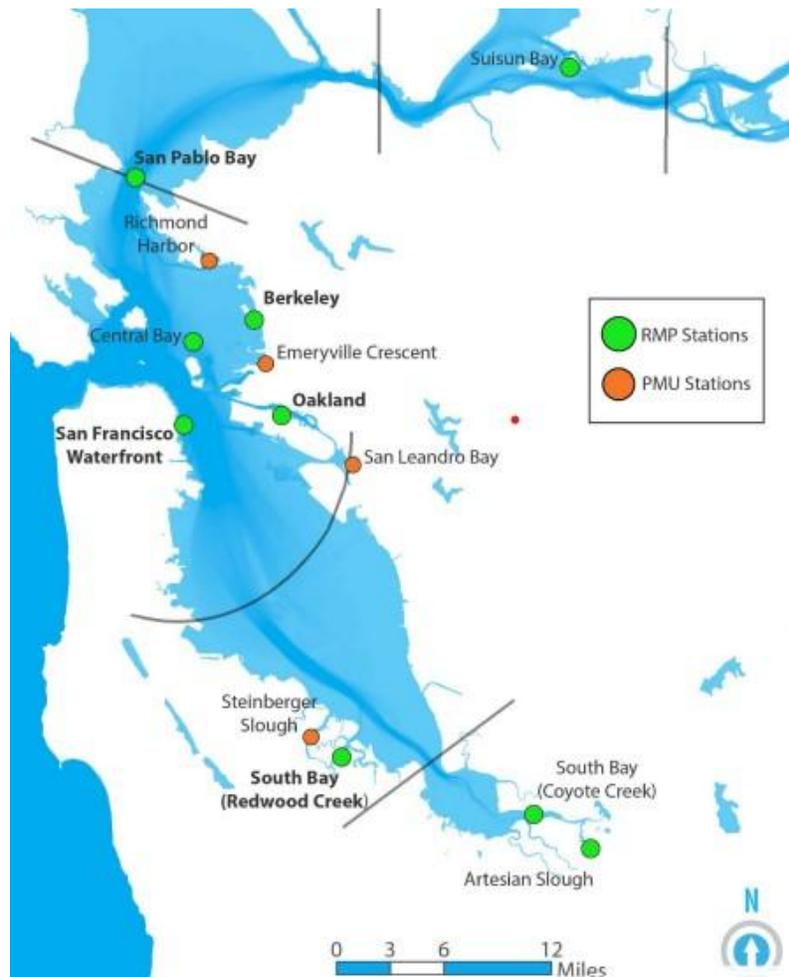


Figure 2. Locations of samples for San Francisco Bay fish, 2019. Green dots indicate historical RMP sampling locations; orange dots denote Priority Margin Unit (PMU) locations that were sampled as part of an RMP special study. Artesian Slough includes a freshwater area above a weir. Berkeley, San Francisco Waterfront, Oakland, San Pablo Bay, and South Bay (Redwood Creek) are historical stations that have been consistently sampled since 1994.

Analytical Methods

PFAS Targeted Analysis

For targeted quantification of PFAS (Table 2), sport fish tissue samples will be spiked with isotopically labeled surrogate standards, then extracted with methanolic potassium hydroxide solution, with acetonitrile, and finally with methanolic potassium hydroxide solution, each time collecting the supernatants. The supernatants are combined, treated with ultra pure carbon powder and evaporated to remove methanol. The resulting solution is diluted with water and cleaned up by solid phase extraction using weak anion exchange cartridges. The extracts will then be spiked with recovery standards, and analyzed by liquid chromatography/mass spectrometry (LC-MS/MS).

Analysis of sample extracts will be performed on a UPLC-MS/MS (ultrahigh performance liquid chromatography) reversed phase C18 column using a solvent gradient. The column is coupled to a triple quadrupole mass spectrometer run at unit mass resolution in the Multiple Reaction Monitoring (MRM) mode, using negative electrospray ionization. Final sample concentrations are determined by isotope dilution/internal standard quantification. Each compound is determined as the total of linear and branched isomers where branched standards are available to confirm their retention time.

Table 2. Targeted PFAS analytes.

Perfluoroalkyl carboxylates	Perfluorobutanoic acid (PFBA) Perfluoropentanoic acid (PFPeA) Perfluorohexanoic acid (PFHxA) Perfluoroheptanoic acid (PFHpA) Perfluorooctanoic acid (PFOA) Perfluorononanoic acid (PFNA) Perfluorodecanoic acid (PFDA) Perfluoroundecanoic acid (PFUnA) Perfluorododecanoic acid (PFDoA) Perfluorotridecanoic acid (PFTrDA) Perfluorotetradecanoic acid (PFTeDA)
Perfluoroalkyl sulfonates	Perfluorobutanesulfonic acid (PFBS) Perfluoropentanesulfonic acid (PFPeS) Perfluorohexanesulfonic acid (PFHxS) Perfluoroheptanesulfonic acid (PFHpS) Perfluorooctanesulfonic acid (PFOS) Perfluorononanesulfonic acid (PFNS) Perfluorodecanesulfonic acid (PFDS) Perfluorododecanesulfonic acid (PFDoS)
Fluorotelomer sulfonates	1H, 1H, 2H, 2H-perfluorohexane sulfonic acid (4:2 FTS) 1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (6:2 FTS) 1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2 FTS)
Fluorotelomer carboxylates	2H, 2H, 3H, 3H-perfluorohexanoic acid (3:3 FTCA) 2H, 2H, 3H, 3H-perfluorooctanoic acid (5:3 FTCA) 2H, 2H, 3H, 3H-perfluorodecanoic acid (7:3 FTCA)
Perfluorooctane sulfonamides	Perfluorooctanesulfonamide (PFOSA) N-Methylperfluorooctanesulfonamide (N-MeFOSA) N-Ethylperfluorooctanesulfonamide (N-EtFOSA)
Perfluorooctane sulfonamidoacetic acids	N-Methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA) N-Ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA)

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Perfluorooctane sulfonamidoethanols	N-Methylperfluoro-1-octanesulfonamidoethanol (N-MeFOSE) N-Ethylperfluoro-1-octanesulfonamidoethanol (N-EtFOSE)
Ether carboxylates	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propionic acid (HFPO-DA) Decafluoro-3H-4,8-dioxanonoate (ADONA, DONA) Perfluoro-3,6-dioxaheptanoate (NFDHA) Perfluoro-3-methoxypropanoate (PFMPA) Perfluoro-4-methoxybutanoate (PFMBA)
Ether sulfonates	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (9Cl-PF3ONS) 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS) Perfluoro(2-ethoxyethane)sulfonic acid (PFEESA)

Budget

Table 3. Budget

Expense	Estimated Hours	Estimated Cost
<i>Labor</i>		
Study Design, Stakeholder Engagement	20	3,000
Sample Retrieval	14	1,700
Data Technical Services		10,500
Analysis and Reporting	180	26,100
<i>Subcontracts</i>		
SGS AXYS		28,800
<i>Direct Costs</i>		
Materials		150
Travel		250
Shipping		2,000
<i>Grand Total</i>		72,500

Budget Justification

The project budget can be reduced by limiting the number of samples analyzed, reducing analytical costs and limiting the types of trends (geographic and temporal) that can be examined and reported.

*PFAS in Archived Sport Fish – ECWG 2022**SFEI Labor*

Labor hours are estimated for SFEI staff to manage the project, develop the study design, retrieve the samples from the short-term archive, ship the samples, analyze data, review toxicological risks, present findings, prepare a technical report on the findings and recommendations for S&T monitoring, and preparation of a manuscript.

Data Technical Services

Standard RMP data management procedures will be used and data will be uploaded to CEDEN. Additional funds are included to explore data handling options relevant to comparison of new analyses with the original 2014 and 2009 PFAS data, developed using a method with fewer analytes and higher detection limits.

Sample Collection

Archived samples will be used to minimize costs.

Laboratory Costs

SGS AXYS analytical costs are \$480 per sample for targeted PFAS analysis. The analytical budget of \$28,800 includes analysis of a total of 60 samples, including field samples, field duplicates, and standard reference tissues.

Reporting

The deliverable will consist of a report (draft due Fall 2023, final due Winter 2023) that includes the data, interpretation of spatial patterns and temporal trends, and recommendations relevant to future RMP Status and Trends sport fish sample collection. This could also include a manuscript for publication.

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