RMP Emerging Contaminants Workgroup Meeting

April 19-20, 2023
9:00 AM – 3:00 PM

Hybrid Meeting

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https://us06web.zoom.us/j/85241812574

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DAY 1 AGENDA - April 19th

1.	**Introductions and Goals for This Meeting** The goals for this meeting: • Provide updates on recent and ongoing ECWG activities (today & tomorrow) • Discuss CEC Strategy Revision and future direction of the program (today) • Review Status and Trends monitoring data (today) • Discuss ongoing stormwater CECs projects; joint meeting with the Sources, Pathways, and Loadings Workgroup (tomorrow) • Recommend which special study proposals should be funded in 2024 and provide advice to enhance those proposals (tomorrow) Meeting materials: Guidelines for Inclusive Conversations, page 8 2022 ECWG Meeting Summary, pages 9-28	9:00 Amy Kleckner

2.	**Information: RMP CECs Science Update** The ECWG science lead will present a brief update on current CECs activities and an overview of the RMP workgroup structure. Desired Outcome: Informed Workgroup	9:15 Rebecca Sutton
3.	**Discussion: CEC Strategy Revision** The workgroup will review and discuss the suggested implementation of last year's guidance concerning ECWG management questions and the tiered risk-based framework, as well as other recommended changes to the CEC Strategy. Specific topics for discussion include: ● Reactions to refined management question regarding temporal trends (10 min) ● Discussion of potential elevation of pathways focus through inclusion as a specific element within the overall strategy (20 min) ● Review of ecotoxicology and human health approach (20 min) ● Review of tiered risk-based framework and monitoring and management recommendations (20 min) ● Discussion of non-detect data handling options (30 min) ● Feedback on appropriate level of information to provide for each class of CECs (20 min) ● Discussion of multi-year plan, including plans for future (20 min) Meeting materials: Draft sections of CEC Strategy Revision document Desired Outcome: Feedback on strategy elements and tiered risk-based framework refinements, desired level of information on emerging contaminant classes	9:45 Rebecca Sutton, Ezra Miller
	Short Break	10:30
3.	**Discussion: CEC Strategy Revision (cont.)** See description above.	10:45 Rebecca Sutton
	Lunch	12:00
4.	**Information: Update on PFAS Sewershed Source Investigations** The workgroup will hear an update on preliminary results from a BACWA funded study to investigate PFAS sources to wastewater. As part of this Phase 2 effort, POTW study participants collected sewershed samples from diverse residential communities, and various industries including industrial laundry, electronics manufacturing, hospitals, and car wash facilities. Sewershed samples were analyzed using targeted PFAS and total oxidizable precursor analyses. Desired Outcome: Informed Workgroup	12:40 Diana Lin, Miguel Mendez

5.	**Information: Update on PFAS in Bay Fish** The workgroup will review updated data on PFAS in San Francisco Bay sport fish. This study examined over 50 archived samples from four fish species collected at 10 locations in three sampling rounds in 2009, 2014, and 2019. The expanded breadth of available data from this study provides the means for a more comprehensive assessment of spatial variation in PFAS in Bay fish, and a robust baseline for evaluating long-term trends. Findings will further inform PFAS management actions to protect the health of humans and aquatic life. These results will be presented at SETAC Europe in May 2023 and will be converted into a manuscript for journal publication. Desired Outcome: Informed Workgroup	1:20 Miguel Mendez
6.	**Information: Quaternary Ammonium Compounds (QACs) Update** The workgroup will hear an update with recent findings on QACs in wastewater. QACs have broad uses including as antimicrobial active ingredients in cleaning products, with increased use observed due to the pandemic. The scope of this QACs monitoring project has significantly expanded thanks to Dr. Arnold's National Science Foundation grant to support study of QACs in wastewater in Minnesota and the Bay Area. Desired Outcome: Informed Workgroup	1:40 Bill Arnold, Anna Mahony (UMinn)
	Short Break	2:00
7.	**Information: In-Bay Fate Modeling** The workgroup will learn about progress on a 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. Desired Outcome: Informed Workgroup	2:15 Jay Davis
8.	**Discussion: Integrated Watershed-Bay Modeling Strategy and Pilot Study** The project team will provide an update on this project to inform a brief discussion of the priority ECWG management questions that modeling could help answer. Desired Outcome: Feedback on priority ECWG management questions, potential modeling applications	2:30 Tan Zi
9.	**Information: Setting the Stage for Day 2** The workgroup will briefly review goals for tomorrow.	2:55 Rebecca Sutton
	Adjourn	3:00

DAY 2 (part 1) AGENDA - April 20th - 9am to noon

Joint Meeting of
Emerging Contaminants Workgroup &
Sources, Pathways, and Loadings Workgroup

Hybrid Meeting

REMOTE ACCESS
https://us06web.zoom.us/j/89729866795

Meeting ID: 897 2986 6795

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10.	**Summary of Yesterday and Goals for Today** The goals for today's meeting: • Brief recap of yesterday's ECWG discussions and outcomes • MORNING: Discuss ongoing stormwater CECs projects; this is a joint meeting of the Emerging Contaminants and Sources, Pathways, and Loadings Workgroups (ECWG & SPLWG) • AFTERNOON: Recommend which ECWG special study proposals should be funded in 2024 and provide advice to enhance those proposals; ECWG meeting	9:00 Amy Kleckner
11.	**Information: Stormwater CECs Screening Study Findings** We have completed sample collection and chemical analysis associated with our multi-year study to screen urban stormwater for occurrence of five classes of CECs: PFAS, bisphenols, organophosphate esters, ethoxylated surfactants, and a suite of stormwater CECs that includes tire-derived ingredients. We are now collaborating with University of Washington scientists Ed Kolodziej and Kathy Peter on data interpretation and manuscript preparation. In this agenda item, we will review high level findings to inform future RMP stormwater CECs monitoring and modeling activities. Desired Outcome: Informed Workgroup	9:15 Rebecca Sutton
	Short Break	10:15

12.	**Discussion: Stormwater Groundwork Management Level Review** This agenda item will cover: ● Review of the management drivers, timelines, and information needs related to CECs in stormwater ● Review guidance on the five-year planning budget for Stormwater CECs integrated modeling and monitoring work ● Discussion of near-term priority management questions for CECs in stormwater Meeting materials: Near-term priority management questions Desired Outcome: Consensus on near-term priority management questions	10:30 Kelly Moran
13.	**Information: Stormwater Groundwork Project Update** This agenda item will cover: ● Overview of project elements ● Update on the progress of modeling relevant projects ● Update on the sampling locations database ● Update on remote sampler development Desired Outcome: Informed Workgroup	11:10 Kelly Moran, Tan Zi, Alicia Gilbreath, Don Yee
	Lunch	12:00

DAY 2 (part 2) AGENDA - April 20th - 12:30 to 3pm

Emerging Contaminants Workgroup
Proposal Review and Prioritization

Hybrid Meeting

REMOTE ACCESS (same as previous)
https://us06web.zoom.us/j/89729866795

<table>
<tr><td>14.</td><td>Summary of Proposed ECWG Special Studies for 2024

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.

2024 RMP ECWG Special Study Proposals include:

● Stormwater CECs Monitoring & Modeling - $300,000
● PFAS Synthesis & Strategy - $107,000
● PFAS and NTA of Marine Mammal Tissues (year 2) - $126,500
● PFAS in Bay Water and Sediment using the TOP Assay - Three options, $97,700, $67,200, $27,200
● Tire Contaminants in Bay Water (year 3) - $50,000
● OPEs, Bisphenols, and Other Plastic Additives in Wastewater - Two options, $95,400, $48,400
● NTA of Bay Fish (year 1) - $48,000

Special Study Proposals for other workgroups that are relevant to ECWG include:

● Remote sampler purchase (SPLWG)
● In-Bay contaminant modeling (PCBWG)

Meeting materials: 2024 Special Studies Proposals, pages 29-93</td><td>12:30
Rebecca Sutton, Alicia Gilbreath, Diana Lin, Ezra Miller, Kelly Moran, Miguel Mendez, Tan Zi</td></tr>
<tr><td>15.</td><td>Discussion of Recommended Studies for 2024 - General Q&A, Prioritization

The workgroup will discuss and ask questions about the proposals presented. The goal is to gather feedback on the merits of each proposal and how they can be improved.

The workgroup will then consider the studies as a group, ask questions of the Principal Investigators, and begin the process of prioritization by stakeholders.</td><td>1:15
Amy Kleckner</td></tr>
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16.	**Closed Session - Decision: Recommendations for 2024 Special Studies Funding** RMP Special Studies are identified and funded through a three-step process. Workgroups recommend studies for funding to the Technical Review Committee (TRC). The TRC weighs input from all the workgroups and then recommends a slate of studies to the Steering Committee (SC). The SC makes the final funding decision. For this agenda item, the ECWG is expected to decide (by consensus) on a prioritized list of studies to recommend to the TRC. To avoid an actual or perceived conflict of interest, the Principal Investigators for proposed special studies are expected to leave the meeting during this agenda item. Desired Outcome: Recommendations from the ECWG to the TRC regarding which special studies should be funded in 2024 and their order of priority.	2:10 Eric Dunlavey
17.	**Report Out on Recommendations**	2:50 Eric Dunlavey
	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 Amy Kleckner (amyk@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 Agreements[1]

- 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 11-12, 2022
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

Adam Wong (SFEI)
Alicia Gilbreath (SFEI)
Allie King (SFEI)
Anna Mahony (U. of Minnesota)
Anne-Cooper Doherty (DTSC)
Bernard Crimmins (Clarkson University)
Blake Brown (CCCSD)
Bonnie de Berry (EOA/SCVURPPP/BASMAA)
Bridgette DeShields (Integral Consulting Inc.)
Coreen Hamilton (SGS AXYS)
David Robertson (City of San Jose)
Diana Lin (SFEI)
Don Gray (EBMUD)
Don Yee (SFEI)
Dawit Tadesse (SWRCB)
Karin North (City of Palo Alto)
Ed Kolodziej (U. of Washington)
Eric Dunlavey (City of San Jose)
Erica Kalve (SWRCB)
Eunha Hoh (SDSU)
Ezra Miller (SFEI)
Frances Bothfeld (WA Dept. of Ecology)
Gaurav Mittal (SFBRWQCB)
Greg LeFevre (U. of Iowa)
Hannah Ray (Green Science Policy Institute)
James Chhor (SWRCB)
Jay Davis (SFEI)
Jaylyn Babitch (City of San Jose)
Jennifer Branyan (UC Davis)
Jennifer Teerlink (CDPR)
June-Soo Park (DTSC)
Rebecca Sutton (SFEI)

Kathy Peter (U. of Washington)
Kelly Moran (SFEI)
Kristian Fried (Integral Consulting Inc.)
Lester McKee (SFEI)
Lilly Sabet (SDSU)
Lisa Austin (Geosyntec Consultants)
Luisa Valiela (EPA Region 9)
Lydia Jahl (Green Science Policy Institute)
Maggie Monahan (SFBRWQCB)
Maggie Stack (SDSU)
Manoela de Orte (SWRCB)
Mary Lou Esparza (CCCSD)
Martin Trinh (SFEI)
Mary Cousins (BACWA)
Melissa Foley (SFEI)
Michael Gross (USGS)
Miguel Mendez (SFEI)
Miriam Diamond (U. of Toronto)
Olivia Magana (SWRCB)
Reid Bogert (BASMAA/San Mateo CCAG)
Richard Looker (SFBRWQCB)
Richard Grace (SGS AXYS)
Robert Budd (CDPR)
Robert C. Wilson (City of Santa Rosa)
Sara Huber (SWRCB)
Sarabeth George (SWRCB)
Sarah Amick (U.S. Tire Manufacturers Assoc.)
Simona Balan (DTSC)
Simret Yigzaw (City of San Jose)
Stephanie Jarmu (OEHHA)
Susan Hurley (OEHHA)
Tammy Qualls (Qualls Environmental Consulting)
Tan Zi (SFEI)
Terry Grim (CIL)
Tom Mumley (SFBRWQCB)
Topher Buck (DTSC)
Xueyuan (Helen) Yu (San Diego RWQCB)

DAY ONE - April 11

1. Introductions and Goals for This Meeting

Melissa Foley began 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. She also presented the group with guidelines for inclusive conversations. Melissa then introduced the workgroup advisors and continued with a brief roll call for the various groups present to introduce themselves.

Melissa then reviewed the ECWG two-day agenda and gave 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 current projects, prioritization of special study proposals, and future directions.

2. Discussion: CEC Strategy Update

Rebecca Sutton started off the workgroup meeting with the first of two updates, discussing current CECs efforts by the RMP and State Water Board, with further discourse on the 2022 CEC Strategy Revision and future directions occurring on Day 2. She began by introducing the SFEI team, particularly noting the addition of Martin Trinh as an Environmental Analyst.

Rebecca's outline of current CECs 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, respectively. Rebecca began by highlighting the status of Bay monitoring projects, including completion of sample collection for a study of PFAS in Bay water and a new SEP to monitor PFAS and chlorinated paraffins in Bay sediment. She continued by noting efforts in wastewater monitoring, including continuing studies on quaternary ammonium compounds (QACs) and ethoxylated surfactants, as well as PFAS via phase 2 monitoring conducted on behalf of the Bay Area Clean Water Agencies (BACWA). Rebecca also commented on PFAS in stormwater data, which have been held up due to a laboratory issue; analyses will now be completed by Eurofins TestAmerica in the Sacramento area, allowing for analysis of a broader set of PFAS.

Further, Rebecca noted recent conferences (SETAC in Portland and Pacifichem) attended by the CECs group to share findings and learn about global efforts relevant to the RMP. She also identified a recent publication of organophosphate esters (OPEs) and bisphenols (Shimabuku et al. 2022) as well as a non-targeted analysis of margin and ambient sediment (Chang et al. 2021). She mentioned a couple of forthcoming deliverables such as draft manuscripts on chemicals and particles related to tires from the Pacific Northwest Consortium on Plastics and a review of QACs led by the Green Science Policy Institute. In addition, draft RMP reports on bisphenols in various matrices, sunscreens in wastewater effluent, and PFAS in Bay water will be completed this summer.

Rebecca followed up with discussion of two projects connected to the State Water Board (SWB) CEC Program. The first study involves synthesizing and analyzing available state CECs water quality data in CA waters using a tiered risk-based framework similar to that of the Bay RMP to inform high level recommendations for monitoring and management priorities for the state. The overall study is an ambient ecosystem evaluation (not including pathways) using a class-based approach, spotlighting nine specific chemical and use classes to better understand data poor chemicals, with hundreds of identified compounds. This includes review of the latest CECs scientific literature to guide future monitoring targets and use of forward looking tools such as advanced analytical techniques and non-targeted analysis. Rebecca reviewed the tiered risk-based framework with particular focus on the ecotoxicity threshold selection utilizing ecosystem-level thresholds (e.g., PNECs). She noted key differences in the State framework compared to the RMP, including the use of risk quotients from Possible to Very High Concern (i.e., no secondary factors like persistence), with the tiers not linked to specific monitoring recommendations. The report has been completed and will help inform potential refinements in the RMP framework, to be discussed on Day 2.

The second effort, co-funded by 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. The original EcoPanel was convened a decade ago to suggest CECs for monitoring. Recently, the EcoPanel was reconvened to review state data and overall progress and suggest a tailored monitoring program, including discussion of potential synergy with other SWB CEC efforts and expansion of recommended analytes to include “new” emerging contaminants. Moving forward, the panel will be discussing the selection framework for SWB CEC database, use of other data sources, potential use of a binning approach at the regional or statewide level, and the process of on- and off-ramping contaminants.

Meeting participants inquired about the specific choice of ecotoxicity thresholds and placement of contaminants within the tiered risk-based framework. Dan Villeneuve commented on the choice of ecotoxicity thresholds, particularly where there were no thresholds available, resulting in a contaminant classified as Possible Concern only. Miriam Diamond continued with a question on the approach for high concern compounds, particularly incorporation of secondary factors, with Rebecca noting that secondary factors are not included in the framework used in the state report, and instead that the monitoring and management recommendations are informed by these factors. Tom Mumley mentioned that the state report is intended to inform a still developing statewide CECs effort, with continued development and discussion of the emerging framework. A future ECWG meeting could feature an update on this state CECs work.

3. Discussion: There’s PFAS in the Bay: Where is it coming from?

Dr. Miriam Diamond of the University of Toronto presented recent work examining the sources of PFAS in indoor and outdoor settings, with a focus on outdoor materials that are potentially contributing to PFAS in stormwater entering the Bay. Previous studies in the Bay, especially RMP efforts, have found increased levels of PFAS, particularly PFOS, in water, sediment, and biota (seals and cormorants). Concentrations of PFAS have been found to be elevated near sites receiving wastewater effluent and urban runoff, where levels are the highest and with the greatest diversity of detected PFAS. There are a plethora of PFAS uses across indoor and outdoor environments, including over 200 use categories such as cosmetics, food contact materials, medical devices, electronics, personal care products, paints, and many other products. Some outdoor uses of PFAS in coatings and construction materials are marketed with green claims of increased durability due to their persistence. A diversity of PFAS are in commerce, including those released during use as “processing aids” and used as side-chains of polymers. These PFAS are persistent, and many are volatile and mobile in the environment. Current and ongoing research on outdoor sources and transport pathways can inform a conceptual model of PFAS in Bay Area stormwater, as well as the interpretation of data.

Discussion centered around specific PFAS analytes and related uses, with Heather Stapleton noting the potential for the presence of diPAPs in paints, of concern due to potential breakdown to FTOHs. Jennifer Teerlink mentioned the potential for PFAS presence in pesticides, which the State of Maine is in the process of eliminating. Heather Stapleton also mentioned the use of an uncommon biosolids processing treatment known as Zimpro, which can transform precursor PFAS to end products. In the Bay Area, only the San Mateo Treatment Plant had this biosolids treatment process, and it may no longer be in use. Lee Ferguson mentioned PFAS are also used as an emulsifier, and Derek Muir noted polychlorofluoroethylenes as lubricants with high release potential. Miriam Diamond highlighted observations of volatile fluorinated siloxanes in China.

4. Information: Stormwater CECs Monitoring Approach

Alicia Gilbreath and Kelly Moran updated the group on the developing CEC monitoring approach for stormwater, a joint project of the ECWG and SPLWG. Compared to the current methodology for legacy contaminants (PCBs and Hg), the updated approach would expand the focus beyond particles to include dissolved contaminants; include diverse sources and physicochemical properties; monitor contaminants with ongoing use; and move back to simpler monitoring questions. Near-term priority questions were identified: the first to help elucidate the presence of specific CECs in local stormwater runoff, and the second to understand the local watershed runoff load to the Bay compared to other pathways for specific identified CECs. An overview of the monitoring approach focused on the development of a prioritization framework for CECs for stormwater monitoring, and the development of a sampling design process with effective integration of modeling analysis. The project would produce a report to help guide future monitoring efforts in stormwater by describing a generalized approach (expected to be completed in Fall 2023). Ongoing and future RMP projects highlight the focus on combining modeling and monitoring to best and most cost-effectively understand the entire watershed.

Discussion shifted toward the prioritization of CECs for stormwater monitoring and potential high-weight factors to consider, including placement in the RMP tiered risk-based framework, known outdoor use and release, availability of analytical methods, and relevance to anticipated management decisions. Meeting participants discussed the varying factors and potential CECs to begin considering, with Derek Muir highlighting a need for tire-related chemicals and vehicle related fluids as priorities. Ed Kolodziej added PPD antioxidants, which are well known to be contained in rubbers and elastomers. Dan Villenueve asked whether the effort also considered particle bound contaminants, and Kelly Moran noted it was included through a focus on measurements in total water, rather than filtered samples. Lee Ferguson noted the potential for use of NTA data generated for the Bay to help inform monitoring priorities, with many meeting participants agreeing.

Kelly Moran continued by noting the differences between monitoring and modeling, highlighting the complex and iterative process of incorporating both together, building from simple conceptual models and limited monitoring data to obtain early answers to management questions. In areas where more detail is needed, initial data will be used to build dynamic models (again a process integrated with monitoring design) to provide refined answers to management questions. She also presented a draft conceptual model for the fate and transport of pollutants from sources to different matrices across the Bay Area including water, land, and air. In order to best obtain a large amount of samples in a cost effective manner, remote automated samplers, potentially a microsampler developed by the EPA and USGS, would be an important addition to this study. Kelly discussed the potential timeline for this foundational work from approach development in 2022 to actual studies integrating monitoring and modeling beginning in fall 2023. She also noted the choice to pilot PFAS for this approach due to the class being of moderate concern, a potential issue in Bay sport fish, interests of varying stakeholders and state agencies, and early data indicating the stormwater load is important to understanding PFAS contamination in the Bay. She ended by opening the discussion to the preliminary approach for stormwater CECs and the choice of PFAS as a pilot.

While there was general support for trialing this stormwater monitoring approach on PFAS, several participants suggested consideration of other contaminants to pilot concurrently. Tom Mumley expressed a management need for including other contaminants, with Lee Ferguson noting the potential utility of comparing relative ratios of contaminants. Melissa Foley highlighted the value of the contaminant class by class approach, and potential concerns for sampling multiple types of CECs when these have not yet been evaluated in terms of sources and pathways via conceptual models. Derek Muir wondered about the additional costs associated with adding tire contaminants to the pilot, given the potential toxicity and availability of a conceptual model. Kelly Moran acknowledged that expansion of the contaminants piloted would readily increase costs and lead to a longer wait to answer the prioritized questions for the stormwater study design. Anne Cooper Doherty indicated the need for identifying important pathways for contaminant discharge to inform DTSC selection of priority products within the Safer Consumer Products program. Tom Mumley expresses interest in exploring expansion of the study and allocating additional funds in an effort to streamline monitoring design and understand contaminant loads into the Bay.

Multiple experts highlighted the need to test the remote samplers and containers rigorously prior to full deployment (e.g., through analysis of field blanks), mentioning possible contamination from use of OPEs in tubing and PFAS in multiple components. Ed Kolodziej recommended future consideration of time-resolved sampling. Miriam suggested ancillary measurements such as metals could be useful for interpretation, and Derek suggested archiving stormwater samples for future analyses.

5. Information: Ethoxylated Surfactants in Bay Water, Wastewater, and Stormwater – Method Development Update

Dr. Lee Ferguson of Duke University updated the group on development of the most comprehensive ethoxylated surfactants analytical method, aiming to also analyze short-chain compounds in San Francisco Bay water, wastewater, and stormwater. Ethoxylated surfactants are commonly detected in the aquatic environment, with widespread uses in consumer products such as paints and detergents. Fatty alcohol ethoxylates (AEO) and alkylphenol ethoxylates (APEO) are two groups known to exist in the environment, with longer chain length varieties frequently used in products. Long-chain APEOs are likely to transform to higher persistence short-chain APEOs and alkylphenols. Already, these have been detected in previous studies of wastewater effluent, stormwater, and ambient water with different analytes in the class detected. There are several challenges with the simultaneous analysis of alkylphenols and AEO/APEOs, with different techniques being used for method development. Mixed-mode size exclusion chromatography has been used to allow for chromatographic resolution of ethoxylates. The use of high-resolution selected ion monitoring has enhanced method sensitivity and allowed for concurrent quantification of ethoxylated surfactants. Additionally, polarity switching has also allowed for consecutive elution of AEO/APEOs and octylphenol and nonylphenol. Moving forward, method development will continue with use of isotope-labeled standards and calibration of ethoxylated surfactant mixtures for accurate detection of short-chain compounds. This novel method will be used to re-analyze previously collected aqueous samples in the Bay (wastewater, stormwater, and ambient Bay water) as well as newly collected stormwater samples. Derek Muir asked about the detection limits for these techniques and if they are below monitoring trigger levels, which Lee noted are generally in the ng/L range (well below noted trigger levels for those compounds). Anne Cooper Doherty expressed enthusiasm for the new data in beginning to fill important data gaps identified by DTSC.

6. Information: Quaternary Ammonium Compounds (QACs) in Wastewater

Dr. Bill Arnold of the University of Minnesota presented the preliminary findings of the QACs in wastewater and the environment study, with a focus on wastewater effluent data from Minnesota and Bay Area treatment plants and Bay Area surface water. QACs are a broad category of compounds separated into several subclasses of ammonium compounds: benzalkyldimethyl (BACs), dialkyldimethyl ammonium compounds (DADMACs), ethylbenzylalkyl (EtBACs), and alkyltrimethyl (ATMACs). These compounds have been used since the 1930s in a wide range of industrial, agricultural, and consumer products, especially as antimicrobials. The emergence of the COVID-19 pandemic has increased the use of QACs, known to be toxic to aquatic species and contribute to the development of antibiotic resistance in bacteria. Bill briefly reviewed the extraction methods, noting that the compounds stick to filter materials requiring additional steps to accurately discern concentrations in samples.

This study is important to understand the most common QACs in wastewater and ambient water as well as understand the temporal trends of QACs in wastewater throughout the pandemic. Of five wastewater treatment plants examined in Minnesota and the Bay Area, the most visible trends in total QAC load in influent and effluent were increases in Plant A throughout the pandemic, while Plant D showed total QAC loads were highest during and after COVID cases spiked. In contrast, QAC levels in Plants Y and Z fluctuated throughout the pandemic and Plant X remained relatively consistent throughout. Compared to prepandemic concentrations, QACs have increased or stayed the same since previous detections in 2019. Overall, these results showed roughly > 98% of QACs are removed during treatment, though µg/L concentrations are reaching the environment, with BACs and then DADMACs the most commonly detected QACs. Preliminary results of Bay ambient water show low levels of QACs are present. Moving forward, Bill has obtained additional National Science Foundation (NSF) funding to expand the study for an additional two years (through 2023). Due to this development, the CECs team is recommending a change to the deadline for the RMP project deliverable, a technical memo, from August 2022 to August 2024.

Several meeting participants asked questions about the study, with Miriam Diamond inquiring about other potential sources of QACs, due to the widespread use of surfactants, including potential outdoor sources. Anne Cooper Doherty noted DTSC is currently doing a systematic look to understand where QACs are being used. Derek Muir inquired about the potential effects of detected concentrations, with Bill highlighting the uncertainty of current trigger levels and a need for further development of toxicological thresholds for QACs. Jay Davis also noted that Bill will study QACs in sediment to understand its fate in the ambient environment, and echoed the benefits of continued sample collection. The group unanimously agreed with the extension of the RMP deliverable.

7. 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, ensure data are relevant to management needs, and identify opportunities to strengthen connectivity between matrices. Melissa highlighted the variety of expert advisors and stakeholders involved to effectively redesign monitoring efforts towards CECs. She briefly reviewed the priority CEC and S&T management questions, and identified the five monitoring matrices water, sediment, and biota (sport fish, bird eggs, and bivalves). Melissa reviewed the different elements that make up the program, including pilot studies, core monitoring, and piggyback studies.

For water, CECs will be added to dry season Bay-wide sampling in order to assess their status and trends. CEC wet weather pilot sampling will be added to evaluate the importance of the stormwater pathway at near-field stations, while persistence will be evaluated at ambient stations. Wet and dry season monitoring of CECs in Lower South Bay will allow for comparisons where different pathways are present, and will focus on urban CECs. Non-targeted analysis will be added to screen for CECs at the recommendation of the advisors. For the sediment matrix, the outlined goals are the assessment of the status and trends for emerging contaminants, and testing conceptual models that indicate urban CEC concentrations decrease from near-field to margins to open Bay stations. Sediment will be analyzed for CECs every five years across identified categories of stations. Based on recommendations from the Emerging Contaminants Workgroup, PBDE sampling is expected to end in 2023, while fipronil and legacy pesticide sampling will cease immediately.

For biota, CECs will be added to assess bioaccumulation, track trends, archive samples for future analyses, and collaborate with efforts across other matrices. For sport fish, PFAS will be added to the regular suite of analytes monitored every 5 years. For bird eggs, the proposal is to maintain cormorant monitoring and discontinue tern monitoring. Sampling would be conducted every three years at three core stations throughout the Bay. Per the recommendation from the Emerging Contaminants Workgroup, PBDEs will be monitored in 2022 for a final time, while PFAS analysis will continue. Prey fish will be piloted with collections concurrent with near field and margins sediment samples. This would occur every five years with a focus on PFAS and bisphenols for the pilot project. The bivalve design will forgo sampling in channel stations in favor of switching to archiving tissue from shore-based collections, leveraging current efforts by the Nutrient Management Strategy. Harbor seals may be considered as an additional tissue matrix, beginning as a special study to explore potential inclusion into S&T, likely with sampling done every five to ten years. The RMP has collected seal tissue samples over the years, including via live capture and archived tissue. A special study has been proposed for 2023 to inform longer-term designs. Melissa ended with a review of the revised sampling schedule, highlighting the opportunity to look for CECs close to pathways in the coming year of sampling with sediment, prey fish, and seals occurring the following year.

Participants discussed the S&T review, with Jay noting that for NTA in water, there is not an established sampling frequency. Tom also added that there is still opportunity for inclusion of North Bay open water monitoring to add further data to this effort. Miriam Diamond wondered what criteria are guiding sampling frequency, noting the importance of establishing guidelines to help best make decisions. She noted the need for a flexible sampling design to fit the needs of the changing chemicals landscape, particularly if intermediate sampling may be needed to observe the impacts of management decisions.

8. Information: Strategy for Development of an In-Bay Fate Model to Support Contaminant and Sediment Management in San Francisco Bay

Jay Davis reviewed the In-Bay Modeling Strategy he helped develop with Craig Jones and Don Yee, which is a product of the PCBWG. This modeling strategy marks the beginning of a major multi-year endeavor that is also connected with the EC and Sediment Workgroups. This effort builds on previous work, leveraging NMS modeling and establishing a foundation for future collaboration. There is a focus on PCBs due to their established contamination of fish species, especially shiner surfperch, known to be most contaminated in Bay margin areas. A simple one-box model of PCBs in San Leandro Bay suggested that reduction of inputs from the watershed would help advance recovery. The recently drafted strategy highlights the desired outputs to address management questions, which include distribution fields for contaminant loads, sediment recovery depth profiles, rates of sediment accumulation in areas of interest, sediment contaminant concentrations over time, surface sediment and contaminant distributions, and biota contaminant concentrations. Jay highlighted important management questions for ECWG to help predict spatial and temporal extent of potential impacts of CECs and areas of interest to monitor CECs through the S&T in water and sediment. Funds from the EPA Water Quality Improvement Fund could help jump start this project in the coming years.

There were a few questions regarding the strategy, with Derek noting the potential inclusion of non-aroclor PCBs and working with SGS AXYS to use their high quality methods. Jay confirmed that all 209 PCB congeners are monitored. Heather Stapleton inquired about a potential explanation for shiner surfperch having such high levels of PCBs compared to other fish. Jay commented that concentrations are correlated to sediment levels, with the small home ranges for this species focused in the margins where sediment is relatively highly contaminated.

9. Information: Integrated Watershed Bay Modeling Strategy and Pilot Study

Tan Zi presented on the integrated watershed Bay modeling strategy and pilot study, an important effort across four workgroups: ECWG, PCBWG, Sediment WG, and SPLWG. The primary motivation of this study is to have a systematic view (from watershed to Bay) of the Bay water quality by effectively integrating current watershed and in-Bay modeling capacities and to identify priorities of future modeling studies to support different RMP workgroups. In the first year, this project will develop a strategy to integrate different models to better support future modeling and monitoring. For the second year, this project will implement and test the strategy on one or more pollutants associated with one or more management questions through the pilot study. The development of this strategy will help elucidate the current capabilities of available models (and related confidence in the model), planning for near future efforts with enhanced capacity, and setting out long-term goals. Overall, this should produce an integrated modeling framework with a roadmap identifying connections with ECWG for the next five years. There are a variety of models currently available and this project will aid in identifying what will work best to answer ECWG management questions, including a focus on sources, pathways, and loadings, as well as the related processes that may affect transport and fate. Miriam Diamond noted the importance of evaluating the models using data-rich compounds to verify they are mechanistically sound, and would be interested in further discussion with those working on the project.

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 spotlighted the beginning of the discussion on the 2022 CEC Strategy Revision, update on the tires strategy, and the review and prioritization of special study proposals.

DAY TWO - April 12

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. Discussion: 2022 CEC Strategy Revision - Management Questions, Tiered Risk-based Framework, Future Priorities

Rebecca Sutton began the second day of the meeting with discussion on the revision of the CEC strategy. This is a direct result of increased funding available to revise the strategy this year, and already an ECWG Strategy Subgroup of stakeholders and experts met in February to discuss potential pathways to consider for the strategy revision. She reminded the group that this is one of several opportunities for feedback on the revision (deadline 06/30/22). Rebecca highlighted the three significant components of the revision: management questions, tiered risk-based framework, and future priorities. Overall, this is a preliminary discussion for a larger group, with a goal for today to identify topics to bring to the ECWG Strategy Subgroup.

Rebecca briefly reviewed each of the management questions, spotlighting how each contributes to guiding the CECs framework and projects. The Strategy Subgroup noted the questions were generally good, though further information on the context of each question would be useful. This could include a small paragraph detailing the interpretation of each management question to RMP work. The Subgroup also recommended improvement of the temporal trends question to include pathways and expand on understanding the reason for any noted trend. Dan Villenueve considered the revision a good idea and wanted to understand the implication of the inclusion of the additional text to RMP work. Derek Muir posited that trends in pathways could include examination of concentrations and/or loads. Tom Mumley agreed with a broader examination of the Bay and addition of this as a driver. Lee Ferguson wondered if the data are there, or would be there, to assess temporal trends in a systematic way, as there is a clear disparity in data availability across classes.

Rebecca continued with a review of the potential revisions to the tiered risked-based framework, focused on the impacts to prioritization as a whole, and noting continued discussion on this topic via the Subgroup. The first revision is to add a very high concern tier to provide better nuance concerning prioritization of contaminants and to correlate with the state framework. Redefinition of risk-based thresholds, especially clear identification of a risk quotient, with secondary factors (persistence, cumulative impacts, and trends) also informing classification. Elevation of fish consumption concerns is another important addition to risk characterization. The addition of the three noted revisions so far would likely lead to a change in some CECs of moderate concern to high concern (PFAS and OPEs). Another revision would differentiate the low and possible concern tiers by monitoring priority. This would create two possible concern groups: one for CECs recommended for periodic screening and another for those that have been deprioritized. The low concern tier would be split into three groups, including the two noted in possible concern plus a transitional group for CECs to help indicate level of priority for follow up work. The final revision would modify existing monitoring recommendations and remove the management recommendation for each tier.

The resulting discussion began with talk of the use of the 90th percentile concentration in the risk quotient as an updated risk screening, with Heather Stapleton noting the assumption of a normal distribution of data, and suggesting it would be useful to discuss with a statistics expert to ensure it is protective enough. Dan Villeneuve had concerns about the use of 90th percentiles because they may not be completely representative, particularly for using risk quotients based on 90th percentiles for some thresholds and medians for others. He also recommended developing guidance on the minimum amount of data needed. Miriam echoed Dan's concern about using a mixture of risk quotients based on 90th percentile and median concentrations, and noted the possibility of datasets that have similar medians but significantly different 90th percentiles. Her experience suggests the range of concentrations is more meaningful for exposure to biota, relative to the median. Because management actions take time to develop, it is important to identify concerns early. Derek Muir supported a more precautionary approach like using 90th percentile concentrations, and highlighted issues with method detection limits and uncertainty in both the numerator and denominator of a quotient. Bill Arnold further commented as to whether the level of uncertainty from the risk quotient calculation could be determined and considered. Don Yee responded to some of the concerns about data quantity and quality, suggesting that use of a 90th percentile concentration might be considered sufficiently protective particularly when monitoring is biased towards higher exposure scenarios such as in the Lower South Bay, and that issues could arise should these data become “diluted” by additional monitoring across subembayments. Nevertheless, if sufficient data are available, if 10% exceed a toxicity threshold, that can indicate concern. Jennifer Teerlink commented on a need for further thought on what pathways (or matrices) are the most useful for risk assessment, especially as it relates to acute versus chronic exposure and toxicity. Tom Mumley noted the importance of data quantity and quality, spotlighting the need for data handling to be informed by best available practices. In particular, concerns relating to fish consumption should be consistent with regulatory frameworks for other contaminants. Tom Mumley and Miriam Diamond disagreed with the suggestion to remove recommendations concerning management, since it is important for ongoing monitoring to inform management decisions. Careful attention to the language in the revision is appropriate because the RMP is a monitoring program, not a management program.

Moving forward, Rebecca commented on the wide variety of potential CECs special study proposals expected at next year's meeting, indicating themes including pathways monitoring, marine mammals, tire and roadway contaminants, non-targeted analysis, toxicology, PFAS, OPEs, and bisphenols. She also discussed the themes that will be evident in the ECWG Multi-Year Plan (MYP): leveraging the S&T study redesign to monitor CECs, continued focus on PFAS across multiple matrices, strategic use of NTA, and greater consideration of the air pathway, especially as it relates to stormwater. The MYP is in development, and will be shared with the Strategy Subgroup for discussion at a later date.

13. Discussion: Tires Strategy Update

Kelly Moran discussed the update to the RMP Tires Strategy, a cross-workgroup multi-year plan to address tire-related water pollution. She began by spotlighting the importance of examining tire wear particles for contaminants, such as 6PPD that can transform to 6PPD-quinone in the environment and be toxic to wildlife (particularly coho salmon). She continued by showcasing the recent projects done at SFEI, especially the "Synthesis of Microplastic Sources and Pathways to Urban Runoff," funded jointly by the Ocean Protection Council (OPC) and RMP. There has also been a plethora of requests for presentations on the microplastics work across a variety of national and international conferences as well as state and federal agency discussions. With the increasing interest in microplastics and tire particles, Kelly commented that these presentations are normally very well attended.

This further correlates with the rapid rise of tire research, with more papers on tires published in the first four months of 2022 than the entire year of 2021 combined. Most emerging research on tires focuses on aquatic toxicity, though there is a growing body examining runoff treatment options. Already several tire chemicals beyond 6PPD-quinone have been identified as of interest to DTSC to help better understand contamination from tires.

Alicia Gilbreath discussed the preliminary chemical results obtained from monitoring studies of ambient Bay water and stormwater. In these studies, various sites were sampled across the Bay including open Bay, nearfield Bay, and urban runoff sites. The amount of data available to review was limited due to a dearth of storm events. In the Bay summer and stormwater reference sites, only trace concentrations of tire contaminants were found. In urban stormwater samples and samples from nearfield Bay sites (post-storm), concentrations of both

6PPD-quinone and N,N'-diphenylguanidine (DPG) were highest. Tire related chemicals were detected in wet season open Bay samples (collected ~1 week after storm) at concentrations indicating significant dilution, though both compounds were detected. Overall, urban runoff showed higher concentrations, with declines spatially and temporally away from stormwater sites and storm events for these two contaminants.

Ezra Miller continued the presentation with a discussion of new toxicity information on tires. Within the literature, there is a growing body of toxicity evidence for tire particles and tire-related contaminants based on exposure levels at environmentally relevant concentrations, which result in observed negative health outcomes. Ezra briefly reviewed some toxicology basics related to dose-reponse to add needed context to the toxicology updates. Although LC50s are not PNECs, they are still important to consider as they indicate potential population effects for a single species. When there is no PNEC or chronic toxicity data, a default assessment factor of 10 or 100 is applied to the LC50 to provide a protective threshold. In addition, stormwater exposure occurs in repeat pulses, and toxicity depends on exposure duration, making it difficult to understand the toxicokinetics and toxicodynamics of tire contaminants like 6PPD-quinone. The concentrations of tire related contaminants in the Bay (presented by Alicia) are helpful in identifying whether steelhead trout in the Bay could experience sublethal exposure and toxicity conditions. Toxicity evidence is building for tire wear due to exposure levels at environmentally relevant concentrations, resulting in negative health outcomes. In addition, runoff tends to be a complicated mixture of different contaminants, which could lead to an altered toxicity of co-exposed contaminants.

The five-year plan for the RMP tires strategy serves as a short-term supplement to the RMP's current MYPs for the ECWG, MPWG, and SPLWG. Over the next five years, this strategy will seek to answer priority questions and inform relevant management policies and decisions with a draft due sometime this year. The timeline of the plan is centered around upcoming management decisions including the DTSC Safer Consumer Products Program Workplan, the OPC tires sector pollution prevention strategy, and the US EPA Trash Free Waters Program - tires workplan. Currently, the focus is on tire chemicals in SF Bay, reflecting the prior year's stakeholder feedback to limit study of tire particles. The draft five-year special studies plan will include continued monitoring of known chemical groups in the wet season as well as identification of new chemicals for monitoring in the coming years. These studies, along with relevant literature, will aid in advancing scientific information to management agencies.

Several meeting participants noted a need for continued work on the interactions between tire related chemicals and particles in conjunction with the tire chemicals entering environmental matrices. It may be appropriate to reevaluate the initial guidance to focus exclusively on tire chemicals without considering the particles themselves. Tom Mumley noted a cause for concern for tire-related chemicals, spotlighting the importance to understand the potential problem clearly in the Bay. Ed Kolodziej identified an important data gap in understanding the separation of chemicals from the particle, with surface degeneration an important factor; improved understanding will provide information needed to effectively tackle this issue.

14. Summary of Proposed ECWG Studies for 2023

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 seven high-priority proposals, with a brief review of three special study proposals relevant to ECWG from other RMP WGs including SPLWG, MPWG, and PCBWG.

The proposal for the second year of the stormwater CECs monitoring strategy continues to develop a novel, long-term stormwater monitoring approach to effectively address CECs. The updated approach would expand the focus beyond particles (most relevant to legacy contaminants) to include dissolved contaminants, consider diverse sources and physicochemical properties, monitor contaminants with ongoing use, and simplify monitoring questions relative to those designed for legacy contaminants. The two major elements of this strategy focus on development of an approach for prioritizing CECs for stormwater monitoring and updated CEC-specific sampling methodology for stormwater including integration of modeling and relevant stakeholder needs.

The CECs in Stormwater: PFAS proposal was presented next, an application of the stormwater CECs monitoring strategy. This study focuses on PFAS, a priority CEC, to establish an important foundation for monitoring and modeling with the resulting design advancing the estimation of the annual load of PFAS entering the Bay via stormwater. This approach would examine available PFAS knowledge to develop a conceptual model and examine prior data to help inform monitoring design. This study would also serve as an important pilot of remote sampling methods for stormwater.

The following proposal was the second year of ethoxylated surfactants analysis in multiple matrices, aimed at filling the data gaps in ethoxylated surfactant analyses described in the presentation by Lee Ferguson. Based on prior screening data, this second year will focus on wastewater with influent, effluent, and upstream sampling at one facility, and only effluent from two facilities, using the expanded analytical method under development.

PFAS and non-targeted analysis of marine mammal tissues, the first of a two year study, was showcased next. This study aims to inform S&T study design by determining if it is appropriate to add marine mammals while monitoring PFAS, a contaminant of high priority. In addition, improved analytical methods, particularly for non-targeted analysis, are likely to provide new insights into the presence of CECs in marine mammal tissues. This would be a two year pilot study with collection of tissues from the Marine Mammal Center. Two different labs have been identified to examine liver and serum as well as blubber, to get a complete understanding of the fate of CECs.

Several meeting participants had questions regarding this proposal, with Lee Ferguson inquiring on the current capabilities of examining serum for fluorinated compounds. Bernie Crimmins discussed the method and its capability to effectively examine serum. Miriam Diamond mentioned if it would be possible to use archived samples if this study is not approved this year, though Rebecca noted the use of archived samples is not yet certain due to the need to review collection and storage materials and available sample masses. Tom Mumley suggested expanding the analysis to include other contaminants, especially for status and trends monitoring. Rebecca noted that the use of non-targeted techniques would allow identification of a broad range of contaminants; expansion of the study for more targeted contaminant monitoring could be considered, though it may be difficult to obtain sufficient mass of certain samples. Jay Davis underlined the importance of the non-targeted component to allow for CEC screening at the top of the food web.

The next study was the first year of a two-year study examining tire contaminants in Bay water during the wet season. Initial samples have indicated the presence of the tire contaminant 6PPD-quinone in Bay water, with further results needed to classify the contaminant under the tiered risk-based framework. In addition, these findings can help evaluate the pilot wet season monitoring effort. The study would examine eight near-field stations and 4-5 open Bay stations, leveraging S&T monitoring. Anne Cooper Doherty was interested in learning more about the analyte list, with Ed Kolodziej responding that there are roughly six tire related chemicals in the method and several CECs considered typical in stormwater.

The proposal on mining NTA data for additional targets for future study aims to leverage existing NTA datasets to elucidate new study ideas. This would also include in depth review of literature and database information on sources and toxicity of at least 40 contaminants.

PFAS in archived sport fish was the final proposal presented, with an aim to fill data gaps relevant to human health concerns, especially of disadvantaged communities, and provide more data for trends analysis. This study could also serve to inform S&T study design. Several different fish will be examined from archives in 2009, 2014, and 2019 from sites all across the Bay to better understand PFAS sport fish contamination in the Bay.

15. Discussion of Recommended Studies for 2023 - General Q&A, Prioritization

Melissa Foley introduced the item by reviewing the process for prioritization and recommendation of special study proposals. 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 three of the high priority studies previously presented.

<u>CECs in Stormwater: PFAS</u>

Heather Stapleton commented on potential sources of PFAS to stormwater from construction and other urban PFAS. She recommended expanding monitoring to include diPAPs and fluorotelomer alcohols. Dan Villeneuve thought the proposal should be marked as time sensitive and urgent due to its use in understanding sampler needs for similar studies. Lee Ferguson expressed concern with the use of AOF, indicating efforts so far using the method have not been fruitful; instead, he recommended a focus on the TOP method. Rebecca noted AOF in stormwater is a pilot for understanding PFAS method and comparison to wastewater. Miriam indicated further support of the TOP method, particularly as PFAS polymers are not quantified via targeted methods. Derek suggested characterizing trifluoroacetic acid.

PFAS and non-targeted analysis of marine mammal tissue
Derek Muir supported use of both Bernie's and Eunha's lab for non-targeted analysis of marine mammal samples. He also noted it would be useful to compare these measurements to those of PFAS in wastewater. Tom Mumley would like to further consider the addition of other analytes to this study.

Tire and roadway contaminants in wet season Bay water
A meeting participant inquired about potential synergy with the stormwater strategy, including identification of sampling methods and locations. Kelly Moran noted this would be an ideal scenario, and that this study is designed to leverage the Bay S&T pilot study design. Tom Mumley reiterated that he did not want to rule out potential consideration of particles.

16. Closed Session - Decision: Recommendations for 2023 Special Studies Funding

Karin North led the closed door discussion. Following extensive discussion, studies were prioritized. The resulting recommendations are shown in the following prioritization tables:

Study Name	Budget	Modified Budget	Priority	Comments
Stormwater monitoring strategy for CECs (year 2 of 2)	$55,000		1	
Ethoxylated surfactants in ambient water, margin sediment, wastewater, Part 2 (year 2 of 2)	$30,000		2	
Tire and roadway contaminants in wet season Bay water (year 1 of 2)	$40,000		3	

Mining nontargeted analysis data for additional targets for future study	$45,000		4	Potential for add-on to follow up on specific contaminants that are observed. Possible limited pro bono work from Lee to try to update the NTA table. Should not lose sight that there are likely other things out there (other than PFAS) that we may need to monitor.
CECs in stormwater: PFAS	$180,000		5	EPA 1633 focused on AFFF; potential to add other PFAS to the study (dipaps and fluorotelomer alcohols)? TOP method would capture these compounds. Dipaps specifically could give info about pathways. Maybe don't do AOF and focus on TOP due to interpretation challenges with AOF (reason to include is because it is a pilot and SWRCB want to look at a broader suite of methods). AOF helpful to compare pathway to wastewater (included in BACWA study). Add GCMS for TFA and TFRA? Use sampling pilot to look at other CECs, particularly for blanks and recovery ($35-40k for additional CEC pilot)? Use savings from not doing AOF to test additional CECs with the remote samplers. Add tire contaminants to pilot. Also potentially add other stormwater contaminants - metals (copper, nickel, zinc) as a useful indicator. Further dialogue to discuss the design and depth of conceptual model development.
PFAS and nontargeted analysis of marine mammal tissues (year 1 of 2)	$115,500		6	Additional contaminants? Non-targeted analysis important for identifying other CECs to include in S&T monitoring. Could blubber analysis be done on GCGC high-res?
PFAS in archived sport fish	$72,500		7	PFAS is part of future S&T work; archive samples may be less useful for EJ communities than future analysis.
Total	$538,000	$0		

17. Report out on Recommendations

After the closed door session, proposal authors were invited back to the meeting to hear the final prioritization decisions. Karin North summarized the discussed suggestions and recommendations. The proposals for continued activity on two year studies were prioritized because they are ongoing. The proposal to monitor chemical tire contaminants during the wet season was the next priority because it is time sensitive. The NTA data mining proposal was next because it is relatively low cost and high impact. The proposal on stormwater (with revisions) was a high priority but was placed further down on the list because the Water Board assumed it could be funded via a variety of mechanisms (including the RMP). Additional feedback will be obtained during the SPLWG meeting. Proposals on marine mammals and sport fish were essentially a tie; monitoring marine mammals was of interest because these are top predators, while an examination of PFAS in archived sport fish was of interest due to the intersection with environmental justice.

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).

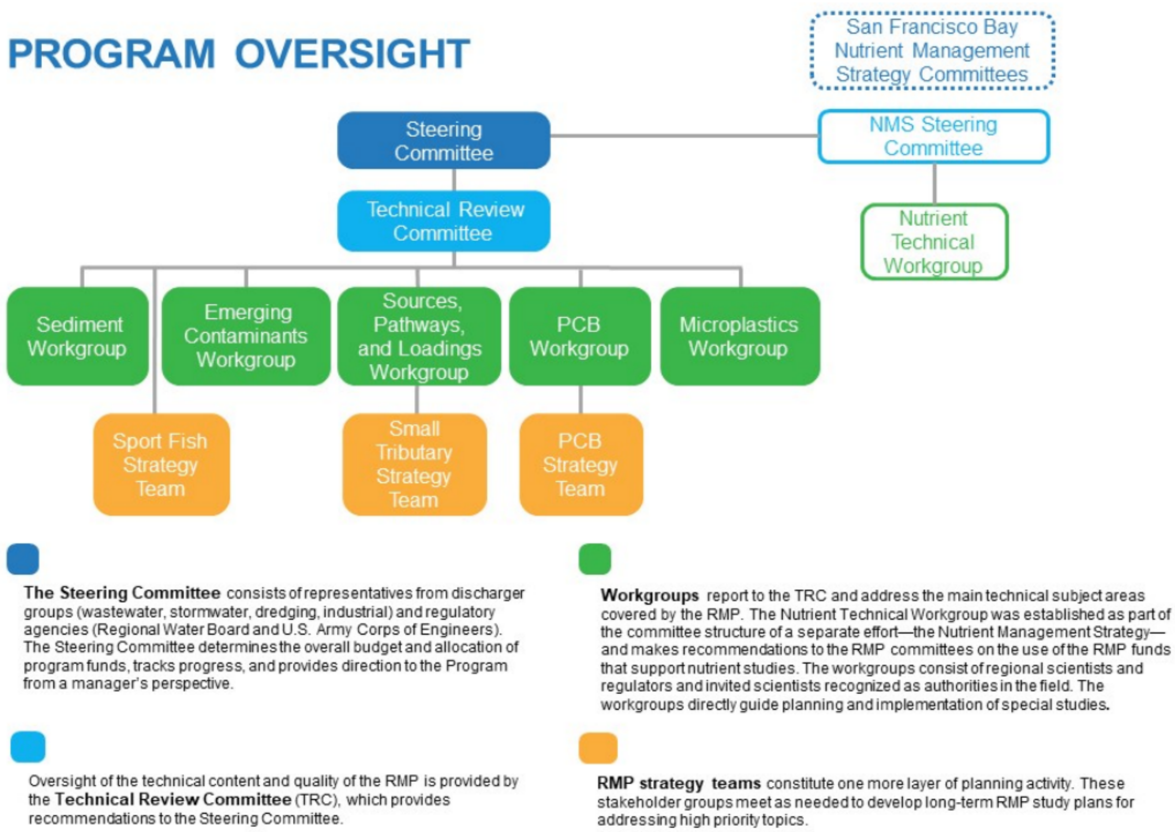
The annual planning cycle begins with a workshop in October in which the Steering Committee articulates general priorities among the information needs on water quality topics of concern. In the second quarter of the following year the workgroups and strategy teams forward recommendations for study plans 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.

Figure 1. Collaboration and adaptation in the RMP is achieved through the engagement of stakeholders and scientists in frequent committee and workgroup meetings.



Special Study Proposal: Stormwater Contaminants of Emerging Concern (CECs) Monitoring and Modeling 2024

Summary: This project will begin implementing the RMP stormwater CECs integrated modeling and monitoring program. The program framework is being developed through the RMP 2022 & 2023 "Stormwater CECs Approach" project that is slated for completion in late 2023. A second project currently underway, the 2023 "Stormwater CECs Monitoring Groundwork" project, is completing a series of necessary tasks to support development of robust, practical, and cost-effective systems for stormwater CECs monitoring. The Groundwork project feeds into the Stormwater CECs Approach development, which is being guided by a Stormwater CECs Stakeholder-Science Advisor Team (SST).

This proposal is a placeholder for completing and implementing the integrated modeling and monitoring program in wet season 2023/2024 (October 2023-September 2024) that will be defined by the Stormwater CECs Approach. It includes scopes and budgets for four specific tasks for which we request early release of funds to initiate implementation in summer 2023. It briefly outlines remaining tasks, which will be developed in concert with the completion of the Approach. These tasks will be developed under the oversight of the SST in parallel with the Approach and brought to the TRC and SC for approval.

Estimated Cost:	$300,000 RMP + $100,000 WQIF ($400K total; early release of RMP funds requested)
Oversight Group:	ECWG and SPLWG, Stormwater CECs Stakeholder-Science Advisor Team
Proposed by:	Kelly Moran, Tan Zi, Alicia Gilbreath, Rebecca Sutton
Time Sensitive:	Yes because it supports completion of the Stormwater CECs Approach and initiates implementation of the Stormwater CECs monitoring program in wet season 2023/2024.

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Scopes and budgets for remaining project tasks	Fall 2023-Spring 2024
Task 2. Stakeholder and science advisor engagement —Informal stakeholder and advisor meetings —SST meetings —Two RMP presentations (ECWG/SPLWG and SC/TRC) —Conference presentation	 Fall 2023-Fall 2024 Fall 2023-Summer 2024 Spring-Summer 2024 Fall 2024
Task 3. CECs Model Development Groundwork Reporting: General workplan for future phases of CECs modeling efforts (to be integrated into the Stormwater CECs Approach Draft Report)	Draft Fall 2023 Final Spring 2024
Task 4. Stormwater CECs work integrated scientific systems development and cross-task and cross-project team coordination	Fall 2023-Summer 2024
Remaining project tasks. Deliverables to be identified in task scopes	To be determined

Background

In 2022 and 2023 the RMP funded a two-year study to develop a stormwater CECs monitoring approach (“Stormwater CECs Approach”). Due to high CECs monitoring costs and technical challenges, a well-thought out, carefully focused approach is essential. Early work on the Approach project identified essential groundwork necessary to move forward with CECs monitoring in a robust, practical, and cost-effective manner. That groundwork is underway. Its schedule is driving the workflow and timing for completion of the Stormwater CECs Approach, slated for fall 2023.

This proposal complements a separate proposal for purchasing and/or building remote samplers capable of collecting stormwater during storm events. These samplers, which increase our sampling capacity and reduce sample collection cost, are a cornerstone of the Stormwater CECs Approach. That proposal is under the purview of the SPLWG, which will review it during its May 2023 meeting.

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	N/A
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Design and implement CECs monitoring, including piloting new integrated modeling and monitoring approach and piloting use of remote samplers.	Implementing monitoring projects to address near-term priority stormwater CECs management questions, such as to determine whether stormwater pathway loads of various CEC families are large or small relative to other pathways flowing into 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?	Design and initiate monitoring capable of informing general understanding of changes in CECs presence in the stormwater pathway.	Understanding the changes in presence of CECs in the stormwater pathway.
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

We propose to pilot implementation of the new Stormwater CECs Monitoring Approach in wet season 2023/2024. A cornerstone of the Approach is the integration of modeling and monitoring designs to maximize the value of each sampling event. Consequently, this project proposal includes both monitoring and modeling.

Until the completion of the Approach this fall, details of the necessary work remain undetermined. This proposal is primarily a placeholder. It describes the general scope and nature of the work envisioned to pilot implementation of the Approach this winter. It includes complete scopes and budgets for four specific tasks for which we request early release of funds to initiate implementation in summer 2023. Remaining tasks, which are briefly outlined below, will be developed in concert with the Approach, under the oversight of the Stormwater CECs Stakeholder-Science Advisor Team (SST). The SST includes representatives from the Steering Committee and Technical Review Committee, as well as science advisors and stakeholders.

<u>Task 1: Develop scopes and budgets for remaing project tasks</u>
We will develop scopes and budgets for remaining tasks in concert with the Stormwater CECs Approach development, under the oversight of the SST. These will subsequently be provided to the SC for final approval. These will necessarily be developed in phases, with the early focus being to ensure that monitoring can occur in wet season 2023/2024 (e.g., pilot monitoring design and its implementation) and the later focus on the less time-sensitive elements (e.g., implementing the next phase of the multi-year phased modeling effort). Each task proposal will be presented in context of the overall project budget to ensure sufficient funds will be available for all priority tasks.

<u>Task 2: Stakeholder and science advisor engagement</u>
We will convene additional meetings of the SST to support this project in parallel with completion of the Stormwater CECs Monitoring Approach and to refine the program based on the pilot experience in wet season 2023/2024. We anticipate holding two or three SST meetings in addition to extensive informal individual and small group engagement with stakeholders and advisors as we finalize and pilot the Stormwater CECs Approach. We will provide a project update at spring 2024 RMP workgroup meeting(s) and plan to share findings at a stormwater or monitoring oriented conference such as the California Stormwater Quality Association (CASQA) Conference in fall 2024.

<u>Task 3: CECs model development groundwork</u>
The goals for this project element are to: 1) prepare a general workplan for CECs stormwater modeling efforts, 2) design the load modeling approaches and model structures for one pilot CEC, and 3) identify and verify model assumptions for the selected CEC (which will necessarily be quite different than those used for PCBs, mercury, and sediment) through literature review and monitoring data analysis. The outcome of this task, a general workplan for future phases of CECs modeling efforts,

will be integrated into the Stormwater CECs Approach Draft Report, to be prepared in fall 2023.

Integrating CECs model development groundwork into this proposal will ensure the RMP will be able to move forward with its cost-saving and value-enhancing vision of integrating modeling with monitoring as it develops a CECs monitoring program. This task will also provide the modeling support necessary to complete the Stormwater CECs Approach Project in 2023.

<u>Task 4: Stormwater CECs Work Integrated Scientific Systems Development and Cross-Task and Cross-Project Team Coordination</u>
Project team meetings to keep this multi-faceted project on track, to develop operating systems (workflows and shared team physical and electronic resources) supporting the long-term implementation of integrated stormwater CECs modeling and monitoring, and to ensure consistency and coordination among the interlinked elements of this and related stormwater and Bay CECs monitoring and modeling projects. We anticipate (almost) biweekly high-level meetings with staff from the emerging contaminants, stormwater monitoring, modeling, project leadership, and RMP science leadership teams and occasional (every 2-3 months) meetings with a larger group of key scientific staff to work through scientific issues on specific project elements.

<u>Remaining tasks</u>
Our current vision is that the unbudgeted project funds would address the elements listed below, which will be developed in parallel with the completion of the Stormwater CECs Approach. The list could expand or change depending on the details of the Approach.

A. *Pilot implementation of the CECs monitoring approach,* which we anticipate to include:
    a. Develop a pilot monitoring design for wet season 2023/2024 consistent with the Stormwater CECs Monitoring Approach and addressing the near-term priority management questions. This task may include integration with Status & Trends monitoring design and identification of and site visits to reference site sampling locations.
    b. Sample collection, which includes activities like obtaining permits, installing remote samplers, collecting samples, and shipping the samples to the analytical laboratory.
    c. Chemical analysis for CEC parameters specified in the monitoring design.
    d. QA/QC review of data.
    e. Data interpretation at a level sufficient for use in evaluating outcomes and to inform future monitoring design. We do not anticipate a full report on the pilot year data, as we expect the Approach will establish a multi-year reporting and data interpretation process.

B. *Modeling*. Complete development of CECs model development plan and implement first year of that plan (CY 2024), which we anticipate to include:
   a. Prepare a specific load modeling plan for the selected pilot CEC;
   b. Prepare conceptual model for one high priority CEC approved by the SST.
C. *Potentially refine design of remote samplers and/or methods for their installation*, if these activities are not fully addressed in the separate remote samplers proposal to be reviewed by SPLWG.

Budget

The Project budget will include Labor, subcontract(s) (laboratories), and direct costs. Hours and costs for tasks not listed below will be estimated when the task scopes are developed.

Expense	Estimated Hours	Estimated Cost
Labor		
Task 1: Develop scopes and budgets for remaining project tasks	50	$10,000
Task 2: Stakeholder and science advisor engagement	220	$42,500
Task 3: CECs model development groundwork	379	$55,000
Task 4: Stormwater CECs work integrated scientific systems development and cross-task team coordination	175	$32,000
Remaining tasks	TBD	TBD
Laboratory and Other Direct Costs (Approximate)		
Laboratory		TBD
Equipment, sampling-related travel, shipping		TBD
Conference presentation travel		$2,000
Remaining tasks (primarily monitoring-related expenses)		$258,500
Grand Total		**$400,000**

<u>Budget Justification</u>

SFEI Labor
Labor hours for SFEI staff to complete all project elements.

Data Technical Services
Standard RMP data management procedures will be used. The monitoring design will specify whether data will be uploaded to CEDEN.

Laboratory Costs
Laboratory costs are anticipated to include analysis of field and QA/QC samples. Specific laboratory partner(s) will be identified in the task-specific scopes and budgets.

Other Direct Costs
Other direct costs are anticipated to include travel, shipping, and other miscellaneous sampling-related equipment. Estimates of other direct costs will be provided in the task-specific budgets. We anticipate purchasing or building the remote samplers to be used for this project under a separate project to be reviewed by SPLWG.

Early Funds Release Request
If this project is approved, we request early release of funds for use in 2023 to support parallel projects and to initiate monitoring during the 2023/2024 wet season.

Reporting

Reporting for Task 1, Scopes and budgets for remaining project tasks, will be the scopes and budgets presented for SST review and SC approval. Reporting for Task 2 will include summaries from SST meetings, the two RMP presentations, and the conference presentation. Reporting for Task 3, the CECs model development groundwork task, will be integrated into the Stormwater CECs Approach draft report to be completed in fall 2023 and final report to be completed by spring 2024.

Reporting for remaining tasks (e.g., presentations, written report[s]) will be determined in conjunction with the scope and budget for each task. Reporting may be combined with deliverables for other related projects.

Special Study Proposal: PFAS Synthesis and Strategy Revision

Summary: Per- and polyfluoroalkyl substances (PFAS) are a class of fluorine-rich chemicals that are used widely in industrial processes and consumer and industrial products, leading to widespread environmental contamination around the world. Since the previous RMP PFAS synthesis and strategy effort completed in 2018, the RMP has collected, and is in the process of collecting significant additional data and information about PFAS in the Bay and Bay pathways. Additionally, concerns relating to the persistence of PFAS, the high toxicity of well-studied members of this class, and the pattern of regrettable substitution observed in industry, have led scientific and regulatory bodies to recommend broad, class-based monitoring and management approaches. With these recent scientific and management developments, as well as the elevation of PFAS as a broader class in the RMP's tiered risk-based framework, an updated comprehensive synthesis of PFAS Bay monitoring data and a strategy for future monitoring is needed. This proposed synthesis and strategy revision would provide an updated synthesis of PFAS monitoring data in the Bay, identification of priority information gaps needed to inform monitoring and management, development of a conceptual model framework identifying source categories associated with pathways for PFAS to reach the Bay, and an updated strategy for RMP monitoring of PFAS.

Estimated Cost:	$107,000
Oversight Group:	ECWG
Proposed by:	Diana Lin, Ezra Miller, Kelly Moran, Rebecca Sutton
Time Sensitive:	Yes to inform ongoing state-wide PFAS monitoring and management strategies

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Presentation and discussion at ECWG to identify management drivers	April 2024
Task 2. Compile datasets, standardize, and conduct data analysis and evaluations	January - June 2024
Task 3. Concise literature review to inform data evaluations and strategy development	June - December 2024
Task 4. Draft Report	March 2025
Task 5. Gather comments on Draft Report strategy during ECWG	April 2025
Task 6. Final Report	July 2025

Background

Per- and polyfluoroalkyl substances (PFAS), a family of thousands of synthetic, fluorine-rich compounds commonly referred to as “forever chemicals,” are known for their thermal stability, non-reactivity, and surfactant properties. All PFAS are highly persistent or, in the case of precursors, degrade to substances that are highly persistent. Some PFAS, particularly the long-chain compounds, bioaccumulate and are associated with a wide variety of toxic effects in wildlife and humans. These unique compounds have widespread uses across consumer, commercial, and industrial products, resulting in widespread occurrence in the environment and wildlife across the globe. However, data gaps remain on PFAS sources and environmental fate, as thousands of compounds are registered for use, yet fewer than 50 have been the subject of significant monitoring in environmental media (Wang et al., 2019).

Concerns relating to the persistence of PFAS, the high toxicity of well-studied members of this class, and the pattern of regrettable substitution observed in industry, have led scientific and regulatory bodies to recommend broad, class-based monitoring and management approaches. The RMP has followed that recommendation. Previously, long-chain PFAS like PFOS and PFOA were classified as Moderate Concern within the RMP’s tiered risk-based framework, while all other PFAS were classified as Possible Concern (Sedlak et al., 2018). Reclassification of all PFAS as Moderate Concern was agreed upon during the 2020 ECWG meeting, consistent with the rapidly evolving scientific and regulatory response to PFAS as a broad class of priority compounds for management actions (Miller et al., 2020). Due to their Moderate Concern classification, the 2022 RMP Status and Trends (S&T) redesign added PFAS monitoring to every matrix; previously, PFAS were only monitored in bird eggs and sport fish as part of S&T monitoring.

Since the previous RMP PFAS synthesis and strategy effort (Sedlak et al., 2018), the RMP and RMP partners have collected or are in the process of collecting data on PFAS in many Bay matrices, including water (Mendez et al., 2022; ongoing), sediment (ongoing), sport fish (Buzby et al., 2019), prey fish (ongoing), bird eggs (ongoing), marine mammals (ongoing), wastewater (Mendez et al., 2021; ongoing), and stormwater (ongoing). Additionally, the RMP participated in a pro bono project to develop a multi-box mass balance model to predict the long-term distribution and concentrations of PFOS and PFOA in water, sediment, and fish (Sánchez-Soberón et al., 2020). These recent advances in our understanding of PFAS in San Francisco Bay matrices and pathways already go above and beyond the monitoring strategy outlined by Sedlak et al. (2018). Additionally, ongoing implementation of the State Water Board’s PFAS Action Plan (https://www.waterboards.ca.gov/pfas/) has generated a wealth of PFAS data.

Management of PFAS has also changed to reflect the growing use of a class-wide approach since the 2018 RMP PFAS synthesis and strategy effort. In California, the Department of Toxic Substances Control’s Safer Consumer Products Program has established a clear rationale for management actions directed at the entire PFAS class

(Bălan et al., 2021), and has begun to apply this approach, starting with carpets and rugs made or sold in California. Similarly, state bans on PFAS in paper-based food packaging and products intended for infants and children, both of which take effect in 2023, rely on a class-wide approach, rather than bans of individual compounds. At the federal level, the US EPA has adopted a PFAS Strategic Roadmap to begin to more fully address this complex class of contaminants. Management of PFAS as a class has also been recommended by several countries within the European Union, via a proposal to prohibit the production, marketing, and use of the class throughout Europe, with exceptions for essential uses such as medical applications.

With these recent scientific and management developments, as well as the elevation of PFAS as a broader class in the RMP's tiered risk-based framework, an updated comprehensive synthesis of PFAS Bay monitoring data and strategy for future monitoring is needed. This proposed synthesis and strategy revision would provide an updated synthesis of PFAS monitoring data in the Bay, identification of priority information needs to support monitoring and management, and an updated strategy for RMP monitoring of PFAS. Recommendations will also inform efforts beyond the RMP, including State and Regional Water Boards' monitoring and management strategies moving forward.

Study Objectives and Applicable RMP Management Questions

The purpose of this study is threefold. First, the project will provide an updated synthesis of existing Bay PFAS data collected by the RMP and other scientists into one document. This will allow better accessibility of recent PFAS data.

Second, this project will conduct a concise literature review to provide more context in evaluating Bay data, to inform monitoring design, and to identify priority information gaps for management of PFAS in the Bay.

Third, this project will propose a monitoring strategy for the RMP for PFAS that integrates with ongoing RMP modeling and monitoring work (e.g., integrated stormwater CECs modeling and monitoring, integrated Bay and watershed modeling, in-Bay fate modeling).

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?	- Synthesize various data sets and update risk evaluation - Identify monitoring data needs for RMP water quality managers to evaluate impacts	- What type of analytical methods (e.g., target, total oxidizable precursor, non-target) are needed to inform management decisions?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	- Synthesize recent data on stormwater and effluent pathways - Synthesis of relevant air monitoring data from other studies - Develop conceptual model for major sources and pathways of PFAS to the Bay -Summarize product categories likely associated with each transport pathway to the Bay	- What are PFAS levels in wastewater and urban stormwater runoff? - How important is air transport? - Is groundwater from contaminated sites a significant pathway to the Bay? - What are the priority information gaps to characterize major sources and pathways?
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?	- Summarize identified PFAS analytes in the environment - Identify new PFAS that have not been monitored in the Bay	- Where are the areas of greatest concern in the Bay?
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	- Evaluate temporal trends in Bay matrices and pathways	- Do available monitoring data indicate an increasing or decreasing trend?
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	- Summarize ongoing and anticipated management actions that may directly impact PFAS in the Bay	- What management actions will be most effective at reducing PFAS in the Bay?
6) What are the effects of management actions?	- Summarize ongoing and anticipated management actions that may directly impact PFAS in the Bay	- Will management actions have the intended effects? - Are management actions targeting the most important sources and pathways?

Approach

Synthesis

The synthesis will focus on studies from the last 10 years (2012-2023). Key datasets that will be compiled include monitoring data from Bay water, sediment, wastewater, stormwater, and biota. This will include the following RMP studies, which were conducted after the completion of the previous PFAS Synthesis (Sedlak et al., 2018).

- Bay water. Ambient Bay water samples collected in 2021 (Mendez et al., 2022). Additional deep Bay water and near-shore samples will be collected as part of the S&T program (dry season cruise 2023; WY2022-2024, as available).
- Sediment. Archived sediment collected from 2018 Status & Trends program and 2020 North Bay margins study (to be analyzed via a SEP-funded study). Additional sediment samples will be collected as part of the S&T program in 2023.
- Sport fish. Sport fish samples collected in 2019 (Buzby et al., 2019) and archived sport fish samples from 2009 - 2019 analyzed to evaluate trends.
- Prey fish. Samples will be collected in 2023 as part of the S&T program.
- Bird eggs. Samples collected in 2018 and 2022 as part of the S&T program.
- Marine mammals. Samples from 2023 that will be analyzed via targeted and non-target analysis.
- Stormwater. Stormwater samples collected during WY2020-2022 as part of RMP multi-year CEC stormwater screening study (Kolodjiez et al., in prep).
- Wastewater. Wastewater influent, effluent, biosolids, and sewershed samples collected winter of 2020 and summer of 2022 as part of BACWA PFAS Phase 1 (Mendez et al., 2021) and Phase 2 Study.

The synthesis will also compile available Bay monitoring data collected by others that are published in peer-reviewed journals and grey literature technical reports from reputable sources.

Literature Review

A concise and focused literature review will be synthesized to put the Bay Area monitoring data in context and inform the monitoring strategy. The understanding gained through this review of the major pathways of PFAS contamination and PFAS product categories most likely associated with each pathway will be summarized in the context of a conceptual model framework. The targeted literature review will include the following components:

- Evaluation of Bay data in the context of monitoring data from other regions
- Summary of advances in analytical methods for monitoring PFAS
- Summary of published PFAS product categories and other sources (e.g., groundwater contamination) likely associated with each transport pathway to the Bay
- Summary of known and important transport and fate processes for each transport pathway and in the Bay itself

- Identification and prioritization of major information gaps relevant for monitoring and modeling design and management information needs.

<u>Strategy</u>
A monitoring strategy will be developed for the RMP within the context of, and integrated with, regional monitoring and modeling, and designed to provide science to support management efforts. The monitoring strategy will provide recommendations for study design (e.g., matrix, spatial distribution, frequency, and analytical methods) appropriate for answering a range of study questions relevant to stakeholder-identified management priorities. We will vet the proposed strategy with selected PFAS advisors (in addition to the existing set of ECWG advisors), as well as the ECWG and TRC.

Budget

Table 2. Budget

Expense	Estimated Hours	Estimated Cost
Labor		
Synthesis	140	$23,300
Literature Review and Strategy	255	$42,300
Reporting	220	$40,400
Honoraria		
2 science advisors		$1,000
Grand Total		**$107,000**

<u>Budget Justification</u>

Labor hours are estimated for SFEI staff to manage the project, gather input from stakeholders and advisors, synthesize RMP and peer-reviewed datasets, conduct literature review, develop monitoring strategy, and prepare deliverables.

Reporting

The deliverable will consist of a report (draft due March 2025, final due July 2025) that includes synthesis summary tables, interpretation of results in context of literature review and conceptual model, and recommended monitoring strategy. Project updates will also be presented at the 2024 and 2025 April ECWG meetings.

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Special Study Proposal: PFAS and Nontargeted Analysis of Marine Mammal Tissues Year 2

Summary: A recent review of the RMP Status and Trends (S&T) Monitoring Program design led to the recommendation to explore the addition of Bay marine mammals, such as harbor seals, to the species included in periodic S&T monitoring. To inform the potential inclusion of marine mammals to the long-term S&T program, this two-year study includes examination of PFAS in multiple tissues of two local species, harbor seals and harbor porpoises. This proposal adds nontargeted analysis of PFAS and hydrophobic halogenated compounds to the pilot study, providing a means to identify unanticipated contaminants that may merit follow-up targeted monitoring. 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. This proposal is for the second year of this two-year project.

Estimated Cost:	$126,500 for Year 2 (Year 1 was $115,500, funded via S&T)
Oversight Group:	ECWG
Proposed by:	Ezra Miller and Rebecca Sutton (SFEI), Bernard Crimmins (AEACS, Clarkson University), Eunha Hoh (San Diego State University)
Time Sensitive:	Yes (multi-year study already underway)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Update sampling plan as necessary	January 2024
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 richardii*) 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 harbor seals in the South Bay 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 perfluorooctane sulfonate (PFOS) following its phase-out in the US; however, perfluorooctanoic acid (PFOA) and other long-chain carboxylates have not shown similar declines (Sedlak et al., 2017).

To explore whether it would be appropriate to add marine mammals to the S&T study design for PFAS monitoring, the RMP is piloting monitoring of marine mammal tissues, leveraging existing recovery and sample collection efforts by the Marine Mammal Center (Sausalito, CA) of two resident Bay species, Pacific harbor seals and harbor porpoises (*Phocoena phocoena*).

Two tissues, serum and liver, are being monitored for PFAS. Improved targeted 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 tissues 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 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 observed almost 200 halogenated organic contaminants, 81% of which are not routinely monitored by traditional targeted methods (Cossaboon et al., 2019).

To build on previous RMP marine mammal tissue monitoring and to more fully understand the occurrence of contaminants in top Bay predators, we propose a continuation of the current study leveraging the Marine Mammal Center sample collection efforts to evaluate concentrations of nontarget PFAS and identify nontarget nonpolar contaminants in harbor seal and harbor porpoise tissues.

Results may indicate the presence of PFAS and other contaminants accumulating in Bay wildlife that are not typically analyzed in targeted monitoring studies. Alternatively, this study may 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). Tissues from animals found along the nearby coast will be collected but may not be analyzed, depending on the number of animals recovered from within San Francisco Bay. Tissues from additional animals may be collected and archived if more than ten animals of each species are recovered from within San Francisco Bay.

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 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 broader geographic trends. Nontargeted PFAS analysis will determine if targeted 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 versus 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 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.

<u>Analytical Methods</u>

PFAS Targeted Analysis

For targeted quantification of PFAS (SGS AXYS; 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) 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, samples 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 analyzed 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 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.

Table 3. Summary of study design

Species	**Tissue**	**Max # of Samples**	**PFAS Targeted** SGS AXYS	**PFAS Nontargeted** Crimmins lab	**Hydrophobic Nontargeted** Crimmins lab and Hoh lab
Harbor seal	Serum	20	x		
	Liver	10	x	x	
	Blubber	10			x
Harbor porpoise	Serum	10	x		
	Liver	10	x	x	
	Blubber	10			x

Budget

Table 4. Estimated costs (estimated hours are for both years; estimated costs reflect only the second year).

Expense	Estimated Hours (2023-2024)	Estimated Cost (2024 only)
Labor		
Study Design	40	NA[1]
Sample Collection	48	3,000
Data Technical Services		10,000
Analysis and Reporting	180	18,000
Subcontracts		
AEACS, LLC		50,000
San Diego State University		25,000
SGS AXYS		19,000
Direct Costs		
Equipment		NA
Travel		0
Shipping		1,500
Grand Total		**126,500**

<u>Budget Justification</u>

This proposal describes year two of a two-year study with a total budget of $242,000 (year 1 funded for $115,500). 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. Increasing the number of samples for targeted analyses would only modestly increase the budget; however, increasing the number of samples for nontargeted analyses would require larger budget increases.

[1] Not applicable because covered by Year 1 funding

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 $582 per liver sample and $521 per serum sample. The analytical budget of $19,000 includes analysis of blood and liver tissues from 20 specimens, one liver field duplicate for each species, and two standard reference tissues, for a total of 25 samples, plus up to 10 additional serum samples from live harbor seal pups.

The Crimmins Laboratory (AEACS, Clarkson University) will 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) will 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 draft[2] 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.

[2] 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: Per- and Polyfluoroalkyl Substances (PFAS) in Ambient Bay Water and Sediment using the Total Oxidizable Precursors (TOP) Assay

Summary: Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are fluorine-rich, chemically stable compounds widely used in consumer, commercial, and industrial applications, and are ubiquitous in the environment. Two of the most studied PFAS, perfluorooctanoic sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are considered highly toxic, and other members of the class are predicted to have similar toxicity. The RMP has found PFAS in biota, water, and sediment as well as stormwater and wastewater. The RMP classifies PFAS as a Moderate Concern in the tiered risk-based framework due to concentrations in Bay biota linked to potential risks. A recently completed RMP analysis of PFAS in Bay water supported the continued prioritization of Bay monitoring for this class. However, most of the studies to date have focused on targeted methods analyzing up to 40 individual PFAS. The use of the total oxidizable precursors (TOP) assay provides a means to indirectly quantify a broad suite of PFAS precursors that break down to detectable compounds. This method has been used in recent Bay Area wastewater studies to demonstrate the presence of significant concentrations of unknown PFAS in this pathway. We propose a study to assess the levels of PFAS precursors in Bay water and sediment to supplement existing Status and Trends (S&T) monitoring of target PFAS and better characterize the presence of this class. Multiple options for sample collection are provided in response to potential constraints regarding Water and Sediment Cruise scheduling and available resources.

Estimated Cost:	$97,700; Dry & Wet Season Sampling (Bay Water & Sediment) $67,200; Dry & Wet Season Sampling (Bay Water Only) $27,200; Wet Season Sampling Only (Bay Water Only); Multi-year
Oversight Group:	ECWG
Proposed By:	Miguel Méndez, Rebecca Sutton
Time Sensitive:	Yes, leveraging S&T water monitoring in 2023 and 2024.

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Develop Sampling Plan	July 2023[1]
Task 2. Field Sampling – Bay Water & Sediment (*Dry Season*)	August-Sept. 2023
Task 3. Lab Analysis (*Dry Season*)	December 2023
Task 4. QA/QC and Data Management (*Dry Season)*	February 2024
Task 5. Preliminary Findings Presented at ECWG	April 2024
Task 6. Field Sampling – Bay Water (*Wet Season*)	Winter-Spring 2024[2]
Task 7. Lab Analysis (*Wet Season*)	June 2024[2]
Task 8. QA/QC and Data Management (*Wet Season*)	August 2024[2]
Task 9. Draft Report	November 2024
Task 10. Final Report	February 2025

[1]*Due to the timing of the dry season cruise, an early indication of funding likelihood is needed to prepare for sampling.*
[2]*Rows in gray are additional tasks related to sampling during the wet season.*

Background

Per- and polyfluoroalkyl substances (PFAS), a family of thousands of synthetic, fluorine-rich compounds commonly referred to as “forever chemicals,” are known for their thermal stability, non-reactivity, and surfactant properties. These unique substances have widespread uses across consumer, commercial, and industrial products, resulting in widespread occurrence in the environment and wildlife across the globe. Their highly persistent and recalcitrant nature, coupled with potential bioaccumulation and toxicity risks, raise concerns of negative impacts on wildlife and human health.

PFOS and PFOA, the most well-studied PFAS, have been the regulatory focus based on their extensive toxicity profiles highlighting a range of toxic effects, multi-year half-lives in human blood, and bioaccumulation in aquatic food webs (DeWitt, 2015; Sunderland et al., 2019). In the US, production of PFOS was phased out by 2002, and production of PFOA was phased out by 2015. With the increasing use of replacements for these compounds, it is important to understand the greater breadth of PFAS in the environment, particularly through a focus on PFAS precursors. These are compounds, both known and unknown, that have the potential to form perfluorinated carboxylic acids (PFCAs; i.e., PFOA) and/or perfluorinated sulfonic acids (PFSAs; i.e., PFOS), as they degrade in the environment.

Over the past two decades, ubiquitous environmental detections of PFAS have been documented by studies worldwide. Since 2004, the RMP has detected PFAS across matrices in San Francisco Bay with a series of monitoring projects on harbor seals, cormorants, fish, bivalves, sediment, and surface water. A recent 2021 study of PFAS in Bay surface water found 11 PFAS (of 40 analyzed) across 22 sites (Mendez et al., 2022). The sums of detected PFAS for all sites had median and maximum levels of 10 and 29 ng/L, respectively. South and Lower South Bay sites, strongly influenced by wastewater and stormwater due in large part to long residence times, exhibited statistically significant greater sums of PFAS when compared to the rest of the Bay. Sediment has not been measured as consistently as other matrices within the Bay, with the most recent study in 2014 finding various PFAS present (Sedlak et al., 2018). PFOS was detected most frequently and in the highest concentrations.

However, most of these studies have focused on targeted methods analyzing up to 40 individual PFAS. In contrast, a recent regional study of influent, effluent, and biosolids on behalf of the Bay Area Clean Water Agencies (BACWA) detected various PFAS across each matrix using targeted analysis of PFAS, as well as the Total Oxidizable Precursor (TOP) assay to indirectly measure unknown perfluoroalkyl acid precursors (Mendez et al., 2021). The TOP assay permits an assessment of the overall levels of persistent PFCAs and PFSAs that will form in a matrix following transformation of precursors to terminal products; this information is essential for evaluating the broader exposure and risks to Bay wildlife from PFAS. In the BACWA study, influent and biosolids samples examined using the TOP assay indicated the sum of PFAS concentrations roughly doubled compared to sums of only targeted analytes. These findings suggest that there are significant amounts of unidentified precursors in wastewater and likely other matrices. A second phase of the wastewater study will examine target and TOP results from sewershed sites representing residential neighborhoods and specific industries, as well as in influent, effluent, and biosolids.

Additionally, an ongoing study of PFAS in archived sediment samples is also using updated targeted analysis and the TOP assay to more thoroughly assess levels in the Bay. Analyzing samples from RMP margins sediment cruises in 2017 and 2020, this study will provide robust baseline data that can be used to evaluate changes with time.

The use of the TOP assay is a step towards understanding the broader range of PFAS that are present in the environment. Though more comprehensive methods of detecting PFAS beyond those observed via the TOP assay exist, these methods are significantly less sensitive (much higher detection limits). An initial screening of wastewater samples using one of these methods (AOF; adsorbable organic fluorine) that is underway will provide information to indicate its potential utility in Bay water sampling.

To better understand the occurrence, fate, and potential risks to ecological and human health posed by PFAS, we propose a study to apply the TOP assay to Bay water and sediment samples. These results can be compared to the RMP S&T 2023 and 2024 dry and wet season monitoring of PFAS in Bay water using targeted methods, as well as near-field and margins monitoring of sediment. The results will characterize the occurrence and potential risks posed by a broader sum of PFAS in the Bay. The findings will also inform the State Water Board's statewide investigation of PFAS.

Study Objectives and Applicable RMP Management Questions

The purpose of this study is to assess the concentrations of PFAS and precursors in Bay waters to improve our understanding of risks to wildlife and people. Comparisons to concentrations measured in previous years along with synonymous monitoring of surface water and sediment using targeted analysis will provide a greater understanding of the presence, transport, and fate of PFAS in the Bay. Additionally, we will compare levels of PFAS in different embayments, and across matrices, to monitor potential spatial patterns of contamination. This new study will expand on the limited targeted analysis of 40 analytes to indirectly evaluate the presence PFAS precursors.

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?	Monitor PFAS precursors in Bay water and sediment relative to target PFAS. Compare concentrations of PFAS precursors and aquatic toxicity thresholds, where available.	Are PFAS precursors present in the Bay at concentrations above detection limits? Do PFAS precursors in the Bay have the potential to contribute to PFAS impacts to aquatic life?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Compare current precursor concentrations to those previously detected in stormwater and wastewater.	Are there any particular trends from pathways to Bay water and sediment?
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	Compare levels and proportions relative to target PFAS across subembayments.	Do specific subembayments or regions appear to have greater levels of contamination?
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	Comparison to other studies of PFAS in Bay water and sediment	Establish baseline of PFAS precursors in Bay water and sediment
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

To accomplish the dry season Bay water and sediment sample collection, additions to the 2023 water and sediment cruise Sampling and Analysis Plans would need to be completed before the Steering Committee makes funding decisions for special studies (August 10th meeting). The Technical Review Committee can provide preliminary guidance on the relative importance of this effort at a meeting on June 20th, which can provide an indication as to whether to move forward pending funding.

<u>Bay Water Sampling</u>

Collection of ambient water samples will be coordinated with the recently updated RMP S&T dry season water monitoring cruise in the summer of 2023 and/or wet season monitoring activities in the winter of 2023-24. All samples will be grab samples of ambient Bay water (125 mL, HDPE), consistent with previous efforts.

During the dry season water cruise, 22 sites will be sampled, a combination of 6 fixed stations and 16 random stations across all five Bay segments, along with a field duplicate and two field blanks. Wet season sampling consists of 13 overall samples, with 7 at near-field sites and 6 at deep Bay stations. The near-field sites include 3 in-Bay stations near stormwater inputs (two storm events) plus one station near wastewater input (only one storm). Four deep Bay sites will be sampled within three weeks of one of the same storms sampled at the near-field locations, including a duplicate and field blank. Overall, 38 samples will be collected and shipped overnight to SGS AXYS, where they will be frozen to extend hold time to 90 days.

Sediment Sampling

Collection of near-field and margins sediment samples will be coordinated with the recently updated RMP S&T sediment monitoring cruise in the summer of 2023. The top 5 cm of sample will be collected using a 0.1 m^2 modified Van Veen sediment grab. In areas where sampling from the boat is not possible, overland access to the site and direct scooping from the target depth of surface sediment may be used.

A total of 20 sites will be sampled for this study during the sediment cruise including 12 margins sites and 8 near-field sites along with a field duplicate and field blank. These sites will be targeted to include areas in the Lower South Bay, where PFAS have been shown to be in greater concentrations in previous studies, as well as any areas not covered in the archived sediment study. Overall, 22 samples will be collected and shipped overnight to SGS AXYS, where they will be frozen to extend hold time to a year.

Analytical Methods

Samples will be analyzed by SGS AXYS (Sidney, BC, Canada) using SGS AXYS method MLA-111 to quantify 40 known PFAS, including breakdown products of various unknown precursors, using the TOP assay (Table 2). Both aqueous and solid samples are spiked with isotopically labeled surrogate standards before oxidation. Following this step, solids are extracted with methanolic ammonium hydroxide and treated with carbon. Aqueous and solid extracts are then oxidized using base and heat activated persulfate. Once cooled and pH-adjusted, the reaction mixture is spiked with isotope labeled quantification standards, extracted, and cleaned up using manual vacuum manifold or automated PromoChrom weak anion exchange SPE. Sample extracts are analyzed by ultrahigh performance liquid chromatography coupled to a triple quadrupole mass spectrometer (UPLC-MS/MS). Final sample concentrations are determined by isotope dilution/internal standard quantification. Reporting limits vary across noted PFAS groups (Table 2).

Table 2. PFAS Analytes in MLA-111 (SGS AXYS)

PFAS Classification/ *Analyte Type*	**PFAS Abbreviation**	**PFAS Name (Conjugate Base in parentheses)**	**Aqueous RLs (ng/L)**	**Solid RLs (ng/g)**
Perfluoroalkyl Carboxylates (PFCAs)/ *Product and non-reacting target*	PFBA	Perfluorobutanoic acid (Perfluorobutanoate)	13	0.8
	PFPeA	Perfluoropentanoic acid (Perfluoropentanoate)	7	0.4
	PFHxA	Perfluorohexanoic acid (Perfluorohexanoate)	3	0.2
	PFHpA	Perfluoroheptanoic acid (Perfluoroheptanoate)		
	PFOA	Perfluorooctanoic acid (Perfluorooctanoate)		
	PFNA	Perfluorononanoic acid (Perfluorononanoate)		
	PFDA	Perfluorodecanoic acid (Perfluorodecanoate)		
	PFUnA	Perfluoroundecanoic acid (Perfluoroundecanoate)		
	PFDoA	Perfluorododecanoic acid (Perfluorododecanoate)		
	PFTrDA	Perfluorotridecanoic acid (Perfluorotridecanoate)		
	PFTeDA	Perfluorotetradecanoic acid (Perfluorotetradecanoate)		
Perfluoroalkyl Sulfonates (PFSAs)/ *Non-reacting target*	PFBS	Perfluorobutanesulfonic acid (Perfluorobutanesulfonate)	3	0.2
	PFPeS	Perfluoropentanesulfonic acid (Perfluoropentanesulfonate)		
	PFHxS	Perfluorohexanesulfonic acid (Perfluorohexanesulfonate)		
	PFHpS	Perfluoroheptanesulfonic acid (Perfluoroheptanesulfonate)		
	PFOS	Perfluorooctanesulfonic acid (Perfluorooctanesulfonate)		
	PFNS	Perfluorononanesulfonic acid (Perfluorononanesulfonate)		
	PFDS	Perfluorodecanesulfonic acid (Perfluorodecanesulfonate)		
	PFDoS	Perfluorododecanesulfonic acid (Perfluorododecanesulfonate)		
Fluorotelomer Sulfonates/ *Reacting precursors*	4:2 FTS	1H, 1H, 2H, 2H-perfluorohexane sulfonic acid (1H, 1H, 2H, 2H-perfluorohexane sulfonate)	13	0.8
	6:2 FTS	1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (1H, 1H, 2H, 2H-perfluorooctane sulfonate)		
	8:2 FTS	1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (1H, 1H, 2H, 2H-perfluorodecane sulfonate)		

PFAS Classification/ *Analyte Type*	**PFAS Abbreviation**	**PFAS Name (Conjugate Base in parentheses)**	**Aqueous RLs (ng/L)**	**Solid RLs (ng/g)**
Fluorotelomer Carboxylates/ *Reacting precursors*	3:3 FTCA	2H, 2H, 3H, 3H-perfluorohexanoic acid (2H, 2H, 3H, 3H-perfluorohexanoate)	13	0.8
	5:3 FTCA	2H, 2H, 3H, 3H-perfluorooctanoic acid (2H, 2H, 3H, 3H-perfluorooctanoate)	83	5
	7:3 FTCA	2H, 2H, 3H, 3H-perfluorodecanoic acid (7:3 FTCA, 2H, 2H, 3H, 3H-perfluorodecanoate)		
Perfluorooctane Sulfonamides/ *Reacting precursors*	PFOSA	Perfluorooctanesulfonamide	3	0.2
	N-MeFOSA	N-Methylperfluorooctanesulfonamide		
	N-EtFOSA	N-Ethylperfluorooctanesulfonamide		
Perfluorooctane Sulfonamido-acetic Acids/ *Reacting precursors*	N-MeFOSAA	N-Methylperfluoro-1-octanesulfonamidoacetic acid (N-Methylperfluoro-1-octanesulfonamidoacetate)	3	0.2
	N-EtFOSAA	N-Ethylperfluoro-1-octanesulfonamidoacetic acid (N-Ethylperfluoro-1-octanesulfonamidoacetate)		
Perfluorooctane Sulfonamido Ethanols/ *Reacting precursors*	N-MeFOSE	N-Methylperfluoro-1-octanesulfonamidoethanol	33	2
	N-EtFOSE	N-Ethylperfluoro-1-octanesulfonamidoethanol		
Per- and Polyfluoroether Carboxylates/ *Varies (2nd and 4th on list are unstable)*	HFPO-DA (GenX)	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propionic acid	13	0.8
	ADONA	Decafluoro-3H-4,8-dioxanonoic acid (Decafluoro-3H-4,8-dioxanonoate)		
	NFDHA	Perfluoro-3,6-dioxaheptanoic acid (Perfluoro-3,6-dioxaheptanoate)	7	0.4
	PFMBA	Perfluoro-4-methoxybutanoic acid (Perfluoro-4-methoxybutanoate)		
	PFMPA	Perfluoro-3-methoxypropanoic acid (Perfluoro-3-methoxypropanoate)	13	0.8
Perfluoroalkyl-ether Sulfonates/ *Varies (First two on list are unstable and may not oxidize completely)*	9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (9-chlorohexadecafluoro-3-oxanonane-1-sulfonate)	13	0.8
	11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11-chloroeicosafluoro-3-oxaundecane-1-sulfonate)		
	PFEESA	Perfluoro(2-ethoxyethane)sulfonic acid (Perfluoro(2-ethoxyethane)sulfonate)	3	0.2

Budget

Table 2. Proposed Budgets

Expense	Estimated Hours (Range)	Dry & Wet Seasons (Water & Sediment)	Dry & Wet Seasons (Water Only)	Wet Season Request (Water Only)
Labor				
Study Design	15-45	$6,300	$4,200	$2,100
Sample Collection	20-65	$9,100	$6,300	$2,800
Data Technical Services		$17,000	$12,200	$5,200
Analysis and Reporting	55-185	$25,900	$18,200	$7,700
Subcontracts				
SGS AXYS		$31,400	$19,900	$6,800
Direct Costs				
Travel		$2,000	$1,400	$600
Shipping		$6,000	$5,000	$2,000
Grand Total		**$97,700**	**$67,200**	**$27,200**

Alternatives

Pilot monitoring of targeted PFAS in Bay water and sediment as well as ongoing studies of precursors in wastewater and archived sediment provide an excellent opportunity for a holistic review of a greater breadth of PFAS. Dry season monitoring cruises (water and sediment) are planned to occur this summer, requiring a quick turnaround of study design and inclusion in current sampling and analysis plans for the noted cruises. This study could also occur over several years, with wet season sampling serving as a pilot for the TOP assay in Bay water. The following year would include dry season monitoring of water and sediment, which could be limited to sites of interest based on past data.

Budget Justification

SFEI Labor
Labor hours are estimated for SFEI staff to manage the project, develop the study design, support sample collection, analyze data, briefly review toxicological risks, present findings, and write a report including recommendations on future related monitoring.

Data analysis can include examination of any trends related to chain length (particularly, short vs. long-chain PFAS precursors), spatial trends, and investigation into the influence of different pathways based on a comparison to TOP data from studies in wastewater and stormwater. Costs for sample collection are minimized through leveraging of sampling during the RMP S&T 2023 dry and wet season water cruises as well as the near-field and margins sediment cruises.

Data and Technical Services
Standard RMP data management procedures will be used for this project. Data will not be uploaded to CEDEN.

Laboratory Costs (SGS AXYS)
Analytical costs per sample are estimated at $522 (including additional data package and disposal fees). For 22 samples from dry season monitoring, with a duplicate and two field blanks, the total analytical cost is ~$13,100. Additional analysis of 13 wet season samples, with a duplicate and field blank, is ~$6,800. For analysis of 22 sediment samples, including a duplicate and field blank, is ~$11,500. For all analyses, the total is $31,400. This study leverages target PFAS results covered by S&T monitoring for both Bay water and sediment.

Early Funds Release Request
We request early release of funds for use in 2023 to coordinate with dry and/or wet season S&T monitoring activities.

Reporting

Preliminary results of dry season sampling will be presented to the ECWG at the spring 2024 meeting. A draft report will be prepared by 11/30/24, which will incorporate data from both sampling efforts and be reviewed by the ECWG and TRC. Comments will be incorporated into the final report, published by 02/28/25.

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Special Study Proposal: Tire and Roadway Contaminants in Wet Season Bay Water Year 3

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 and 2022. 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, the third and final year in a multi-year monitoring effort, 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's tiered risk-based framework for emerging contaminants. Results will be shared with the California Department of Toxic Substances Control's Safer Consumer Products Program, which seeks data to support its evaluation of tire chemical ingredients.

Estimated Cost:	$50,000
Oversight Group:	ECWG
Proposed by:	Ezra Miller, Kelly Moran, and Rebecca Sutton (SFEI); Ed Kolodziej (University of Washington)
Time Sensitive:	Yes, year three of multi-year study, leverages S&T pilot wet season water monitoring (2024)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Update sampling plan	August – September 2023
Task 2. Field sampling – wet season Bay water samples	Fall 2023 – Spring 2024
Task 3. Lab analysis	Fall 2023 – Summer 2024
Task 4. QA/QC, data management, and data upload	October 2024
Task 5. Presentation at ECWG	April 2025
Task 6. Draft report	June 2025
Task 7. Final 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 a 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 coho salmon (*Oncorhynchus kisutch*) LC50, the concentration at which half the individuals die after a few hours of exposure in laboratory experiments. While coho salmon are now absent from Bay tributaries, steelhead (*Oncorhynchus mykiss*), a threatened species, are observed in some streams (e.g., Guadalupe River, Alameda Creek), and are similarly susceptible to toxic effects from this contaminant at concentrations somewhat higher than coho (Brinkmann et al. 2022; French 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). This concentration approached the European Chemicals Agency 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 prioritized emerging contaminants in the Bay, including bisphenols, organophosphate esters (OPEs), and per- and polyfluorinated alkyl substances (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 Baystations far from stormwater inputs.

Tire-derived contaminants have only been monitored in Bay water during fall 2021 and in the first two years of the pilot S&T wet season monitoring (fall 2022 through spring 2023). These limited data suggest that tire-derived contaminants appear in the Bay in the wet season and potentially persist for many days after a storm event. These results are in distinct contrast to limited detections in dry season samples, indicating the importance of wet season monitoring. 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's 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 third year 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 the 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 present in urban stormwater, these data may also be used to inform RMP watershed and 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 water to improve our understanding of risks to aquatic life. These compounds may then be classified within the RMP's 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 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?	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 versus 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 in the Bay?	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	N/A
6) What are the effects of management actions?	N/A	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 withplanned S&T monitoring.

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

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 green dots). In total, during the 2023-2024 wet season, we anticipate collecting a total of seven samples from the in-Bay near-field pathway sites, not including field blanks and duplicates. For stormwater sampling in the watershed, SFEI generally uses at least 0.5 inches of rain in six hours as its sampling criterion. Sampling at the in-Bay stations will be completed within two tidal cycles of the storm at locations meeting this criterion.

Samples will also be collected at four deep Bay stations (Figure 1 blue dots) within three weeks of at least one of the same storms sampled at the near-field locations. In total, during the 2023-2024 wet season, we anticipate collecting a total of four samples from the deep Bay stations, 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.

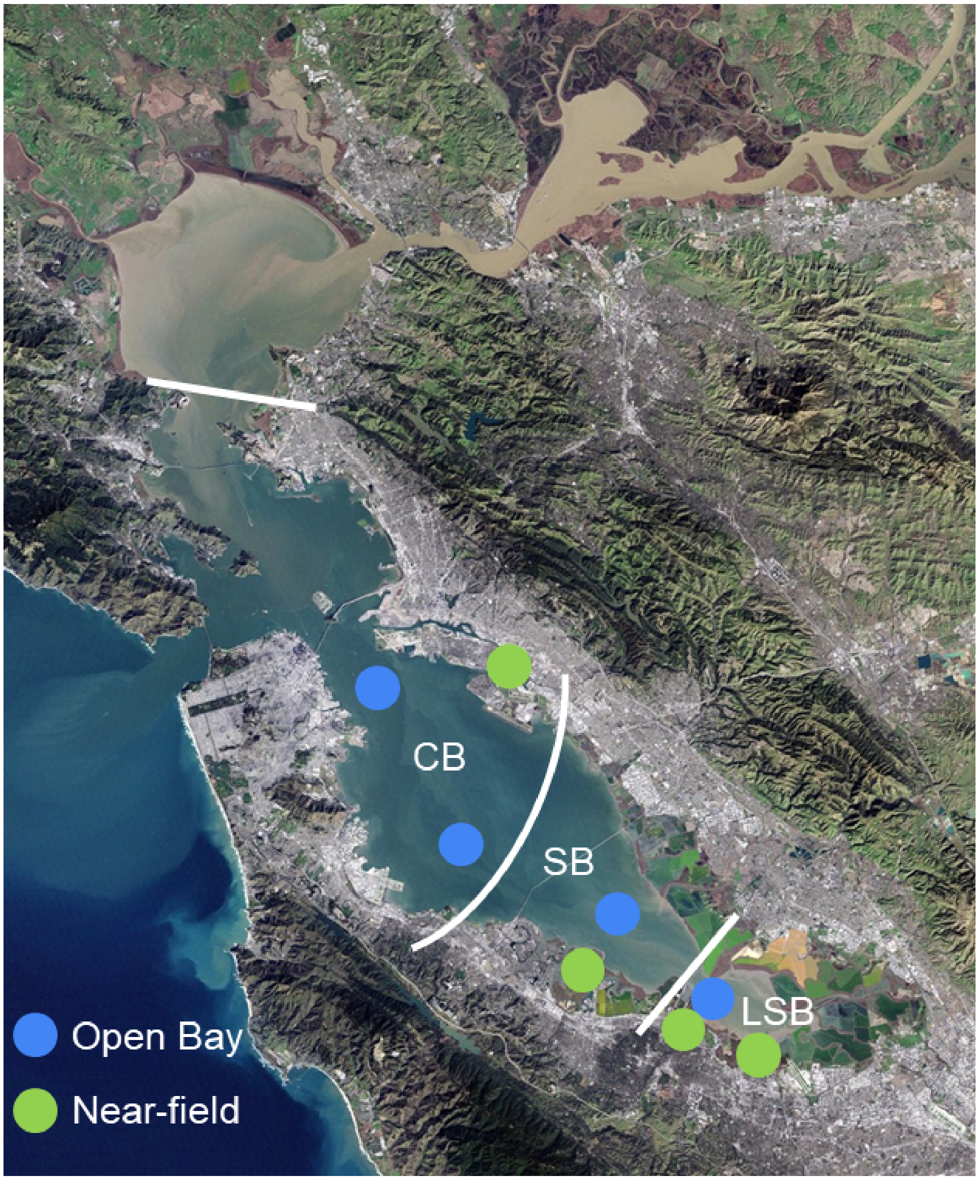

Figure 1. Proposed station selection for pilot wet season Status and Trends monitoring effort for water year 2024. Blue circles identify deep Bay stations; green circles identify in-Bay near-field stations (near San Leandro Creek, Redwood Creek, Stevens Creek, and Palo Alto municipal wastewater outfall). CB – Central Bay; SB – South Bay; LSB – Lower South Bay.

<u>Analytical Methods</u>

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). A broad range of compounds will be monitored, including pharmaceuticals, pesticides, and several tire-derived analytes such as 6PPD-quinone and DPG (Table 2). This suite of representative tracers for urban runoff includes a broad range of contaminants with different physical-chemical parameters (e.g., various chemical functionalities, a wide range of polarities and biodegradation potential). The compounds were selected to represent three primary urban sources/pathways: residential use, roadways, and wastewater.

Table 2. Targeted analytes.

Analyte Group	Analytes
Tire-derived Compounds	1,3-diphenylguanidine (DPG) hexa-(methoxymethyl)melamine (HMMM) N-cyclohexyl-1.3-benzothiazole-2-amine (NCBA) 6PPD-quinone
Benzotriazoles	benzotriazole 5-methyl-1-H-benzotriazole 2-amino-benzothiazole 2-hydroxy-benzothiazole 2-(4-morpholinyl)-benzothiazole
Urban Use Pesticides	clothianidin imidacloprid thiamethoxam carbendazim iprodione diuron prometon
Pharmaceuticals and Personal Care Product Ingredients	caffeine cetirizine cotinine *N,N*-diethyl-*meta*-toluamide (DEET) triclosan
Commercial/Industrial Compounds	1,3-dicyclohexylurea

Budget

Table 3. Proposed Budget

Expense	Estimated Hours	Estimated Cost
Labor		
Study Design and Coordination (details for this project)	25	4,250
Stormwater Sample Collection (additional costs for this project)	25	3,500
Data Technical Services	35	5,000
Analysis and Reporting	100	22,500
Subcontracts		
University of Washington		10,000
Direct Costs		
Equipment		1,000
Shipping		3,750
Grand Total		**50,000**

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.

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 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 $10,000.

Reporting

Results will be presented to the ECWG at the spring 2025 meeting; data will be incorporated into a 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 report will be reviewed by the ECWG, TRC, and SC. Comments will be incorporated into the final report, due September 30, 2025.

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Special Study Proposal: Organophosphate Esters, Bisphenols, and Other Plastic Additives in Bay Area Wastewater

Summary: Plastic additives are an extensive group of chemicals used in the production of plastics for a variety of consumer, commercial, and industrial applications. Many of the chemical classes that comprise plastic additives, especially organophosphate esters (OPEs) and bisphenols, are ubiquitous in the environment. In addition, many of these compounds are known to be toxic and exhibit a variety of effects on humans and animals. The RMP has previously found OPEs and bisphenols in wastewater, stormwater, and ambient Bay water. The RMP currently classifies both as a Moderate Concern within the RMP tiered risk-based framework for emerging contaminants. To build on these previous efforts, we propose a study to assess the concentrations of OPEs, bisphenols, and other plastic additives in Bay Area wastewater effluent. Analysis of OPEs is a particularly high priority to allow for an assessment of the relative importance of stormwater versus wastewater pathways to the Bay. Leveraging a study of OPEs to include other plastic additives is a cost-effective way to gain more information on a broader list of widely used and potentially toxic compounds.

Estimated Cost:	Monitor OPEs, Bisphenols, & Plastic Additives in Effluent: $95,400 Monitor OPEs *Only* in Effluent: $48,400
Oversight Group:	ECWG
Proposed by:	Miguel Méndez, Rebecca Sutton
Time Sensitive:	No

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Develop Sampling Plan	June 2024
Task 2. Field Sampling – Wastewater	August - Sept. 2024
Task 3. Lab Analysis	March 2025
Task 4. QA/QC and Data Management	June 2025
Task 5. Draft Report	September 2025
Task 6. Final Report	January 2025
Task 7. Presentation at ECWG	April 2026

Background

Plastic additives are an extensive group of chemicals, and can include antioxidants, flame retardants, plasticizers, UV stabilizers, and several other compounds (Chen et al., 2021). Many plastic additives share physical and chemical properties such as high hydrophilicity and mobility in the environment, which make them more difficult to remove via traditional wastewater treatment methods, leading to contamination of receiving waters. Plastic additives enter the environment through several different pathways from their substantial consumer and industrial uses, notably from wastewater and stormwater.

As some of the plastic additives manufactured and used in the greatest quantities globally, organophosphate esters (OPEs) are found ubiquitously in the environment. OPEs have emerged as a new generation of flame retardants due to the phase-out of polybrominated diphenyl ethers (PBDEs). Triester OPEs (tri-OPEs) are the most commonly used and studied, though diester variations (di-OPEs) are also observed and are metabolites of tri-OPEs. OPEs have been linked to many toxic effects such as endocrine disruption, neurotoxicity, adverse fertility effects, and carcinogenicity, with three OPEs—tris(2-chloroethyl) phosphate (TCEP), tris(2,3-dibromopropyl)phosphate (TDBPP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP)—listed as carcinogens on California's Proposition 65 List (OEHHA, 2023; Wei et al., 2015). Still, the full scope of toxicity of OPEs, particularly for di-OPEs, is not completely understood.

Bisphenols are another well-known class of plastic additives with similar properties to OPEs. They have also been detected ubiquitously in the environment due to their widespread production and use. Bisphenol A (BPA), the best studied of the bisphenols, has been shown to have estrogenic effects, and is on California's Proposition 65 List due to its developmental toxicity and female reproductive toxicity (Björnsdotter et al., 2017; OEHHA, 2023).

In 2017, the RMP biennial Status and Trends water cruise included analysis of 22 OPEs and 16 bisphenols in samples collected from 22 sites throughout the Bay during the dry season (Shimabuku et al., 2022). A pro bono add-on included preliminary characterization of 18 other plastic additives. Fifteen of 22 OPEs were detected, with six found in 100% of samples. The sum of all OPEs ranged from 35-290 ng/L (median 100 ng/L) across all Bay sites. In particular, concentrations of TDCIPP ranged from 2.8-23 ng/L, in the range of or above the marine predicted no effect concentration (PNEC) of 0.46 ng/L at many Bay sites (Xing et al., 2019). These detections were consistent with a previous screening study of flame retardants in surface water, sediment, bivalves, and harbor seal blubber conducted in 2013, which reported exceedances of toxicity thresholds for both TDCIPP and triphenyl phosphate (TPhP; Sutton et al., 2019).

Only BPA and bisphenol S (BPS) were quantified in 91% and 41% of sites, respectively, of the 16 bisphenols analyzed. Total concentrations of BPA (sum of particulate and dissolved contributions) ranged from <0.7–35 ng/L, while concentrations BPS ranged from <1–120 ng/L. These levels of bisphenols are in the range of a PNEC for BPA, 60 ng/L. Based on these findings, along with available toxicity data and potential for increasing use, OPEs and bisphenols have been classified as Moderate Concern within the RMP tiered risk-based framework for emerging contaminants.

All 18 additional plastic additives were detected in the 2017 survey, with 9 of 10 analyzed found in greater than 50% of samples. The sum of all additional plastic additives detected ranged from 220-3800 ng/L (median: 940 ng/L) across all Bay sites. One additive, tri(2-ethylhexyl) trimellitate (TOTM; also known as tris(2-ethylhexyl)benzene- 1,2,4-tricarboxylate) exceeded its marine PNEC of 6 ng/L at four sites, with a maximum concentration over an order of magnitude higher than its PNEC. Aquatic toxicity information as well as environmental occurrence data for many of these compounds is limited.

Several studies have identified wastewater and stormwater as important pathways of OPEs and bisphenols. A previous 2014 study of OPEs (Sutton et al., 2019) included a pilot evaluation in effluent from three wastewater treatment plants (WWTPs); 12 of 13 analytes were detected. The sum of all OPEs ranged from 3100-7900 ng/L with tris(1-chloro-2-propyl)phosphate (TCPP) and tris(2-butoxyethyl) phosphate (TBOEP) showing significantly higher levels compared to other analytes. A 2020 study of bisphenols in wastewater effluent from six wastewater treatment facilities detected 5 of 17 bisphenols (Mendez et al., 2022). BPA, BPF, and BPS were predominantly detected and the sum of bisphenols for all WWTP effluent samples had median and maximum concentrations of 96 and 246 ng/L. OPEs and bisphenols have also been detected in stormwater with further screening anticipated to better understand the importance of this pathway to Bay contamination. Other plastic additives have not been previously measured in local wastewater or stormwater, though based on these limited findings, they are likely to also be found in these pathways.

This proposal outlines a study to monitor OPEs, bisphenols, and additional plastic additives in wastewater effluent to continue building our understanding of pathways of these contaminants to the Bay. The results of this study can be compared to previous monitoring in wastewater and Bay water as well as forthcoming stormwater data to understand the relative influence of these pathways to the Bay. Analysis of OPEs is a particularly high priority to fill the data gap concerning effluent concentrations and loads, essential for an assessment of the relative importance of stormwater versus wastewater pathways to the Bay. The results from this study will further inform and refine the placement of OPEs, bisphenols, and other plastic additives in the RMP's tiered risk-based framework.

Study Objectives and Applicable RMP Management Questions

The purpose of this study is to assess the concentrations of OPEs, bisphenols, and additional plastic additives in wastewater effluent to improve our understanding of the sources and pathways of these contaminants into the Bay. Since pathways generally contain higher concentrations of contaminants due to their more direct connection to sources in urban settings, wastewater is an ideal matrix for early and broad detection of compounds that have been more recently incorporated into consumer and industrial products. Comparisons to concentrations measured in previous years in wastewater effluent will aid in this analysis. Comparing concentrations and estimated loadings for the wastewater and stormwater pathways can identify the relative importance of these pathways to Bay contamination. This study will expand analysis of OPEs, including di-OPEs, and can also include many additional plastic additives including bisphenols and others.

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	N/A
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Characterize levels of OPEs, bisphenols, and other plastic additives in effluent	Concentrations and estimated loadings from effluent can be compared to similar values from stormwater to assess the relative importance of these pathways to the Bay. The presence of different CECs in each pathway may provide clues as to potential 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?	N/A	N/A
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	Comparison to previous studies of OPEs and bisphenols in wastewater effluent.	Analysis of time trends related to concentrations and/or loadings of OPEs and bisphenols in effluent. This study will provide baseline information that can be used to evaluate changes with time for other plastic additives.
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

Wastewater Effluent Sampling

The primary goal will be to assess dominant effluent flows to the Bay. We propose to do this by collecting effluent from the six largest wastewater treatment facilities: Central Contra Costa Sanitary District (CCCSD), East Bay Dischargers Authority (EBDA), East Bay Municipal Utility District (EBMUD), Palo Alto Wastewater Treatment (PA), and San Jose-Santa Clara Regional Wastewater Facility (SJSC). These facilities account for ~70% of wastewater effluent flows to the Bay. At each facility, 24-hour composites of effluent will be collected into glass containers twice during Fall 2024. Samples will be collected during the week to avoid any variation from the weekend.

Analytical Methods

Samples will be analyzed by Dr. Da Chen’s laboratory (at Jinan University and Southern Illinois University), which previously analyzed bisphenols and OPEs in Bay water, as well as bisphenols in wastewater samples. Dr. Chen’s team will use their existing water method, which uses a Shimadzu HPLC coupled to an AB Sciex 5500 Q Trap MS/MS (Toronto, Canada). This method can include analysis of up to 160 plastic additives, including a suite of 24 OPEs, 16 bisphenols, 41 phthalates, 10 non-phthalate plasticizers, 40 antioxidants, and 29 UV stabilizers (Chen et al., 2021).

Table 2. OPEs, bisphenols, and other plastic additives analytes included in prior study (Chen et al., 2021); specific analyte list may be refined as part of study design.

Group	Analyte	Full Name
Organophosphate Esters	BPA-BDPP	Bisphenol A bis(diphenylphosphate)
	BPDPP	t-butylphenyl diphenyl phosphate
	CDP	Cresyl diphenyl phosphate
	EHDPHP	2-Ethylhexyl-diphenyl phosphate
	IDDPP	Isodecyl diphenyl phosphate
	RDP	Resorcinol bis(diphenyl phosphate)
	T2IPPP	Tris(2-isopropylphenyl) phosphate
	T35DMPP	Tris(3,5-dimethylphenyl) phosphate
	TBOEP	Tris(2-butoxyethyl) phosphate
	TBP	Tributyl phosphate
	TCEP	Tris(2-chloroethyl) phosphate
	TCIPP	Tris(2-chloroisopropyl) phosphate
	TCrP	Tricresyl phosphate
	TDBPP	Tris(2,3-dibromopropyl) phosphate
	TDCIPP	Tris(1,3-dichloro-2-propyl) phosphate

Group	Analyte	Full Name
Organophosphate Esters	TEHP	Tris(2-ethylhexyl) phosphate
	TEP	Triethyl phosphate
	TPhP	Triphenyl phosphate
	TPrP	Tripropyl phosphate
	V6	Tetrakis(2-Chloroethyl)dichloroisopentyldiphosphate
Bisphenols	BPA	4,4'-(1-Methylethylidene) bisphenol
	BPAF	4,4'-(Hexafluoroisopropylidene) diphenol
	BPAP	4,4′-(1-Phenylethylidene) bisphenol
	BPB	4,4'-(1-Methylpropylidene) bisphenol
	BPBP	4,4'-(Diphenylmethylene) diphenol
	BPC	2,2-Bis(4-hydroxy-3-methylphenyl) propanone
	BPC-dichloride	4,4'-(2,2-Dichlorovinylidene)bisphenol
	BPE	4,4'-Ethylidenebisphenol
	BPF	4,4'-Methylenebisphenol
	BPG	4-[2-(4-hydroxy-3-propan-2-yl-phenyl)propan-2-yl]-2-propan-2-yl-phenol
	BPM	4,4′-(1,3-Phenylenediisopropylidene) bisphenol
	BPP	4,4'-[1,4-Phenylenebis(1-methylethane-1,1-diyl)] bisphenol
	BPPH	5,5'-Isopropylidenebis(2-hydroxybiphenyl)
	BPS	Bis(4-hydroxyphenyl) sulfone
	BP-TMC	4,4'-(3,3,5-Trimethyl-1,1-cyclohexanediyl) bisphenol
	BPZ	4,4'-Cyclohexylidenbisphenol
Phthalates	BBzPh	Butylbenzyl phthalate
	iBCHPh	Isobutylcyclohexyl phthalate
	DAPh	Diallyl phthalate
	DBPh	Di-n-butyl phthalate
	DiBPh	Diisobutyl phthalate
	DiBzPh	Dibenzyl phthalate
	DiDPh	Diisodecyl phthalate
	DEPh	Diethyl phthalate
	DEHPh	Bis(2-ethylhexyl) phthalate
	BMPPh	Bis(4-methyl-2-pentyl) phthalate
	DHPh	Dihexyl phthalate
	DiHPh	Diisohexyl phthalate
	DNPh	Dinonyl phthalate
	DiNPh	Diisononyl phthalate
	DPePh	Di-n-pentyl phthalate

Group	Analyte	Full Name
Phthalates	DiPePh	Diisopentyl phthalate
	DPhPh	Diphenyl phthalate
	DPiPh	Diphenyl isophthalate
	DPrPh	Di-n-propyl phthalate
	DiPrPh	Diisopropyl phthalate
	DUPh	Diundecyl phthalate
Mono-phthalates	MBPh	Mono-n-butyl phthalate
	MiBPh	Monoisobutyl phthalate
	MBzPh	Monobenzyl phthalate
	MCHPh	Monocyclohexyl phthalate
	MEPh	Monoethyl phthalate
	MEHPh	Monoethylhexyl phthalate
	MHePh	Mono-2-heptyl phthalate
	MHxPh	Monohexyl phthalate
	MiNPh	Monoisononyl phthalate
	MOPh	Mono-n-octyl phthalate
	MPePh	Mono-n-pentyl phthalate
	MiPrPh	Monoisopropyl phthalate
	MEHHPh	Mono (2-ethyl-5-hydroxyhexyl) phthalate
	MEOHPh	Mono (2-ethyl-5-oxohexyl) phthalate
	MCPPh	Mono (3-carboxypropyl) phthalate
Non-phthalate plasticizers Non-phthalate plasticizers	ATBC	Acetyl tri-n-butyl citrate
	DiBA	Diisobutyl adipate
	DBA	Dibutyl adipate
	DiDeA	Diisodecyl adipate
	DiDeAz	Diisodecyl azelate
	DEHA	Bis(2-ethylhexyl) adipate
	DHeNoA	Di(n-heptyl,n-nonyl) adipate
	DINCH	Di-isononylcyclohexane-1,2-dicarboxylate
	TCaT	Tricapryl trimellitate
	TOTM	Trioctyl trimellitate
UV stabilizers: benzothiazoles	2-Me-BTH	2-Methylbenzothiazole
	2-Mo-BTH	2-(Morpholinothio)-benzothiazole
	2-Me-S-BTH	2-(Methylthio)-benzothiazole
	2-OH-BTH	2-Hydroxybenzothiazole

Group	Analyte	Full Name
UV stabilizers: benzotriazoles	1-H-BTR	1-Hydrogen-benzotriazole
	5-Cl-BTR	5-Chloro-benzotriazole
	5-Me-1-H-BTR	5-Methyl-1-hydrogenbenzotriazole
	1-OH-BTR	1-Hydroxybenzotriazole
	UV-234	2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol
	UV-320	2-(3,5-Di-tert-butyl-2-hydroxyphenyl) 2H-benzotriazole
	UV-326	2-Tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol
	UV-327	2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol
	UV-328	2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol
	UV-350	2-(3-Sec-butyl-5-tert-butyl-2-hydroxyphenyl)benzotriazole
	UV-P	2-(2-Hydroxy-5-methylphenyl) benzotriazole
	UV-PS	2-(5-Tert-butyl-2-hydroxyphenyl) benzotriazole
UV stabilizers: benzophenone	BP1	2,4-Dihydroxybenzophenone
	BP3	2-Hydroxy-4-methoxybenzophenone
	BP4	2-Hydroxy-4-methoxybenzophenone-5-sulfonic acid hydrate
	BP6	2,2-Dihydroxy-4,4-dimethoxybenzophenone
	BP8	2,2′-Dihydroxy-4-methoxybenzophenone
	4-OH-BP	4-Hydroxybenzophenone
UV stabilizers: others	4-MBC	3-(4-Methylbenzylidene) camphor
	BMDM	4-Tert-Butyl-4′-methoxydibenzoylmethane
	IAMC	Isoamyl 4-methoxycinnamate
	OC	2-Ethylhexyl 2-cyano-3,3-diphenyl-2-propenoate
	ODPABA	Octyl dimethyl-p-aminobenzoic acid
	OMC	Ethylhexyl methoxycinnamate
Antioxidants	BHA	2(3)-Tert-butyl-4-hydroxyanisole
	BHT-OH	2,6-Di-tert-butyl-4-(hydroxymethyl)phenol
	BHT-CHO	3,5-Di-tert-butyl-4-hydroxybenzaldehyde
	BHT-COOH	3,5-Di-tert-butyl-4-hydroxybenzoic acid
	3,5-DTBH	11-Methyldodecyl3-[4-hydroxy-3,5-bis(2-methyl-2-propanyl)pheny]propanoate
	4-tOP	4-(1,1,3,3-Tetra-methylbutyl)phenol
	AO245	hydroxy-3-methyl-5-(2-methyl-2-propanyl)phenyl]propanoate}
	AO259	1,6-Hexanediylbis{3-[4-hydroxy-3,5-bis(2-methyl-2-propanyl)phenyl]propanoate}
	AO425	2,2'-Methylenebis(4-ethyl-6-tert-butylphenol)
	AO565	4-[[4,6-Bis(octylsulfanyl)-1,3,5-triazin-2-yl]amino]-2,6-ditert-butylphenol

Group	Analyte	Full Name
Antioxidants	AO697	(1,2-Dioxo-1,2-ethanediyl)bis(imino-2,1-ethanediyl)bis{3-[4-hydroxy-3,5-bis(2-methyl-2-propanyl)phenyl]propanoate}
	AO1035	Sulfanediyldi-2,1-ethanediylbis{3-[4-hydroxy-3,5-bis(2-methyl-2-propanyl)phenyl]propanoate}
	AO1081	2,2'-Thiobis(6-tert-butyl-p-cresol)
	AO1098	N,N'-1,6-Hexanediylbis{3-[4-hydroxy-3,5-bis(2-methyl-2-propanyl)phenyl]propanamide}
	AO1222	Diethyl 3,5-di-tert-butyl-4-hydroxybenzyl phosphonate
	AO2246	2,2'-Methylenebis(6-tert-butyl-4-methylphenol)
	AO3790	Tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate
	AO22E46	2,2'-(1,1-Ethanediyl)bis[4,6-bis(2-methyl-2-propanyl)phenol]
	AO44B25	4,4'-Butylidenebis(6-tert-butyl-m-cresol)
	AO-TBM6	4,4'-Thiobis(6-tert-butyl-m-cresol)
	diAMS	Bis[4-(2-phenyl-2-propyl)phenyl]amine
	DBHA	Dibenzylhydroxylamine
	DET	N,N'-diethylthiourea
	DTG	1,3-Di-o-tolylguanidine
	DPG	1,3-Diphenylguanidine
	DPT	1,3-Diphenyl-2-thiourea
	DPPD	N,N'-Diphenyl-1,4-benzenediamine
	PANA	N-Phenyl-1-naphthylamine
	BBOT	2,2'-(2,5-Thiophenediyl)-bis(5-tert-butylbenzoxazole)
	MMBI	Methyl-2-mercaptobenzimidazole

Budget

Table 3. Budget

Expense	Estimated Hours (Range)	OPEs, Bisphenols, & Plastics Additives	OPEs Only
Labor			
Study Design	20	$2,800	$2,800
Sample Collection	40	$5,600	$5,600
Data Technical Services		$10,000	$6,200
Analysis and Reporting	120-250	$35,000	$16,800
Subcontracts			
Dr. Da Chen, Jinan/SIU		$35,000	$11,200
Direct Costs			
Equipment		$1000	$500
Travel		$2,000	$2,000
Shipping		$4,000	$2,500
Grand Total		**$95,400**	**$48,400**

Budget Justification

SFEI Labor
Labor hours are estimated for SFEI staff to manage the project, develop the study design, support sample collection, analyze data, review toxicological risks, present findings, and write a report including recommendations on future related monitoring.

Data analysis can include examination of any temporal trends, spatial trends, and investigation into the influence of wastewater and stormwater on noted concentrations and estimated loadings in the Bay. Costs for sample collection include SFEI staff assisting facilities to collect samples.
Data and Technical Services
To minimize costs, data will undergo RMP QA/QC review and be formatted for CEDEN but not uploaded.

Laboratory Costs (Dr. Da Chen, Jinan/SIU)
Analytical costs per sample are estimated at $700 for only OPEs and ~$2,190 for all analytes. For 12 field samples of only OPEs monitoring, with two field duplicates and two field blanks, the total analytical cost is $11,200. For monitoring of OPEs, bisphenols, and plastic additives, 16 samples would total $35,000.

Reporting

A draft report will be prepared by 09/31/25 and be reviewed by the ECWG and TRC. Comments will be incorporated into the final report, published by 1/31/26. Full results will be presented to the ECWG at the spring 2026 meeting.

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Special Study Proposal: Non-targeted Analysis of San Francisco Bay Fish

Summary: Contaminants in sport fish may have both human health and ecological implications. The RMP has been monitoring selected contaminants in sport fish for many years but has never done any non-targeted analysis of this matrix. This two-year study would leverage 2024 Status and Trends sport fish monitoring to collect sport fish samples for non-targeted analysis. This type of analysis will provide a means to identify unanticipated contaminants that may merit follow-up targeted monitoring and compare San Francisco Bay fish contaminant profiles with those of fish from other locations such as the Great Lakes. Anticipated study outcomes would include priorities and recommendations for future investigations of newly identified CECs of potential concern observed in sport fish.

Estimated Cost:	$110,000 for two-year study ($48,000 for Year 1)
Oversight Group:	ECWG
Proposed by:	Ezra Miller & Rebecca Sutton (SFEI), Bernard Crimmins (AEACS, Clarkson University)
Time Sensitive:	Yes, leverages S&T sport fish monitoring (2024)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Work with S&T Sport Fish Strategy Team to develop sampling plan	January 2024
Task 2. Sample collection	Summer 2024
Task 3. Lab and data analysis	Fall 2024 - Spring 2026
Task 4. Presentation to ECWG and TRC	April 2026
Task 5. Draft manuscript	June 2026
Task 6. Final manuscript	September 2026

Background

Sport fish in San Francisco Bay are an important matrix in which to understand the contaminant profile, as they are consumed by both people, particularly in low-income and immigrant communities practicing subsistence fishing, as well as by apex predators like cormorants and harbor seals. The RMP began sport fish monitoring in 1997, and Status and Trends samples are collected every five years (most recently in 2019) during the summer season. Data collected through this monitoring program not only provide updates on the status and long-term trends of contaminants in Bay sport fish, but are also used to update human health consumption advisories and evaluate the effectiveness of regulatory and management efforts to reduce the impacts of contaminants of concern in the Bay (Buzby et al. 2019).

Status and Trends sport fish contaminant monitoring by the RMP is focused on a limited list of contaminants: mercury, polychlorinated biphenyls (PCBs), dioxins, selenium, polybrominated diphenyl ethers (PBDEs), and select per- and polyfluoroalkylated substances (PFAS). However, investigations of sport fish and other wildlife collected from other highly urbanized coastal sites indicate that these regularly monitored contaminants represent only a small fraction of the total number of bioaccumulative contaminants present in aquatic life. While the RMP has been monitoring sport fish for many years, to date there has never been any non-targeted analysis of Bay sport fish.

Non-targeted analysis, a key element of the RMP's CEC strategy, can help to provide a measure of assurance that the RMP is not missing unexpected yet potentially harmful contaminants simply because of failures to predict their occurrence based on use or exposure prioritization criteria. This type of non-targeted study can lay the foundation for future targeted CECs monitoring by helping to identify new potential contaminants of concern without *a priori* knowledge of their occurrence. The RMP has conducted successful non-targeted analysis of nonpolar, fat-soluble compounds in bivalve tissue and seal blubber (Sutton and Kucklick 2015), and polar, more water-soluble compounds in Bay water and wastewater effluent (Sun et al. 2020; Overdahl et al. 2021), as well as in fire-impacted stormwater (Miller et al. 2021). Non-targeted analysis of marine mammal tissues is also currently underway as part of a pilot study to inform the RMP's Status and Trends program design.

The proposed study will employ a non-targeted analytical approach to examine samples of Bay sport fish to assess the contaminant profiles in the food chain and identify potential additional contaminants for future monitoring.

Results may indicate the presence of contaminants accumulating in Bay food chains that are not typically analyzed in targeted monitoring studies. Alternatively, should results reveal that most compounds of concern for wildlife and human health are already included in targeted monitoring, this study 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?	Screen CECs identified via non-targeted analysis for potential toxicity concerns, future monitoring needs, and data gaps.	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 variations in site 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 non-targeted analysis for the presence of unanticipated transformation products.	Do the results of non-targeted analysis indicate transformation of parent compounds into unanticipated contaminants with potential concerns for Bay wildlife or human health?
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

Approach

<u>Bay Fish Sampling</u>

Although the RMP Status and Trends (S&T) biota monitoring design was updated in 2022, the design for sport fish remains largely the same, with samples collected every five years. This project will involve collection of additional fish samples in conjunction with the planned 2024 S&T sport fish monitoring, using an "opportunistic" sampling approach planned with the help of the sport fish S&T team as they develop their sampling and analysis plan this fall (fall 2023).

Core RMP sport fish species include white croaker, shiner surfperch, white sturgeon, striped bass, halibut, northern anchovy, and jacksmelt. Other species are targeted primarily based on information needed to update Bay fish advisories. Species that have been sampled include Pacific herring, Pacific sardine, staghorn sculpin, brown rockfish, blue rockfish, barred surfperch, bat ray, rubberlip perch, black perch, cabezon, Pacific sanddab, diamond turbot, petrale sole, starry flounder, and monkeyface prickleback. Largemouth bass and common carp, which are only found in freshwater in the extreme Lower South Bay, have also been sampled near the San Jose wastewater outfall to track CECs and mercury.

The five existing core S&T stations that have always been sampled as part of S&T monitoring will continue to be monitored, including San Pablo Bay, Berkeley, Oakland, San Francisco Waterfront, and South Bay (may include Redwood Creek, Artesian Slough, and/or Coyote Creek) (Figure 1 green dots). This project would likely sample both expected relatively less contaminated sites such as San Pablo Bay and Berkeley, as well as sites with expected higher contaminant loads such as San Leandro Bay and the South Bay. Shiner surfperch are a good species for spatial comparisons, as they will also be collected from the Priority Margin Unit locations to track PCB trends (Figure 1 orange dots).

Fish are collected using a variety of techniques, including gill nets, otter trawls, and hook and line depending on location and species sought. For most analytes, multiple fish are used to make composite samples. Mercury and selenium in white sturgeon and mercury in striped bass, however, are analyzed in tissue from individual fish, so this project could also potentially take that approach depending on the target species.

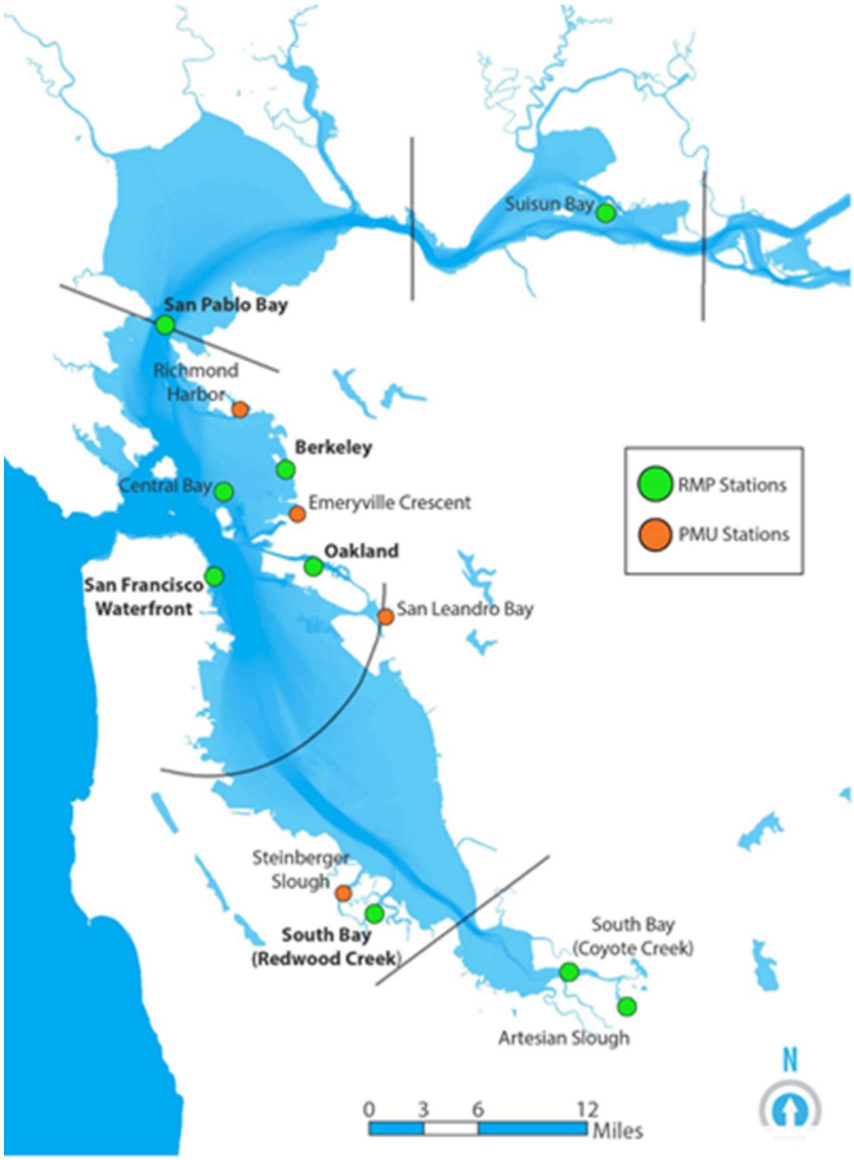

Figure 1. RMP S&T sport fish sampling locations. The green circles with bold names represent the five core stations included in the S&T Program (South Bay includes three locations – Redwood Creek, Artesian Slough, and Coyote Creek). Shiner surfperch will be collected from the Priority Margin Unit locations to track PCB trends (orange circles).

<u>Analytical Methods</u>

For non-targeted screening (Crimmins lab; AEACS, Clarkson University), fish tissue samples will be processed and analyzed using two non-targeted methods: one to look for non-polar compounds, and another to look for polar compounds, especially fluorinated polar compounds such as PFAS.

For non-polar compounds, DCM will be eluted through desiccated fish tissue 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).

Polar compound non-targeted analysis will be performed in accordance with Crimmins et al. (2014) and Fakouri Baygi et al. (2021). Tissue homogenates will be extracted using methods described in Point et al. (2019) and then analyzed 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.

The contaminant profiles for San Francisco Bay sport fish will be compared to profiles acquired previously from Great Lakes sport fish using the same sample preparation and analytical methods.

Budget

Table 2. Budget

Expense	Estimated Hours	Estimated Total Cost	Year 1 Request
Labor			
Study Design and Coordination	60	10,000	8,000
Sample Collection (additional costs for this project)	15	25,000	25,000
Data Technical Services		0	0
Analysis and Reporting	120	20,000	0
Subcontracts			
AEACS, LLC		50,000	10,000
Direct Costs			
Equipment		2,000	2,000
Shipping		3,000	3,000
Grand Total		**110,000**	**48,000**

Budget Justification

This proposal describes a two-year study with a total budget of $110,000 (split between the two years).

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, and assist with manuscript development.

Data Technical Services
Standard RMP data management procedures have not been developed for non-targeted data. These data will not be uploaded to CEDEN.

Sample Collection
Costs are minimized by leveraging Status and Trends sport fish sampling; nevertheless, fish composite sampling costs are estimated at $2,000 - $3,000 per sample (2019 costs were $1,873 for the usual species and $2,810 for hard-to-sample species). The budget therefore covers up to 12 samples, depending on species.

Laboratory Costs
The Crimmins Laboratory (AEACS, Clarkson University) can provide non-targeted analysis using two different methods on up to 12 fish tissues for a total cost of $50,000 (including 25% indirect rate). This budget includes both analysis and manuscript preparation. The majority of the analysis and reporting would take place during year 2 of the study.

Reporting

Results will be presented to the ECWG at the spring 2025 meeting, and may also be presented at a TRC meeting; a draft manuscript led by the Crimmins lab will serve as the RMP technical report for this project (draft for RMP review due September 2025, submission-ready draft[1] due December 2025).

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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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