

RMP Sources Pathways and Loading Workgroup Meeting Package

1.	Agenda	pgs. 1 - 6
2.	2020 SPLWG Meeting Summary	pgs. 7 - 15
3.	SPLWG Special Study Proposal: Small Tributaries Pollutants of Concern Reconnaissance Monitoring and Discrete Monitoring to Support Modeling	pgs. 16 - 25
4.	SPLWG Special Study Proposal: Regional Model Development to Support Assessment of Watershed Loads and Trends	pgs. 26 - 32
5.	SPLWG Special Study Proposal: CECs Remote Sampler Development and Pilot Testing	pgs. 33 - 37
6.	ECWG Special Study Proposal: Tracking Ethoxylated Surfactants in Wastewater and Stormwater	pgs. 38 - 46
7.	ECWG Special Study Proposal: Stormwater Contaminants of Emerging Concern (CECs) Monitoring Strategy	pgs. 47 - 54
8.	ECWG Special Study Proposal: Contaminants of Emerging Concern (CECs) in Urban Stormwater	pgs. 55 - 64
9.	ECWG Special Study Proposal: Tire and Roadway Contaminants in Wet Season Bay Water	pgs. 65 - 71
10.	ECWG Special Study Proposal: Wet Season Non-Targeted Analysis (NTA) of Bay Water and Stormwater	pgs. 72 - 79
11.	MPWG Special Study Proposal: Tire Particle/Contaminant Fate and Transport	pgs. 80 - 92
12.	MPWG Special Study Proposal: RMP Tires Strategy	pgs. 93 - 101

RMP Sources Pathways and Loading Workgroup Meeting Agenda

May 26, 2021, 9:30 am - 2:00 pm

May 27, 2021, 9:30 am - 2:00 pm

Remote Work Group meeting

Remote Access: Zoom Meeting

<https://zoom.us/j/200409313>

May 26th, DAY 1, 9:30-2:00

	Title	Time	Staff
1	Introduction and Goals for this meeting <ul style="list-style-type: none"> Welcome, introductions, ground rules, goals for today Overview of RMP planning <p>The goals for this meeting:</p> <ul style="list-style-type: none"> Provide context for RMP Sources, Pathways, and Loadings program Provide updates on RMP SLPWG 2020/21 activities Review study proposals for 2022 and receive advice to enhance those proposals Recommend a prioritized list of special studies and SEP concept proposals for 2022 <p>Attachment: 2020 SPLWG Meeting Summary (pages 7-15)</p>	9:30	Melissa Foley (SFEI)
2a	Information: Review of management questions <p>SF Bay Water Board staff will provide an overview of the management and policy priorities that are important considerations when planning future research as context for the meeting and proposal development and ranking.</p> <p>Desired Outcome: Informed workgroup</p>	9:45	Richard Looker (Water Board)
2b	Information: Overview of related stormwater program activities and objectives <p>BASMAA member agencies are key partners for the RMP who conduct monitoring in relation to the Small Tributaries Loading Strategy (STLS) and the municipal regional stormwater permit (MRP). Representatives will provide an update on their recent</p>	10:00	Chris Sommers (BASMAA)

	activities and management priorities to provide context for the meeting and proposal development and ranking. Desired Outcome: Informed workgroup		
3	Scientific Updates on Current Projects: Introduction	10:15	Melissa Foley (SFEI)
3a	Scientific Update: Stormwater Monitoring Update on coordination between the SPL, EC, and PCBs workgroups to sample and identify high leverage watersheds for PCBs, Hg, and CECs; presentation of 2021 results. Desired outcome: Informed workgroup	10:20	Alicia Gilbreath (SFEI)
	Break	10:40 - 10:45	
3b	Scientific Update: Regional LSPC Model Development to Support Watershed Loads Update on the development of the hydrology and sediment models, discuss plan for sediment and modeling in 2021, set expectations for model performance, and provide linkages to the future development of pollutant models. Desired outcome: Informed workgroup	10:45	Tan Zi (SFEI)
3c	Scientific Update: Advanced Data Analysis Update on final products of the Advanced Data Analysis project and expected/potential uses in the future. Desired Outcome: Informed workgroup	11:15	Lester McKee / Lisa Sabin (SFEI)
3d	Scientific Update: Integrated Monitoring and Modeling Strategy Update on the progress of the integrated strategy. Discuss plan for continuing effort the rest of 2021. Desired outcome: Informed workgroup	11:45	Tan Zi, Kelly Moran, Lester McKee, (SFEI)
	Break for Lunch	12:15 - 12:45	
4	Proposals: Introduction Summary of process for discussing proposals during Day 2. A broader discussion of all proposals will be held on Day 2 in Agenda Item 3a. Formal recommendations for funding will be	12:45	Melissa Foley (SFEI)

	made on Day 2 during Agenda Item 3b. Desired Outcome: Informed workgroup		
5	<p>Other Workgroup Proposals with Connections to SPLWG:</p> <p>The RMP Emerging Contaminants and Microplastics workgroups reviewed five stormwater-related RMP special study project proposals at their April meetings:</p> <ul style="list-style-type: none"> • Stormwater monitoring strategy for CECs (ECWG) • CECs in stormwater (year 4 of 4) (ECWG) • Wet season non-targeted analysis of Bay Water (ECWG) • Tire-related contaminants in Bay Water (ECWG) • Ethoxylated surfactants in wastewater and stormwater (ECWG) • Tires strategy (MPWG) • Tire particle/contaminant fate and transport (MPWG) <p>Each of these special study proposals will be briefly presented. Feedback from the lead workgroups will be summarized. The workgroup will have time to discuss and ask questions about the proposals.</p> <p>Desired outcome: Inform the workgroup, receive technical comments, answer clarifying questions.</p> <p>Attachments</p> <ul style="list-style-type: none"> • Agenda package, pages 38-101 	12:55	Kelly Moran (SFEI)
6	Recap of Day 1 and Expectations for Day 2	1:50	Melissa Foley (SFEI)
	Adjourn	2:00	

May 27th, DAY 2, 9:30-2:00

	Title	Time	Staff
1	Introduction <ul style="list-style-type: none"> Welcome, introductions, ground rules, goals for today Recap on Day 1 outcomes/ action items Summary of process for discussing proposals. 	9:30	Melissa Foley (SFEI)
2a	Proposal: Stormwater Monitoring for Continued Reconnaissance and to Support Modeling Justification/proposal for WY2022 stormwater monitoring work. Desired outcome: Feedback from advisors and stakeholders on the merits of this proposal and how it can be improved. Attachments <ul style="list-style-type: none"> Proposal 2: Agenda package, pages 16-25 	9:45	Alicia Gilbreath (SFEI)
2b	Proposal: Regional Model Development to Support Watershed Loads and Trends Justification/proposal for pollutant model development in 2022. Desired outcome: Feedback from advisors and stakeholders on the merits of this proposal and how it can be improved. Attachments <ul style="list-style-type: none"> Proposal 3: Agenda package, pages 26-32 	10:00	Tan Zi (SFEI)
2c	Proposal: CECs Remote Sampler Development and Pilot Testing Justification/proposal for CECs remote sampler development in WY2022. Desired outcome: Feedback from advisors and stakeholders on the merits of this proposal and how it can be improved. Attachments <ul style="list-style-type: none"> Proposal 4: Agenda package, pages 33-37 	10:15	Alicia Gilbreath (SFEI)
2d	Proposal: SEP project concept level proposals in a programmatic context Review current SEP projects list and propose new ideas for possible funding through supplemental environmental projects (SEPs) in a programmatic context.	10:30	Lester Mckee/ Alicia Gilbreath (SFEI)

	<p>Desired outcome: Feedback from advisors and stakeholders on the merits of each proposal and any needed improvements; Should any be elevated for consideration for special studies funding in 2022? List of SPLWG-approved new ideas for possible future SEP funding.</p> <p>Attachments</p> <ul style="list-style-type: none"> • Proposal 5: proposed SEP projects write-up • Agenda package, forthcoming 		
3a	<p>Discussion (Open): Recommended studies for 2022</p> <p>Desired Outcomes: The workgroup will review and critique the proposals presented within the broader programmatic context of a 5-year Bay stormwater and watershed information needs as outlined in the SPLWG work plan and other RMP workgroup (SWG, PCBWG, ECWG, MPWG) plans.</p>	11:00	Melissa Foley (SFEI)
	Break for Lunch	12:15 - 12:45	
3b	<p>Decision (Closed): Recommendations for 2022 special studies funding and SEP list</p> <p>RMP Special Studies are identified for funding through a three-step process. Strategy teams/ Workgroups reach a consensus and recommend studies for funding to the Technical Review Committee (TRC). The TRC weighs input from all workgroups and then recommends a slate of studies to the Steering Committee (SC). The SC makes the final funding decision. To avoid an actual or perceived conflict of interest, the Principal Investigators for proposed special studies will leave the meeting during this item.</p> <p>Desired Outcomes: Recommendations from the SPLWG to the TRC regarding which special studies should be funded in 2022 and their order of priority.</p>	12:45	Facilitation by Chris Sommers (EOA)
3c	Report out on Recommendations	1:45	Chris Sommers (EOA)
	Adjourn	2:00	

Final reports since last WG meeting

- Gilbreath, A.N., Hunt, J.A., and McKee, L.J., 2020. Pollutants of concern reconnaissance monitoring final progress report, water years 2015 - 2019. A technical report prepared for the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP). Contribution No. 987. San Francisco Estuary Institute, Richmond, California.
<https://www.sfei.org/documents/pollutants-concern-reconnaissance-monitoring-water-years-2015-2018>
- Zi, T., McKee, L., Yee, D., Foley, M., 2021. San Francisco Bay Regional Watershed Modeling Progress Report, Phase 1. Report prepared for the Sources Pathways and Loadings Workgroup of the Regional Monitoring Program for Water Quality. SFEI Contribution No.1038. San Francisco Estuary Institute, Richmond, CA.

Reports for SPLWG Review

- Pollutants of Concern Reconnaissance Monitoring Water Years 2015-2020. Draft Progress Report.

Forthcoming Reports

- McKee, L.J., and Gilbreath, A.N., 2021. Small Tributaries Pollutants of Concern Reconnaissance Monitoring: Application of loads and yields-based and congener-based prioritization methodologies. SFEI Contribution No. xxx. San Francisco Estuary Institute, Richmond, California.



RMP Sources Pathways and Loadings Workgroup Meeting

May 27-28, 2020 (teleconference)

Meeting Summary

Advisors	Affiliation
Barbara Mahler	USGS
Tom Jobes	Independent
Jon Butcher	Tetra Tech

Attendees:

- Alicia Gilbreath (SFEI)
- Autumn Bonnema (MLML)
- Bonnie de Berry (EOA)
- Bridgette DeShields (Integral)
- Bryan Frueh (City of San Jose)
- Chirs Sommers (SCVURPPP / EOA)
- Don Yee (SFEI)
- Jay Davis (SFEI)
- Lester McKee (SFEI)
- Lisa Austin (Geosyntec)
- Lisa Sabin (SCVURPPP / EOA)
- Luisa Valiela (EPA)
- Melissa Foley (SFEI)
- Nina Buzby (SFEI)
- Rebecca Sutton (SFEI)
- Richard Looker (SFBRWQCB)
- Tan Zi (SFEI)
- Tom Mumley (SFBRWQCB)
- Xavier Fernandez (SFBRWQCB)

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

Day 1

1a. Information: Review of management questions

Melissa Foley began the meeting by presenting recommendations on effectively using the remote Zoom platform. After going over the meeting's agenda, Melissa noted the difference in items being covered in each of the two days. While introducing the group's expert advisors, Melissa acknowledged the group's newest advisor - Dr. Jon Butcher from Tetra Tech. Melissa then provided an overview of the RMP goals and budget, outlining for the participants how the workgroup fits into the program organization and budget. When speaking about the program

budget, Melissa highlighted the difference between the cost of proposed studies and the amount will likely be funded by the RMP governance committees.

1b. Information: Overview of related stormwater program activities and objectives

Richard Looker from the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB or Water Board) provided further context to the group on the management questions the Water Board is hoping to answer through the work of the SPLWG. Noting that last year's discussion suggested transitioning away from PCB-centric efforts, Richard emphasized the goal to seek a balance between legacy and emerging contaminant work. Related to future needs, Richard communicated a desire to model and monitor effectiveness of control measures, urging the group to start thinking about the information needed to address such a task. Richard recognized that the RMP would likely not be the sole funder of these activities, but that this would be a good group to discuss the options.

Chris Sommers then provided the group with an overview of the drivers and needs of current stormwater work; specifically pollutants of concern (POC) monitoring efforts and determining how to track benefits of control efforts over time. Related to the POC monitoring, Chris noted that there are discussions to update the MRP permit (MRP 2.0 to MRP 3.0) with likely implementation in 2021. Additionally, Chris explained a predictive modeling approach known as Reasonable Assurance Analysis (RAA) that has a planned document release for September 2020. When asked about the future of RAA work, Chris responded that future steps will involve tracking and verifying predicted changes over time.

The discussion moved on to the nexus of SPLWG with other RMP groups (e.g., STLS, workgroups). Because the SPLWG is not a pollutant-specific WG, there are often connections to other workgroup efforts. Melissa Foley emphasized the importance of being able to coordinate and engage in a cost-effective manner, given the growth of many workgroup efforts. Chris also commented on the STLS goals to which the group's special studies will contribute, including identifying additional source areas, improving data analysis techniques, and evaluating trends in pollutant loadings in relation to stormwater.

2a. Proposals: Introduction

Melissa Foley began the item by reviewing the SPLWG's priority management questions and providing an update on 2020 special study efforts. Related to 2020 work, the group was informed that the uniquely dry year put a damper on POC reconnaissance monitoring efforts. Melissa then gave a brief overview of the 2021 special study proposals, namely who would be presenting each proposal in the following items. The proposal funding STLS coordination and management, however, would not be presented. Melissa explained that since the funding is critical to STLS function, it would not be considered in the later prioritization exercise by the

TRC. Prior to hearing the proposal presentations, Melissa presented the group with guiding questions to consider so the proposed projects could fit within the likely funding allocation for the group.

2b. Proposal: Reconnaissance characterization monitoring

Alicia Gilbreath presented an overview of the reconnaissance monitoring proposal, highlighting that the main item for discussion should be what monitoring is needed to support the SPLWG's direction in future years. As context, Alicia reminded the group of past load monitoring efforts from 2003-2010 and 2012-2014 that were more intensive in comparison to the 2011, 2015-2020 reconnaissance efforts. Due to limited funding, Alicia presented the recommendation to continue reconnaissance monitoring due to the data applicability to BASMAA and cost sharing opportunities with emerging contaminant work. Because of the limited work that occurred in 2020, there is \$55,000 leftover in the budget to carry over to 2021 efforts making the actual funding needs of the work \$65,000 (full cost \$120K).

The majority of the following discussion amongst the workgroup participants focused on the differences between loads and reconnaissance monitoring. Alicia provided further details on loadings efforts, noting that the number of sites would be dependent on the funding amount, and that they would likely be past load monitoring sites and/or previous reconnaissance monitoring locations. Jon Butcher also brought up the possibility of collecting depositional sediment along with reconnaissance monitoring for later PCB congener and/or aroclor analysis.

2c. Proposals: Advanced Data Analysis (ADA)

Lester McKee presented the proposal to continue advanced data analysis efforts on reconnaissance monitoring data that began in 2018. The continuation of funding would allow for statistical analysis on more datasets and complete reporting efforts. Lester encouraged the group to consider any possible improvements to the methods and whether there was value in finishing the analysis on remaining data. While presenting the methods and results from the current ADA efforts, Lester highlighted the relationship between PCB aroclor patterns and particle concentrations. He suggested that aroclor signatures could be used to indicate upstream sources. Lester also presented the group with a timeline of the current efforts, including a draft report towards the end of the summer.

In presenting the proposal, Lester offered the group two options on how to continue the work: (1) finish the current efforts and get a comparative ranking for all sites, or (2) add aroclor analysis of soil and sediment samples to complete more upstream source tracking. In response to these options, the group discussed the utility of the current ADA results - specifically how they will support BASMAA decision-making. The discussion covered various technical aspects related to the analysis methods, which reflected the complexity and difficulty associated with ranking catchments to determine locations worth management actions.

2d. Proposal: Regional Model Development to Support Watershed Loads and Trends

The newest member of the SPLWG team at SFEI, Tan Zi, presented the proposal to continue efforts on the regional watershed model. Putting the work in context, Tan reviewed the group's multi-year modeling plan and timeline of modeling deliverables. Tan also provided an overview of his progress on the hydrology model, next steps for sediment and POC calibration, and challenges with development. In the following discussion, Richard Looker and Tom Mumley expressed the Water Board's desire to broaden the range of contaminants that the workgroup addresses. What developed was a group consensus that the modeling work on hydrology and sediment could provide a foundation for various other applications/contaminants in the future. In order to make the most of this model going forward, the group agreed that an integrated monitoring and modeling strategy should be a priority.

SFEI staff noted that the current contaminants being used to develop the model, mercury and PCBs, are ideal given their difference in distribution and source-release-transport processes. In order to develop the model with emerging contaminants in mind, the participants agreed that there would also need to be an understanding of what such modeling needs would be, specifically conceptual model insight. Through the Zoom platform's chat function, there were discussions in support of incorporating CECs into the 2021 modeling proposal.

2e. Summary of proposals in a programmatic context and group discussion

Lester McKee reviewed all three of the proposals, noting which category of workgroup efforts - pilot studies, field programs, modeling tools, outcomes - each was aligned with. He also reminded the group of the prioritization goal for the following day of the meeting, and asked what balance of aspects is a priority for the workgroup and will best suit ongoing programmatic needs.

The participants discussed the utility of the potential data to come from the proposals. Notably, Lisa Austin and Lisa Sabin expressed a potential interest in the ADA findings, but that they would be able to determine the urgency of continued work after seeing the upcoming report. Lisa Austin also commented that the ADA method development will possibly inform future BASMAA work.

Day 2

Melissa Foley began the second day of the meeting by welcoming participants, outlining goals for the day, and the steps that would be followed for the closed door session. She also provided

a recap of the first day of the meeting, commenting that after the previous day's discussions, SFEI staff had added an integrated modeling and monitoring strategy to the proposal lineup. Melissa then went over the day's agenda and reminded participants about the potential for Supplemental Environmental Project (SEP) funding and the process for getting studies on the list.

3. Proposal: SEP project concept level proposals

Lester McKee presented the group with SEP ideas, starting by reviewing the workgroup's management questions and how they relate to outside work and other RMP efforts. While providing details on each of the potential SEP studies, Lester explained the motivations for adding them to the SEP list. For example, conducting additional monitoring to support modeling efforts is not quite ready to be a full special study, but SEP funding would allow for a few fixed sites suitable for trend tracking.

Tom Mumley voiced an initial concern towards projects for green stormwater infrastructure and strategic efforts. Previous discussions have revealed that such studies wouldn't be considered 'RMP-based' unless they have a strong Bay-monitoring component and/or specific deliverables. Workgroup members then provided comments on the six proposed SEP ideas, excluding the green stormwater infrastructure projects. Comments ranged from improving clarity on final deliverables, coordination opportunities, and possible alternative funding sources. As a method of approval, the participants were also asked to voice dissent on any of the projects.

4a. Discussion (Open): Recommended studies for 2021

As a preface to the discussion, Melissa presented the group with coronavirus contingency planning for the proposals. Comments from the group lead to the understanding that discussion of the proposals should proceed considering the 'normal times' scenario. Chris Sommers suggested that the TRC could handle any possible changes on a quarterly or monthly basis.

Multiple participants brought up the fact that the ADA work would be the least time sensitive, and any delay would allow for stakeholders to digest and interpret the upcoming technical report. Tom Jobs noted that if ADA results would help inform regional model development, a phased approach could be more beneficial.

The group also took time during the item to begin to flesh out the scope of the new integrated modeling strategy proposal. The study funding would cover staff time and input from workgroup experts. Lester McKee provided some initial thoughts on what sorts of information would be most helpful to have on CECs and Rebecca Sutton, lead of the ECWG, responded with some examples of existing contaminant knowledge. The conversation elucidated both a long-term goal to better understand how to direct data collection that addresses modeling needs, as well as a coordination task on how to fit all the pieces together. To help make headway absent of a formal strategy, Tom Mumley encouraged thinking about possible iterative efforts.

Towards the end of the item the group discussed whether funding for STLS management could be decreased. Melissa provided context that the funds for such efforts have been decreasing each year, so the proposed \$30K was a lower amount compared to the previous year. She suggested that the group return to that question after the closed door prioritizations - providing more insight on what studies the STLS would be weighing in on.

4b. Decision (Closed): Recommendations for 2021 special studies funding and SEP list

Study Name	Proposed Budget	Final Budget	Priority	Comments
STLS Program Management	\$30,000	\$30,000	-	Review of all ongoing projects in SPLWG and collaboration on data collected outside of the RMP; important for collaboration; important but expensive; could consider incorporating these costs into the projects themselves, possibly starting in 2022; separate line item is cleaner; move inter-workgroup coordination meetings to integrated strategy budget.
Small Tributaries Loading POC Watershed Reconnaissance Monitoring*	\$120,000	\$65,000	3	Loads monitoring is more useful for the modeling, so a shift in the near term should be considered; BASMAA gets a lot of use out of monitoring - should RMP pay to do this; serves a lot of needs and has value; 2020 light on sampling, so finish work in 2021 before moving to loads monitoring; serves two working groups (SPLWG and ECWG); BASMAA supplements the monitoring done by the RMP; addresses priority management questions for the group (high leverage source areas); less time sensitive than modeling or integrated strategy; use 2019 and 2020 leftover funds to supplement 2021 budget
POC Data Interpretation - Advanced Data Analysis	\$30,000 - \$50,000	\$15,000 - \$50,000	4	Not time sensitive; is phasing important or doable?; push to 2022 to give BASMAA a chance to see what else is needed for the method; more valuable if we wait before investing in another year; potential and application of project is great and helps prioritize source areas; integrating sediment (\$50k) would be great for counties without a lot of water data; consider costs of normalization and aroclors pieces and consider costs to optimize outputs; congener analysis may

				be a lower priority of the project; update proposal with normalization and aroclors components, with and without sediment
Regional Model Development to Support Watershed Loads and Trends	\$150,000	\$150,000	1	High priority (all advisors); critical to keep this project moving; make sure there are budget options for the project ; dividing tasks will slow down the overall project
Integrated Monitoring and Modeling Strategy - CEC Conceptual Model	\$30,000	\$50,000	2	Important to understand what you need the model to do now rather than later after the model is developed; phase in CECs based on available information and knowledge about them; should it be part of the regional model development effort? may be different participants, so it might make sense to keep it as a separate effort; important for saving time and money in the future on the model; time sensitive and important to get started on this; will need to communicate clearly to SFEI staff what this looks like; Chris Sommers and Richard Looker to help SFEI develop brief proposal with funding level options (\$30k-\$60k)
	<u>\$360,000 to 380,000</u>	<u>\$340,000</u>		

4c. Report out on Recommendations

Chris Sommers reported the results of the closed session discussions, noting that the lower ranking for ADA work was a result of the group's desire to wait for the reporting of the current work. Additionally, the group tasked SFEI with providing more detail on the cost of aroclor-related work in comparison to sediment efforts for the ADA. Chris also explained that while SEP projects were not ranked, there was discussion earlier in the day that provided input on whether or not they should be included/added to the project list. The group was supportive of adding all proposed projects to the SEP list except the green stormwater infrastructure projects. Lester ended the meeting by outlining a brief timeline and next steps towards planning and authoring a new proposal to present to the Bay RMP Technical Review Committee in June for the integrated modeling strategy. The first step would include input from stakeholders, Chris Sommers and Richard Looker, to get some initial ideas on what the work could look like.

Adjourn

About the RMP

RMP ORIGIN AND PURPOSE

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

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

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

RMP PLANNING

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

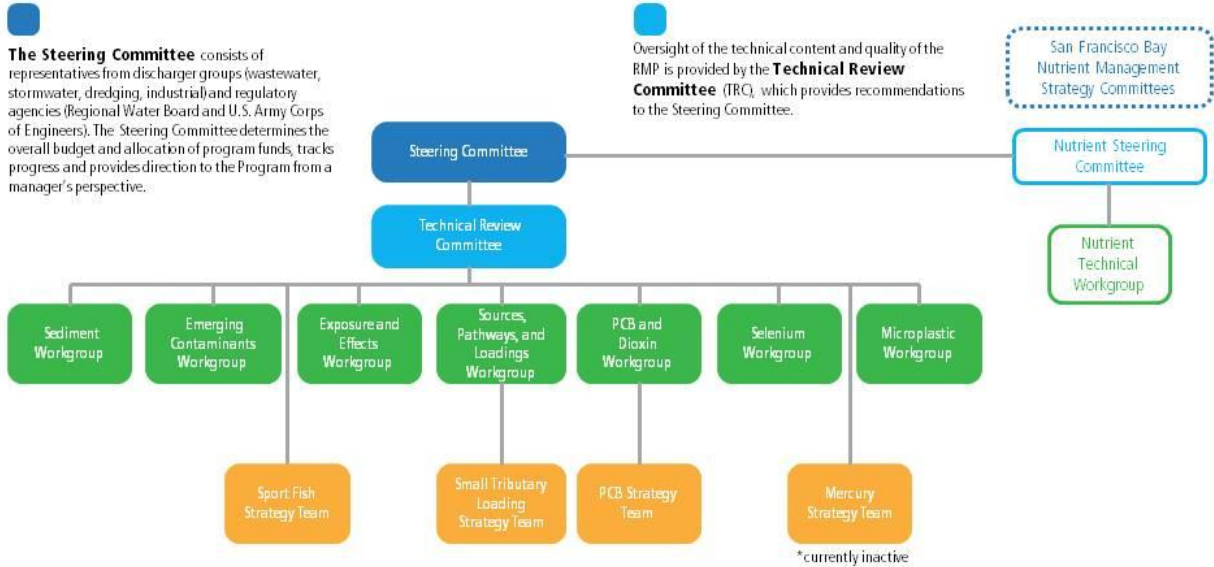
The annual planning cycle begins with a workshop in October in which the Steering Committee articulates general priorities among the information needs on water quality topics of concern. In the second quarter of the following year the workgroups and strategy teams forward recommendations for study plans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

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

PURPOSE OF THIS DOCUMENT

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

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



SPLWG Special Study Proposal: Small Tributaries Pollutants of Concern Reconnaissance Monitoring and Discrete Monitoring to Support Modeling

Summary: The RMP has monitored stormwater throughout the region using multiple techniques over the last 19 years. With the exception of 2011, from 2002 to 2014, intensive loads monitoring during multiple storms and years was carried out to compute loads in single watersheds and support modeling to estimate regional loads. In contrast, in 2011 and from 2015 to 2021, a reconnaissance monitoring style (single storm composite samples) was adopted to identify high leverage watersheds of potential management interest. At this time, data to support both goals (identifying high leverage watersheds and regional modeling) are relevant to current management needs. This project proposal addresses both needs by presenting a flexible monitoring design that includes both reconnaissance monitoring and discrete sampling at existing flow stations to support modeling.

Stormwater monitoring for pollutants of concern occurs in coordination with stormwater monitoring for the Emerging Contaminants Workgroup (ECWG) (for specific emerging contaminants), the PCB Workgroup (PCBWG) and potentially future work overseen by the Sediment Workgroup (SedWG). Decisions about where to monitor during each storm will be supported by a decision tree that will be developed in consultation with those WG leads.

This is primarily a field study and the level of effort will be tailored to the amount of budget available. There is no phasing proposed.

Estimated Cost: \$93k (and at least \$50k carryover from WY 2021) (at least \$143k total)

Oversight Group: STLS/SPLWG

Proposed by: A Gilbreath, D Yee, T Zi and L McKee (SFEI)

Time Sensitive: Somewhat. This is a continuation of a multi-year study to identify PCB and Hg sources to inform management actions. More urgently, any discrete data collected at existing flow stations could immediately support the regional watershed modeling development effort intended for 2022 and 2023.

Proposed Deliverables and Timeline

Deliverable	Due Date
Selected site list and preparation for sampling	09/2021
Wet season water samples collected and sent to the labs for analysis	04/2022
Laboratory analysis, QA & Data Management	09/2022
Interpretation & reporting for BASMAA	02/2023
Draft report	03/2023
Final report	06/2023

Background

The San Francisco Bay Hg and PCB TMDLs call for a 50% reduction in Hg loads by 2028 and a 90% reduction in PCB loads by 2030. In supporting these TMDLs, the Municipal Regional Permit for Stormwater (MRP) (SFRWQCB, 2009) called for a range of actions, including gaining a better understanding of which Bay tributaries contribute the most loading to sensitive areas of biological interest on the Bay margin, better quantification of sediment and trace contaminant loads on a watershed basis and regionally, a better understanding of how and where trends might best be measured, and an improved understanding of which management measures may be most effective in reducing impairment. In response to the MRP requirements and information needs, the Small Tributaries Loading Strategy (STLS) outlined a set of management questions (SFEI, 2009) that was the guide for the region's stormwater-related activities. These activities included a statistical analysis of land use and PCB and Hg source areas to support the selection of monitoring locations, monitoring for concentrations and loads in eight watersheds, and a statistical analysis of optimal sampling design for loads and trends.

Then in 2015, the SPLWG prepared a “multi-year synthesis” of the work completed from 2000-2014 (McKee et al., 2015) and, consistent with the issuance of MRP 2.0 (SFRWQCB, 2015), provided new recommendations for a shift in emphasis of the program to focus on:

1. characterizing concentrations in a greater number of watersheds and subwatersheds with older urban and industrial land uses,
2. allocating some of the sampling resources to a small number of monitoring sites with existing flow monitoring gauges to help broaden the data set for regional model calibration and to inform decisions about cleanup potential, and
3. developing a trends monitoring strategy that includes a menu of designs for assessing trends at varying scales and circumstances.

It was envisioned that as the trends strategy matured and pollution abatement efforts and implementation projects began to accrue, the overall small tributary load monitoring program would transition from a focus on finding high leverage watersheds to measuring concentration and loading trends (McKee et al., 2015). One of the remaining challenges, however, was deciding which watersheds and source areas to target for management efforts. In response, the Sources, Pathways, and Loadings Workgroup (SPLWG) developed methods to take a deeper dive into existing data by looking at PCB congener patterns (Davis et al., 2019), and loads and yields of PCBs and Hg (McKee et al., 2019). The results of this Advanced Data Analysis project are being finalized now.

In parallel, the recommendations and visions described in the synthesis document (McKee et al., 2015) were further refined and developed with the completion of a PCB trends statistical model and sampling design for the Guadalupe River (Melwani et al., 2018). Further, the SPLWG prepared the RMP Small Tributaries Loading Strategy: Modeling and Trends Strategy (Wu et al., 2018) and the Modeling Implementation Plan-Version 1.0 (Wu and McKee., 2019). These documents recommended a path forward for developing a trends monitoring and modeling program that included a sampling design that has sufficient power (> 80%) to detect 25% or greater trends over a 20-year period, a regional dynamic model using LSPC (the C++ version of HSPF), and the use of the modeling framework and outcomes for driving decisions about further sampling design.

The Year 1 report for the regional dynamic LSPC model (hydrology calibration) (Zi et al., 2021) provides a preliminary plan for the use of existing stormwater data for calibrating and verifying the water quality model (planned for 2022 and 2023). In the first quarter of 2021 a new RMP project called, “Integrated watershed modeling and monitoring implementation strategy” with oversight by both the ECWG and the SPLWG, is developing these ideas further as the use of models and sampling designs for CECs is being considered. A preliminary recommendation from that effort is consistent with the earlier recommendations (McKee et al., 2015) to allocate some sampling resources to watersheds where there are existing flow monitoring gauges to help broaden the data set for regional model calibration, to inform decisions about cleanup potential, and possibly to support CECs information needs.

This proposal aims to address the ongoing need for water quality sampling data

- to characterize concentrations in a greater number of watersheds and subwatersheds with older industrial land uses, including new sites (**Objective 1**),
- at sites where there are suspected false negatives or where the Advanced Data Analysis results provided evidence that the data collected were insufficient to categorize the site with confidence (**Objective 2**), and
- in watersheds with existing flow monitoring gauges to provide calibration and verification data for the Regional Model (**Objective 3**).

Study Objectives and Applicable RMP Management Questions

This study will provide information essential to understanding concentrations of PCBs, Hg, and SSC at a broad number of sites around the Bay, using two designs: the targeted land-use specific reconnaissance sampling and discrete grab sampling at existing flow stations. The objectives of the project and how the information will be used are shown in Table 1 relative to the SPLWG high-level management questions.

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

Management Question	Study Objective	Example Information Application
Q1: What are the loads or concentrations of Pollutants of Concern (POCs) from small tributaries to the Bay?	Use manual sampling to collect discrete grab samples at existing flow stations. Use this data to calibrate/verify the Regional Model.	How do concentrations of POCs vary with flow during the course of a storm?
Q2: Which are the “high-leverage” small tributaries that contribute or potentially contribute most to Bay impairment by POCs?	N/A	N/A
Q3: How are loads or concentrations of POCs from small tributaries changing on a decadal scale?	N/A	N/A
Q4: Which sources or watershed source areas provide the greatest opportunities for reductions of POCs in urban stormwater runoff?	Use remote samplers to collect samples at new locations as a screening method to determine if they are likely high-leverage. Use these results to rank these locations relative to each other and sources. Use manual water composite sampling methods to revisit previously sampled locations	Where are the highest leverage watersheds for potential management action? How variable are concentrations from storm to storm?
Q5: What are the measured and projected impacts of management action(s) on loads or concentrations of POCs from small tributaries, and what management action(s) should be implemented in the region to have the greatest impact?	Provide a regional map of concentrations and loads for baseline comparison to the effects of BMP application.	Where should BMPs be located to have the greatest benefit for water quality?

Approach

A wet weather field monitoring program is proposed to continue during the winter months of WY 2022 sampling at watersheds, subwatersheds, or finer scales to assess management priority as well as to support the development of the Regional Model. The sampling program will largely mimic the program implemented during WYs 2011, and 2015-2021 (McKee et al., 2012; Gilbreath et al., 2021 in review), with some modifications of collecting discrete samples at some sites.

1. Site selection and monitoring design based on Objective:
 - a. To address Objective 1 to find new high-leverage watersheds or sub-watershed areas, Countywide stormwater programs will be consulted to help select sites. At these sites, remote samplers will be used, where feasible, although manual sampling can also be used. Samples will be collected during a rainfall event that is forecast to exceed 0.5 inches of rainfall in a 6-hour period using a Hamlin Sampler or Walling Tube, dependent on site logistics (Walling Tubes are best suited for a natural bed while Hamlin Samplers are superior in storm drains or concrete channels). If any of the selected sites meet the criteria for CECs sampling and manual sampling is chosen as the method, the CECs in stormwater project will piggyback on the POC sampling and the two projects will split field costs.
 - b. To address Objective 2 to re-sample locations where additional information is necessary to inform ranking, the results from the Advanced Data Analysis will be used in consultation with the Countywide stormwater programs. At these sites, manual water composite sampling methods will be used to allow direct comparison to the prior data. One composite stormwater sample will be collected during a rainfall event that is forecast to exceed 0.5 inches of rainfall in a 6-hour period using a manual sampling techniques using either a DH-81, D-95 or ISCO pumping sampler (appropriately lab cleaned and prepared) to take time-paced sub-samples during the storm that are composited on site. If any of the selected sites meet the criteria for CECs sampling, the CECs in stormwater project will piggyback on the POC sampling and the two projects will split field costs.
 - c. To address Objective 3 to sample locations with existing flow stations to support modeling, the STLS as a whole, the individual Countywide stormwater programs and the RMP CECs team will be consulted. At these sites, discrete grab samples will be collected throughout the course of a storm, aiming for sample collection on the rising, peak, and falling stages of the hydrograph. Samples will be collected during a rainfall event that is forecast to exceed 0.5 inches of rainfall in a 6-hour period using manual sampling techniques. Discrete samples will be collected using

either a D-95 suspended using a crane and winch assembly (larger water bodies) or a DH-81 or ISCO pumping sampler (smaller or wadable water bodies). Like the first two Objectives, if any of these sites meet the criteria for CECs sampling, the CECs in stormwater project will piggyback on the POC sampling and the two projects will split field costs.

2. Number of sites relative to monitoring design

The number of sites sampled will depend on site logistics, the ratio of methods (composite manual sample:remote sample:discrete grab sample), proximity of sites to one another, budget, and other factors. However, we estimate we can achieve between 7-18 sites with a budget of \$143k (\$93k plus at least \$50k carryover from WY 2021). Some options for ratios of methods are shown in Table 2 below.

Table 2. Options for combinations of sampling methods for WY 2022.

	Remote Sample Sites	Composite Sample Sites	Discrete Grab Sites
Option 1	4	4	4
Option 2	0	0	7
Option 3	8	10	0

This sampling program is being coordinated with reconnaissance monitoring for the ECWG and PCBWG. Some reconnaissance sites for SPLWG will share the field costs for CECs sampling in cases where the two projects piggyback on each other at the same sites. PCBWG also has reconnaissance sampling sites in priority margin units and the data is managed, analyzed and reported on by the SPLWG-funded reconnaissance monitoring report (PCBWG pays for the analytical costs of these samples).

3. Analytes

The 2021 analyte list will be continued (PCBs, Hg, SSC) in WY 2022. In addition, CECs will be sampled and paid for through any ECWG stormwater special stud(ies) selected for RMP implementation.

Budget

The following budget represents estimated costs for this proposed special study (Table 3), assuming composite samples are collected at approximately two-thirds of the sites and discrete grab samples (five per site) are collected at approximately one-third of the sites (representing Option 1 in Table 2). Efforts and costs can be scaled back by reducing the number of sampling sites.

Table 3. Proposed budget.

Expense	Estimated hours	Estimated Cost
Labor		
Project Staff	450	\$50,000
Project Management	80	\$13,000
Data Management	175	\$20,000
Reporting	107	\$15,000
Subcontracts		
SGS AXYS Analytical, Brooks Applied Laboratories, USGS		\$40,000
Direct Costs		
Equipment		\$1,000
Travel		\$1,000
Shipping		\$3,000
Grand Total	812	\$143,000

Budget Justification

Field Costs: This special study proposal has a budget of \$143,000, which includes up to \$50,000 devoted to stormwater sample collection (site selection and reconnaissance, permit applications, development of sample collection protocols, and field work for approximately 7-18 sites).

Every effort will be made to minimize field costs through monitoring multiple sites per team per storm, and leveraging existing stormwater monitoring activities of the RMP.

Laboratory Costs: Up to 40 independent samples (depending on methods chosen) will be analyzed, including field duplicates and a field blank. Analyses will be conducted for PCBs, mercury, and suspended sediment concentration.

Data Management Costs: Data services will include quality assurance and upload to CEDEN.

Reporting Costs: Preparation of a draft and final report on the results will be completed.

Reporting

The outcome of the study will be a concise technical report. The main objective will be to report and rank concentrations and particle ratios observed at each location and compare these to existing data (reporting related to Objective 1). The methods developed in the Advanced Data Analysis project may be applied and used to compare sites in which multiple storms were sampled over multiple years (reporting related to

Objective 2). The technical report will include any discrete data collected that can be used to support modeling, and will also include the approximation of a time-weighted composite in order to rank the concentrations and particle ratios against other site composites (reporting related to Objective 3). The quality assured data will also be delivered to the modeling team for inclusion in the Regional Watershed Model calibration and verification.

References

- BASMAA, 2011. Small Tributaries Loading Strategy Multi-Year Plan (MYP) Version 2011. A document developed collaboratively by the Small Tributaries Loading Strategy Work Group of the Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP): Lester McKee, Alicia Gilbreath, Ben Greenfield, Jennifer Hunt, Michelle Lent, Aroon Melwani (SFEI), Arleen Feng (ACCWP) and Chris Sommers (EOA/SCVURPPP) for BASMAA, and Richard Looker and Tom Mumley (SFRWQCB). Submitted to the Water Board, September 2011, in support of compliance with the Municipal Regional Stormwater Permit, provision C.8.e.
http://www.swrcb.ca.gov/rwqcb2/water_issues/programs/stormwater/MRP/2011_AR/BASMAA/B2_2010-11_MRP_AR.pdf
- Davis, J. A.; Gilbreath, A. N. 2019. Small tributaries pollutants of concern reconnaissance monitoring: pilot evaluation of source areas using PCB congener data. SFEI Contribution No. 956. San Francisco Estuary Institute: Richmond, CA.
<https://www.sfei.org/documents/small-tributaries-pollutants-concern-reconnaissance-monitoring-pilot-evaluation-source>
- Gilbreath, A.N., Hunt, J.A., Yee, D., and McKee, L.J., 2021 (in final revisions). Pollutants of concern (POC) reconnaissance monitoring final progress report, water years (WYs) 2015 - 2020. A technical report prepared for the RMP, SPLWG, STLS. Contribution No. XXXX. San Francisco Estuary Institute, Richmond, CA.
- McKee, L.J., Gilbreath, A.N., Hunt, J.A., and Greenfield, B.K., 2012. Pollutants of concern (POC) loads monitoring data, Water Year (WY) 2011. A technical report prepared for the RMP, SPLWG, STLS. Contribution No. 680. San Francisco Estuary Institute, Richmond, CA.
<http://www.sfei.org/documents/pollutants-concern-poc-loads-monitoring-data-water-year-wy-2011>
- McKee, L.J. Gilbreath, N., Hunt, J.A., Wu, J., and Yee, D., 2015. Sources, Pathways and Loadings: Multi-Year Synthesis with a Focus on PCBs and Hg. A technical report prepared for the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP), Sources, Pathways and Loadings Workgroup (SPLWG), Small Tributaries Loading Strategy (STLS). SFEI Contribution No. 773. San Francisco Estuary Institute, Richmond, CA.
http://www.sfei.org/sites/default/files/biblio_files/MYSR%20Final%20Report.pdf
- McKee, L.J., Gilbreath, A.N., Hunt, J.A., Wu, J., Yee, D., and Davis, J.A., 2019. Small tributaries pollutants of concern reconnaissance monitoring: Loads and yields-based

- prioritization methodology pilot study. SFEI Contribution No. 817. SFEI, Richmond, California.
<https://www.sfei.org/documents/small-tributaries-pollutants-concern-reconnaissance-monitoring-loads-and-yields-based>
- Melwani, A.R., Yee, D., McKee, L., Gilbreath, A., Trowbridge, P., and Davis, J.A., 2018. Statistical Methods Development and Sampling Design Optimization to Support Trends Analysis for Loads of Polychlorinated Biphenyls from the Guadalupe River in San Jose, California, USA, Final Report.
<https://www.sfei.org/documents/statistical-methods-development-and-sampling-design-optimization-support-trends-analysis>
- Melwani, A., Lent, M., Greenfield, B., and McKee, L.J., 2010. Optimizing sampling methods for pollutant loads and trends in San Francisco Bay urban stormwater monitoring. A technical report for the Sources Pathways and Loading Workgroup of the Regional Monitoring Program for Water Quality. San Francisco Estuary Institute, Oakland, CA. Final Draft.
<https://www.sfei.org/documents/optimizing-sampling-methods-pollutant-loads-and-trends-san-francisco-bay-urban-stormwater>
- SFEI, 2009. RMP Small Tributaries Loading Strategy. A report prepared by the strategy team (L McKee, A Feng, C Sommers, R Looker) for the Regional Monitoring Program for Water Quality. Contribution No. 585. San Francisco Estuary Institute, Oakland, CA.
http://www.sfei.org/sites/default/files/biblio_files/Small_Tributary_Loading_Strategy_FINAL.pdf
- SFRWQCB, 2009. California Regional Water Quality Control Board San Francisco Bay Region Municipal Regional Stormwater NPDES Permit, Order R2-2009-0074, NPDES Permit No. CAS612008. Adopted October 14, 2009.
http://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/stormwater/Municipal/index.shtml
- SFRWQCB, 2015. California Regional Water Quality Control Board San Francisco Bay Region Municipal Regional Stormwater NPDES Permit, Order No. R2-2015-0049, NPDES Permit No. CAS612008. November 19, 2015.
http://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/stormwater/Municipal/R2-2015-0049.pdf
- Wu, J., Trowbridge, P., Yee, D., McKee, L., and Gilbreath, A., 2018. RMP Small Tributaries Loading Strategy: Modeling and trends Strategy 2018. Contribution No. 886. San Francisco Estuary Institute, Richmond, California.
<https://www.sfei.org/documents/rmp-small-tributaries-loading-strategy-trends-strategy-2018>
- Wu, J., and McKee, L.J., 2019. Modeling Implementation Plan-Version 1.0. A technical report prepared for the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP). Contribution No. 943 San Francisco Estuary Institute, Richmond, California.
<https://www.sfei.org/documents/regional-watershed-model-implementation-plan>

Zi, T., McKee, L., Yee, D., and Foley, M., 2021. San Francisco Bay Regional Watershed Modeling Progress Report, Phase 1. Report prepared for the Sources Pathways and Loadings Workgroup of the Regional Monitoring Program for Water Quality. SFEI Contribution #xxx. San Francisco Estuary Institute, Richmond, CA. www.xxx

SPLWG Special Study Proposal: Regional Model Development to Support Assessment of Watershed Loads and Trends

Summary: The 2018 Small Tributary Loading Strategy (STLS) prioritized further assessment of the spatial and regional estimates and temporal trends in contaminant loads, and developed a multi-year plan for model development. Although initially conceived as a tool for evaluating PCB and Hg trends, advice provided at the May 2019 SPLWG meeting placed greater emphasis on developing a model to support better estimates of loads of sediment and other contaminants in addition to PCBs and Hg. The focus in 2021 is on developing and calibrating the sediment model. This proposal is for funding in 2022 for the fourth year of the multi-year modeling plan and focuses on developing the contaminant model. The two main objectives of the model development are to: 1) create a flexible watershed modeling platform for general contaminant simulation; and 2) answer management questions related to PCBs, Hg, and emerging contaminants). The model will initially be used to evaluate PCBs and Hg loadings at watershed and regional scales. The trial using these two well sampled pollutants will provide a proof of concept for other contaminants. The developed model structure can be a basis for and further modified for other contaminants in the future. Trends associated with control measures, land-use changes, or other scenarios could then be explored.

Estimated Cost: \$90K 2022/\$60K 2023 if phased over 2022 and 2023 (\$150K complete in full in 2022)

Oversight Group: STLS/SPLWG

Proposed by: Tan Zi and Lester McKee (SFEI)

Time Sensitive: Yes - this is the fourth year of a sequential multi-year study

Proposed Deliverables and Timeline

Option 1 - Model development phased over 2022 and 2023

Option 2 - Model development completed in full in 2022

Deliverable	Completion Date (Option 1)	Completion Date (Option 2)
Model data collation and preparation	04/2022	02/2022
Model setup and initial calibration	12/2022	07/2022
Model final calibration	09/2023	09/2022
Draft modeling report for peer review	10/2023	10/2022
Final modeling report and data sharing portal	12/2023	12/2022

Background

The San Francisco Bay TMDLs call for a 50% reduction in Hg loads by 2028 and a 90% reduction in PCB loads by 2030, respectively. In supporting these TMDLs, the Municipal Regional Permit for Stormwater (MRP) (SFRWQCB, 2009; SFRWQCB, 2015) called for the implementation of control measures to reduce PCB and Hg loads from urbanized tributaries. In addition, the MRP has identified additional information needs associated with improving understanding of sources, pathways, loads, trends, and management opportunities for contaminants. In response to the MRP requirements and information needs, the Small Tributary Loading Strategy (STLS) was developed, outlining a set of management questions (MQs) that have been used as the guiding principles for the region's stormwater-related activities (Table 1; SFEI, 2009; Wu et al., 2018).

Over the past decade, the RMP Sources, Pathways, and Loadings Workgroup (SPLWG) and BASMAA have focused on getting answers to MQ1, MQ2, and MQ4 in relation to PCBs and Hg. In recognition of the need to answer MQ3, the STLS team updated the Strategy in 2018 to include a trends component, mainly for PCBs. The new Modeling and Trends Strategy identified the development of a regional watershed model as a priority, with an initial focus on PCB and Hg loading, but developed in a way that would facilitate its use for evaluation of trends. Although there is a more general objective to support multiple pollutants, initially the model will be developed for PCBs and Hg simply because we have the most loading data for these pollutants. But the regional model could also be developed to include other pollutants, such as contaminants of emerging concern (CECs) and nutrients, and provide a mechanism for evaluating the potential for management actions and management impact on future pollutant loads or concentrations in support of MQ5.

The 2018 Modeling and Trends Strategy included a multi-year work plan that would obtain initial answers to loading questions by 2022, and the trends or other questions in years beyond with additional funding. The first step of this plan, completed in 2019, was to develop a Modeling Implementation Plan (MIP) to guide model development, which included model platform selection and development procedures and a timeline (Wu and McKee, 2019). Subsequently, RMP funding was provided for 2020 to support hydrologic model setup and calibration, which have been completed (Zi et al., 2021). The sediment model is under development and will be completed in 2021. This proposal is for 2022 funding to implement the fourth year of the multi-year work plan, which includes completing the calibration and validation of the regional model for the PCB and Hg, and working with the ECWG to plan and develop a flexible modeling basis for CECs.

Study Objectives and Applicable RMP Management Questions

This study will provide information essential to understanding spatial and temporal characteristics of sediment and contaminant loads, at the scales of both individual watersheds and the region as a whole in relation to the SPLWG high-level management questions.

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

Management Question	Study Objective	Example Information Application
Q1: What are the loads or concentrations of Pollutants of Concern (POCs) from small tributaries to the Bay?	Complete a regional hydrology and sediment model to serve as the basis for POC modeling and as the first stage of regional model development to support trends evaluation.	The model will produce an estimate of flow and sediment concentrations and loads at each individual watershed.
Q2: Which are the “high-leverage” small tributaries that contribute or potentially contribute most to Bay impairment by POCs?		Estimates produced by the regional model at each individual watershed can be compared to explore relative loading rates and how those pass into specific priority margin areas, operational landscape units, or RMP Bay segments.
Q3: How are loads or concentrations of POCs from small tributaries changing on a decadal scale?		Time series of flow and sediment loads for 1999-2018 can be used to assess trends for individual watersheds and the region as a whole.
Q4: Which sources or watershed source areas provide the greatest opportunities for reductions of POCs in urban stormwater runoff?		Model outputs of flow and sediment will help identify high yield areas that can be targeted for management actions.
Q5: What are the measured and projected impacts of management action(s) on loads or concentrations of POCs from small tributaries, and what management action(s) should be implemented in the region to have the greatest impact?		Management actions, both existing and planned or anticipated, could be evaluated in the model through scenario runs.

Approach

A phased approach is being employed to develop the regional model, starting with hydrology, followed by suspended sediment, and then by contaminants. Table 2 lays out the roadmap for the whole project from inception (2015) through to the end of the multi-year plan as it currently stands. The tasks proposed represent the third phase of model development and will primarily cover development and calibration of the contaminant model with a focus on PCBs and Hg, which have the best data available, as examples, and aiming to set up a more general modeling framework for other contaminants (emerging contaminants and nutrients). Overall, the following roadmap lays out a standard model development and application process.

Two timeline options have been provided for the proposed tasks. Option one is to complete the proposed tasks in one year, and the alternative option is to span the proposed tasks over two years (Option 1 and Option 2). The timeline, budget, and deliverables of the two options were provided in Table 2.

Table 2. Timeline and budget for major milestones of the modeling multi-year plan.

Year	Budget (\$k)	Deliverable	Completion Date (Option 1)	Completion Date (Option 2)
2015-2018	235	Loads and trends strategy conception; Conceptual model development; Statistical analysis of PCB trends in Guadalupe River; Completion of Small Tributaries Loading Strategy: Modeling and trends Strategy.	2018	2018
2019	60	Modeling Implementation Plan	2019	2019
2020	100	Hydrology calibration completed	08/2020	08/2020
2021	150	Sediment model calibration completed and report ready for review	08/2021	08/2021
2022 (2022 and 2023 if phased)	5	Refine WQ model structure to ensure it can be broadly applied to a variety of pollutants based on a review of pertinent conceptual model documents and the findings from the Integrated Monitoring and Modeling Strategy that is currently being developed for CECs, sediment, nutrients, PCBs, and Hg, the integrated watershed and Bay modeling SEP project that is proposed, as well as any other pertinent projects currently being proposed by the WGs for 2022 funding	02/2022	02/2022
	15	Proof of concept model preparation using the best available datasets (PCBs and Hg): Model data collation and preparation	04/2022	02/2022
	70	Proof of concept model preparation using the best available data sets (PCBs and Hg): Model setup and initial calibration	12/2022	07/2022
	30	Proof of concept model preparation using the best available data sets (PCBs and Hg): Model final calibration and validation (will add new monitoring data (if available))	09/2023	09/2022
	30	Modeling report and data sharing portal with the objective of making the model publically available, gathering user experience, and planning for other pollutants.	12/2023	12/2022

2023 (2024 if the previous work is phased into two years)	150	Collation of additional control measure data and receipt of updated land use; Model application runs for answering RMP questions. Possibly start modeling CECs. Options may include: <ul style="list-style-type: none"> a) Model refinements for better representation of spatial variability b) Model refinements for assessing trends-associated control measure implementation and land use change c) Characterization of sedimentation process in flood control channels d) Assessment of future scenario loading estimates e) Model development for other contaminants f) Linking and doing model runs to support models of physical and biological processes on the Bay margins or in the Bay 	12/2024	12/2023
--	-----	---	---------	---------

Comparison of Two Options

The two proposed timeline options are aimed to provide a more adjustable modeling work plan to fit all the work plans that SPLWG proposed. The goal and the contents of the work are the same between the two options. However, there are some pros and cons for each plan. Option 1 (completing the project over two years) has the advantage that potentially more data from the monitoring activities in Water Year 2022 would be available as verification data. This plan may also benefit from advances on the CECs stormwater monitoring strategy (planned for 2022 and 2023) to help structure the POC modeling such that it is more suitable for CECs modeling in future. Option 2 aims to complete the PCBs and Hg modeling in just one year, thus it can support PCBs and Hg management and be used or modified by RMP stakeholders for their own needs sooner than Option 1. The other advantage of Option 2 is higher project efficiency. Benefits of a shorter project timeline include continued engagement of the lead scientist (reducing the need to drop a project and then ramp up on it again), and more efficient “realtime” advice and review from the science advisors and the stakeholders. Should Option 1 be selected but Water Year 2022 is a dry year, modeling activities could be accelerated using the staff resources that were unallocated due to the lack of stormwater monitoring.

Budget

The following budget represents estimated costs for this special study (Table 3).

Table 3. Proposed budget.

Expense	Estimated Hours	Estimated Cost
Project Staff (Modeling)	700	\$100,000
RMP staff and stakeholder interactions and SPLWG review	80	\$25,000
Project/Contract management		
Data technical services	120	\$15,000
GIS services	80	\$10,000
Total	980	\$150,000

Budget Justification

Labor Costs: Staff time to perform calibration/verification, process model results, and write up technical reports; to collect and process GIS data and construct a webpage; consult on water quality and control measure data and get technical support from related other parties; and senior staff contributions and review.

Reporting Costs: RMP staff will produce a model development report to document all aspects of model development, including input data, key assumptions, calibration/verification, and model results.

Reporting

- Annual Model Development presentations to STLS and SPLWG will be prepared.
- Draft modeling report for peer review
- Final modeling report
- Data and modeling results will be made available for the public.

References

- SFRWQCB, 2009. California Regional Water Quality Control Board San Francisco Bay Region Municipal Regional Stormwater NPDES Permit, Order R2-2009-0074, NPDES Permit No. CAS612008. Adopted October 14, 2009.
http://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/stormwater/Municipal/index.shtml
- SFRWQCB, 2015. California Regional Water Quality Control Board San Francisco Bay Region Municipal Regional Stormwater NPDES Permit, Order No. R2-2015-0049, NPDES Permit No. CAS612008. November 19, 2015.
http://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/stormwater/Municipal/R2-2015-0049.pdf

- Wu, J., Trowbridge, P., Yee, D., McKee, L., and Gilbreath, A., 2018. RMP Small Tributaries Loading Strategy: Trends Strategy 2018. Contribution No. 886. San Francisco Estuary Institute, Richmond, CA.
https://www.sfei.org/sites/default/files/biblio_files/STLS%20Trends%20Strategy%202018%20FINAL.pdf
- Wu, J., and McKee, L.J., 2019. Modeling Implementation Plan-Version 1.0. A technical report prepared for the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP). Contribution No. 943 San Francisco Estuary Institute, Richmond, California.
<https://www.sfei.org/documents/regional-watershed-model-implementation-plan>
- Zi, T., McKee, L., Yee, D., Foley, M., 2021. San Francisco Bay Regional Watershed Modeling Progress Report, Phase 1. Report prepared for the Sources Pathways and Loadings Workgroup of the Regional Monitoring Program for Water Quality. SFEI Contribution No.1038. San Francisco Estuary Institute, Richmond, CA.

SPLWG Special Study Proposal: CECs Remote Sampler Development and Pilot Testing

Summary

The SPLWG is collaborating with the Emerging Contaminants Workgroup (ECWG) to develop and pilot test a remote sampler for CECs. This proposed project would select, modify, and pilot test remote samplers that are suitable for collection of samples for this purpose. Examples of current commercial autosamplers that could be considered include the ISCO 3700C, Hach AS950, Global WS700 series, and YSI ProSample PM. Time is budgeted for selecting and modifying a remote sampler, developing methods for deployment and retrieval, running quality control samples (i.e. field blanks) through the equipment to evaluate which CECs the remote sampler is appropriate for, and deploying samplers during storm events at two to six locations for side-by-side field testing with manually collected composite samples. This investigation - proposed for WY 2022 - is cost-efficient because it piggybacks on the CECs in stormwater monitoring project, which will be in its fourth and final year.

Estimated Cost: \$30k (Option A), \$36k (Option B)

Oversight Group: STLS/SPLWG/ECWG

Proposed by: Alicia Gilbreath, Lester McKee, Don Yee, Kelly Moran, Rebecca Sutton (SFEI)

Time Sensitive: Yes - since this project is piggybacking on CECs in stormwater monitoring. Field labor during storm events and data management of the manually-collected side-by-side samples will be covered by the RMP-funded CECs in stormwater monitoring project.

Proposed Deliverables and Timeline

Deliverable	Due Date
Development/selection/modification of remote sampler	09/2021
Field blank testing	10/2021
Pilot testing side-by-side with manual sampling	03/2022
Presentation at SPLWG and ECWG on the results and proposal/decision whether to continue with pilot study into WY 2023	4/2022

Background

There is a clear need to further characterize CECs entering the Bay via the stormwater pathway. The current multi-year stormwater CECs monitoring project, initiated in 2018, identified the presence of CECs of moderate and potential concern in urban runoff (Sutton et al. 2019a; Sutton et al. 2019b; Tian et al. 2021). Available data from this and other RMP CECs sampling are relatively limited, but provide an increasingly strong body of evidence that stormwater is a major pathway for CECs to enter San Francisco Bay (e.g., Sedlak et al. 2018; Sutton et al. 2019a; Miller et al. 2020). Given the importance of this pathway, it is likely that monitoring CECs in stormwater will continue to be needed.

One of the largest costs of stormwater sampling is for the labor associated with two staff being out in the field for an extended period during storms. Over the years, we have found ways of reducing this cost by sampling two field locations that are near each other, alternating between them during a storm, addressing the needs of multiple work groups by taking samples for analysis of a greater number of pollutants, and developing a remote sediment sampler that allows staff to be absent during the storm. Unfortunately, a remote sediment sampler is only suitable for pollutants like PCBs and Hg that are dominantly particle-bound. This proposal aims to develop and test a remote sampler that is suitable for capturing dissolved phase as well as particle-bound pollutants.

A similar successful effort was led by SPLWG during WYs 2015-2018 when we pilot-tested two remote sediment samplers for the feasibility of collecting PCBs and Hg samples during storms without a staff person present (Gilbreath et al., 2019). Those two samplers work by capturing suspended sediment throughout the course of a storm event. Now that they are designed and tested, the samplers are relatively inexpensive (one being \$750 and the other \$400) and can be deployed into the waterway and retrieved in less than one hour plus travel time to and from the field. The remote PCB and Hg samplers were pilot-tested by deploying them side-by-side as composite samples were also manually collected, and the results were compared and found to have a strong enough correlation that the method was accepted for use.

This project would carry out a similar process of method development as followed for the particle-bound contaminants but focused on collection of total water rather than just a sediment sample. We would select, modify, and pilot test remote samplers that are suitable for collection of a wide range of contaminants with a specific interest in application for characterizing CECs in stormwater, many of which have large dissolved phase components.

This proposal is timely and cost-efficient because field labor during storm events and data management will be covered by the RMP-funded CECs in stormwater monitoring project. Also, the chemical analysis of samples collected manually for comparison to the

remote sampler samples will also be covered by the CECs in stormwater monitoring project. Being able to utilize a remote sampling technique for CECs will expand the RMP's annual stormwater sampling capacity while minimizing costs.

Study Objectives and Applicable RMP Management Questions

The goal of this project is to choose, develop/modify, and test a remote sampler for stormwater CECs that would include two basic elements:

- the ability to be deployed and left unattended throughout a storm event, and
- the ability to collect whole water samples without blank contamination.

The near-term objectives of the sampling approach will be to (a) choose and modify the componentry of the remote sampler to minimize the possibilities of CEC contamination from the sampler itself, (b) test the sampler for blank contamination, (c) deploy during storm events at two (Option A) to six (Option B) sites and collect side-by-side samples with manually collected composite samples, and (d) compare the concentrations obtained from the remote and manual samples to evaluate the robustness of the remote sampling technique.

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

Management Question	Study Objective	Example Information Application
Q1: What are the loads or concentrations of Pollutants of Concern (POCs) from small tributaries to the Bay?	Develop a remote sampler to collect CECs samples. Test side-by-side with manual sampling.	What are the concentrations of CECs in the small tributaries?
Q2: Which are the "high-leverage" small tributaries that contribute or potentially contribute most to Bay impairment by POCs?	Indirect, via answering Q1 for a range of watersheds.	Identify watersheds warranting more intensive CECs monitoring
Q3: How are loads or concentrations of POCs from small tributaries changing on a decadal scale?	N/A	N/A
Q4: Which sources or watershed source areas provide the greatest opportunities for reductions of POCs in urban stormwater runoff?	Indirect, via answering Q1 for a range of watersheds	Confirm/refute conceptual models of expected CECs from various land use/ watershed characteristics.
Q5: What are the measured and	N/A	N/A

projected impacts of management action(s) on loads or concentrations of POCs from small tributaries, and what management action(s) should be implemented in the region to have the greatest impact?		
---	--	--

Approach

RMP staff will work together to identify candidate remote samplers and modify the componentry of the samplers as necessary to make them suitable for CECs sampling. RMP staff will collect equipment blanks to test for contamination well in advance of the wet season. For the analytes in which equipment blank testing indicated no contamination, the sampler will be utilized side-by-side with manual sampling in storm events at 2-6 sites during WY 2022. The field trial with paired manual sampling will provide an opportunity to test operations under actual field conditions and observe possible failure modes. Example testing and observation activities include finding suitable locations; testing the attachment methods for the sampler body; observing obstructions of the sampling tube inlet during operation; observing potential failures such as leaks or flooding of the equipment causing short circuits or malfunction, insufficient power to collect for the whole storm duration, and programming or sensor errors leading to filling the bottles too fast (full before a storm ends) or too slow (collection of too little volume). These trials, with concurrent manual sampling, will allow observation of the failures as they happen or soon after, and the possibility to reconfigure the sampler during the deployment to prevent loss of equipment or to improve collection effectiveness.

Budget

The following budget represents estimated costs for this special study (Table 2).

Table 2. Proposed budget.

Expense	Estimated Hours	Estimated Cost
Project Staff	110	\$18,000
Equipment costs		\$6,000
CECs sample chemical analysis		\$6,000 (Option A) \$12,000 (Option B)
Grand Total	110	\$30,000 (Option A) \$36,000 (Option B)

Budget Justification

Labor Costs: 110 hours of staff time to research and develop the remote sampler, run equipment blanks and present to ECWG and SPLWG in spring 2022.

Early Funds Release Request

If this project is approved, we request early release of funds for use in 2021. We would like to test this remote sampler in Water Year 2022 (which begins fall of 2021).

Therefore, we must begin identification and modification of the remote sampler in summer 2021, and blank testing in summer/fall 2021.

Reporting

The data for the remote sampler and manually-collected samples will be compared and presented to SPLWG and ECWG in spring of 2022.

References

- Gilbreath, A.N., Hunt, J.A., Yee, D., and McKee, L.J., 2019. Pollutants of concern (POC) reconnaissance monitoring final progress report, water years (WYs) 2015 - 2018. A technical report prepared for the RMP, SPLWG, STLS. Contribution No. 942. SFEI, Richmond, CA.
<https://www.sfei.org/documents/pollutants-concern-reconnaissance-monitoring-water-years-2015-2018>
- Miller, E., Shimabuku, I., Mendez, M., Buzby, N., and Sutton, R., 2020. "RMP Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2020 Update." Contribution No. 1007. San Francisco Estuary Institute, Richmond, California.
- Sedlak, M., Sutton, R., Wong, A., Lin, D., 2018. "Per and Polyfluoroalkyl Substances (PFASs) in San Francisco Bay: Synthesis and Strategy." Contribution No. 867. San Francisco Estuary Institute, Richmond, California.
- Sutton, Rebecca, Diana Lin, Meg Sedlak, Carolynn Box, Alicia Gilbreath, Rusty Holleman, Liz Miller, et al. 2019a. "Understanding Microplastic Levels, Pathways, and Transport in the San Francisco Bay Region." Contribution No. 950. San Francisco Estuary Institute, Richmond, California.
- Sutton, Rebecca, Da Chen, Jennifer Sun, Denise J. Greig, and Yan Wu. 2019b. "Characterization of Brominated, Chlorinated, and Phosphate Flame Retardants in San Francisco Bay, an Urban Estuary." *Science of The Total Environment* 652 (February): 212–23.
<https://doi.org/10.1016/j.scitotenv.2018.10.096>.
- Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. "A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon." *Science*, December, eabd6951. <https://doi.org/10.1126/science.abd6951>.

Special Study Proposal: Tracking Ethoxylated Surfactants in Wastewater and Stormwater

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

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

Estimated Cost: \$83,415

Oversight Group: ECWG

Proposed by: Diana Lin, Miguel Mendez, Rebecca Sutton (SF EI)

Time Sensitive: No

PROPOSED DELIVERABLES AND TIMELINE

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

Background

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

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

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

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

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

produced. Alcohol ethoxylates are often used as replacement products because they degrade faster and are expected to be less toxic (Soares et al., 2008).

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

The RMP funded special studies in 2019 to analyze a broad set of ethoxylated surfactants in ambient Bay water, margin sediment, wastewater, and stormwater using HPLC-MS/MS (Ferguson et al., 2000). Samples were analyzed for the ethoxylate series C₁₂₋₁₄EO, C₁₆EO, C_{12(Br)}EO, NPEs and OPEs. NPEs and OPEs were among the most important ethoxylate series in each matrix, though ethoxylate chain units of one and two were below reporting limits and nonylphenol and octylphenol were not analyzed. These short chain compounds are more toxic than the long chain parent compounds and are expected to represent a significant fraction of the total NPEs, particularly in wastewater effluent (Soares et al., 2008).

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

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

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

analyzed because the predominant removal mechanism for these compounds from wastewater is through solids removal (Soares et al., 2008).

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

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

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

Study Objectives and Applicable RMP Management Questions

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Compare ethoxylated surfactant occurrence data with toxicity information reported in the scientific literature. Evaluate future monitoring needs and toxicity data gaps.	Do findings suggest ethoxylated surfactants should be classified as high, moderate, low, or possible concern within the RMP’s tiered framework.
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Compare concentrations observed in wastewater and stormwater runoff. Investigate the temporal pattern in wastewater effluent and biosolids. Compare concentrations observed at different stormwater watersheds to glean insights regarding the influence of sources or land use types. Compare concentrations to measurements of other urban areas.	How do concentrations in wastewater compare with urban stormwater runoff, and what does that suggest about relative loads? Do discharge patterns indicate intermittent or continuous sources? Can discharge patterns be compared to expected industrial releases to wastewater? What are the key sources or land uses that are associated with

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

Approach

Sample Collection

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

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

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

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

Analysis

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

Data Interpretation

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

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

Stormwater data will be evaluated along with the broader set of ethoxylated surfactants and other prioritized CECs funded through a separate study. Screening data will be evaluated based on land-use type; specific indicators of source types, such as road density, will be used for an initial investigation into key sources or land uses associated with these compounds.

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

Budget

Table 3. Proposed Budget.

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

Budget Justification

Project management

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

Study design and sample collection

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

Data Management Costs

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

Analysis and Reporting

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

Laboratory Costs

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

Direct Costs

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

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

Reporting

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

References

Department of Toxic Substance Control (DTSC) and California Environmental Protection Agency (CalEPA). 2018. Product-Chemical Profile for Nonylphenol Ethoxylates in Laundry Detergents. May. Discussion Draft.

Ferguson, P. L.; Iden, C. R.; Brownawell, B. J. 2001. Analysis of nonylphenol and nonylphenol ethoxylates in environmental samples by mixed-mode high-performance liquid chromatography-electrospray mass spectrometry. *J Chromatogr A* 938, (1-2), 79-91.

Hou, F., Tian, Z., Peter, K.T., Wu, C., Gipe, A.D., Zhao, H., Alegria, E.A., Liu, F., Kolodziej, E.P., 2019. Quantification of organic contaminants in urban stormwater by isotope dilution and liquid chromatography-tandem mass spectrometry. *Anal Bioanal Chem* 411, 7791–7806. <https://doi.org/10.1007/s00216-019-02177-3>

Klosterhaus, S., Grace, R., Hamilton, M.C., Yee, D. 2013b. Method validation and reconnaissance of pharmaceuticals, personal care products and alkylphenols in surface waters, sediments, and mussels in an urban estuary. *Environ Int* 54: 92-99.

Lamprea, K., Bressy, A., Mirande-Bret, C., Caupos, E., Gromaire, M.-C., 2018. Alkylphenol and bisphenol A contamination of urban runoff: an evaluation of the emission potentials of various construction materials and automotive supplies. *Environ Sci Pollut Res* 25, 21887–21900. <https://doi.org/10.1007/s11356-018-2272-z>

Soares, A., Guieysse, B., Jefferson, B., Cartmell, E., Lester, J.N., 2008. Nonylphenol in the environment: A critical review on occurrence, fate, toxicity and treatment in wastewaters. *Environ Inter* 34, 1033–1049. <https://doi.org/10.1016/j.envint.2008.01.004>

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

U.S. Environmental Protection Agency (EPA). 2010. Nonylphenol (NP) and Nonylphenol Ethoxylates (NPEs) Action Plan [RIN 2070-ZA09].

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

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

Estimated Cost: \$105,000 over 2 years (\$50,000 for 2022; \$55,000 for 2023)
Oversight Groups: ECWG & SPLWG
Proposed by: Kelly Moran, Rebecca Sutton, Lester McKee, Alicia Gilbreath, and Tan Zi (SFEL)
Time sensitive: No. However, this strategy will inform future monitoring, which could begin with piloting a few strategy elements as early as Water Year 2023 (October 2022 - September 2023) if this strategy is initiated in 2021.

PROPOSED DELIVERABLES AND TIMELINE

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

Background

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

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

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

Study Objectives and Applicable RMP Management Questions

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

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

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

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Develop an approach for prioritizing CECs for stormwater monitoring.	Using conceptual models to identify which CECs of potential or moderate concern for the Bay have sufficient outdoor exposure to occur in urban runoff. Using stormwater monitoring to identify CECs of potential concern for the Bay to inform future Bay monitoring design.
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Develop a CECs monitoring approach capable of generating data suitable for characterizing the presence of priority CECs in stormwater and estimating loads of selected stormwater priority CECs loads to the Bay.	Characterizing the presence of a CEC of potential or moderate concern in stormwater. Obtaining sufficient stormwater monitoring data to estimate loads of selected priority CECs to the Bay.
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	N/A	N/A
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?	N/A	N/A
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	Develop a CECs monitoring approach capable of generating data suitable for estimating stormwater priority CECs loads discharged to the Bay.	Predicting trends based on monitoring data and/or other factors (e.g., use trends, environmental and societal changes).
6) What are the effects of management actions?	Develop a CECs monitoring approach capable of generating data suitable for estimating stormwater priority CECs loads discharged to the Bay.	Predicting trends based on monitoring data and modeling of the effects of management actions. Providing data to support modeling to inform monitoring design refinements to most quickly and/or more cost-effectively measure reductions.

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

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

Approach

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

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

1. Approach for prioritizing CECs for stormwater monitoring

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

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

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

2. Approach for Stormwater CECs sampling design

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

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

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

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

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

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

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

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

Budget

Table 3. Estimated costs for Stormwater CECs Monitoring Strategy.

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

Budget Justification

Labor Costs

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

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

Early Funds Release Request

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

Reporting

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

References

- McKee, L., Feng, A., Sommers, C., Looker, R., 2009. “RMP Small Tributaries Loading Strategy.” Contribution No. 585. San Francisco Estuary Institute, Richmond, California..<http://www.sfei.org/documents/rmp-small-tributaries-loading-strategy>
- Miller, E., Shimabuku, I., Mendez, M., Buzby, N., and Sutton, R., 2020. “RMP Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2020 Update.” Contribution No. 1007. San Francisco Estuary Institute, Richmond, California.
- Sedlak, M., Sutton, R., Wong, A., Lin, D., 2018. “Per and Polyfluoroalkyl Substances (PFASs) in San Francisco Bay: Synthesis and Strategy.” Contribution No. 867. San Francisco Estuary Institute, Richmond, California.
- Sutton, Rebecca, Diana Lin, Meg Sedlak, Carolyn Box, Alicia Gilbreath, Rusty Holleman, Liz Miller, et al. 2019a. “Understanding Microplastic Levels, Pathways, and Transport in the San Francisco Bay Region.” Contribution No. 950. San Francisco Estuary Institute, Richmond, California.
- Sutton, Rebecca, Da Chen, Jennifer Sun, Denise J. Greig, and Yan Wu. 2019b. “Characterization of Brominated, Chlorinated, and Phosphate Flame Retardants in San Francisco Bay, an Urban Estuary.” *Science of The Total Environment* 652 (February): 212–23. <https://doi.org/10.1016/j.scitotenv.2018.10.096>.
- Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2020. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” *Science*, December, eabd6951. <https://doi.org/10.1126/science.abd6951>.
- Wu, J., Trowbridge, P., Yee, D., McKee, L., and Gilbreath, A., 2018. “RMP Small Tributaries Loading Strategy: Trends Strategy 2018.” Contribution No. 886. San Francisco Estuary Institute, Richmond, California.

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

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

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

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

Oversight Group: ECWG and SPLWG

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

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

PROPOSED DELIVERABLES AND TIMELINE

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

Background

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

Findings from this study indicated that water samples from the stormwater-influenced site, San Leandro Bay, contained a broad array of unique contaminants with strong signals suggesting higher concentrations (Overdahl et al. 2021; Sun et al. 2020). One example of a contaminant identified with high confidence is 1,3-diphenylguanidine (DPG), a rubber vulcanization agent derived from vehicle tires. The European Chemicals Agency established predicted no effect concentrations (PNEC) for DPG of 30 µg/L in freshwater and 3 µg/L in marine waters (ECHA 2018). While the non-targeted analysis provides only qualitative data, the high relative strength of the DPG signal suggested that this contaminant has the potential to be present at concentrations similar to these PNECs.

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

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

In addition to vehicle and roadway CECs, four additional classes of emerging contaminants have been identified in recent RMP studies and ECWG discussions as critical data gaps for stormwater, and are included as part of this pioneering exploration of CECs in stormwater.

Urban Runoff CECs – A direct outcome of the effort to identify the cause of coho mortality in Puget Sound was the development of a list of target analytes consisting of contaminants of concern that are characteristic of urban stormwater. While there are a number of targeted CEC lists designed around the influence of wastewater (e.g., focused on pharmaceuticals and

other compounds typically disposed of down the drain), this is the first CEC list targeting the influence of urban runoff in aquatic habitats. Unique contaminants with sources specific to vehicle traffic include the previously mentioned DPG and 6PPD-quinone, as well as hexa(methoxymethyl)melamine (HMMM), a component of tire resin, which can occur in highway runoff at concentrations approaching 10 µg/L (Peter et al. 2018).

Per- and polyfluoroalkyl substances (PFAS) – PFAS are classified as Moderate Concern for the Bay. A conceptual model of sources of PFAS to stormwater includes outdoor textiles, synthetic turf, construction materials, paints, plastic items, automotive fluids and waxes, and urban litter (e.g., food packaging), as well as industrial products such as fire-fighting foams. Atmospheric deposition is also possible. The RMP's PFAS Synthesis and Strategy (Sedlak et al. 2018) reviewed two studies of stormwater that have been conducted in the Bay Area: a seven site study conducted in water year 2010 (October 2009 through September 2010), and a 10 site study conducted in water year 2011. A relatively small number of PFAS were monitored; in addition, the watersheds monitored were not specifically selected to provide representative data for these contaminants in the Bay Area. The PFAS Synthesis and Strategy recommends stormwater monitoring as an RMP priority for future work.

Organophosphate ester (OPE) plastic additives/ flame retardants – OPEs were recently classified as Moderate Concern for San Francisco Bay. A conceptual model of sources of these contaminants to stormwater includes outdoor products such as construction and building materials, as well as volatilization from a broader assortment of consumer goods to the air followed by deposition to urban streams. Samples collected during two storms (water year 2014) at two Bay Area stormwater sites indicated the presence of OPEs at concentrations generally comparable to those found in wastewater (Sutton et al. 2019). An RMP report that reviews available data for this class of CECs recommends stormwater monitoring as a priority for the RMP (Lin and Sutton 2018).

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

Ethoxylated surfactants – Ethoxylated surfactants include alkylphenol ethoxylates (classified as Moderate Concerns for the Bay), as well as alcohol ethoxylates and others. A conceptual model of sources of ethoxylated surfactants to stormwater includes outdoor use of automotive cleaners, lubricants and other fluids, as well as pesticides, plastics, paints, construction materials, and many other products. The non-targeted analysis of San Francisco Bay sites described previously also identified a number of ethoxylated surfactants with strong signals in the stormwater-influenced site, San Leandro Bay (Overdahl et al. 2021; Sun et al. 2020). The RMP funded a 2019 special study to screen Bay water, sediment, and wastewater for ethoxylated surfactants; results from the two studies will be complementary.

This proposal describes the final year in a multi-year monitoring effort. The current wet season, Year 3 in terms of funding, was intended to include a significant amount of monitoring and laboratory analysis, but this was constrained due to relatively dry weather and the COVID-19 outbreak, similar to Year 2. As a result, there is a significant level of

unused funding in the Year 2 and 3 budgets, which will be carried forward towards monitoring in Year 4, as well as all associated laboratory analysis.

Study Objectives and Applicable RMP Management Questions

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

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

Approach

Stormwater Sample Collection

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

Up to 20 samples (including field blank and duplicate samples) will be collected as part of Year 4 sample collection. Samples will consist of grabs or composites. Composites collected using an ISCO pump are preferred for the new stormwater CECs analyte list developed by Dr. Kolodziej. For the other types of contaminants, the ISCO pump may lead to procedural contamination. For these contaminants, one or more grab samples will be collected at each site, and may be composited in the field or laboratory.

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

Chemical Analysis

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

Stormwater CECs: Unfiltered samples will be analyzed by the Kolodziej Laboratory (University of Washington) with a newly developed, targeted analytical method using multi-residue solid phase extraction (SPE) and liquid chromatography with tandem mass spectroscopy (LC-MS/MS; Hou et al. 2019). Approximately 35 compounds will be monitored, including pharmaceuticals, pesticides, and several vehicle-specific analytes such as 6PPD-quinone, DPG, and HMMM. This suite of representative tracers for urban runoff includes a broad range of contaminants with different physical-chemical parameters (e.g., various chemical functionalities, wide range of polarities and biodegradation potential). The compounds were selected to represent three primary urban sources: residential use, roadways, and wastewater.

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

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

Organophosphate ester (OPE) plastic additives/flame retardants: Both dissolved and particulate phase samples will be analyzed under supervision of the Chen Laboratory (Jinan University). Samples will be extracted in the U.S. by a partner laboratory, then Dr. Chen and his staff will characterize contaminants within the aqueous and solid phases using highly sensitive liquid chromatography–triple quadrupole mass spectrometry (LC-QQQ-MS/MS) based analysis methods (Chen et al. 2012; Chu et al. 2011). Dr. Chen has agreed to undertake method development to add recently identified OPEs, including isopropylated and tert-butylated triarylphosphate esters (ITPs and TBPPs; Phillips et al. 2017) to his extensive list of target analytes.

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

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

Data Interpretation

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

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

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

Budget

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

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

Budget Justification

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

Planning and Stakeholder Engagement Costs

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

Field Costs

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

Data Management Costs

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

Analysis and Reporting Costs

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

After the manuscripts are complete, RMP staff will produce a summary document for stakeholders, which describes the results and their implications for water quality management. Year 2 and 3 funds for analysis and reporting remain and will be carried over to Year 4 activities.

Laboratory Costs

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

Reporting

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

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

References

- Barzen-Hanson KA, Davis SE, Kleber M, Field JA. 2017. Sorption of fluorotelomer sulfonates, fluorotelomer sulfonamido betaines, and a fluorotelomer sulfonamido amine in National Foam Aqueous Film-Forming Foam to soil. *Environ Sci Technol* 51(21):12394-12404.
- Chen D, Letcher RJ, Chu S. 2012. Determination of non-halogenated, chlorinated and brominated organophosphate flame retardants in herring gull eggs based on liquid chromatography – tandem quadrupole mass spectrometry. *J Chromatogr A* 1220: 169-174.
- Chu S, Chen D, Letcher RJ. 2011. Dicationic ion-pairing of phosphoric acid diesters post-liquid chromatography and subsequent determination by electrospray positive ionization-tandem mass spectrometry. *J Chromatogr A* 1218(44): 8083-8088.
- ECHA (European Chemicals Agency). 2018. Brief Profile: 1,3-diphenylguanidine. <https://echa.europa.eu/brief-profile/-/briefprofile/100.002.730>
- Hou, F., Tian, Z., Peter, K.T., Wu, C., Gipe, A.D., Zhao, H., Alegria, E.A., Liu, F., Kolodziej, E.P., 2019. Quantification of organic contaminants in urban stormwater by isotope dilution and liquid chromatography-tandem mass spectrometry. *Anal Bioanal Chem* 411, 7791–7806.
- Houtz E, Sedlak D. 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environ Sci Technol* 46(17):9342-9349.
- Lin D, Sutton R. 2018. Alternative Flame Retardants in San Francisco Bay: Synthesis and Strategy. SFEI Contribution 885. San Francisco Estuary Institute, Richmond, CA.
- McGuire ME, Schaefer C, Richards T, Backe WJ, Field JA, Houtz E, Sedlak DL, Guelfo JL, Wunsch A, Higgins CP. 2014. Evidence of remediation-induced alteration of subsurface poly- and perfluoroalkyl substance distribution at a former firefighter training area. *Environ Sci Technol* 48(12):6644-6652.
- Overdahl, K.E., Sutton, R., Sun, J., DeStefano, N.J., Getzinger, G.J., Ferguson, P.L., 2021. Assessment of emerging polar organic pollutants linked to contaminant pathways within an urban estuary using non-targeted analysis. *Environ. Sci.: Processes Impacts* 10.1039.D0EM00463D.
- Peter KT, Tian Z, Wu C, Lin P, White S, Du B, McIntyre JK, Scholz NL, Kolodziej EP. 2018. Using high-resolution mass spectrometry to identify organic contaminants linked to urban stormwater mortality syndrome in coho salmon. *Environ Sci Technol* 52(18): 10317-10327.
- Phillips AL, Hammel SC, Konstantinov A, Stapleton HM. 2017. Characterization of

individual isopropylated and tert-butylated triarylphosphate (ITP and TBPP) isomers in several commercial flame retardant mixtures and house dust standard reference material SRM 2585. *Environ Sci Technol* 51(22):13443-13449.

Sedlak M, Sutton R, Wong A, Lin D. 2018. Per and Polyfluoroalkyl Substances (PFASs) in San Francisco Bay: Synthesis and Strategy. SFEI Contribution 867. San Francisco Estuary Institute, Richmond, CA.

Shimabuku I, Sutton R, Chen D, Wu Y, Sun J. 2020. Flame Retardants and Plastic Additives in San Francisco Bay: A Targeted Monitoring of Organophosphate Esters and Bisphenols. SFEI Contribution 925. San Francisco Estuary Institute, Richmond, CA.

Sun, J.; Sutton, R.; Ferguson, L.; Overdahl, K. 2020. New San Francisco Bay Contaminants Emerge. SFEI Contribution 931. San Francisco Estuary Institute: Richmond, CA.

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

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

Tian, Z., Zhao, H., Peter, K.T., Gonzalez, M., Wetzel, J., Wu, C., Hu, X., Prat, J., Mudrock, E., Hettinger, R., Cortina, A.E., Biswas, R.G., Kock, F.V.C., Soong, R., Jenne, A., Du, B., Hou, F., He, H., Lundeen, R., Gilbreath, A., Sutton, R., Scholz, N.L., Davis, J.W., Dodd, M.C., Simpson, A., McIntyre, J.K., Kolodziej, E.P., 2021. A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon. *Science* 371, 185–189.

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

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

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

PROPOSED DELIVERABLES AND TIMELINE

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

Background

A number of potentially toxic tire-derived contaminants have been observed in Bay Area stormwater, including the newly discovered coho salmon toxicant, 6PPD-quinone, derived from a tire preservative (Tian et al. 2021). Four of nine Bay Area stormwater samples collected in WY2019 contained levels of 6PPD-quinone that exceeded the LC₅₀, the concentration at which half the coho salmon die after a few hours of exposure in laboratory experiments. While coho salmon are now absent from Bay tributaries, steelhead (*Oncorhynchus mykiss*), a threatened species, are observed in some streams (e.g., Guadalupe River, Alameda Creek), and their susceptibility to this contaminant has not yet been established. Another tire-derived contaminant, the rubber vulcanization agent 1,3-diphenylguanidine (DPG), was detected in stormwater at levels up to 1.8 µg/L (SFEI, unpublished data). The European Chemicals Agency established predicted no effect concentrations (PNEC) for DPG of 30 µg/L in freshwater and 3 µg/L in marine waters (ECHA 2018). Monitoring of 6PPD-quinone, DPG, and other tire-derived contaminants is possible through a recently developed method designed to evaluate emerging contaminants in stormwater (Hou et al. 2019).

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

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

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

Study Objectives and Applicable RMP Management Questions

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

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Monitor tire-derived contaminants and other stormwater-associated CECs in Bay water.	Do these compounds have the potential to cause impacts to aquatic life? Which compounds are of greatest concern?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Evaluate concentrations in Bay water relative to RMP stormwater monitoring.	Are Bay water concentrations near stormwater and wastewater influenced sites consistent with the hypothesis that stormwater is the dominant pathway?
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	Compare concentrations in near-field vs. mid-Bay sites.	Are these stormwater-derived contaminants rapidly removed from Bay water?
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?	N/A	
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	N/A	
6) What are the effects of management actions?	N/A	

Approach

Bay Water Sampling

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

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

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

Analytical Methods

Unfiltered samples will be analyzed by the Kolodziej Laboratory (University of Washington) with a newly developed, targeted analytical method using multi-residue solid phase extraction (SPE) and liquid chromatography with tandem mass spectrometry (LC-MS/MS; Hou et al. 2019). Approximately 35 compounds will be monitored, including pharmaceuticals, pesticides, and several tire-derived analytes such as 6PPD-quinone and DPG. This suite of representative tracers for urban runoff includes a broad range of contaminants with different physical-chemical parameters (e.g., various chemical functionalities, wide range of polarities and biodegradation potential). The compounds were selected to represent three primary urban sources: residential use, roadways, and wastewater.



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

Budget

Table 2. Proposed Budget

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

Budget Justification

SFEI Labor

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

Data Technical Services

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

Sample Collection

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

Laboratory Costs (Ed Kolodziej, University of Washington)

Analysis of 23 samples, including two field blanks and two field duplicates, as well as assistance with interpretation, are included in a subcontract for \$10,000.

Reporting

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

References

- ECHA (European Chemicals Agency). 2018. Brief Profile: 1,3-diphenylguanidine. <https://echa.europa.eu/brief-profile/-/briefprofile/100.002.730>
- Hou, F., Tian, Z., Peter, K.T., Wu, C., Gipe, A.D., Zhao, H., Alegria, E.A., Liu, F., Kolodziej, E.P., 2019. Quantification of organic contaminants in urban stormwater by isotope dilution and liquid chromatography-tandem mass spectrometry. *Anal Bioanal Chem* 411, 7791–7806.
- Houtz E, Sedlak D. 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environ Sci Technol* 46(17):9342-9349.
- Sutton R, Sedlak M, Sun J, Lin D. 2017. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2017 Revision. SFEI Contribution 815. San Francisco Estuary Institute, Richmond, CA.
- Sutton R, Chen D, Sun J, Greig D, Wu Y. 2019. Characterization of Brominated, Chlorinated, and Phosphate Flame Retardants in an Urban Estuary. *Sci Total Environ* 652: 212-223.
- Tian, Z., Zhao, H., Peter, K.T., Gonzalez, M., Wetzel, J., Wu, C., Hu, X., Prat, J., Mudrock, E., Hettinger, R., Cortina, A.E., Biswas, R.G., Kock, F.V.C., Soong, R., Jenne, A., Du, B., Hou, F., He, H., Lundeen, R., Gilbreath, A., Sutton, R., Scholz, N.L., Davis, J.W., Dodd, M.C., Simpson, A., McIntyre, J.K., Kolodziej, E.P., 2021. A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon. *Science* 371, 185–189.

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

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

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

PROPOSED DELIVERABLES AND TIMELINE

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

Background

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

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

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

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

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

In contrast, because of the comprehensive nature of the non-targeted methods proposed herein, should few unexpected contaminants be identified, the RMP would then have

considerable evidence that existing CEC monitoring is already focusing on the highest priority contaminants for the Bay.

Study Objectives and Applicable RMP Management Questions

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

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Identify water contaminants not yet characterized by targeted monitoring efforts. Evaluate future monitoring needs and toxicity data gaps.	Identify additional contaminants that may merit further monitoring.
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Comparison of Bay water near stormwater inputs vs. ambient mid-Bay water with respect to non-targeted detections. Initial comparison of sites influenced by the stormwater pathway.	Compare the suite of contaminants detected in stormwater to those in ambient Bay water near stormwater inputs and mid-Bay post-storms. Identify regional or pathway-related differences in the presence of newly identified contaminants.
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	Investigate the influence of the stormwater pathway for water contaminants.	Identify differences in detection that may suggest persistence, degradation, or additional pathways for specific contaminants.

4) Have the concentrations of individual CECs or groups of CECs increased or decreased?	N/A	
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	N/A	
6) What are the effects of management actions?	N/A	

Approach

Bay Water Sampling

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

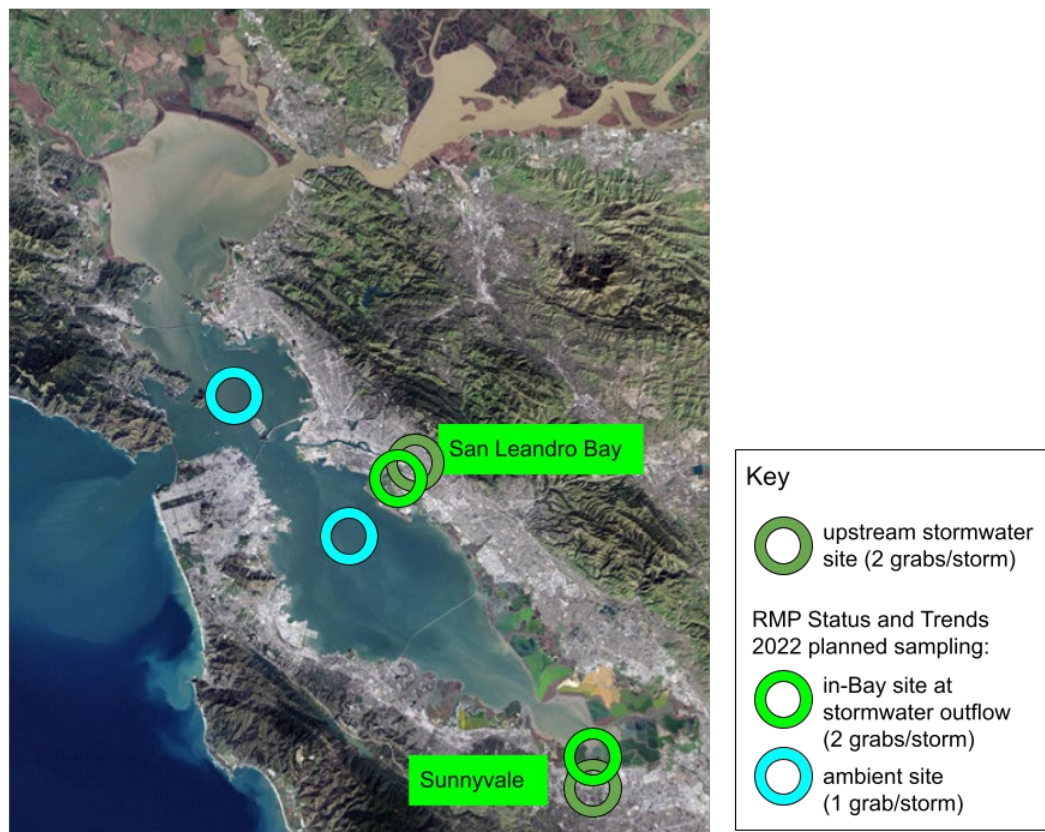


Figure 1. Proposed sampling locations, based on current Status and Trends 2022 pilot wet season sampling design planned at San Leandro Bay, Sunnyvale, and ambient sites.

Analytical Methods

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

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

Samples will be extracted for comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC/TOF-MS) using previously described methods (Chang et al., in review). Briefly, vacuum-filtered storm water samples will be extracted using OASIS HLB SPE with acetone and dichloromethane. The samples will further be dried with sodium

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

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

Budget

Table 2. Proposed Budget

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

Budget Justification

Field Costs

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

Reporting Costs

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

Laboratory Costs

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

Data Management Costs

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

Reporting

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

References

- Chang, D., Richardot, W.H., Miller, E.L., Dodder, N.G., Sedlak, M.D., Hoh, E., Sutton, R., in review. Non-targeted Analysis of Stormwater Runoff Following the 2017 Northern San Francisco Bay Area Wildfires.
- Dodder, N.G., Mehinto, A.C., Maruya, K.A., 2015. Monitoring of Constituents of Emerging Concern (CECs) in California's Aquatic Ecosystems – Pilot Study Design and QA/QC Guidance (SCCWRP Technical Report 854). Southern California Coastal Water Research Project, Costa Mesa, CA.
- Du, B., Lofton, J.M., Peter, K.T., Gipe, A.D., James, C.A., McIntyre, J.K., Scholz, N.L., Baker, J.E., Kolodziej, E.P., 2017. Development of suspect and non-target screening methods for detection of organic contaminants in highway runoff and fish tissue with high-resolution time-of-flight mass spectrometry. *Environ. Sci. Process. Impacts* 19, 1185–1196. <https://doi.org/10.1039/C7EM00243B>
- Overdahl, K.E., Sutton, R., Sun, J., DeStefano, N.J., Getzinger, G.J., Ferguson, P.L., 2021. Assessment of emerging polar organic pollutants linked to contaminant pathways within an urban estuary using non-targeted analysis. *Environ. Sci. Process. Impacts* 10.1039/D0EM00463D. <https://doi.org/10.1039/D0EM00463D>
- Peter, K.T., Tian, Z., Wu, C., Lin, P., White, S., Du, B., McIntyre, J.K., Scholz, N.L.,

- Kolodziej, E.P., 2018. Using High-Resolution Mass Spectrometry to Identify Organic Contaminants Linked to Urban Stormwater Mortality Syndrome in Coho Salmon. *Environ. Sci. Technol.* 52, 10317–10327. <https://doi.org/10.1021/acs.est.8b03287>
- Sun, J., Sutton, R., Ferguson, P.L., Overdahl, K.E., 2020. New SF Bay Contaminants Emerge (SFEI Contribution No. 931). San Francisco Estuary Institute, Richmond, California.
- Sutton, R., Sedlak, M., Sun, J., Lin, D., 2017. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2017 Revision (SFEI Contribution No. 815). San Francisco Estuary Institute, Richmond, CA.
- Tian, Z., Zhao, H., Peter, K.T., Gonzalez, M., Wetzel, J., Wu, C., Hu, X., Prat, J., Mudrock, E., Hettinger, R., Cortina, A.E., Biswas, R.G., Kock, F.V.C., Soong, R., Jenne, A., Du, B., Hou, F., He, H., Lundeen, R., Gilbreath, A., Sutton, R., Scholz, N.L., Davis, J.W., Dodd, M.C., Simpson, A., McIntyre, J.K., Kolodziej, E.P., 2021. A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon. *Science* 371, 185–189. <https://doi.org/10.1126/science.abd6951>
- Ulrich, E.M., Sobus, J.R., Grulke, C.M., Richard, A.M., Newton, S.R., Strynar, M.J., Mansouri, K., Williams, A.J., 2019. EPA’s non-targeted analysis collaborative trial (ENTACT): genesis, design, and initial findings. *Anal. Bioanal. Chem.* 411, 853–866. <https://doi.org/10.1007/s00216-018-1435-6>

Special Study Proposal: Tire Particle/Contaminant Fate and Transport

Summary: The Tires Conceptual Model project, which was funded in 2020 and is currently underway, is identifying several key data gaps crucial to identification and design of management actions. All of these data gaps relate to release of contaminants from tire particles and their fate and transport. This project proposes to fill the highest priority of those data gaps – particle surface area measurements – and to complete related, relatively inexpensive additional tests (morphology, particle size distribution, and density) to support conducting the particle surface area measurements and to inform future monitoring and management efforts.

Results from this project are expected to determine whether tire wear particles that travel primarily through the air (smaller particles) or the particles that fall on or near the road (larger particles) have the greatest overall surface area, and thus the greatest potential to support formation and release of tire-related pollutants like 6PPD-quinone into stormwater and the Bay. This information has tremendous implications for tire-related mitigation strategies. The information will also improve interpretation of tire-related toxicity data from the scientific literature that we would like to use to support the RMP. It will also inform monitoring approaches for tire particles and tire-related contaminants.

The results from this project will have implications for both the proposed Tires Strategy and the proposed Stormwater CECs Monitoring Strategy. This project is being recommended in parallel with the Tires Strategy because it provides foundational information for the strategy, informs and improves science generated by others that we hope to use to support the RMP, and provides information that will be immediately useful to state management agencies addressing (1) pollutants that leach from rubber particles (California Department of Toxic Substances Control [DTSC]) and (2) the particles themselves (California Ocean Protection Council [OPC]).

Because tire-wear microplastics release tire-related water pollutants into stormwater, this is a cross-workgroup strategy proposal involving the Microplastics Workgroup (MPWG), the Emerging Contaminants Workgroup (ECWG), and the Sources, Pathways, and Loadings Workgroup (SPLWG). It will address MPWG, ECWG, and SPLWG management questions.

Estimated Cost: \$110,000

Oversight Groups: MPWG, ECWG & SPLWG

Proposed by: Kelly Moran and Rebecca Sutton (SFEI), Jasquelin Peña (UC Davis)

Time sensitive: Yes. Provides information to support upcoming management decisions by DTSC and OPC; informs identification and evaluation of possible mitigation strategies for tire-related stormwater pollutants like 6PPD-quinone; and will inform next steps for the proposed Tires Strategy and Stormwater CECs Monitoring Strategy.

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Laboratory analysis	Spring 2022
Task 2. Present update to the MPWG, SPLWG and ECWG	Spring 2022
Task 3. Semi-Annual updates to STLS	2022
Task 4. Draft report to the MPWG, SPLWG and ECWG	Summer-Fall 2022
Task 5. Final report and draft manuscript	December 31, 2022

Background

Every vehicle on the road sheds tiny particles from its rubber tires into the environment. As they disperse into the environment, these microplastic particles convey tire tread ingredients into the air, runoff, and eventually into San Francisco Bay. With funding from the Moore Foundation, the RMP, and other organizations, an SFEI study found black, rubbery particles in urban stormwater (Sutton et al. 2019). These were the most common microparticles in urban stormwater runoff. The source of these particles appears to be tires. Modeling studies indicate tire wear may be one of the top sources of microplastics to the environment globally (Boucher and Friot 2017; Kole et al. 2017; Sieber et al. 2020).

Chemicals that leach from tire tread also appear in urban runoff, including in the San Francisco Bay area (Peter et al. 2018; 2020; Tian et al. 2021). One of these chemicals, 6PPD-quinone (a degradate of a tire antioxidant) causes pre-spawn mortality in wild populations of coho salmon (Tian et al. 2021).

The RMP-funded Tires Conceptual Model project currently underway identified several key data gaps crucial to identification and design of management actions. All of these data gaps relate to release of contaminants from tire particles and their fate and transport. This project proposes to fill the highest priority of those data gaps – particle surface area measurements – and to complete related, relatively inexpensive additional tests (morphology, particle size distribution, and density) to support conducting the particle surface area measurements and to inform future monitoring and management efforts.

The proposed project will answer the following critical questions:

1. Which tire wear particles - the ones that travel primarily through the air (smaller particles) or the particles that fall on or near the road (larger particles) - have the greatest overall surface area, and thus the greatest potential to support formation and release of tire-related pollutants like 6PPD-quinone into stormwater and the Bay?
2. What particle size and transport pathway should be prioritized for tire-related mitigation strategies?
3. How does the type of particle used by researchers affect interpretation of tire-related toxicity data from the scientific literature that we would like to use to support the RMP?
4. What is the best approach for sampling tire particles and tire contaminants in RMP monitoring?

The information generated by this project will allow us to identify the transport pathways of greatest importance for water quality, to better understand the potential for chemical ingredients and transformation products like 6PPD-quinone to leach from tires, and to identify the tire wear particle size range of greatest importance from the water quality perspective. It will also allow us to design any future monitoring more accurately and cost-effectively. While this information has fundamental importance and is relatively low cost to obtain, we did not identify any other plans by other scientists to obtain it.

A similar set of measurements undertaken early in the Brake Pad Partnership proved crucial to the design and success of the joint science studies that led to California's law that nearly phases out copper in vehicle brake pads.

By quickly conducting this study and broadly sharing results, we believe the RMP investment will greatly improve the value of the other work occurring at no cost to the RMP, such as toxicity studies being undertaken at labs around the world. Without this information, we would expect study designs by others may continue to be a bit off-target from the water quality perspective (e.g., using non-representative materials in toxicity tests, focusing on particle sizes that may not be of greatest importance for water quality).

The background below explains the importance of these measurements, starting with background about tire particle sizes.

Tire wear particle sizes and transport pathways

Tire wear particles span a broad range of sizes, extending from tiny, primarily air-transported particles small enough to be inhaled ($<10\ \mu\text{m}$) up to particles so large ($>100\ \mu\text{m}$) that they deposit quickly after release. Figures 1 and 2 show tire wear particle size distributions measured (using transmission optical microscopy) in a road simulator laboratory from tires abraded by a rotating asphalt surface (Kreider et al. 2010). Figure 1 shows the tire wear particle size distribution by volume; Figure 2 shows the same distribution as a function of number of particles (irregular lines). While only a few tire wear particle size distributions have been published, multiple researchers have noted bimodal distributions and explored the differences between larger and smaller particles (Wagner et al. 2018).

Figure 1. Tire Wear Particle Size distribution (by volume) from Kreider et al. (2010). Blue lines indicate sieve sizes used in Bay Area microplastics monitoring: 125 μm (stormwater) and 355 μm (surface water). Purple line indicates air quality regulatory threshold (PM₁₀).

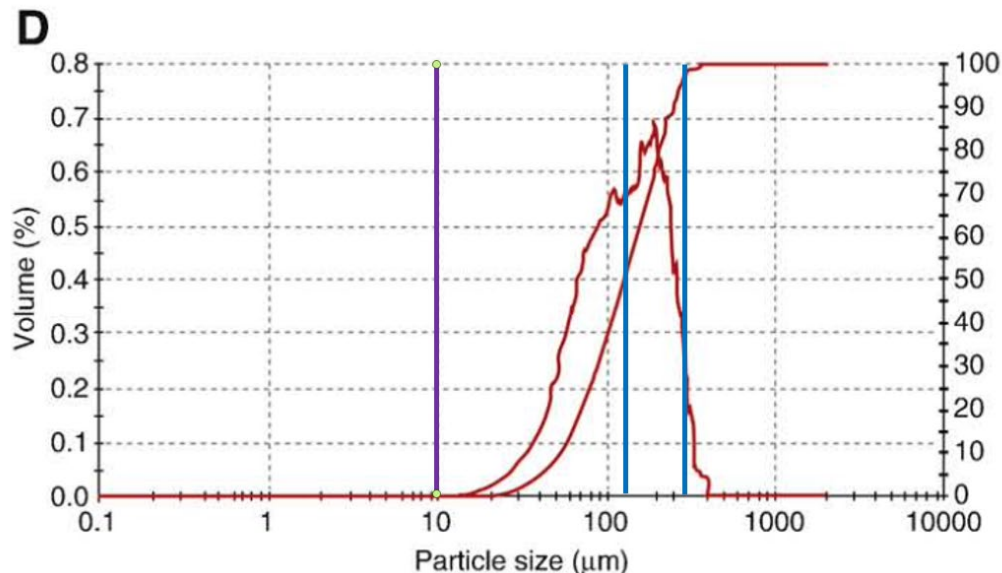
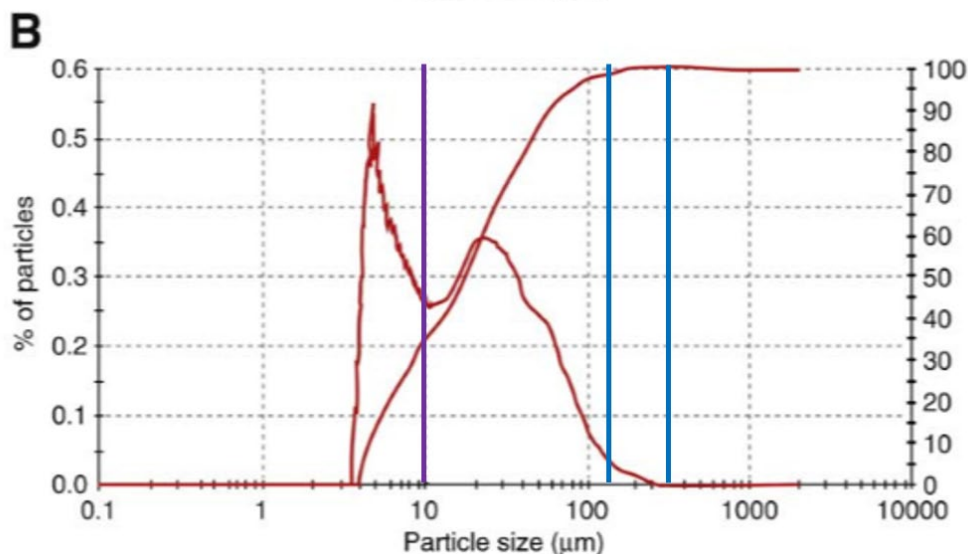


Figure 2. Tire wear particle size distribution (by number of particles) from Kreider et al. 2010. Blue lines indicate sieve sizes used in Bay Area microplastics monitoring: 125 μm (stormwater) and 355 μm (surface water). Purple line indicates air quality regulatory threshold (PM₁₀).



Specific Surface Area

Specific surface area (total surface area per unit mass) is a key indicator of potential for release and/or transformation of chemicals contained in environmental particles like tire wear debris. The greater the surface area, the greater the potential for degradate formation and chemical release from the particle.

The few published scanning electron micrograph photos of tire wear debris reveal rough, irregular surfaces, which suggests that these particles may have surface areas much higher than those on tire materials used in various tire leaching and tire toxicity research (e.g., cryomilled particles and ground whole tires used for turf infill). Clarifying these differences would allow us to better interpret information from the literature (particularly toxicity test data).

Management efforts seeking to minimize release of tire-related contaminants will be most effective if they target the particle size fraction containing the majority of the specific surface area.

Another friction-formed material, brake pad wear debris, provides an example of the importance of specific surface area. Due to its micro-roughness, brake pad wear debris has a surface area >150 times greater than most of the powdered reference materials. Hur et al. (2003) found higher copper leaching from brake wear debris containing only 10% copper than any copper-containing reference material (copper oxides, sulfides, or brass). They attributed the higher leaching (despite much lower copper content) to the higher surface area of the wear debris (31 m²/g for wear debris; 0.059-1.4 m²/g for copper-containing reference materials purchased from chemical laboratory suppliers) (Hur et al. 2003).

Surprisingly, tire wear debris specific surface area has not been reported in the literature.

Morphology

One line of evidence in identifying tire wear particles – and in beginning to understand their transport in stormwater runoff – involves examining particle morphology. Scanning electron micrograph (SEM) images and tomography are two ways of examining particle morphology. Morphology is a qualitative indicator of specific surface area. Because morphology can relate to the particle formation process, it may not be consistent across all tire wear particle sizes. Morphological differences in tire wear debris, if they occur, can guide the process of selecting sieve sizes to create particle size fractions for specific surface area measurements.

Density

Tire wear particle density has been roughly estimated (not based on direct measurements) to be in the range of 1.25-1.8 g/cm³ (Wagner et al. 2018). We were unable to identify published density measurements of tire wear particles (with or without encrustations). Density measurements can inform sampling methods to ensure tire particles are fully recovered and counted. Density will inform conceptual modeling (and possible future numeric modeling) of tire particle transport.

Knowing tire wear particle density and the most environmentally relevant size fraction would allow optimization of any future RMP tire-related monitoring to collect the particles most relevant for water quality.

Comparison between tire wear particles and substitute laboratory test materials

Due to the lack of availability of representative samples of real tire wear particles, scientists have used a variety of substitute materials in studies reported in the scientific literature. Better understanding how real particles compare to these test particles (particularly how their

sizes and surface areas compare) will allow us to better interpret scientific work done by others, particularly aquatic toxicity studies.

Study Objectives and Applicable RMP Management Questions

The objectives of this project are:

- (1) To identify the tire-wear particle size fraction of greatest importance from the water quality perspective, which in turn will identify the tire particle/contaminant transport pathway of greatest importance, thereby focusing consideration of management actions.
- (2) To better understand the potential for chemical ingredients and degradates to leach from tire-wear particles.
- (3) To obtain information that will improve interpretation of sometimes conflicting scientific literature around tire particle contaminants, leachates, and aquatic toxicity.
- (4) To inform design of future tire particle/contaminant-related monitoring and modeling.

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

Management Question	Study Objective	Example Information Application
1) How much microplastic pollution is there in the Bay and in the surrounding ocean?	To inform design of future tire particle/contaminant-related monitoring and modeling.	Modify sample collection, preparation, and analysis procedures in future microplastics monitoring to maximize recovery of tire particles and allow for more comprehensive assessment of microplastic abundance.
2) What are the health risks?	<p>To obtain information that will improve interpretation of sometimes conflicting scientific literature around tire particle contaminants, leachates, and aquatic toxicity.</p> <p>To better understand the potential for potentially harmful chemical ingredients and degradates to leach from tire-wear particles.</p>	<p>Inform monitoring data interpretation, particularly how we use tire particle toxicity information in the literature.</p> <p>Improve designs of studies conducted by others (e.g., tire particle toxicity testing), making the data more useful to RMP stakeholders.</p>
3) What are the sources, pathways, loadings, and processes leading to microplastic pollution in the Bay?	To identify the tire-wear particle size fraction of greatest importance from the water quality perspective, which in turn will identify the tire particle/contaminant transport pathway of greatest importance.	Understand whether tire-wear particles transported by air or those deposited near roads have greater potential to leach contaminants into stormwater.

4) Have the concentrations of microplastics in the Bay increased or decreased?	N/A	N/A
5) Which management actions may be effective in reducing microplastic pollution?	To identify the tire-wear particle size fraction of greatest importance from the water quality perspective, which in turn will identify the tire particle/contaminant transport pathway of greatest importance, thereby focusing consideration of management actions.	Identify and prioritize potential management actions appropriate for the most important tire particle size fraction. Develop improved conceptual models (and inform future numeric models) to predict possible reductions from various management action options.

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

Management Question	Study Objective	Example Information Application
1) What are the loads or concentrations of pollutants of concern from small tributaries to the Bay?	To inform the design of future tire particle/contaminant-related monitoring and modeling.	Modify sample collection, preparation, and analysis procedures in future microplastics monitoring to maximize recovery of tire particles and allow for more comprehensive assessment of microplastic abundance.
2) Which are the “high-leverage” small tributaries that contribute or potentially contribute most to Bay impairment by pollutants of concern	N/A	N/A
3) How are loads or concentrations of pollutants of concern from small tributaries changing on a decadal scale?	N/A	N/A
4) Which sources or watershed source areas provide the greatest opportunities for reductions of pollutants of concern in urban stormwater runoff?	To identify the tire-wear particle size fraction of greatest importance from the water quality perspective, which in turn will identify the tire particle/contaminant transport pathway of greatest importance.	Identify and prioritize potential management actions appropriate for the most important tire particle size fraction.
5) What are the measured and projected impacts of management action(s) on loads or concentrations of pollutants of concern from the small tributaries, and what	To identify the tire-wear particle size fraction of greatest importance from the water quality perspective, which in turn will identify the tire particle/contaminant transport	Identify and prioritize potential management actions appropriate for the most important tire particle size fraction. Develop improved conceptual models (and inform future

management action(s) should be implemented in the region to have the greatest impact?	pathway of greatest importance, thereby focusing consideration of management actions.	numeric models) to predict possible reductions from various management action options.
---	---	--

Table 3. Study objectives and questions relevant to RMP ECWG management questions

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	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?	To identify the tire-wear particle size fraction of greatest importance from the water quality perspective, which in turn will identify the tire particle/contaminant transport pathway of greatest importance.	Understand whether tire-wear particles transported by air or those deposited near roads have greater potential to leach contaminants into stormwater.
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	To better understand the potential for chemical ingredients and degradates to leach from tire-wear particles.	Identify the places in the road area and outdoor environment where tire contaminants are most likely to be released.
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?	N/A	N/A
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	N/A	N/A
6) What are the effects of management actions?	To identify the tire-wear particle size fraction of greatest importance from the water quality perspective, which in turn will identify the tire particle/contaminant transport pathway of greatest importance, thereby focusing consideration of management actions.	Identify and prioritize potential management actions appropriate for the most important tire particle size fraction. Develop improved conceptual models (and inform future numeric models) to predict possible reductions from various management action options.

Approach

We propose to:

- (1) Examine and compare morphology and specific surface areas of black, rubbery particles collected in stormwater, tire wear debris, and other tire materials that are being used in scientific studies conducted by others.
- (2) Determine the size fraction of tire wear debris that accounts for the majority of the specific surface area.
- (3) Measure tire particle density.
- (4) Use these data and information from the scientific literature to interpret these results
- (5) Share these insights with RMP stakeholders and the scientific community.

The particles we propose to test include:

- Tyre Collective in-laboratory road simulator and test track tire wear particles. The Tyre Collective, a start-up company developing an on-vehicle device to collect tire wear debris, will be generating tire wear particles during its product development process. Their 10% scale laboratory system using a composite formulation of 100% tread material generates wear debris from a sandpaper “road” surface (a debris generation method used by others, e.g., Kreider et al. 2010). The on-road collection system is in development, with the intent of capturing particles from several full-sized vehicle tires on a test track. These systems have the potential to capture a wide range of particle sizes, but neither are designed to provide full or perfect particle size distributions.
- Stormwater black, rubbery particles collected in conjunction with a separate grant-funded study being conducted by SFEI. (Particles from the Sutton et al. 2019 study can only be used for SEMs). These will be separated from non-rubber runoff debris via density separation. We anticipate these particles will be from the larger size fraction of the tire wear particle size distribution.
- Road surface black, rubbery particles to be collected by SFEI as part of this proposed project. The particles are planned to be swept or vacuumed off of pavement on a high-traffic road segment during the dry season (see AP-42; McKenzie et al. 2008). Subsequently, they will be separated from non-rubber road debris via density separation. Due to the collection method, these samples will likely include only the larger particles.
- Laboratory test particles of tires that are commonly used by scientists conducting tire particle toxicity tests. These are anticipated to include lab-generated tire tread particles (potentially from Washington State University and Oregon State University) and artificial turf infill particles (milled whole tires), which we plan to obtain from tire recyclers and/or collect from artificial turf fields.

We propose to work with UC Davis Professor Jasquelin Peña to conduct the following measurements:

- Specific Surface Area (SSA) – Brunauer–Emmett–Teller (BET) specific surface area measurements
- Morphology – Scanning Electron microscope (SEM) images and tomography
- Particle Size Distribution – Inverted phase contrast microscope
- Density – Bulk density (mass/volume)

We propose to work with Dr. Jasquelin Peña, Associate Professor in the Department of Civil and Environmental Engineering at U.C. Davis. Professor Peña also has a faculty scientist appointment in the Energy Geosciences Division at the Lawrence Berkeley National Laboratory. She has been working in the field of environmental and molecular geochemistry since 2001. With nearly two decades of experience applying molecular-scale science, environmental mineralogy, and biogeochemistry to investigate interfacial processes, particle structure, and surface reactivity, she has extensive experience in the proposed types of particle characterization measurements. Her laboratory owns or has access on the U.C. Davis campus to the specialized equipment needed for this work, such as the equipment necessary for specific surface area measurements and microscopic imaging.

In the initial phase of the study, we will examine particle morphology and measure particle size distributions. We intend to measure the particle size distribution in each sample via inverted phase contrast microscopy. We plan to use scanning electron microscope images and tomography to look at particle morphology. These relatively inexpensive measurements provide quick insight into the relative surface areas of the different tire particles – as well as the ability to examine the particle to determine if there is a relationship between particle size and morphology. We hypothesize that particles in different size segments are formed by different processes, such that some segments may have larger surface areas as a function of mass than other size segments. We also hypothesize that real tire-wear debris and environmental tire particles have greater specific surface area than the laboratory test particles. The morphology work will address these hypotheses.

Subsequently, based on the preliminary morphology examination and particle size distributions, we plan to divide the tire wear particles (from the Tyre Collective and perhaps from road samples) into size-based fractions to explore surface area as a function of size. We will also measure specific surface area of the particles used in laboratory studies, which will allow us to compare the lab particles to environmental tire particles.

A density-based separation process is currently used to extract tire and other microplastic particles from environmental mixtures. Because tires are denser than most microplastics, this procedure may not collect all tire particles. Surprisingly, the density of tire particles has not been specifically reported in the literature – it is usually listed as a range and often reflects tire material encrusted with road debris (which may also need to be addressed in separation procedures). We plan to measure the density of our various samples; this inexpensive test will inform our future monitoring designs. Density will be a useful input for any future modeling of tire wear particle transport.

We plan to work with Dr. Peña's lab to prepare a report and short manuscript presenting and interpreting the results. The manuscript would be designed to be a short communication for submission to a quick-publishing journal. To maximize the value of the results, we will also present them at a scientific conference attended by researchers working on tire particle/contaminants fate, transport, and toxicity.

Budget

The following budget represents estimated costs for this proposed special study (Table 4).

Table 4. Estimated costs.

Expense	Estimated Hours	Estimated Cost
<i>Labor</i>		
Project Staff	300	\$54,000
Senior Management Review	12	\$3,000
<i>Direct Costs</i>		
Shipping/sample collection		\$2,000
UC Davis (J. Peña Lab)		\$51,000
<i>Grand Total</i>		\$110,000

Budget Justification

Labor Costs

SFEI labor will primarily be spent on data review and interpretation in the context of the relevant scientific literature; preparing the report and manuscript; obtaining and shipping samples; project management, preparing presentations for the ECWG, SPLWG, and MPWG meetings and a scientific conference; and updates for the STLS. Senior scientists will help guide the process and review interim products. Project staff hours and costs reflect the need for specialized work.

Direct Costs

Most of the UC Davis costs (\$41k) are to fund a graduate student to conduct the testing and professor supervision (2 academic quarters); the remaining \$10,000 will be used for specialized equipment and supplies (most of this is for the specific surface area measurements). UC Davis labor will primarily be spent on conducting SEM, tomography, BET, particle size and density measurements; sample handling, preparation, separation and storage; analyzing data with computer-based tools; and preparing sections of the report and manuscript. In addition to conducting specialized testing of tire particles, work will include trials of sample preparation methods to address extended de-gassing of rubber particles in preparation for BET measurements.

Early Funds Release Request

If this project is approved, we request early release of funds (by September 2021). This will allow information to be available in time to support upcoming management decisions by DTSC and OPC (multiple decisions anticipated between now and 2025), and to inform the development of the RMP's proposed Tires Strategy and Stormwater CECs Monitoring Strategy.

Reporting

Deliverables will include a) a progress update presentation, to be presented to the MPWG, SPLWG, and ECWG in spring 2022; b) a draft report to be provided to the MPWG, SPLWG, and ECWG in summer or fall 2022; and c) a final report and draft manuscript (a brief article aimed at a quick-publish journal), to be completed December 31, 2022. The project budget includes quarterly verbal updates to the STLS and a scientific conference presentation to encourage others (whose work will be useful but will not be funded by the RMP) such that they can consider study results when designing future scientific studies.

References

- Boucher, Julien, and Damien Friot. 2017. “Primary Microplastics in the Oceans: A Global Evaluation of Sources.” Gland, Switzerland: IUCN.
- Hur, Jin, Soobin Yim, and Mark A. Schlautman. 2003. “Copper Leaching from Brake Wear Debris in Standard Extraction Solutions.” Electronic Supplementary Information (ESI) Available: Thermodynamic Equilibrium Speciation Results from the Geochemical Model MINTEQA. See <http://www.rsc.org/suppdata/em/B3/B303820c/>. *Journal of Environmental Monitoring* 5 (5): 837. <https://doi.org/10.1039/b303820c>.
- Kole, Pieter Jan, Ansje J. Löhr, Frank Van Belleghem, and Ad Ragas. 2017. “Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment.” *International Journal of Environmental Research and Public Health* 14 (10): 1265. <https://doi.org/10.3390/ijerph14101265>.
- Kovochich, Michael, Monty Liong, Jillian A. Parker, Su Cheun Oh, Jessica P. Lee, Luan Xi, Marisa L. Kreider, and Kenneth M. Unice. 2021. “Chemical Mapping of Tire and Road Wear Particles for Single Particle Analysis.” *Science of The Total Environment* 757 (February): 144085. <https://doi.org/10.1016/j.scitotenv.2020.144085>.
- Kreider, Marisa L., Julie M. Panko, Britt L. McAtee, Leonard I. Sweet, and Brent L. Finley. 2010. “Physical and Chemical Characterization of Tire-Related Particles: Comparison of Particles Generated Using Different Methodologies.” *Science of The Total Environment* 408 (3): 652–59. <https://doi.org/10.1016/j.scitotenv.2009.10.016>.
- McKenzie, Erica R., Carol M. Wong, Peter G. Green, Masoud Kayhanian, and Thomas M. Young. 2008. “Size Dependent Elemental Composition of Road-Associated Particles.” *The Science of the Total Environment* 398 (1–3): 145–53. <https://doi.org/10.1016/j.scitotenv.2008.02.052>.
- Peter, Katherine T., Fan Hou, Zhenyu Tian, Christopher Wu, Matt Goehring, Fengmao Liu, and Edward P. Kolodziej. 2020. “More Than a First Flush: Urban Creek Storm Hydrographs Demonstrate Broad Contaminant Pollutographs.” *Environmental Science & Technology* 54 (10): 6152–65. <https://doi.org/10.1021/acs.est.0c00872>.
- Peter, Katherine T., Zhenyu Tian, Christopher Wu, Peter Lin, Sarah White, Bowen Du, Jenifer K. McIntyre, Nathaniel L. Scholz, and Edward P. Kolodziej. 2018. “Using High-Resolution Mass Spectrometry to Identify Organic Contaminants Linked to Urban Stormwater Mortality Syndrome in Coho Salmon.” *Environmental Science & Technology* 52 (18): 10317–27. <https://doi.org/10.1021/acs.est.8b03287>.
- Sieber, Ramona, Delphine Kaweck, and Bernd Nowack. 2020. “Dynamic Probabilistic Material Flow Analysis of Rubber Release from Tires into the Environment.”

- Environmental Pollution* 258 (March): 113573.
<https://doi.org/10.1016/j.envpol.2019.113573>.
- Sommer, Frank, Volker Dietze, Anja Baum, Jan Sauer, Stefan Gilge, Christoph Maschowski, and Reto Gieré. 2018. “Tire Abrasion as a Major Source of Microplastics in the Environment.” *Aerosol and Air Quality Research* 18 (8): 2014–28.
<https://doi.org/10.4209/aaqr.2018.03.0099>.
- Sutton, Rebecca, Diana Lin, Meg Sedlak, Carolyn Box, Alicia Gilbreath, Rusty Holleman, Liz Miller, et al. 2019. “Understanding Microplastic Levels, Pathways, and Transport in the San Francisco Bay Region.” SFEI Contribution No. 950. Richmond, CA: San Francisco Estuary Institute.
https://www.sfei.org/sites/default/files/biblio_files/Microplastic%20Levels%20in%20SF%20Bay%20-%20Final%20Report.pdf.
- Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon.” *Science* 371 (6525): 185–89.
<https://doi.org/10.1126/science.abd6951>.
- Wagner, Stephan, Thorsten Hüffer, Philipp Klöckner, Maren Wehrhahn, Thilo Hofmann, and Thorsten Reemtsma. 2018. “Tire Wear Particles in the Aquatic Environment - A Review on Generation, Analysis, Occurrence, Fate and Effects.” *Water Research* 139 (August): 83–100. <https://doi.org/10.1016/j.watres.2018.03.051>.

Special Study Proposal: RMP Tires Strategy

Summary: We propose to develop a cross-workgroup strategy for the RMP’s efforts around tire microplastics and tire-related water pollutants. The Tires Conceptual Model project, which was funded in 2020 and is currently underway, is identifying key information gaps around the connections between tires and aquatic habitats. The next step is to establish a short-term RMP strategy and multi-year plan spanning up to 5 years, based on stakeholder needs and the special capabilities of the RMP. This project is being recommended in parallel with other tire and stormwater CECs projects because of the high level of stakeholder interest in tire-related water pollution.

To prepare the strategy, we will identify relevant, specific management policies or decisions that are being evaluated, and priority RMP stakeholder tire-related science information needs that are not being addressed by others. We will then outline and work with experts and RMP stakeholders to refine a set of recommended RMP special studies related to tires for the years 2023-2028. Because tire-wear microplastics release tire-related water pollutants into stormwater, this is a cross-workgroup strategy proposal involving the Microplastics Workgroup (MPWG), the Emerging Contaminants Workgroup (ECWG), and the Sources, Pathways, and Loadings Workgroup (SPLWG). This inter-workgroup strategy will be designed as a short-term companion to the MPWG, ECWG, and SPLWG multi-year plans. Tire-related work that is needed after the 5-year horizon of this strategy would be integrated into future workgroup-specific strategies and multi-year plans. It will address RMP MPWG, ECWG, and SPLWG management questions.

Estimated Cost: \$25,500

Oversight Groups: MPWG, ECWG, & SPLWG

Proposed by: Kelly Moran and Rebecca Sutton

Time sensitive: Yes. Responds to high stakeholder interest in tire-related water pollution by identifying the RMP’s role in supporting science-based management actions. Provides information to support DTSC’s science-based Safer Consumer Products regulatory program, which intends to regulate chemicals in tires (a series of decisions are anticipated from 2021-2026).

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	<i>Due Date</i>
Task 1. Present draft strategy to the MPWG, SPLWG, ECWG and SC	Spring 2022
Task 2. Semi-Annual updates to STLS	Fall 2021; Spring 2022
Task 3. Final strategy	October 2022

Background

Every vehicle on the road sheds tiny particles from its rubber tires into the environment. As they disperse into the environment, these microplastic particles convey tire tread ingredients into the air, runoff, and eventually into San Francisco Bay. With funding from the Moore Foundation, the RMP, and other organizations, SFEI found black, rubbery particles in urban stormwater that appeared to be from tires (Sutton et al. 2019). These were the most common microparticles in urban stormwater runoff. Modeling studies indicate tire wear may be one of the top sources of microplastics to the environment globally (Boucher and Friot 2017; Kole et al. 2017; Sieber, Kawecki, and Nowack 2020). Total environmental emissions from tires likely exceed emissions of other well-known pollutant classes like pharmaceuticals and pesticides (Wagner et al. 2018).

Chemicals that leach from tire tread also appear in urban runoff, including in the San Francisco Bay area (Peter et al. 2018; 2020; Z. Tian et al. 2021). One of these chemicals, 6PPD-quinone (a degradate of a tire antioxidant) causes pre-spawn mortality to coho salmon (Tian et al. 2021).

Emerging concerns around exposures to tire particles and tire tread chemical ingredients have fueled intensifying investigations by researchers around the world, who are studying their toxicity, chemistry, and occurrence in organisms and environmental compartments. Non-targeted chemical analysis has identified potentially toxic tire ingredients and degradates in leachates and environmental media (Peter et al. 2018; 2020; Seiwert et al. 2020; Overdahl et al. 2021). Aquatic toxicologists have examined toxicity of leachates (Capolupo et al. 2020; Gualtieri et al. 2005; Halle et al. 2020; Kolomijeca et al. 2020) and have initiated studies on toxicity of the particles themselves. Environmental monitoring has revealed the presence of tire particles in air, aquatic environments and organisms (Baensch-Baltruschat et al. 2020; Leads and Weinstein 2019; Sutton et al. 2019; Z. Tian et al. 2017). Investigation of potential management measures like runoff treatment and alternatives for toxic ingredients has also begun (e.g., McIntyre et al. 2015; California Department of Toxic Substances Control 2021a; 2021b).

The RMP-funded Tires Conceptual Model project currently underway identified several key data gaps – all related to tire particles and rubbery stormwater particles. The next step is to establish the RMP's priorities, based on baseline scientific information, stakeholder needs, and the special capabilities of the RMP.

If funded, the proposed Tire Particle/Contaminant Fate and Transport Project will provide key information to focus the development of the Tires Strategy.

This project is specially designed to provide a timely response to high stakeholder interest in tire-related water pollution by working with affected agencies and science experts to define the RMP's role in supporting science-based management actions for tires. RMP scientists have received inquiries about tires from US EPA, state agencies, regional and local agencies, NGOs, the press, and legislators. The proposal seeks to maximize the RMP's ability to provide timely support to key efforts, like DTSC's science-based Safer Consumer Products regulatory program, which has initiated efforts to regulate chemicals in tires to protect

aquatic life (California Department of Toxic Substances Control 2021a; 2021b). DTSC will be making a series of science-based management decisions anticipated to occur between now and 2026.

Establishing a special, short-term Tires Strategy will allow the RMP to provide a timely response to stakeholder interest and management agency needs without diverting resources from long-term RMP priorities. Once the strategy is in place, its implementation can be integrated within the existing RMP structure. Determining how to complete the integration of work crossing three RMP workgroups (MPWG, ECWG, and SPLWG) in a cost-effective manner will be crucial to the strategy's success.

Study Objectives and Applicable RMP Management Questions

The goal of this project is to develop a multi-year plan for the RMP's activities around tire microplastics and tire-related water pollutants.

The objectives of this project are:

- (1) To identify the specific management policies or decisions regarding tire particles and tire tread chemical ingredients that are anticipated to occur in the next few years.
- (2) To identify priority RMP stakeholder tire-related science information needs that are not being addressed by others.
- (3) To outline a list of recommended RMP special studies related to tires for the years 2023-2028, based on addressing scientific information gaps that are within the RMP's purpose and mission and that not being addressed by others.
- (4) To vet and refine the five-year plan with RMP science advisors and stakeholders through the RMP workgroup process.

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

Management Question	Study Objective	Example Information Application
1) How much microplastic pollution is there in the Bay and in the surrounding ocean?	N/A	N/A
2) What are the health risks?	Summary literature review of toxicity data.	Identify tire-related monitoring priorities.
3) What are the sources, pathways, loadings, and processes leading to microplastic pollution in the Bay?	List of recommended RMP special studies related to tires to address scientific information gaps.	Identify tire-related monitoring (and any modeling support) necessary to improve understanding of pathways, processes, and load estimates for tire microplastics discharged to the Bay in stormwater.
4) Have the concentrations of microplastics in the Bay increased or decreased?	N/A	N/A

5) Which management actions may be effective in reducing microplastic pollution?	List of recommended RMP special studies related to tires to address scientific information gaps.	Identify studies to inform selection and design of tire-related management actions.
--	--	---

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	List of recommended RMP special studies related to tires to address scientific information gaps.	Identify tire-related chemical monitoring priorities.
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	List of recommended RMP special studies related to tires to address scientific information gaps.	Identify tire-related monitoring (and any modeling support) necessary to improve understanding of pathways, processes, and load estimates for tire microplastics discharged to the Bay in stormwater.
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	List of recommended RMP special studies related to tires to address scientific information gaps.	Identify any low-cost tire particle and tire tread chemical ingredient characterization necessary to understand their physical, chemical, and biological processes that may affect the transport and fate (e.g., density measurements).
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?	N/A	N/A
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	N/A	N/A
6) What are the effects of management actions?	N/A	N/A

Table 3. Study objectives and questions relevant to RMP SPL management questions

Management Question	Study Objective	Example Information Application
1) What are the loads or concentrations of pollutants of concern from small tributaries to the Bay?	List of recommended RMP special studies related to tires to address scientific information gaps.	Identify tire-related monitoring (and any modeling support) necessary to improve understanding of load estimates for tire microplastics discharged to the Bay in stormwater.
2) Which are the “high-leverage” small tributaries that contribute or potentially	N/A	N/A

contribute most to Bay impairment by pollutants of concern		
3) How are loads or concentrations of pollutants of concern from small tributaries changing on a decadal scale?	N/A	N/A
4) Which sources or watershed source areas provide the greatest opportunities for reductions of pollutants of concern in urban stormwater runoff?	List of recommended RMP special studies related to tires to address scientific information gaps.	Identify tire-related monitoring (and any modeling support) necessary to improve understanding of source linkages (e.g., to VMT or land use) and pathways for tire microplastics discharged to the Bay in stormwater.
5) What are the measured and projected impacts of management action(s) on loads or concentrations of pollutants of concern from the small tributaries, and what management action(s) should be implemented in the region to have the greatest impact?	List of recommended RMP special studies related to tires to address scientific information gaps.	Identify studies to inform selection and design of tire-related management actions.

Approach

We propose to build a strategy for future RMP work around tire microplastics and tire-related water pollutants. This strategy will build upon the foundation created by the Tires Conceptual Model project that is currently underway. That project is identifying key information gaps around the connections between tires and aquatic habitats. The next step is to establish priorities, based on stakeholder needs and the special capabilities of the RMP. The project will not create new management questions; it will rely on the existing management questions for the RMP's MPWG, ECWG, and SPLWG.

We propose to use a four-step process to develop the RMP Tires Strategy:

- (1) Engage with relevant management agencies and stakeholders to clarify their tire-related science information needs related to the RMP's function and purpose,
- (2) Engage with the scientific community to evaluate the extent to which the identified science information needs will be addressed independent of the RMP,
- (3) Develop a five-year plan outlining the recommended RMP projects related to tires (e.g., monitoring and potentially one or more special studies), and
- (4) Vet and refine the five-year plan with RMP science advisors and stakeholders through the RMP workgroup process and SC.

The primary effort on the project will be to engage the relevant agencies and stakeholders. From agencies, we will seek to identify a list of specific management policies or decisions that are anticipated to occur in the next few years and if and whether RMP science would

have significant value for their decision-making process. In addition to the Water Boards and urban runoff management agencies (municipalities and Caltrans), agencies that may have an interest in water pollution from vehicle tires include California Department of Toxic Substances Control, California Ocean Protection Council, California Office of Environmental Health Hazard Assessment, US EPA, California Department of Fish & Wildlife, and NOAA Fisheries.

We also intend to engage with others in the scientific community to identify the relevant work they have underway so as to avoid duplication and seek opportunities to leverage RMP resources for any projects recommended to fill key information gaps.

The Tires Strategy will include proposed projects and tasks and projected annual budgets for up to a five-year period starting in 2023. The format will be consistent with other RMP multi-year plans. It will include:

- A list of specific management policies or decisions that are anticipated to occur in the next few years.
- A very brief summary of the latest advances in understanding achieved through the RMP and other programs. This summary will largely be based on the Tires Conceptual Model project, but will add two topics that are beyond the scope of that project: (1) surface water monitoring and (2) aquatic toxicity.
- A list of relevant RMP studies performed within the last five years and studies that are currently underway.
- Brief descriptions of recommended RMP projects.
- Explanation of the rationale for selection of the recommended projects.
- A table summarizing the recommended RMP projects, their timing, and estimated budgets.

The final deliverable will be a brief strategy document accompanying the 5-year budget plan. This inter-workgroup strategy will be designed as a short-term companion to the MPWG, ECWG, and SPLWG multi-year plans. Any tire-related work that is needed after the 5-year horizon of this strategy would be integrated into future workgroup-specific strategies and multi-year plans. A draft of the strategy will be provided for Microplastics, Emerging Contaminants, and Sources Pathways and Loading workgroups, TRC, and SC review. The Small Tributaries Loading Strategy (STLS) Team will be updated on the project twice during the one-year project period.

Budget

The following budget represents estimated costs for this proposed special study (Table 4).

Table 4. Estimated costs.

Expense	Estimated Hours	Estimated Cost
<i>Labor</i>		
Additional Literature Review (Toxicity and monitoring data from elsewhere; topics not included in Tires Conceptual Model project)	18	\$3,000
Strategy Development: Stakeholder and Scientist Engagement; Prepare Draft and Final Strategy	63	\$13,000
Workgroup meetings (MPWG, ECWG, SPLWG) and STLS updates	40	\$8,000
Senior Management Review	6	\$1,500
<i>Grand Total</i>		\$25,500

Budget Justification

Labor Costs

Labor will primarily be spent on consulting with management agencies, relevant experts currently working in the field, and RMP stakeholders. While most of the background scientific information will be developed by the RMP's tires conceptual model project, additional effort will be necessary to identify major findings and gaps in California monitoring data and aquatic toxicity data. Senior managers will help guide the process and review interim products.

Project staff hours reflect the need for teamwork among RMP scientists with expertise in microplastics, CECs and stormwater. As we develop this strategy, we anticipate considerable engagement with regional and state agencies as well as other RMP stormwater, microplastics, and emerging contaminants stakeholders. The budget reflects the need to engage with three RMP workgroups (Microplastics; Emerging Contaminants; and Sources, Pathways, and Loadings) as well as the Small Tributaries Loading Strategy team and the Steering Committee. We also anticipate the need to consult with the RMP's external experts that support the three workgroups.

Early Funds Release Request

If this project is approved, we request early release of funds (by September 2021). This will allow the strategy to inform RMP funding decisions starting in 2022.

Reporting

Deliverables will include a) a draft strategy (a brief document), to be presented to the MPWG, SPLWG, and ECWG and SC in spring 2022; b) two verbal updates to STLS (fall 2021; spring 2022); and c) a final strategy document, to be completed by October 31, 2022.

References

- Baensch-Baltruschat, Beate, Birgit Kocher, Friederike Stock, and Georg Reifferscheid. 2020. “Tyre and Road Wear Particles (TRWP) - A Review of Generation, Properties, Emissions, Human Health Risk, Ecotoxicity, and Fate in the Environment.” *Science of The Total Environment* 733 (September): 137823.
<https://doi.org/10.1016/j.scitotenv.2020.137823>.
- Boucher, Julien, and Damien Friot. 2017. “Primary Microplastics in the Oceans: A Global Evaluation of Sources.” Gland, Switzerland: IUCN.
- California Department of Toxic Substances Control. 2021a. “Three Year Priority Product Work Plan (2021-2023) (Stakeholder Discussion Draft).” Sacramento CA: CalEPA.
- California Department of Toxic Substances Control. 2021b. “Rationale Document for Motor Vehicle Tires Containing Zinc: Discussion Draft.” Sacramento CA: CalEPA.
- Capolupo, Marco, Lisbet Sørensen, Kongalage Don Ranil Jayasena, Andy M. Booth, and Elena Fabbri. 2020. “Chemical Composition and Ecotoxicity of Plastic and Car Tire Rubber Leachates to Aquatic Organisms.” *Water Research* 169 (February): 115270.
<https://doi.org/10.1016/j.watres.2019.115270>.
- Gualtieri, M, M Andrioletti, C Vismara, M Milani, and M Camatini. 2005. “Toxicity of Tire Debris Leachates.” *Environment International* 31 (5): 723–30.
<https://doi.org/10.1016/j.envint.2005.02.001>.
- Halle, Louise L., Annemette Palmqvist, Kristoffer Kampmann, and Farhan R. Khan. 2020. “Ecotoxicology of Micronized Tire Rubber: Past, Present and Future Considerations.” *Science of The Total Environment* 706 (March): 135694.
<https://doi.org/10.1016/j.scitotenv.2019.135694>.
- Kole, Pieter Jan, Ansje J. Löhr, Frank Van Belleghem, and Ad Ragas. 2017. “Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment.” *International Journal of Environmental Research and Public Health* 14 (10): 1265.
<https://doi.org/10.3390/ijerph14101265>.
- Kolomijeca, Anna, Joanne Parrott, Hufsa Khan, Kallie Shires, Stacey Clarence, Cheryl Sullivan, Leah Chibwe, David Sinton, and Chelsea M. Rochman. 2020. “Increased Temperature and Turbulence Alter the Effects of Leachates from Tire Particles on Fathead Minnow (*Pimephales Promelas*).” *Environmental Science & Technology* 54 (3): 1750–59. <https://doi.org/10.1021/acs.est.9b05994>.
- Leads, Rachel R., and John E. Weinstein. 2019. “Occurrence of Tire Wear Particles and Other Microplastics within the Tributaries of the Charleston Harbor Estuary, South Carolina, USA.” *Marine Pollution Bulletin* 145 (August): 569–82.
<https://doi.org/10.1016/j.marpolbul.2019.06.061>.

- McIntyre, J. K., J. W. Davis, C. Hinman, K. H. Macneale, B. F. Anulacion, N. L. Scholz, and J. D. Stark. 2015. “Soil Bioretention Protects Juvenile Salmon and Their Prey from the Toxic Impacts of Urban Stormwater Runoff.” *Chemosphere* 132 (August): 213–19. <https://doi.org/10.1016/j.chemosphere.2014.12.052>.
- Overdahl, Kirsten E., Rebecca Sutton, Jennifer Sun, Noelle J. DeStefano, Gordon J. Getzinger, and P. Lee Ferguson. 2021. “Assessment of Emerging Polar Organic Pollutants Linked to Contaminant Pathways within an Urban Estuary Using Non-Targeted Analysis.” *Environmental Science: Processes & Impacts*, 10.1039.D0EM00463D. <https://doi.org/10.1039/D0EM00463D>.
- Peter, Katherine T., Fan Hou, Zhenyu Tian, Christopher Wu, Matt Goehring, Fengmao Liu, and Edward P. Kolodziej. 2020. “More Than a First Flush: Urban Creek Storm Hydrographs Demonstrate Broad Contaminant Pollutographs.” *Environmental Science & Technology* 54 (10): 6152–65. <https://doi.org/10.1021/acs.est.0c00872>.
- Peter, Katherine T., Zhenyu Tian, Christopher Wu, Peter Lin, Sarah White, Bowen Du, Jennifer K. McIntyre, Nathaniel L. Scholz, and Edward P. Kolodziej. 2018. “Using High-Resolution Mass Spectrometry to Identify Organic Contaminants Linked to Urban Stormwater Mortality Syndrome in Coho Salmon.” *Environmental Science & Technology* 52 (18): 10317–27. <https://doi.org/10.1021/acs.est.8b03287>.
- Seiwert, Bettina, Philipp Klöckner, Stephan Wagner, and Thorsten Reemtsma. 2020. “Source-Related Smart Suspect Screening in the Aqueous Environment: Search for Tire-Derived Persistent and Mobile Trace Organic Contaminants in Surface Waters.” *Analytical and Bioanalytical Chemistry*, May. <https://doi.org/10.1007/s00216-020-02653-1>.
- Sieber, Ramona, Delphine Kaweck, and Bernd Nowack. 2020. “Dynamic Probabilistic Material Flow Analysis of Rubber Release from Tires into the Environment.” *Environmental Pollution* 258 (March): 113573. <https://doi.org/10.1016/j.envpol.2019.113573>.
- Sutton, Rebecca, Diana Lin, Meg Sedlak, Carolyn Box, Alicia Gilbreath, Rusty Holleman, Liz Miller, et al. 2019. “Understanding Microplastic Levels, Pathways, and Transport in the San Francisco Bay Region.” SFEI Contribution No. 950. Richmond, CA: San Francisco Estuary Institute. https://www.sfei.org/sites/default/files/biblio_files/Microplastic%20Levels%20in%20SF%20Bay%20-%20Final%20Report.pdf.
- Tian, Zhaoxue, Uwe Kaminski, Jan Sauer, Christoph Maschowski, Peter Stille, Kuang Cen, Reto Gieré, Frank Sommer, Volker Dietze, and Anja Baum. 2017. “Coarse-Particle Passive-Sampler Measurements and Single-Particle Analysis by Transmitted Light Microscopy at Highly Frequented Motorways.” *Aerosol and Air Quality Research* 17 (8): 1939–53. <https://doi.org/10.4209/aaqr.2017.02.0064>.
- Tian, Zhenyu, Haoqi Zhao, Katherine T. Peter, Melissa Gonzalez, Jill Wetzel, Christopher Wu, Ximin Hu, et al. 2021. “A Ubiquitous Tire Rubber-Derived Chemical Induces Acute Mortality in Coho Salmon.” *Science* 371 (6525): 185–89. <https://doi.org/10.1126/science.abd6951>.
- Wagner, Stephan, Thorsten Hüffer, Philipp Klöckner, Maren Wehrhahn, Thilo Hofmann, and Thorsten Reemtsma. 2018. “Tire Wear Particles in the Aquatic Environment - A Review on Generation, Analysis, Occurrence, Fate and Effects.” *Water Research* 139 (August): 83–100. <https://doi.org/10.1016/j.watres.2018.03.051>.