REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN SAN FRANCISCO BAY

sfei.org/rmp

RMP Emerging Contaminants Workgroup Meeting

April 12-13, 2018
10:00 AM – 4:00 PM

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

DAY 1 AGENDA - April 12th

1.	**Introductions and Goals for This Meeting** (Attachment) The goals for this meeting: • Provide updates on recent and ongoing ECWG activities (today) • Feedback on Draft CEC Strategy 2018 Update, including discussion of modeling efforts and pathways strategy (today & tomorrow) • Discuss the moderate concern chemical class of nonylphenols and nonylphenol ethoxylates (NP/NPEs), and develop a consensus for next steps (today) • Recommend which special study proposals should be funded in 2019 and provide advice to enhance those proposals (tomorrow) Meeting materials: 2017 ECWG minutes (See pages 6-18)	10:00 Phil Trowbridge
2.	**Discussion: CEC Strategy Update** (Attachment) Review of recent RMP activities and overview of Draft CEC Strategy 2018 Update. Strategy discussion will focus on the new CECs added to the tiered risk framework; discussion of modeling will occur in the afternoon, and discussion of the pathways strategy will occur tomorrow. Review potential priorities for tasks to be completed during 2018 using CEC Strategy funds already allocated by the RMP. Desired Outcome: Initial Feedback on the Draft CEC Strategy 2018 Update Deadline: April 30, 2018 Meeting materials: CEC Strategy 2018 Update - Draft (attached separately)	10:10 Rebecca Sutton
3.	**Information: Summary of Exposure and Effects Workgroup Meeting** Review major findings and recommended next steps from the April 11th EEWG meeting concerning bioanalytical tools. Desired outcome: Informed workgroup	10:40 Phil Trowbridge with contributing EEWG members

4.	**Information: Interaction of Alkylphenols and Alkylphenol Ethoxylates on Endocrine Responses to Pesticides in Fish** Nonylphenols and nonylphenol ethoxylates are classified as moderate concern contaminants for the Bay, in large part due to their potential to contribute to hormone disruption. The RMP has not monitored these compounds in Bay matrices in recent years. Dr. Schlenk, an expert advisor to the RMP's EEWG, will review relevant science regarding the occurrence and ecotoxicological risks of the broader contaminant class, alkylphenols and alkylphenol ethoxylates, to inform a strategy for future monitoring of these chemicals. Desired Outcome: Informed workgroup	11:00 Dan Schlenk
5.	**Discussion & Decision: Potential Monitoring Strategy for Nonylphenols and Nonylphenol Ethoxylates** The workgroup will discuss data needs and review and refine a proposed monitoring strategy to fill those needs in the coming years. Desired Outcome: Consensus strategy for monitoring of nonylphenols and nonylphenol ethoxylates	11:30 Rebecca Sutton
	Lunch (provided)	12:00
6.	**Information & Discussion: CECs Model Development** Brief description of two models that are available to support the RMP's CEC strategy: 1) a watershed model that can be used to estimate pollutant loads into the Bay from stormwater; and 2) a hydrodynamic model that simulates ambient concentrations in Bay subembayments based on pollutant loads from wastewater and stormwater pathways and assuming conservative behavior. The workgroup can then discuss general CECs modeling needs, and possible approaches for future modeling efforts. Desired outcome: Workgroup priorities for development and use of models. Meeting materials: CEC Strategy 2018 Update - Draft (attached separately)	12:40 Rebecca Sutton, Jing Wu
7.	**Information: Identification, Sources, and Risks of Novel and Emerging Contaminants in Urban Stormwater** (Attachment) This presentation will focus upon understanding the chemical composition of urban stormwater using mass spectrometry, with a particular focus on organic contaminants and their impacts on health of aquatic organisms, especially salmonids. Discussion will include stormwater screening and the details of a standardized list of CECs specific to urban stormwater and related receiving waters that has been developed by Dr. Kolodziej. A 2019 RMP special study proposal to implement an initial screening for these targeted analytes in Bay Area stormwater will be discussed tomorrow, part of a larger effort to screen stormwater from major urban areas along the West Coast using this new list of analytes. Desired Outcome: Workgroup feedback on selection of an initial, standardized set of CECs for stormwater monitoring	1:20 Ed Kolodziej, University of Washington

	Meeting materials: Target Analytes for Urban Stormwater (attached separately)	
7.	**Information: Pharmaceuticals in Bay Area Wastewater** Review preliminary findings from pharmaceuticals monitoring data for wastewater collected at seven local facilities. Desired outcome: Workgroup insights to refine analysis of data	2:00 Diana Lin, Jennifer Sun
	Short Break	2:30
8.	**Information: Preliminary Data on CECs in San Francisco Bay** Review preliminary findings from CECs monitoring in ambient Bay water samples as well as South and Lower South Bay margins water and sediment samples. Desired outcome: Workgroup insights to refine analysis of data	2:45 Diana Lin, Jennifer Sun, Rebecca Sutton
9.	**Information: Partitioning and Persistence of Volatile Methylsiloxanes in Aquatic Environments: A Case Study for the Bay** Volatile methylsiloxanes (VMS) have caused some concern among environmental chemists and regulators because of their continuous presence in aquatic environments, high affinity for organic carbon, and potential for bioaccumulation. Differences in reported organic carbon/water partition ratios (K_{oc}) for VMS vary by an order of magnitude. These differences have important implications in modeling calculations of overall persistence, and the calculated overall residence times may differ by more than 200 days. Such differences are large enough to lead to misclassifications of VMS as non-persistent or persistent chemicals. In our study in the SF Bay, we aim to collect sediment samples across the Bay and create a mass-balance model, which will help us calculate the environmentally relevant K_{oc} and estimate the overall residence times of VMS in the Bay. The findings from this study will help us reduce some of the uncertainties associated with calculations of persistence for VMS. Desired outcome: Workgroup feedback on design of pro bono study to be conducted by Dr. Panagopoulos with funding from the Sweden-America Foundation; additional collaborators include Dr.s June-Soo Park and Juan Villa Romero (DTSC).	3:30 Dimitri Panagopoulos, USEPA & DTSC visiting researcher
	Adjourn	4:00

DAY 2 AGENDA - April 13th

1.	**Summary of Yesterday and Goals for Today** (Attachment) The goals for today's meeting: • Feedback on CEC Strategy 2018 Update, particularly the pathways strategy • Recommend which special study proposals should be funded in 2019 and provide advice to enhance those proposals	10:00 Phil Trowbridge

2.	**Discussion: CEC Pathways Monitoring Strategy** (Attachment) Discussion of draft RMP strategy for monitoring of pathways including wastewater and stormwater. In addition, potential priorities for tasks to be completed during 2018 using existing CEC Strategy funds will be discussed. Desired Outcome: Initial feedback on Draft CEC Strategy 2018 Update Deadline: April 30, 2018 Meeting materials: CEC Strategy 2018 Update - Draft (attached separately)	10:10 Rebecca Sutton
3.	**Summary of Proposed ECWG Studies for 2019** The Principal Investigators will present the proposed special studies. Clarifying questions may be posed, however, the workgroup is encouraged to hold substantive comments for the next agenda item. 2019 Special Study Proposals include: ● Emerging Contaminants Strategy ● Stormwater Loading Strategy for CECs ● Roadway Contaminants in Stormwater ● Alternative Organophosphate Flame Retardants Conceptual and Steady-State Model (technical report attached, pages 47-59) ● Fipronil and Fipronil Degradates in the Bay Food Web ● Sunscreens in Water and Fish ● Non-targeted Analysis of Sport Fish, Cormorant Eggs, Harbor Seals (matching funds for Cal Sea Grant proposal, pages 81-87) Meeting materials: ECWG 2019 Special Studies Proposals (See pages 19-87)	11:00 Phil Trowbridge
	Lunch (provided)	12:30
4.	**Discussion of Recommended Studies for 2019 - General Q&A** The workgroup will discuss and ask questions about the proposals presented. The goal is to gather feedback on the merits of each proposal and how they can be improved.	1:00 Phil Trowbridge
5.	**Discussion of Recommended Studies for 2019 - Prioritization** The workgroup will consider the studies as a group, ask questions of the Principal Investigators, and begin the process of prioritization.	2:00 Phil Trowbridge
6.	**Closed Session - Decision: Recommendations for 2019 Special Studies Funding** RMP Special Studies are identified and funded through a three-step process. Workgroups recommend studies for funding to the Technical Review Committee (TRC). The TRC weighs input from all the workgroups and then recommends a slate of studies to the Steering Committee. The Steering Committee makes the final funding decision. For this agenda item, the ECWG is expected to decide (by consensus) on a prioritized list of which studies to recommend to the TRC. To avoid an actual or perceived conflict	3:00 Karin North

	of interest, the Principal Investigators for proposed special studies are expected to leave the room during this agenda item. Desired Outcome: Recommendations from the ECWG to the TRC regarding which special studies should be funded in 2019 and their order of priority.	
7.	**Report out on Recommendations**	3:20 Karin North
	Adjourn	3:30

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RMP Emerging Contaminants Workgroup Meeting

March 30, 2017

San Francisco Estuary Institute
4911 Central Avenue, Richmond, CA

Meeting Summary

Attendees

Science Advisor	Affiliation	Present
Lee Ferguson	Duke University	Yes
Kelly Moran	TDC Environmental	Yes
Derek Muir	Environment Canada	Yes
Heather Stapleton	Duke University	Yes
Bill Arnold	University of Minnesota	Yes

Others Present

Luisa Valiela (USEPA, Region 9)
Tom Mumley (SFBRWQCB)
Dawit Tadesse (SWQCB)
Karin North (City of Palo Alto)
Mary Lou Esparza (Central San)
Jim Ervin (City of San Jose)
Arleen Feng (BASMAA)
Jennifer Teerlink (DPR)
June-Soo Park (DTSC)
Anne Cooper Doherty (DTSC)
Daphne Molin (DTSC)
Shoba Iyer (OEHHA)
Keith Maruya (SCCWRP)
Jiawen She (CDPH)
Yu-Chen Chang (CDPH)
Tom Bruton (Green Science Policy Institute)
Eunha Hoh (San Diego State University)
Miriam Diamond (University of Toronto)
Rebecca Sutton
Meg Sedlak
Diana Lin
Jennifer Sun
Philip Trowbridge
Jay Davis
Don Yee
Lester McKee
Terry Grimm (Cambridge Analytical)
Michael Lyon (LARWQCB)
Denise Greig (Cal Academy)
Mike Elliott (SGS)

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

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1. Introductions and Review of the Agenda

No changes were made to the agenda.

2. Discussion: Revised CEC Strategy

Management Questions
Key discussion points are summarized below:

- **Framing:** The group discussed further expanding the CEC management questions. It should be made clear that the questions will apply separately for each CEC compound class. Tom requested additional description and contextualization of the questions in the strategy, including descriptions of how these questions will be applied and/or addressed using differents study types, how they relate to different types of management activities, and how they will be used to identify potential feasible management actions.
- **Sources, Pathways, and Loadings:** Tom suggested separating the second management question into separate questions about (1) sources, pathways, and loadings; and (2) contaminant fate and transport processes. The strategy should more explicitly emphasize the strategy for monitoring sources. Lee pointed out that process-specific studies are often extremely difficult to conduct. The group then began to discuss other types of studies that would provide the most useful information about sources and pathways to inform management.
- **Prediction/forecasting:** Kelly Moran and Miriam Diamond both described the need to be able to predict what compounds will be of concern, in order to both inform product design and enable more proactive management activities. Tom and Jay suggested adding a question related to forecasting (i.e. what concentrations do we expect to be increasing).
  Kelly Moran described the need to predict what compounds will be of concern and provide feedback for the design of products. Anne Cooper added a specific interest in predictive tools for classes of compounds, to inform assessments of alternative compounds. Kelly explained that DTSC's alternative assessment tools rely in part on predictive information about the environmental impact of alternative compounds; this information is being produced in part by DPR, which has developed some numeric predictive models, as well as EPA, and these models in turn can be informed by information produced by the RMP.
  Jennifer Teerlink indicated that it would be useful for the RMP to also work towards explicitly identifying contaminant pathways that can be most influenced through management actions, and suggested the fourth management question be revised to reflect this linkage.
- **Upstream activities:** Miriam Diamond emphasized the need to be able to predict trends from classes of chemicals based on land use changes, changes in socio-economics, and climate change. In a similar vein, Bill Arnold suggested spending more time on developing conceptual models to help narrow down where studies and management activities should be focused, given that detailed process-oriented studies to understand how compounds behave in the environment can be very complex, expensive, and compound-specific.

Tiered Risk Framework
Downgrading chemicals in the risk framework
The group agreed that any time a compound is downgraded within the tiered risk framework, the default action should be to continue monitoring for a while to confirm levels continue to decrease as expected. Tom Mumley also suggested creating sub-categories of low concern chemicals, for those that are (1) no longer of concern or (2) of low concern or priority for management, but should continue to be monitored. Miriam Diamond also highlighted the value of continuing to monitor compounds like PBDEs not only to

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support scientific conclusions about the effectiveness of management actions, but also to support ongoing public communications demonstrating the effectiveness of management actions.

There was general agreement that PBDEs should be downgraded from Tier 3 to Tier 2, but that monitoring should continue for a few more years to confirm the downward trend and also to demonstrate the effectiveness of regulatory action. The group agreed with the proposal to discontinue PBDE monitoring in bivalves, but to continue monitoring in sediment, bird eggs, and sport fish. Birds are particularly sensitive to PBDEs, which can cause reproductive effects, and Dr. Jianwen She (California DPH) emphasized the value of monitoring eggs of terns, which are top food chain predators.

Karin North agreed that bivalves should be removed from Status and Trends monitoring. Tom Mumley asked what is the most cost-effective strategy to sustain long-term trend monitoring. Keith Maruya said that NOAA's Mussel Watch program may revisit California in 2018, in which case bivalves may be monitored for PBDEs as part of the program..

Moderate concern chemicals
Tom Mumley agreed that any compounds that are in the Tier 3 category should have a full action strategy that is regularly reviewed. Nonylphenol ethoxylates are currently in Tier 3, but a strategy for monitoring and managing these chemicals needs to be developed.

Decisions:

- The group agreed to downgrade PBDE to a Tier 2 low risk compound group, but to recommend continued monitoring these compounds according to the suggested Status and Trends schedule (monitor in sediment, bird eggs, and sport fish, but not bivalves).

<u>Status and Trends</u>
Archive Strategy
Tom Mumley suggested including an explicit archive sample management plan in the CEC strategy, in order to highlight the possibility of using archives to look retrospectively at historical contaminant levels, and to prioritize the level of effort for archiving. Terry Grimm suggested archiving leftover chemical extracts, and Derek Muir indicated that his program archives raw sample extract (i.e., after lipid removal and other cleanup steps, but before standards are added).

Status and Trends Analyte Lists

- Kelly Moran suggested adding neonicotinoids to Status and Trends water sampling if the 2017 special study shows substantial levels of these compounds in ambient Bay water.
- Jennifer Teerlink strongly supported sampling of fipronil in sediment, at least through 2023, which will provide valuable data to DPR to evaluate the effectiveness of management actions.
- Tom Mumley supported conducting periodic non-targeted analysis, but indicated that the RMP (particularly the Steering Committee) would need to discuss how to fund these analyses (i.e., through Status and Trends or special studies, for example).

<u>General Strategy Comments</u>

- **Compound categorization:** Lee Ferguson and Tom Mumley supported separating pharmaceuticals and personal care products into separate categories, and including plastic additives (which also include some organophosphate flame retardants) as a separate category as well. This may require recategorization of alternative flame retardants into multiple groups as well.

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Anne Cooper Doherty requested further discussion in the strategy about chemical class categorization, to help inform DTSC guidance on the use of chemical alternatives.

- **Communication:** Kelly Moran and Jennifer Teerlink suggested that the strategy include an explicit step for coordination, communication and collaboration with partner agencies, such as DTSC and DPR.
- **Compound identification:** Derek Muir suggested using CAS numbers to allow searches of individual compounds of interest within the RMP's previous CEC work. The Multi-Year Plan currently describes previous work only in lumped categories. Derek suggested Rebecca contact Tony Williams, who works on the EPA Chemistry Dashboard that links from CAS numbers of data sources. The RMP could potentially be added as an additional data source.
- **Risk framework categorization:**
    - Tom Mumley suggested indicating which Tier 2 low concern chemicals are (1) no longer of concern or (2) of low concern or priority for management, but should continue to be monitored.
    - Anne Cooper Doherty also suggested differentiating compounds are classified as Tier 2 low concern compounds because (1) they have been monitored and determined to be of low concern, or (2) not enough data is available to make a different classification.
    - The group agreed that the current Tier 1 class of compounds should not be displayed or "ranked" as being below the Tier 2 low risk class. Instead, the current Tier 1 should be a separate category of compounds that require additional study.
- **Risk framework notations:**
    - Jennifer Teerlink suggested using different symbology to indicate whether compound use or monitoring data suggest levels are thought to be increasing or decreasing. Arrows suggest the presence of increasing or decreasing trends in the real world, which is not always what is meant to be implied.
    - Kelly Moran suggested noting which compound classes have related management actions already in place.
    - Tom Mumley suggested creating a separate matrix to include information on use trends, regulatory activities, available monitoring data, and other relevant metadata-type information on all compounds classes.

<u>Alternative Flame Retardants Conceptual Model Needs</u>
Arleen Feng presented a proposal to begin planning to develop larger 2019 Special Study proposal for a conceptual model for alternative flame retardants (AFRs) in stormwater, and requested feedback from the group.

The science advisors emphasized that an AFR conceptual model should take into consideration that AFRs are a broad class of compounds with a wide range of environmental behaviors. PBDEs may not be the appropriate group of compounds to use as a starting point to assess AFRs, particularly if there is a focus on understanding more than sediment-bound contaminants. However, modeling tools can be used to predict AFR behavior and identify optimal sampling locations for the AFRs of interest. A sampling strategy should include partnering with DPR, which may be sampling some of the same locations for their own studies.

Many compounds that are categorized as AFRs, especially organophosphate flame retardants, have other sources; this class in particular has been used as plasticizers for a long time. Other sources should

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be considered in any conceptual model. Miriam Diamond also advocated for using multi-media models, including combining suspended sediment and hydrologic models, at minimum.

3. Information: Non-Targeted Analysis of Polar Compounds in San Francisco Bay Water and Effluent

Lee Ferguson presented preliminary results from the 2016 non-targeted analysis study of polar organic contaminants in ambient Bay water. This study included analysis of grab samples and passive (POCIS) samplers deployed in San Leandro Bay (i.e., stormwater influenced), Napa River (i.e., agricultural runoff influenced), and Coyote Creek (i.e., wastewater influenced).

The analytical screen included about 150 targeted analytes with standards, as well as non-targeted analytical methods that identified on the order of 3,000-5,000 compounds per analysis. Of these compounds, about 1/3 of samples had no MS/MS spectra, due to the complexity of the sample (i.e., the instrument is unable to measure spectra as quickly as compounds are eluted). These compounds were only able to be characterized to a molecular formula level. Detections are generally biased towards compounds present at higher abundances, while lower abundance compounds are more commonly skipped. Of the compounds with spectra, only 6.5% had library spectra matches (m/z cloud, ChemSpider). Those without library spectra matches were tentatively identified where possible using in-silico fragmentation predictions. Results were normalized to internal standards to account for matrix effects, and were also blank subtracted.

Comparisons between grab samples and POCIS samples showed a relatively good correlation between the sampling types, with better agreement for high abundance compounds. However, in San Leandro Bay, grab samples generally showed greater peak intensities than the POCIS samples, suggesting that the passive samplers can become saturated and in some cases may not reflect true contaminant abundances. Grab samples collected during high and low tide on the Napa River also showed substantial differences, with greater intensities found during low tide, with greater influence from runoff vs. Bay water.

Another key result of this study was that the stormwater-influenced site appeared to be more contaminated than the wastewater-influenced site, with higher peak intensities. Lee then presented a series of volcano plots highlighting contaminants identified at each site that were not observed in wastewater. Over 50 compounds not identified in wastewater were identified with high confidence MS/MS library hits in the San Leandro Bay samples, many of which were polyethoxylated compounds. Other highly detected and highly abundant compounds included the fungicide myclobutanil, and vulcanization products (from tires, indicating an urban source), as well as other polymer additives.

In the Napa River, 44 compounds not found in wastewater were identified, with only a single library match for a simazine pesticide breakdown product. Tentative identifications in the Napa River suggested presence of natural products from non-urban runoff. The contaminant profile in Coyote Creek suggested that this area is essentially diluted wastewater, as expected.

Bill Arnold noted that in his passive sampling studies, he has found that comparing both grab and passive samples has been useful, with slightly different contaminant profiles identified in each type of sample. Keith Maruya indicated that many similar compounds have been identified in Southern California as well, using GC analysis methods.

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The group then began to brainstorm potential sources further upstream that could be causing the detections seen in San Leandro Bay. Arleen Feng explained that although San Leandro Bay occasionally receives combined sewer overflow from EBMUD, it was unlikely that overflow occurred during the relatively small or moderate storms that occurred in the spring of 2016 when sampling occurred in that region. Kelly Moran indicated that myclobutanil, the fungicide detected at a particularly high intensity in San Leandro Bay, has been registered for many urban uses, including applications on trees, grasses, ornamental plants, and over-the-counter uses. The lowest toxicity threshold for myclobutanil is 100 ug/L, which Kelly speculated is likely greater than even the high levels that were observed in San Leandro Bay. Carbendazim, another high intensity compound, is a breakdown product of benomyl, a fungicide registered for many urban uses as well.

Derek Muir suggested using the TSCA high production volume compounds to identify compounds and identify any correlations between detections/intensities and production volume. Lee indicated that he typically does not use production volume in his prioritization, to avoid biasing his analyses towards industrial chemicals and away from natural products.

4. Summary of Special Study 2018 Proposals

SFEI staff presented proposals for special studies in 2018, followed by brief clarifying questions. Comments and questions regarding each study are summarized below.

In introducing the proposed 2018 studies, Rebecca highlighted the theme of margins sediment sampling; many studies were designed to leverage the 2017 margins sediment sampling occurring in South Bay and Lower South Bay. It was noted that Dave Schoellhamer's previous work showed that Lower South Bay was a depositional region in general, and Don explained that any scouring that may have occurred during the past wet year was unlikely to completely remove all or most of the top 5 cm of sediment that is collected for this type of sampling. Therefore, margins sampling in the summer of 2017 would be likely to capture relatively recent deposits of sediment and associated contaminants.

<u>CEC Strategy</u>
Miriam Diamond suggested that the strategy include an integration task, to support synthesis of recent work and policy updates for key chemical groups. The group agreed that the CEC strategy can be presented as a mandatory funding line rather than a proposal.

<u>Characterizing Unknown PFAS in Seals and Margin Sediment</u>
Kelly Moran suggested adding a budget line for communications with press and policymakers, given that this class of chemicals is of growing policy interest and this study has the potential to influence policy.

<u>Non-Targeted Analysis of Margin Sediment and Related Studies</u>
The group was supportive of this study, but given the high cost of the overall study, wanted to explore the opportunity to reduce the scale of the study. Lee Ferguson indicated that funding below $20,000 would make it difficult to participate in the study at all.

<u>Nonylphenol Ethoxylates in Margin Sediment</u>
Heather Stapleton suggested that this study may be redundant with the non-targeted analysis work, which was shown in Lee's earlier presentation to detect nonylphenol ethoxylates. However, this targeted study would be able to better quantify the levels of these compounds, and would not cover the shorter chained NP/NPEs that have been previously detected by RMP Status and Trends, but are not detected in Lee's

non-targeted analysis. Miriam Diamond also suggested that there could be a benefit in having the same laboratory (AXYS) measure NP/NPEs again with a new method.

Multiple group members suggested scaling back the study, or conducting monitoring at shallow sites during water or ambient sediment monitoring efforts. Rebecca indicated that scaling back could be possible, given that the purpose of the study is to conduct a screening exercise rather than conduct rigorous statistical analysis to evaluate source types. Lee Ferguson suggested that future studies could focus on a broader range of polyethoxylated surfactants, including alcohol polyethoxylates, which are typically removed in wastewater. However, they may also be present in stormwater, potentially causing endocrine disruption in streams and/ or receiving waters.

Pesticides and Wastewater Contaminants in Margin Sediment and Water

Stakeholders interested in pesticide work were strongly supportive of this study. Jennifer Teerlink and Kelly Moran explained that this study would fill an important gap in DPR's priority sampling, which typically does not look at ambient locations that integrate stormwater and wastewater effluent. DPR does not monitor pesticides in the Bay, despite an expectation that the Bay margins may be some of the most contaminated regions.This study would complement the non-targeted analysis by quantifying pesticide levels, including pyrethroids, with low detection limits. The methods include pesticides that are not professionally applied, as well as strobin fungicides, which are of interest to DPR and other pesticide stakeholders and experts.

Non-Targeted Analysis of RO Concentrate

The group expressed general support for the study idea, but felt that it fell outside the scope of the RMP to fund. Lee Ferguson indicated that samples could potentially be archived after extraction.

Pharmaceuticals in Effluent Report

The group expressed support for this study. Anne Cooper Doherty expressed support from DTSC, which is interested in some of the non-pharmaceutical compounds, such as triclosan. Karin North reiterated that many of the participating wastewater treatment plants would need to rely on the RMP to assist with data QA/QC review. Rebecca explained that the study focused on a subset of the available pharmaceutical analyte lists available through AXYS primarily due to budget constraints - specifically, the study focused on AXYS lists 1,3, 4 and 5.

5. Discussion of Recommended Studies for 2018

The planned budget, if all the proposals were funded, is $550k. The target planning budget is $505k. The workgroups are directed to prioritize studies to different levels, assuming the Steering Committee allocates between 50% and 100% of the target budget. Phil later clarified that about $250k of alternative monitoring requirement funds from wastewater agencies has been specifically earmarked for CEC studies. Karin North also highlighted that Supplemental Environmental Project funds could potentially become available outside of the standard RMP funding process, so projects that are not prioritized for funding today should still be prioritized for potential future funding.

Nonylphenol/Nonylphenol Ethoxylates

Lee Ferguson was asked whether the nonylphenol/nonylphenol ethoxylates had different toxicity levels or mechanisms than the other polyethoxylates that would be covered by the non-targeted analysis, to help determine whether including those compounds in a targeted analysis was important. Lee indicated that the current thinking is that the nonylphenol and the short-chained nonylphenol ethoxylates are not

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necessarily the dominant source of toxicity in this class, and that other polyethoxylates have other mechanisms for toxicity besides degrading to nonylphenol. Lee emphasized the need to look at a broader class of compounds beyond nonylphenol/ethoxylates and their precursors. In particular, toxicity of polyethoxylated alcohols has been poorly studied, in part because they are efficiently removed during wastewater treatment; however, these compounds have been detected in stormwater (i.e., very abundant in stormwater-influenced ambient Bay water) and may be cytotoxic and estrogenic. It was noted that EPA has a framework for estimating toxic equivalency factors for polyethoxylates, but only based on estrogenicity.

<u>Perfluorinated Compounds</u>

Meg explained that the TOP assay and QTOF analyses would provide complementary information about previously unidentified perfluorinated compounds in sediment. In addition, the researchers at Colorado School of Mines will specifically quantify a short list of PFAS compounds such as PFOS, PFOA, etc. The TOP assay degrades precursor compounds to carboxylic acids analogs; the LC-Q-ToF-MS method identifies a broader list of compounds, some of which would not be oxidized and identified using the TOPassay. These methods would be able to provide information about relative abundances of individual compounds.

It was asked whether sediment and water samples should be analyzed concurrently, given that some of these perfluorinated compounds do not sorb to sediments particularly well. Meg explained that previous water sampling has shown largely carboxylic acids that are at levels similar to what is observed elsewhere, but this study focuses on PFOS, which has been found at particularly high levels in South Bay biota and sediments. Previous Bay sediment studies have also found a variety of PFOS and PFOA precursors includingpolyfluoroalkyl phosphoric acid diesters (diPAPs). Derek Muir also noted other studies of river sediments that showed that essentially all the perfluoro compounds of interest, including variants with various additional alkyl groups, are found in sediments, which appears to serve as the primary reservoir for these contaminants, not the water column.

Heather Stapleton asked whether gender, age, and/or size, would be taken into account when measuring PFAS levels in seal serum samples. Literature on human serum samples suggests different body burdens by sex. Meg acknowledged that this is true for humans but that not all species exhibit a difference. To date, RMP data have not identified a significant difference in PFOS in males vs females. Meg also mentioned that PFAS body burdens can be transferred from mother to offspring. The purpose of this study is to identify other PFAS compounds that may be in use beyond the 12 or so that the RMP routinely monitors. Concentrations of PFOS in biota are decreasing and it is not clear what alternatives the market is moving to. In addition, the seal study would also assess trends (since 2012). This study is a smaller screening study to identify novel compounds rather than a robust statistical analysis of levels of specific compounds and potential causes.

<u>Non-Targeted Analysis of RO Concentrate</u>

Miriam Diamond asked whether the RO concentrate non-targeted analysis would miss contaminants that coagulate or settle out in the wetland. Rebecca noted that the water is filtered through a 10 micron filter prior to entering the treatment wetland, which should reduce the level of particulate contaminants. Phil also explained that ultimately the biomat and any particles that settle out are planned to be regularly removed, replaced, and disposed of, so this kind of material may not need to be considered in evaluating compounds that may reach the Bay in discharged effluent.

Kelly asked whether other types of studies might be able to provide similar information to this proposed study. Lee explained that this study is meant to look specifically at the transformation processes occurring during this treatment process. One major objective is to assess whether new compounds of concern are being produced during treatment, and proactively identify potential new contaminants that would not be

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identified through other studies. Karin North and Tom Mumley clarified that the RMP would not fund this study as it does not directly address RMP management questions, although alternate funding sources might be available.

Derek Muir asked why additional targeted compounds (i.e. perfluorocompounds and nonylphenol ethoxylates) are not a larger part of this project. Phil and Rebecca explained that a short list of targeted analytes, including PFOS and PFOA (but not NPEs), have already been included in the Santa Clara Water District funded study. Lee also explained that another purpose of the non-targeted study would be to look at compounds impacted by the advanced oxidation treatment -- i.e. brominated and chlorinated compounds that might be created after oxidation in a high ionic strength solution.

Non-Targeted Analysis of Sediment

Heather Stapleton supported the idea of using two complementary non-targeted analysis methods at once, but asked how the results would be compared, given the complications of using very different workflows. Lee indicated that the labs would be primarily comparing lists of tentative identifications, rather than spectra. A scatterplot comparison between the two labs of the retention time for a compound with a tentative ID match could then serve as confirmation that they have correctly identified the same compound; similarly such a plot showing similar retention time for a compound with two different tentative identifications but the same molecular formula might suggest that additional analysis is needed to evaluate the true structure and identity of that compound.

Eunha also indicated that the two labs already use similar methods of prioritizing which compounds to work towards identifying, and can further work with each other and the RMP to sync this prioritization process to focus, for example, on compounds identified with high frequency or using other methods of interest to the RMP. This way, the two labs can also work in an even more complementary way, with one lab filling gaps that may exist in the others' identification workflow. Exploring methods for merging data between the two labs will be part of the purpose of this project; Lee also cautioned that because these are exploratory methods, the deliverable will not include a validated list of identified compounds. Jennifer Teerlink and Kelly Moran mentioned the importance of having the RMP review the tentative identification list to identify compounds of toxicity concern, or those that could serve as important indicator compounds for different sources.

Pharmaceuticals Data Reporting

Derek Muir asked whether enough data was available to look at trends in pharmaceuticals data. Rebecca clarified that the only previous RMP study of pharmaceuticals in wastewater took place in 2006 at two wastewater treatment plants in Lower South Bay, so comparisons of pharmaceutical levels would be relatively qualitative. The purpose of this study is to serve as a first step to identify whether there are compounds that should be monitored in ambient Bay water. The study will also include a simple conservative tracer model (i.e. no degradation, no transformation, etc.) to conservatively estimate ambient Bay rough concentrations based on wastewater effluent concentrations.

Jennifer Teerlink asked if good information is available about how much recycled water is used for irrigation, which could be used to estimate how much might runoff into the Bay. Karin North indicated that she can provide this information compiled by BACWA, but that likely very little of this irrigation water reaches the Bay, as recycled water is typically used for this purpose during the driest periods of summer and overspray is not permitted.

Pesticides

Kelly Moran asked how the pesticide study leverages the USGS NAWQA study, which will focus on upstream freshwater sites. Becky indicated that the studies would be easier to compare given that the samples would have been collected at the same time. The USGS data will likely not be published until a

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year or two after the RMP data, so efforts to compare across the data sets or conduct modeling would occur at a later time.

Other Studies and Priorities

Miriam Diamond commented that none of the proposed studies appeared to be focused on developing an inventory of contaminant levels, for which the study designs would need to be more representative of what is seen at different types of locations and times in the Bay. She also provided a broader suggestion to develop a criteria matrix to help guide prioritization for the group, including outlining different types of studies and identifying how the proposed studies fit into the universe of various possibilities and priorities. Rebecca, Jay and Karin indicated that no formal scoring system has been used or needed in the past, but it could be considered if stakeholders would like a more formal process.

Kelly Moran brought up two potential ideas for future study: (1) pesticides in wastewater, and (2) antimicrobial compounds in environmental matrices (stormwater, wastewater, and ambient Bay water). Kelly has been compiling a priority list of antimicrobial compounds of interest.

Agency Priorities

DPR strongly supported the pesticide study, which would provide very useful data to inform DPR's current planning process. DTSC indicated a high level of interest in triclosan and PFAS, but also indicated that data on nonylphenol ethoxylates, alcohol ethoxylates, and non-targeted analyses would be useful in informing the development of future plans. Daphne Molin explained that the DTSC's planning process will not prioritize any aquatic chemicals without monitoring data, so non-targeted analyses that will identify potential compounds of concern is extremely important. Data on high priority compounds like triclosan and PFAS may also be useful even if rules are already in motion, in order to help demonstrate the effectiveness of management actions in the future.

Becky explained that sediment archiving is possible if funding is not available in 2018, but a small amount of funds will still be needed to collect the samples and coordinate the archive activities.

6. Closed Session - Decision: Recommendations for 2018 Special Studies Funding

7. Report Out on Recommendations

Study Name	Proposed Budget	Modified Budget	Priority	Notes
EC Strategy	$65,000	$65,000	1	Deliverables should be more specific. Should be for RMP work/products.
PFASs in Seals and Sediment	$78,000	$50,000	5	Collect sediment now and postpone seal collection. Determine new cost. Second option is collect sediment and archive ($10,000).

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NTA in Margin Sediment	$118,000	$101,000	4	Remove dye analysis and DM. Add cost to archive raw extract for future analysis (dye, NPE, etc.).
NPEs in Margin Sediment	$54,000	$10,000	6	Collect now and archive samples. Investigate whether can use extract from NTA. Update cost estimate. NPEs are a State Board priority. Get a quote from Lee for running the NP/NPE at the same time as the NTA.
Pesticides and Wastewater Contaminants in Margin Sediment & Water	$126,000	$126,000	2	
Pharmaceuticals in Wastewater	$30,000	$30,000	3	
NTA of RO Concentrate	$59,000			End goal is evaluating a treatment technology. Should not be a RMP project.
Total Amount	$530,000	$382,000		

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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.

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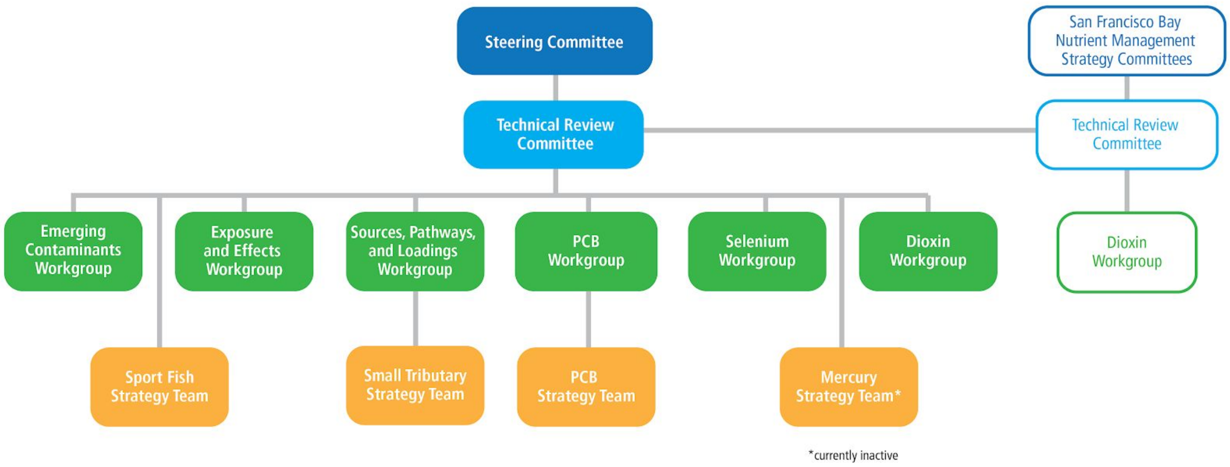
Governance Structure for the Regional Monitoring Program for Water Quality in San Francisco Bay



2019 Emerging Contaminants Special Studies Proposal Abstracts

Study Name	Budget	Summary	RMP Tier	Critical Drivers	Deliverables	Page #
Emerging Contaminants Strategy	$70,000	Annual update of CEC Strategy, including tracking new information, updating the Tiered Framework and Multi-Year Plan. Increasing needs for stakeholder support, coordination of pro bono studies, and development and use of CEC transport model.	All	Essential to coordinate studies relevant to management actions. Inform policy actions at local, state, federal levels. Additional $5k requested for honoraria to fund essential ecotoxicological review of Possible Concern contaminants. Funding request 20% of planning budget.	Technical assistance to stakeholders; Update and share CEC Strategy; Refine monitoring and science strategy related to Possible Concern contaminants, with particular attention to ecotoxicity data gaps.	21 - 26
Stormwater Loading Strategy for CECs	$60,000	Development of urban stormwater loading strategy for CECs, with model study designs including potential representative watersheds and frequency of sampling	All	**Scientific Driver**: There is a significant data gap in our understanding of CEC loads from stormwater; this information is important for monitoring and modeling. **Management Driver**: Better understanding of loads based on watershed types and CEC chemical properties will be important for implementing effective management actions. **Cost Savings**: This project will involve collaboration between SPLWG and ECWG. Developing multi-year storm water monitoring designs will leverage funding by conducting multi-contaminant investigations and possibly leveraging SPLWG activities. **Time Constraints**: Loading studies will likely be on hold until a strategy is agreed upon.	Summary memorandum of monitoring designs for representative watersheds. Presentations to SPLWG and ECWG (Spring 2019). Final Strategy September 2019.	27 - 31
Roadway Contaminants in Stormwater	$130,000	Non-targeted analysis of Bay water samples indicates that stormwater has the potential to contain significant levels of potentially harmful contaminants. An initial West Coast screening effort is being conducted using a new, targeted analyte list of stormwater-derived contaminants developed in response to stormwater-related Coho salmon aquatic toxicity. As part of this screening effort, we propose analyzing Bay stormwater samples, as well as samples from Lagunitas Creek, a less urban reference site that provides key habitat for the endangered Coho salmon.	Analytes include Moderate Concerns, Possible Concerns, Others Not Previously Monitored	**Scientific Driver**: Screen Bay stormwater for presence of stormwater-derived contaminants associated with ecotoxicity concerns. **Management Driver**: Initial data on CECs specifically related to stormwater is expected to inform the need for monitoring or management actions. Identified true sources, such as vehicle tires, could be the subject of green chemistry focus. **Cost Savings**: Study budget funds stormwater sample collection at five sites; samples from additional sites may be collected by leveraging other RMP sampling efforts as well as planned DPR activities. **Time Constraints**: Implementation in 2019 would allow RMP results to be part of West Coast-wide monitoring being coordinated for WY2019.	**Manuscript**: Draft spring 2020, Final summer 2020 **Management-oriented summary document**: Draft spring 2020, Final summer 2020 **Data Management**: Data uploaded to CEDEN	32 - 38
Alternative Organophosphate Flame Retardant Conceptual and Steady-State Model	$99,500	This study will develop a steady-state, multimedia model to better understand the pathways, loadings, and fate of organophosphates in the Bay. The findings from this modeling effort will provide direction for future monitoring and management actions. This study will also fulfill a stormwater permit requirement to conduct a study on alternative flame retardants. As part of this study, Bay Area ambient air samples for the wet and dry season will be collected and analyzed to fill a significant data gap.	Possible Concern	**Scientific Driver**: Develop conceptual understanding of sources, pathways, and fate of organophosphate flame retardants in the Bay **Management Driver**: Fulfills municipal stormwater permit requirement to study alternative flame retardants; quantify loads and uncertainties; prioritize monitoring data needs to reduce uncertainty **Cost Savings**: Reporting costs are signficantly reduced by having collaborators take primary responsibility for reporting through a draft manuscript that will serve as a technical report.	Regular check-ins with STLS team meetings throughout course of project **Technical report** (draft manuscript): Draft May 2020 **Management summary report**: Draft May 2020, Final August 2020	39 - 59

2019 Emerging Contaminants Special Studies Proposal Abstracts

Study Name	Budget	Summary	RMP Tier	Critical Drivers	Deliverables	Page #
Fipronil and Fipronil Degradates in the Bay Food Web	$78,500	Fipronil is a widely used insecticide that has been detected at levels of concern in Bay sediment and pathways; however, limited data are available on fipronil and fipronil degradates in the food web. This study will provide a screening of fipronil and three fipronil degradates in sediment, prey fish, sport fish and harbor seals. The results from this study will be used to evaluate the bioaccumulation and biomagnification potential of these compounds in the Bay food web, and subsequently assess potential human health and wildlife exposures.	Moderate Concern	**Scientific Driver:** Conduct screening to fill data gaps in our understanding of fipronil/degradates bioaccumulation and biomagnification in the food web, and assess human and wildlife exposures. **Management Driver:** Fipronil has been the focus of growing management interest following studies showing increasing use patterns and fipronil/degradates at levels of concern in Bay sediment and pathways. Results can inform DPR's human health risk assessment for fipronil and the statewide Sediment Quality Assessment Framework for human health effects. **Cost Savings:** Sediment and fish sampling will take advantage of concurrent sampling as part of the 2019 RMP Status and Trends sport fish sampling and a planned PCB monitoring study (will be reviewed by the PCB workgroup).	**Technical report**: Draft Fall 2020, Final Winter 2020 **Data Management**: Sediment data uploaded to CEDEN, tissue data maintained internally, available for distribution upon request	60 - 68
Sunscreens in Water and Fish	$127,400	UV sunscreen chemicals are widely used in personal care products (e.g., sunscreens and cosmetics) and commercial products (e.g., paints and plastics). They are discharged to the environment through the washing off of these chemicals during swimming or other outdoor activities, or discharged indirectly via wastewater treatment facilities from showering or bathing activities. These chemicals are also likely to leach from paints and plastics. Several sunscreen chemicals are known to be toxic and can cause endocrine disruption. This project will evaluate sunscreen chemicals in sport fish, prey fish, surface water and wastewater.	Not Previously Monitored	**Scientific Driver**: We do not have any studies of sunscreen chemicals in SF Bay **Management Driver**: City of San Francisco is bringing forward a resolution to request information on sunscreens in SF Bay **Cost Savings**: This project will leverage the 2019 RMP sport fish collection effort **Time Constraints**: This study assumes that we will be able to leverage 2019 sport fish event. If the decision to fund this study is postponed, we lose that opportunity	**Manuscript and management-oriented summary**: Draft Summer 2020, Final Fall 2020	69 - 75
Non-targeted Analysis of Fish and Wildlife	RMP $75,000; Sea Grant $250,000 (3-year study)	Non-targeted analysis (NTA) is part of the triad of methods the RMP is using to identify and track CECs. This study will leverage a proposal that has been submitted to Sea Grant to fund a three-year study evaluating Bay biota using novel non-targeted analyses. A variety of sport fish will be analyzed to assess the importance of feeding habitats (open water vs shallow margins), spatial location, and trophic status. In addition, apex predators such as cormorants (eggs) and harbor seals (blubber) will be used to assess the potential for biomagnification of these CECs in the food web.	Not Previously Monitored	**Scientific Driver**: This study will employ a novel NTA approach to examine Bay biota for persistent and bioaccumultive CECs. A review of the literature will be conducted to assess the possible impact of CECs identified. This study may identify previously unknown and important CECs. **Management Driver:** Results from this study may inform sport fish advisories and/or identify hotspots of new CECs. **Cost Savings**: This project will leverage the 2019 RMP sport fish collection effort as well as the 2018 margin sediment NTA study that is on-going. Information from the margins sediment study will be used to assess bioaccumulation. **Time Constraints:** This study assumes that we will be able to use 2019 sport fish event as a platform to collect samples. If the decision to fund this study is postponed, we lose that opportunity.	**Manuscript and factsheet**: Draft Spring 2021, Final Fall 2021	76 - 87

Special Study Proposal:
Emerging Contaminants Strategy

Summary: Increasing interest in emerging contaminants issues by the San Francisco Bay Regional Water Board, RMP stakeholders, and the general public is reflected in headline news as well as policy actions at local, state, and federal levels. The amount of effort needed to manage the RMP Emerging Contaminants Strategy has increased significantly in recent years. Core deliverables include tracking new information regarding contaminant occurrence and toxicity and updating the RMP's Tiered Risk and Management Action Framework; responding to requests for information and assisting the Water Board with emerging contaminants action plans; and coordination of *pro bono* analyses by partners. Additional funds of $5,000 are requested to provide honoraria to experts in ecotoxicology who will provide guidance concerning prioritization and further study of Possible Concern contaminants. A total of $70,000 is requested; this is the same level of funding as in 2018, and represents 20% of the overall RMP CECs planning budget ($350,000).

Estimated Cost: $70,000

Oversight Group: ECWG

Proposed by: Rebecca Sutton (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Information gathering from a variety of sources throughout the year, including presentations at scientific conferences, to inform Task 5	Year-round
Task 2. Assist Water Board and other RMP stakeholders with science summaries relating to policy including emerging contaminants action plans and comment letters regarding proposed actions of other agencies	Year-round
Task 3. Coordinate *pro bono* studies conducted in collaboration with RMP Status and Trends monitoring activities	Year-round
Task 4. Consult with ecotoxicologists on relative concern associated with Possible Concern contaminants and the potential for the RMP to contribute to studies that establish toxicological thresholds	12/31/2019
Task 5. Update the RMP CEC Strategy document with revised tiered framework tables (integrating new data and external infornation) and multi-year plan, discussion of new RMP data and information gathered (Task 1); present at spring ECWG meeting	Spring 2020
Task 6. Present an update of RMP CEC Strategy, ongoing or completed special and *pro bono* studies, and new studies to the Steering Committee	Spring 2020

Background

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

In 2017, the RMP completed the first major revision of its CEC Strategy document, which outlines a comprehensive, forward-looking approach to addressing CECs in San Francisco Bay (Sutton et al. 2017). The RMP's CECs Strategy consists of three major elements. First, for contaminants known to occur in the Bay, the RMP evaluates relative risk using a Tiered Risk and Management Action Framework. This risk-based framework guides future monitoring proposals for each of these contaminants. The second element of the strategy involves review of scientific literature and other aquatic monitoring programs to identify new contaminants for which no Bay data yet exist. Finally, the third element of the strategy consists of non-targeted monitoring, including broadscan analyses and development of bioanalytical tools.

For the RMP CEC Strategy to remain relevant and timely, it needs annual updates with new information on analytical methods and study findings from the RMP and others. Funds are needed to review new results, track research conducted elsewhere, and keep stakeholders apprised of findings. Coordination of *pro bono* analyses is another rapidly expanding component of the strategy fund. At the same time, it is important for the RMP to provide relevant, objective science to inform the growing number of policy actions concerning emerging contaminants, an increasing demand on staff time.

Beginning in 2017, the RMP directed significantly increased resources for monitoring and special studies relating to emerging contaminants, the result of an optional reduced monitoring schedule for municipal wastewater discharges to the Bay in exchange for increased payments to the RMP. By necessity, the level of funding directed towards emerging contaminants strategy also increased. In 2018, the funding provided to manage the RMP CEC Strategy is $65,000.

In 2019, $70,000 is requested, including an additional $5,000 to provide honoraria to ecotoxicologists to supplement the existing expertise provided by the RMP's Exposure and Effects Workgroup; these experts will provide guidance on prioritization and further study of Possible Concern contaminants, including the potential for the RMP to fund targeted studies to establish toxicity thresholds for contaminants with the greatest potential to pose risks to the Bay.

Study Objectives and Applicable RMP Management Questions

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Compare existing occurrence data with new toxicity information reported in the scientific literature. Evaluate future monitoring needs and toxicity data gaps.	Does the latest science suggest a reprioritization of chemicals as we learn more about them? Which newly identified contaminants merit further monitoring? Which Possible Concern contaminants could be the subject of RMP-funded ecotoxicity studies?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Evaluate new knowledge regarding sources, pathways, and loadings for CECs in the context of a comprehensive conceptual model to allow prioritization of data gaps the RMP can fill.	What are the key sources or pathways that impact concentrations and potential risk of emerging contaminants?
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	Compare levels of parent CECs to degradates in light of processes expected to be active and influential in the Bay. Compare model predictions to monitoring results; assess potential reasons for differences between predicted and measured values. Does new research in other regions provide insight as to key processes that affect the fate of emerging contaminants?	Are relative levels of contaminants and degradates in different matrices or subembayments consistent with our expectations for various contaminant processes?
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	Compare Bay CECs levels measured over time. Do trend data from other regions suggest likely trends in the Bay?	Have specific CECs declined over time? Have functional replacements for these CECs increased?

5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	Evaluate data on production, use, and source trends in the scientific and trade literature as a means of prioritizing potential risk of Bay contaminants in the future, and corresponding monitoring recommendations. Evaluate the expected impacts of changes to population, climate, affluence, and other factors.	Do production, use, and source trends suggest likely changes in the relative risk of specific emerging contaminants? What are the possible effects of changes to population, climate, and affluence on concentrations of CECs and associated risk?
6) What are the effects of management actions?	Evaluate the likely impacts of new management actions on contaminant levels. Which actions may have unintended consequences?	Are additional or different actions needed to reduce levels below aquatic toxicity thresholds?

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

Approach

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

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

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

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

In 2019, additional funding of $5,000 in the form of honoraria is requested to supplement the toxicological expertise already available to the RMP via the Exposure and Effects Workgroup expert advisory panel. The need for additional expertise is anticipated as part of a strategic effort to review Possible Concern contaminants, prioritize those that have the highest potential to pose risks based on available data, and determine whether it would be appropriate for the RMP to fund targeted toxicological studies on these contaminants to develop ecotoxicity thresholds that might allow for a more definitive classification in the High, Moderate, or Low Concern tiers. This effort is expected to begin later in 2018, with external consultations to be scheduled in early 2019; a potential outcome would be a proposed special study to be reviewed as part of 2019 workgroup meetings.

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

Budget

Table 2. 2019 Emerging Contaminants Strategy budget

Deliverables	Budget
Tasks 1-6: Information gathering from a variety of sources throughout the year, including presentations at scientific conferences, to inform Task 5; Assist Water Board and other RMP stakeholders with science summaries relating to policy including emerging contaminants action plans and comment letters regarding proposed actions of other agencies; Coordinate *pro bono* studies conducted in collaboration with RMP Status and Trends monitoring activities; Consult with ecotoxicologists on relative concern associated with Possible Concern contaminants and the potential for the RMP to contribute to studies that establish toxicological thresholds; Update the RMP CEC Strategy document with revised tiered framework tables (integrating new data and external infornation) and multi-year plan, discussion of new RMP data and information gathered (Task 1); present at spring ECWG meeting; Present an update of RMP CEC Strategy, ongoing or completed special and *pro bono* studies, and new studies to the Steering Committee.	$65,000
Task 4: Honoraria for consultation with ecotoxicologists concerning relative concern associated with Possible Concern contaminants and the potential for the RMP to contribute to studies that establish toxicological thresholds.	$5,000

<u>Budget Justification</u>

Significant increases in RMP resources dedicated to CEC special studies, beginning in 2017 and expected to continue in 2019, require greater levels of engagement, outreach, coordination, and integration to assure strategic use of available funds. Funding for this task will allow for strategic thinking using the latest science, so that the RMP can continue to generate the information water managers need to effectively address emerging contaminants in the Bay. An additional request of $5,000 for 2019 would be allocated toward honoraria to fill gaps in ecotoxicity expertise and guide strategic evaluation and special study proposal development related to Possible Concern contaminants. The total request, $70,000, represents 20% of the overall RMP CECs planning budget ($350,000).

Reporting

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

References

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

Special Study Proposal:
Stormwater Loading Strategy for CECs

Summary: For many CECs of interest to the RMP, the two major pathways to the Bay are wastewater and stormwater. The RMP and the wastewater community have devoted considerable resources to understanding CEC concentrations in wastewater effluent. This information has been important for understanding the potential sources as well as estimating CEC loads to the Bay. To date, screening studies have been conducted to determine the presence/absence of CECs in stormwater; however, robust information for calculating loads from this pathway for CECs has not been collected. The goal of this proposal is to develop a stormwater loading strategy for CECs that would include a methodology for identifying representative watersheds and monitoring designs for key CECs with different physico-chemical characteristics and derived from different types of sources or land uses.

Estimated Cost: $60,000

Oversight Groups: ECWG & SPLWG

Proposed by: Meg Sedlak, Diana Lin, Rebecca Sutton, Jing Wu, Alicia Gilbreath, and Lester McKee (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	***Due Date***
Task 1. Development of draft stormwater monitoring strategy for CECs including potential representative watersheds and frequency of sampling	Fall 2018 – Spring 2019
Task 2. Presentation to the SPLWG and ECWG of the Draft strategy	Spring 2019
Task 3. Final Strategy	September 1, 2019

Background

To date, wastewater and stormwater are the two major pathways of CECs of interest to the RMP. Considerable resources have been devoted to understanding CEC concentrations and loads from wastewater effluent; however, comparable data for stormwater do not exist. Most recently, this was identified as a data gap as part of the spreadsheet modeling exercise that was conducted as part of the RMP's PFAS Synthesis and Strategy (Sedlak et al. 2018). To fill in this data gap, stormwater CEC data need to be collected at representative watersheds across the Bay Area to provide a basis for load calculation. The RMP has begun to articulate sources and possible pathways by which CECs may be introduced into the environment in the CEC Strategy 2018 Update (Lin et al. 2018); however, a comprehensive stormwater monitoring strategy that goes beyond a screening level of presence/absence and provides robust data for load calculations needs to be developed.

Stormwater monitoring to calculate CEC loads has been discussed within the ECWG. One major concern from stakeholders is lack of guidance and clarity as to which watersheds and CECs should be targeted for monitoring. Bay Area watersheds feature a wide variety of characteristics, with different land use distributions and varying degree of imperviousness. Moreover, there are many thousands of CECs, derived from a variety of sources or land uses and featuring a broad range of physico-chemical properties. Because it is impossible to monitor everywhere at all times, choosing the right watersheds that are representative of Bay Area watershed characteristics for CECs, and sampling at an appropriate frequency, become critical for the success of the monitoring program to provide needed information for load estimates. Therefore, prior to embarking on monitoring to inform load estimates, a monitoring strategy for loads needs to be developed to provide the rationale and methodology for watershed selection and sampling design.

Study Objectives and Applicable RMP Management Questions

The goal of this project is to develop a strategy for monitoring representative watersheds to assess stormwater loads of CECs to the Bay. An important outcome of the strategy would be the recommended stormwater monitoring designs based on the sources and physico-chemical properties of different types of CECs.

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?		
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	This study will develop a stormwater loading strategy for CECs including model study designs that specify which watersheds to monitor based on CEC and land use characteristics.	Implementing monitoring efforts guided by the model study designs would result in sufficient data to estimate loading from the stormwater pathway for CECs of interest.
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?		
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?		
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?		
6) What are the effects of management actions?		

Approach

We propose to develop a stormwater loads monitoring strategy with study designs that identify representative watersheds to monitor for CECs to provide information for estimating loads to the Bay. This process will require us to consider the following elements, which were described in detail in the recent CEC Strategy 2018 Update (Lin et al. 2018):

- Understand physico-chemical properties of various CECs (e.g., water solubility, partitioning to sediment, volatility, degradation) and identify key CECs for monitoring;
- Identify sources of CECs, particularly the those that are related to land uses;
- Understand watershed characteristics (e.g., land use, size, slope, impervious surfaces) and develop a methodology (or metrics) for identifying representative watersheds for CECs monitoring;
- Develop a monitoring design that includes frequency of sampling, method of sampling, and ancillary data needs (e.g., flow gauge data); and
- Develop a stepwise plan for implementing the designed monitoring program, including the prioritization of targeted watersheds and a timeline.

Budget

Table 2. Estimated costs for Stormwater Loading Strategy for CECs.

Expense	Estimated Hours	Estimated Cost
Labor		
Project Staff	446	49,200
Senior Management Review	16	3,400
Project Management		0
Contract Management		0
Data Technical Services		0
GIS Services	24	3,400
Creative Services		0
IT Services		0
Communications		0
Operations		0
Honoraria		
Expert advisors on CECs in stormwater		4,000
Grand Total		60,000

<u>Budget Justification</u>

Interdisciplinary Effort Requiring Internal Coordination and External Expertise
Project staff hours reflect the need for high levels of coordination 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 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.

At a minimum, this project will develop a monitoring strategy for calculating loads for PFASs and several high priority CECs such as flame retardants. The budget for this project can be reduced by focusing on fewer CECs.

Reporting

Deliverables will include: a) a Draft Strategy document, to be presented to the SPLWG and ECWG in spring 2019; and b) a Final Strategy document, to be completed by September 1, 2019.

References

Lin D, Sutton R, Shimabuku I, Sedlak M, Sun J, Wu J, Holleman R. 2018. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2018 Update. DRAFT.

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

Special Study Proposal: Roadway Contaminants in Stormwater

Summary: Preliminary results from a 2016 Special Study that scanned Bay water samples for contaminants via non-targeted analysis suggests that stormwater has the potential to contain significant levels of potentially harmful contaminants. An independent effort to probe stormwater-related Coho salmon aquatic toxicity in the Puget Sound region has led to development of a targeted list of key CECs in urban stormwaters, which includes contaminants derived from sources such as vehicle tires and urban use pesticides. As part of an initial, West Coast screening effort using this new, targeted analyte list, we propose analyzing stormwater samples collected from major urban watersheds discharging to San Francisco Bay, as well as Lagunitas Creek, a less urban reference site that provides key habitat for the endangered Coho salmon.

Estimated Cost: $130,000

Oversight Group: ECWG

Proposed by: Rebecca Sutton (SFEI) and Ed Kolodziej (University of Washington)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Site selection and reconnaissance, in coordination with SFEI stormwater and STLS teams	Summer 2018
Task 2. Field collection of stormwater samples	Fall 2018 – Spring 2019
Task 3. Laboratory analysis of samples	Summer 2019
Task 4. Review of data	Fall 2019
Task 5. Draft manuscript and management-oriented summary for ECWG meeting	Spring 2020
Task 6. Final manuscript and management-oriented summary	Summer 2020

Background

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

Preliminary findings from this study, presented at both the ECWG meeting (Ferguson et al. 2017) and the RMP Annual Meeting (Sun et al. 2017) last year, indicate that water samples from the stormwater-influenced site, San Leandro Bay, contained a broad array of unique contaminants with strong signals suggesting higher concentrations. Contaminants identified with high confidence include 1,3-diphenylguanidine (DPG), a rubber vulcanization agent derived from vehicle tires, as well as ε-caprolactam, used to make the nylon polymers found in tires and many other products. The European Chemicals Agency has established predicted no effect concentrations (PNEC) for DPG of 30 μg/L in freshwater and 3 μg/L in marine waters (ECHA 2018). While the non-targeted analysis provides only qualitative data, the high relative strength of the DPG signal in San Leandro Bay suggests that this contaminant has the potential to be present at concentrations similar to these PNECs.

These findings indicate that stormwater is a pathway by which unique contaminants from vehicles and roadways make their way to tributaries and near-shore Bay environments. An additional factor influencing a special interest in emerging contaminants from stormwater is that, unlike wastewater, this pathway generally receives no treatment. As a result, limited degradation or trapping of contaminants occurs prior to their discharge to receiving waters. In many urbanized areas, contaminant flows from untreated stormwaters dominate chemical mass discharges to freshwater and marine receiving waters.

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

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

A direct outcome from these non-targeted analytical efforts is the development of a list of targeted analytes developed specifically to assess the stormwater pathway as major contaminant inputs. While there are a number of targeted CEC lists designed around the influence of wastewater (e.g., focused on pharmaceuticals and other compounds typically disposed of down the drain), this is the first major effort to develop a CEC list targeting the influence of urban runoff in aquatic habitats with a coordinated analytical effort. The RMP has the opportunity to take part in a West Coast-wide screening effort, analyzing Bay Area stormwater using this new list of targeted CECs derived from vehicular sources, urban use pesticides, and other ubiquitous urban contaminants.

The endangered Coho salmon, the focus of the Puget Sound research effort, are now absent from all tributaries discharging to the Bay. Steelhead (*Oncorhynchus mykiss*), a threatened species, are observed in some Bay streams (e.g., Guadalupe River, Alameda Creek). Therefore, in addition to a survey of the tributaries that discharge to the Bay, monitoring is recommended for Lagunitas Creek, a less-urban reference site in Marin County (within the jurisdiction of the San Francisco Bay Water Board) that provides spawning habitat for both the endangered Coho salmon and threatened steelhead.

Study Objectives and Applicable RMP Management Questions

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Compare new occurrence data for stormwater CECs with toxicity information reported in the scientific literature. Evaluate future monitoring needs and toxicity data gaps.	Do any stormwater CECs merit additional monitoring in the Bay or a specific classification in the tiered risk framework? What are the potential risks of these emerging contaminants, especially to priority populations of salmonids? Is a need for management actions indicated?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Compare concentrations observed at different sites in the Bay Area to glean possible insights regarding the influence of sources or land use types. Compare Bay Area concentrations to other measurements of other urban areas along the West Coast.	What are the key sources or land uses that most impact stormwater concentrations?
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	N/A	
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	N/A	The data from this study will establish baseline data for stormwater CECs in the Bay Area.

5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?		
6) What are the effects of management actions?	N/A	Are pollution prevention actions needed to reduce levels below aquatic toxicity thresholds?

Approach

Stormwater Sample Collection
For this initial screening effort, up to ten stormwater sites will be sampled. Site selection will occur in consultation with stormwater loading team at SFEI, the RMP's Small Tributaries Loading Strategy team, and the California Department of Pesticide Regulation (DPR). Sites will be selected based on multiple factors including: 1) greater relative estimated discharge volume to the Bay; 2) greater relative urban land use in the watershed, with an emphasis on proximity to roadways; 3) suitability as fish habitat; and 4) reduced sample collection costs due to existing sample collection effort underway as part of other studies.

Sites under consideration for this study include locations along:

- Alameda Creek – large urban watershed with past observations of steelhead;
- Colma Creek – small urban watershed with high percentage of roadways;
- Guadalupe River – larger urban watershed with high percentage of roadways and past observations of steelhead; potential use in DPR study;
- Lower Marsh Creek – small urban watershed;
- San Francisquito Creek – small urban watershed; limited observations of steelhead;
- Confluence of San Joaquin/Sacramento rivers – Bay receives 96% of its freshwater from this watershed;
- South San Ramon Creek – residential watershed; potential use in DPR study;
- Walnut Creek – residential watershed; potential use in DPR study;
- Lagunitas Creek – reference site that drains to Tomales Bay; critical habitat for endangered Coho salmon.

With the primary goal of screening for the presence or absence of target analytes, each site will be sampled during one or two storms. Samples will consist of single grabs or composites of 1 L, collected into pre-cleaned amber glass containers. QA/QC samples collected will include two field duplicates and one field blank. A total of up to 18 samples will be obtained.

Targeted Chemical Analysis
Unfiltered samples will be analyzed with a newly developed, targeted analytical method using multi-residue solid phase extraction (SPE) and liquid chromatography with tandem mass spectroscopy (LC-MS/MS). Approximately 35 compounds will be monitored, including pharmaceuticals, pesticides, and several vehicle-specific analytes such as DPG and HMMM. A description of the analytes is provided as a separate attachment. This suite of

representative tracers for urban runoff includes a broad range of contaminants with different physical-chemical parameters (e.g, various chemical functionalities, wide range of polarities and biodegradation potential). The compounds were selected to represent three primary urban sources: residential use, roadways, and wastewater.

Data Interpretation

We anticipate most of these contaminants will be widely observed in urban areas. However, Lagunitas Creek, the reference site supporting Coho salmon, may have lower levels of many stormwater-derived contaminants. Results for the Bay Area will also be compared to levels observed in other West Coast urban regions. Dr. Kolodziej is coordinating this upcoming sampling effort, which is likely to include southern California, the Portland area, and the Seattle/Puget Sound area.

Levels in Bay Area stormwater will also be compared to available toxicity thresholds and other indicators of aquatic ecosystem health. Findings may highlight concerns, data gaps, and the need for further research as well as potential pollution prevention actions.

Budget

Table 2. 2019 Roadway Contaminants in Stormwater budget

Expense	Estimated Hours	Estimated Cost
Labor		
Project Staff	500	85,000
Senior Management Review	6	1,200
Project/Contract Management *		0
Data Technical Services		15,500
GIS Services	6	600
Subcontracts		
Kolodziej Lab, University of Washington		25,000
Direct Costs		
Equipment		1,200
Travel		500
Shipping		1,000
Grand Total		130,000

* Not needed because core RMP funding provides this service.

Budget Justification

Field Costs
This special study proposal has a budget of $130,000, which includes up to $67,000 devoted to stormwater sample collection (site selection and reconnaissance, permit applications, development of sample collection protocols, field work for five sites, and coordination with other stormwater sample collection efforts at additional sites).

Every effort will be made to minimize field costs through leveraging existing stormwater monitoring activities of the RMP and the California Department of Pesticide Regulation (DPR). DPR plans to monitor three Bay Area stormwater sites for pesticides, and may be able to collect stormwater samples for RMP studies.

Laboratory Costs
The Kolodziej Laboratory (University of Washington) offers this analysis at a cost of $280/sample. Up to 18 independent samples will be analyzed, including field duplicates and a field blank. Additional funds are provided to support data analysis within the context of the broader West Coast screening effort, and preparation of a manuscript describing the findings.

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

Reporting Costs
Preparation of a draft manuscript for publication in a peer-reviewed journal would be led by the analytical partner (Ed Kolodziej, University of Washington), with assistance from RMP staff. After the manuscript is complete, RMP staff will produce a management-oriented summary to describe the results and their implications for RMP stakeholders.

Reporting

Deliverables will include: a) a draft manuscript[1] that serves as an RMP technical report, due spring 2020; b) a management-oriented summary describing the results and their implications, due spring 2020; and c) additions to other RMP publications such as the Pulse.

References

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

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

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Special Study Proposal:
Alternative Organophosphate Flame Retardants Conceptual and Steady-State Model for San Francisco Bay

Summary: Organophosphate alternative flame retardants occur in relatively high concentrations in San Francisco Bay. This study will develop a steady-state, multimedia model to better understand the sources, pathways, loadings, and fate of organophosphates in the Bay. The findings from this modeling effort will provide direction for future monitoring and management actions. This study will also help fulfill a stormwater permit requirement to conduct a study on alternative flame retardants. As part of this study, Bay Area ambient air samples from the wet and dry season will be collected and analyzed to fill a significant data gap regarding atmospheric inputs.

Estimated Cost: $99,500

Oversight Groups: SPLWG and ECWG

Proposed by: Miriam Diamond (U. Toronto), Tim Rodgers (U. Toronto), Diana Lin (SFEI), Rebecca Sutton (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	**Due Date**
Task 1. Finalize technical report (Appendix A)	July 2018
Task 3. Update STLS team with project progress - model assumptions and inputs, model results, sampling design, sampling results, and draft report	November 2018 – May 2020
Task 2. Compilation of model inputs and model implementation	February 2019
Task 4. Finalize study design for air monitoring	December 2018
Task 5. Field sampling	January 2019 – August 2019
Task 6. Lab analysis	November 2019
Task 7. Revised model calibrated with new air data	January 2020
Task 8. Draft reports – draft manuscript and draft summary report	May 2020
Task 9. Final report – final summary report	August 2020

Background - Previous Work

The Municipal Regional Stormwater NPDES Permit requires local stormwater agencies to investigate or support studies on alternative flame retardants. Specifically, the permit language requires agencies "to conduct or cause to be conducted special study that addresses relevant management information needs for emerging contaminants. The special study must account for relevant CECs in stormwater and would address at least PFOS, PFAS, and alternative flame retardants being used to replace PBDEs (NPDES No. CAS612008; p. 83)."

To address this permit requirement, the RMP Small Tributary Loading Strategy (STLS) Team and SPLWG developed and funded a $13,000 special study in 2018 to review available PBDE data and previously developed conceptual models to support a stormwater alternative flame retardants conceptual model. The workplan for this study as well as relevant management questions were developed through the STLS Team. The draft technical report is included as Appendix A, and includes a review of available stormwater and flame retardant monitoring data and existing model platforms. The draft report concluded with the recommendation to develop a steady-state one-box model of organophosphates in the Bay based on the Multimedia Urban Model (MUM). The draft report also identified local air data as an important data gap that should be prioritized for monitoring. The draft report will be finalized after review through SPLWG, ECWG, and TRC.

Study Objectives and Applicable RMP Management Questions

This study will develop a conceptual model for organophosphate flame retardants in the Bay, as well as a steady-state, multimedia model. Recent investigations of flame retardants in San Francisco Bay (Sutton et al., in prep) have identified organophosphates as a priority for investigations. The model will be used to address management questions, assess data gaps, prioritize monitoring data needs, and help fulfill stormwater permit requirements.

As part of a Sources, Pathways, and Loadings Workgroup special study for 2018, management questions specific to this study were developed in collaboration with the RMP STLS Team.

Table 1. Management questions prioritized through STLS.

Management Question	Study Objective	Example Information Application
1) What are estimated contaminant concentrations/masses in Bay water, sediment, and air?	Measure ambient organophosphate air concentrations. Use the model to predict ambient Bay water and sediment concentrations.	Is there agreement between modeled and measured water and sediment concentrations of organophosphates?
2) What are the relative contributions of contaminant loads from air deposition, stormwater, and wastewater effluent?	Compare the estimated loads for each organophosphate modeled.	A sensitivity analysis can determine the relative impact from different loads; sensitivity of the model towards stormwater and wastewater flow estimates can also be evaluated.
3) Do the loads explain ambient concentrations?	Determine whether any disagreement between	Identify key processes or missing processes in

	modeled and measured concentrations is within an acceptable range.	conceptual model. What data needs should be prioritized?
4) What are the likely true sources of loads?	Review the literature and available data on sources and uses of organophosphates to identify likely true sources.	Are true sources amenable to management actions that could reduce Bay contamination?

The specific management questions identified for this proposed study fit within the scope of management questions identified by the RMP, ECWG, and STLS. The first question is essentially RMP MQ2 (What are the concentrations and masses of contaminants in the Estuary and its segments). The second through fourth questions are related to RMP MQ3 (What are the sources, pathways loadings, and processes leading to contaminant-related impacts in the Estuary?), ECWG MQ2 (What are the sources, pathways and loadings leading to the presence of individual CECs or group of CECs in the Bay?) and STLS MQ1 (What are the loads or concentrations of pollutants of concern from small tributaries to the Bay?).

Approach

First, the technical report (Appendix A) will be finalized based on input from SPLWG, ECWG, and TRC. Model development and air sampling, which were the next steps identified in the report, are described below. Major milestones will be shared during STLS team meetings throughout the course of the project.

Model Description

A steady-state, multimedia one-box model of the Bay will be developed that includes compartments for ambient Bay air, water, and sediment. While the one-box model lacks capacity to simulate the heterogeneous geospatial processes within the Bay, it is currently considered to be the best starting point to further our knowledge on the multimedia partitioning behavior of organophosphates given scarce data on pathways and loadings of organophosphates. Model development will start with a simple one-box model to represent the Bay, and additional complexity may be added as justified based on data availability.

The model will include the following elements, and additional elements may be added:

1. Air compartment including:
    a. A one box compartment from the water's surface to the average height of the boundary mixing layer,
    b. Bulk air comprised of gas phase and suspended particulate concentrations,
    c. Prevailing air exchange from the Pacific Ocean
    d. Net exchange with surrounding urban air
    e. Atmospheric compartment mass transfer processes
    f. Chemical degradation
    g. Deposition (wet and dry)
    h. Air-water exchange
2. Water compartment including

   a. Dissolved water and particulate concentrations
   b. Loadings from freshwater tributaries and river inflows
   c. Loadings from wastewater effluent
   d. Tidal exchange with the Pacific Ocean
   e. Water-air and water-sediment mass transfer processes
   f. Chemical degradation
   g. Solids deposition and resuspension
3. Active and buried sediment compartments including
   a. Solids and porewater (water between solids in sediment bed) concentrations
   b. Sediment-water mass transfer processes
   c. Chemical degradation
   d. Sediment resuspension and burial

Model input data

Model parameters and inputs will be based on the following sources as appropriate for modeling organophosphates in the Bay:

- Previously published Bay one-box models (Davis et al., 2007; Oram et al., 2008; Yee et al., 2010)
- Simplification of previously published multi-box waterbody model (Gandhi et al., 2014; Sommerfreund et al., 2010a,b)
- Multimedia Urban Model of organophosphates in Toronto (Rodgers et al., in prep)
- Bay monitoring data (summarized in Appendix A)
- Literature review

Chemical-specific model parameters will be used to model the organophosphates listed in Table 2 because these organophosphates have very different chemical and physical properties (e.g., partitioning estimates based on polyparameter linear free energy relationships (Arp et al., 2008; Endo and Goss, 2014; Goss and Schwarzenbach, 2001)).

During the first phase of model development, loadings from the rivers and small tributaries will be based on available monitoring data (Appendix A) assuming conservative behavior (no degradation, volatilization, or partitioning) until loads reach the ambient Bay "box." Additional boxes may be added to simulate partitioning behavior upstream in these pathways if the model and data support adding this level of complexity.

Table 2: Organophosphates to be included in model and Henry's constant (measure of volatility), water solubility, and octanol-water partition coefficients (Log K_{OW}). Properties from U.S. EPA Chemistry Dashboard.

Acronym	Full Analyte Name	H_{ac} ($Pa\text{-}m^3/mol$)	Water solubility (mg/L)	Log K_{OW}
TCEP	Tris (2-chloroethyl) phosphate	0.01	7,000	1.4
TCPP	Tris (1-chloro-2-propyl) phosphate	0.2	1000	2.6
TDCPP	Tris (1,3-dichloro-2-propyl) phosphate	0.2	7	3.7
TPhP	Triphenyl phosphate	0.2	2	4.6

TnBP	Tri-n-butyl phosphate	0.1	280	3.7
TBEP	Tris (2-butoxyethyl) phosphate	7E-6	0.003	3.75
EHDPP	2-Ethylhexyl diphenyl phosphate	5E-5	0.000005	5.73

<u>Model evaluation and implementation</u>

First, organophosphate loads into the Bay will be calculated from available data on a Bay-wide annual basis. There are limited data points to fully characterize stormwater (n=8 from WY2014, see Appendix A) and wastewater effluent concentrations (n=3 from 2014), and therefore uncertainties as well as best estimates for stormwater and effluent loads will be calculated. Results from this calculation will be used to answer the question about the relative contribution of contaminant loads.

Air concentrations needed to calculate mass balances in the air compartment and loads to Bay water will initially be based on air data from other regions (e.g., Toronto), since there are currently no Bay air data. Air concentrations in the model will be updated after completion of the Bay air sampling and analysis (see below). Additionally, loads will be calculated from river inflows, Pacific Ocean exchanges through the Golden Gate, sediment deposition and resuspension, and sediment burial.

The model results will be evaluated by comparing predicted ambient water and sediment concentrations of organophosphates with monitoring data. Should the model not provide reasonable estimates, a sensitivity analysis will be performed to try to determine the source of the discrepancies (e.g., incorrect approximation of inputs, exchange flows, versus incorrect model structure). With the expectation that the model provides reasonable results, the model will be implemented to help answer management questions developed for this study as described in Table 1.

One of the primary goals for developing an organophosphate model is to help prioritize monitoring data needs. The sensitivity analysis will be used to evaluate how modeled ambient Bay concentrations respond to concentrations in pathways entering the Bay, which will be used to develop recommendations data collection needs. The sensitivity analysis will summarize how ambient Bay concentrations respond to a significant increase or decrease (e.g., reduction to 50% of current value, or two times increase from current value) in:

- Stormwater concentrations/flows
- Wastewater effluent concentrations/flows
- Ambient air concentrations during the wet/dry season
- Ocean exchange concentrations
- Delta river concentrations

A detailed sensitivity analysis will also be used to evaluate the impact of other input parameters in order to highlight information needs to improve the model.

<u>Sampling and Analysis of Air Concentrations</u>

Ambient air concentrations for the Bay Area have been identified as an important data gap, therefore ambient air concentrations will be measured and used in the model. Development of the study design and sample collection will occur concurrently with model development.

Ambient air samples will be collected using polyurethane foam passive samplers (PUF-PAS) from the University of Toronto. The PUF-PAS are consistent with methods used by the Global Atmospheric Passive Sampling (GAPS) study, which is a global monitoring program for persistent organic pollutants required by the Stockholm Convention, with air concentrations published in several scientific peer-reviewed journals (Rauert et al., 2018).

We will develop a detailed study design, which will be reviewed through STLS-team meetings.

Ten samples will be analyzed from field sampling during the wet and dry season, for a total of twenty samples. Up to six sampling locations will be selected throughout the Bay to capture variability in different regions of the Bay. Samplers are typically deployed for 90 days. If possible, two samplers will be deployed above ambient water, such as on buoys or bridges. Sampling sites should be relatively secure such that equipment is unlikely to be stolen, vandalized, or contaminated. Ideally, sampled locations also have meteorological data available, but this is optional. Field blanks will be collected at each site by transporting samples to and from the field in the same way as a field sample, and exposing to the site for a few seconds; only two will likely be analyzed. Additionally, two field replicates will be collected at one site for each season. Samples will be analyzed by the University of Toronto using GC-MS methods.

Budget

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

Table 3. Proposed Budget.

Task	**SFEI costs**	**Subcontract Costs**	**Total Cost**
Model development	$15,000	$33,000	$48,000
Air data study design and collection	$25,600	$12,200	$37,800
Reporting	$13,700		$13,700
Totals	**SFEI total**	**Subcontract total**	**Grand Total**
	$54,300	$45,200	$99,500

<u>Budget Justification</u>

Model development – SFEI and Subcontract (Labor)
University of Toronto will lead model development with support and coordination from SFEI staff. Estimated costs are based on labor needed to complete the following tasks:

- Compile model inputs through literature review and engineering estimates
- Develop model

- Evaluate model predictions with monitoring data
- Conduct detailed sensitivity analysis for model inputs
- Synthesizing model results and data collection priorities
- Update model with new local air data
- Provide project updates and key deliverable: Draft manuscript for submission in peer-review journal, which will serve as the technical report for the project (a small subset of hours needed for this task is included in the budget, the remaining hours needed will be the covered by the U. of Toronto)
- Support SFEI in drafting summary report.

SFEI costs are based on total labor costs to support University of Toronto to develop and compile model inputs, support model development, and implement scenarios to answer study questions, and preparation and attendance at STLS team meetings to provide project updates. SFEI costs also includes labor costs to finalize Appendix A technical report through feedback from SPLWG and ECWG. (110 hrs)

Air data collection – SFEI and Subcontract (Labor and direct)
SFEI will design and implement a field study to collect air samples and ship to U. of Toronto's laboratory for analysis. SFEI labor costs include staff hours needed to develop field sampling plan and deploy and retrieve passive samplers during two sampling events (one during wet and dry season) at six different sites. An additional $2,500 is estimated for direct costs for sample shipment and supplies. (171 hrs + direct costs)

University of Toronto costs are based on analytical costs of $500 per sample ($500 * 20 samples = $10,000, including an additional $2,200 of direct costs for supplies and shipping.

Reporting – SFEI costs only
University of Toronto will lead preparation of a draft manuscript for publication in a peer-reviewed journal, which will serve as a technical report. Reporting costs are significantly reduced by having U. of Toronto take main responsibility for writing. Reporting costs are budgeted only for SFEI staff time to participate in writing of the manuscript, and prepare a separate management-oriented summary document. This also includes additional hours needed to discuss report with STLS team. (100 hrs)

Reporting

Project status updates will be provided at STLS team meetings. Deliverables will include: a) a draft manuscript that serves as an RMP technical report, and b) a plain language RMP management-oriented summary report describing results and recommendations for next steps for data collection and model development. The draft manuscript and draft summary report will be due May 31, 2020, and will be reviewed by SPLWG, ECWG and the TRC. Comments will be incorporated into the final summary report due August 31, 2020. Since it will be difficult to determine the timeline for the manuscript to be published in a peer-reviewed journal, a deadline is not specified for publication of the manuscript.

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Appendix A

REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN SAN FRANCISCO BAY

sfei.org/rmp

Draft Technical Report

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Executive Summary
The Municipal Regional Stormwater NPDES Permit requires local stormwater agencies to investigate or support studies on alternative flame retardants. To address this permit requirement, the RMP Small Tributary Loading Strategy (STLS) Team and the Sources, Pathways and Loadings Workgroup (SPLWG) developed and funded a $13,000 special study project in 2018 to review available PBDE data and previously developed conceptual models to support a stormwater alternative flame retardants conceptual model. This technical report summarizes the results of the study.

Recent RMP monitoring that characterized a wide-range of alternative flame retardants has led to the conclusion that among the many categories of alternative flame retardants, organophosphates should be prioritized for further investigation in the Bay. Monitoring revealed ubiquitous detections of organophosphates at concentrations comparable to or greater than PBDEs, with some levels approaching or exceeding predicted no effect concentrations for marine waters, suggesting concerns for aquatic toxicity.

A limited amount of organophosphate monitoring data has been collected of ambient Bay water (n=12), sediment (n=10), stormwater (n=8), and wastewater effluent (n=3). A modeling effort is recommended to prioritize organophosphate data collection needs to answer RMP management questions. Based on the limited availability of data and wide-ranging multimedia partitioning behavior of organphosphates, a simple, steady-state model that incorporates this behavior would be most appropriate. The model can be used to evaluate the sensitivity associated with different variables, particularly average concentrations used to represent concentrations in ambient air, and loads entering and leaving the Bay. Currently, there are no local ambient air monitoring data, which is expected to be an important pathway for organophosphates. A special study is recommended for 2019 to develop a model and collect ambient air data.

Introduction

Flame retardants are chemical additives incorporated into a broad array of consumer products to meet industry flammability standards. A wide variety of flame retardants are used in building insulation materials, foams used in furniture and other products, electronics, clothing and textiles, and many other consumer products. Widespread use of PBDEs in response to regulatory flammability standards led to unusually high PBDE exposure in San Francisco residents, as well as contamination of San Francisco Bay and its wildlife (She et al., 2008, 2002).

Subsequent state bans and nationwide phase-outs of PBDEs have resulted in declining levels of contamination in the Bay (Sutton et al. 2015). However, PBDEs are being replaced by a diverse array of alternative flame retardants, including brominated, chlorinated, and organophosphate compounds. These alternatives are ubiquitously detected in the Bay and around the world, even in remote regions like the Arctic (Li et al., 2017; Sutton et al., 2017, in prep).

Organophosphate flame retardants can be chlorinated or non-chlorinated, and are used for flame retardancy, as plasticizers, and in other applications. Sutton et al. (in prep) concluded that among the many categories of alternative flame retardants, organophosphates should be prioritized for further investigation in the Bay because of ubiquitous detections comparable to PBDE concentrations, with some levels exceeding or approaching predicted no effect concentrations for marine waters. Organophosphates belong to a class of polar, persistent, and mobile organic compounds that have previously been overlooked due to analytical limitations, but are increasingly being investigated because they are very mobile, potentially difficult to remove through water treatment processes, and a threat to water quality for humans and ecosystems (Reemtsma et al., 2016). In 2015, the USEPA released a workplan to assess the potential risks of chlorinated organophosphates to aquatic organisms and humans (USEPA, 2015).

The Municipal Regional Stormwater NPDES Permit requires local stormwater agencies to investigate or support studies on alternative flame retardants. Specifically, the permit language requires agencies "to conduct or cause to be conducted special study that addresses relevant management information needs for emerging contaminants. The special study must account for relevant CECs in stormwater and would address at least PFOS, PFAS, and alternative flame retardants being used to replace PBDEs (NPDES No. CAS612008; p. 83)." To address this permit requirement, the RMP STLS Team and SPLWG developed a $13,000 special study proposal for 2018 to review available PBDE data and previously developed conceptual models to support a stormwater alternative flame retardants conceptual model.

The 2018 proposal, titled "Planning Support for Stormwater Alternative Flame Retardants Conceptual Model," outlines Tasks A through D to be completed by the project and summarized in a technical report. In subsequent STLS meetings, STLS reviewed the workplan to complete these tasks, briefly summarized below.

- Task A: Develop draft management questions and information needs for alternative flame retardants in stormwater and refine questions through STLS.
- Task B: Review existing data: 1) compile and summarize PBDE stormwater data and summarize lessons learned that may be applicable to organophosphate flame retardants conceptual model development, and 2) review and compile relevant RMP alternative flame retardant data.
- Task C: Review modeling platforms that could be used for exploring and predicting alternative flame retardant behavior (e.g., partitioning) in stormwater to fill information gaps. In short, how can these previously developed modeling platforms be used to develop a conceptual model of organophosphate flame retardants to answer RMP and STLS management questions?

- Task D: Report on the strengths and weaknesses of the available data and conceptual models for addressing alternative flame retardant information needs in relation to stormwater, and propose methods for addressing data gaps.

Results of Tasks A, B, and C are summarized in this report. Task D is addressed in this report and in the 2019 Special Study Proposal: Alternative Organophosphate Flame Retardants Conceptual and Steady-State Model for San Francisco Bay.

Management questions for organophosphates developed with STLS input (Task A)

1. What are relative contaminant concentrations/masses in Bay water, sediment and air?
2. What are relative contributions of contaminant loads from air deposition, stormwater, and wastewater effluent?
3. Do these loads explain ambient concentrations?
4. What are the likely true sources of loads?

Summary of Existing Monitoring Data (Task B)

This section briefly summarizes the availability of PBDE and organophosphate stormwater data for the Bay Area, as well as data for other Bay matrices.

PBDEs

The RMP began monitoring PBDEs in the Bay in 2002, and following the state ban of two PBDE mixtures a few years later, documented declines of PBDE concentrations in Bay wildlife and sediment (Sutton et al., 2017, 2015, in prep). Detections are now generally below thresholds of potential concern. For example, tern egg concentrations are below a reproductive toxicity threshold, and sport fish concentrations are below protective human health thresholds for fish consumption. Because there is limited information about potential adverse impacts of PBDEs in harbor seals, there is some uncertainty as to the potential impact of PBDEs to seals in the Bay.

The RMP developed a PBDE pollutant profile to support future stormwater model development. PBDEs enter surface waters primarily from stormwater runoff and wastewater treatment plant discharges, as well as in minor amounts from rainfall and direct atmospheric deposition (McKee et al., 2014). PBDEs in the terrestrial landscape are primarily atmospherically deposited after emissions from production, use, and disposal and recycling. Efforts to monitor stormwater loads including monitoring ten mixed-use watersheds around the Bay Area for PBDEs in stormwater runoff (Table 1). Most of the Bay Area watersheds have only been studied at the screening level, with less than 8 samples collected. Stormwater measurements of sums of PBDEs from these samples ranged between 0.4 - 430 ng/L, with a mean of means of 41 ng/L (McKee et al., 2014). A preliminary exploration of how measured stormwater concentrations correlated with land use within those watersheds found strong correlations between median PBDE concentration and combined sum of percent High Density Residential and percent Open Compacted spaces (R^2 = 0.77) (McKee et al., 2014). Also, in terms of water concentrations, PBDEs correlated with total mercury, but not with PCBs. Stormwater measurements in Zone 4 Line A, a 100% urban tributary in Hayward, showed strong correlations with turbidity, and in this watershed an estimate of 99.3% of total PBDE loads was transported during storm flow conditions. Additional data would be needed to see if these correlations hold for organophosphates.

Table 1: Mixed-use watersheds previously sampled for PBDEs in stormwater (McKee et al., 2014)

Borel Creek, San Mateo
San Leandro Creek, San Leandro
Santa Fe Channel, Richmond
Sunnyvale East Channel, Sunnyvale
Lower Penetencia Creek, Milpitas
Lower Marsh Creek, Brentwood
Guadalupe River, San Jose
Coyote Creek, Santa Clara County
Zone 4 Line A, Hayward
Zone 5 Line M, Union City

In WY2014, additional stormwater samples (n=8) were collected and analyzed for PBDEs and alternative flame retardants, including other brominated flame retardants, dechlorane-based flame retardants, and organophosphates (Sutton et al., in prep). Summed PBDE concentrations were between 22 - 180 ng/L, within the concentration ranges reported in earlier studies (McKee et al., 2014).

PBDEs likely enter the municipal wastewater pathway when products and dust from products containing flame retardants are washed (Schreder et al., 2014). The most recent monitoring data of PBDEs in wastewater effluent from Sutton et al. (in prep) measured total concentrations of the sum of PBDEs between 6.2 – 49 ng/L based on single grab samples from three participating wastewater treatment facilities in the spring of 2014. This is comparable to wastewater effluent concentrations reported in 2005 which were between 14 – 66 ng/L (Oram et al., 2008).

Organophosphates

Current understanding of organophosphate concentrations in the Bay is based on monitoring data from 2013 and 2014, and summarized briefly here. For further details, see Sutton et al. (in prep). Bay samples, including ambient sediment and water, stormwater, and wastewater, were analyzed for 13 organophosphates, including chlorinated and non-chlorinated types (Table 2). Unlike PBDEs, organophosphates are generally water soluble, and were widely detected in ambient Bay water and sediment.

Table 2: Organophosphates analyzed in Bay samples (Sutton et al. in prep).

Acronym	Full Analyte Name
TEP	Triethyl phosphate
TCEP	Tris (2-chloroethyl) phosphate
TCPP	Tris (1-chloro-2-propyl) phosphate (multiple isomers)
TDCPP	Tris (1,3-dichloro-2-propyl) phosphate (aka “chlorinated tris”)

TPhP	Triphenyl phosphate
TnBP	Tri-n-butyl phosphate
TCrP	Tricresyl phosphate
TPrP	Tripropyl phosphate
TBEP	Tris (2-butoxyethyl) phosphate
TEHP	Tris (2-ethylhexyl) phosphate
EHDPP	2-Ethylhexyl diphenyl phosphate
TDBPP	Tris (2,3-dibromopropyl) phosphate
T2iPPP	Tris (2-isopropylphenyl) phosphate

- Ambient Bay water concentrations
  TCPP was typically the most abundant organophosphate, with total concentrations ranging between 46 - 2,900 ng/L (median 140 ng/L, n=12, 2013). TPhP median concentrations were the second highest (90 ng/L), and ranged between 41-360 ng/L, with the highest concentrations near the predicted no effect concentration of 370 ng/L calculated for marine settings (ECHA, 2018a). Another organophosphate, TDCPP (also known as chlorinated tris) was detected in all samples at concentrations ranging between 14 - 450 ng/L (median 33 ng/L); many of these measurements exceeded the predicted no effect concentration of 20 ng/L for marine settings (ECHA, 2018b). Ambient Bay water concentrations were found to be generally higher than reported for other estuarine and marine settings, such as the Southern California Bight and Maizuru Bay, Japan (Sutton et al., in prep). An additional 21 ambient Bay water samples were collected during the 2017 Status & Trends water cruise, which will provide more data on ambient water concentrations, as well as a data from a site outside the Golden Gate Bridge.

- Ambient Bay sediment concentrations
  TEHP was found in the highest concentration, with a median of 8.2 ng/g dw (n=10). For comparison, the long-term average dry season concentration of BDE-209 from 2002-2011 was 5.4 ng/g dw in the Lower South Bay, which was higher than found in other subembayments (Sutton et al., 2014). Ambient Bay sediment organophosphate concentrations were generally comparable to those reported for other estuarine and marine settings, such as the Southern California Bight and Scheldt Estuary, Holland (Sutton et al., in prep).

- Stormwater concentrations
  Stormwater data are available from two industrial watersheds in Richmond and Sunnyvale, sites selected as part of an initial screening of the urban landscape for identifying high leverage watersheds for PCBs and mercury. These two watersheds were monitored during two separate storm events in WY2014; two samples were collected

during the rising hydrograph of each storm (n = 2x2x2 = 8), and both dissolved and total water concentrations were measured. Several organophosphates were detected in all samples, and TCPP (150 - 2,100 ng/L, median 935 ng/L) and TBEP (220 - 2,000 ng/L, median 900 ng/L) had the highest median concentrations (Table 2).

Table 2: Comparison of available stormwater measurements of PBDEs and organophosphates.

Stormwater	Sum of PBDEs (McKee et al. 2014) and Sutton et al., in prep	Sum of organophosphates (Sutton et al., in prep)
Minimum (ng/L)	0.4	720
Maximum (ng/L)	430	4,900
Mean/Median (ng/L)	41 (mean of means)	2,900 (median)

- Wastewater effluent concentrations
  Effluent samples were collected from three facilities in 2014; TCPP had the highest concentrations, ranging between 2,500 ng/L - 2,700 ng/L (Sutton et al., in prep). Sum of phosphates were between 3,200 – 8,100 ng/L.

Summary of Existing Modeling Platforms (Task C)

This section briefly summarizes modeling platforms that can be used for predicting contaminant behavior in stormwater and the ambient Bay to help guide and prioritize monitoring effort. The models summarized are the One-Box Bay Model, Multimedia Urban Model, San Francisco Bay Hydrodynamic Model, Regional Watershed Spreadsheet Model, and Bay Area Hydrological Model.

One-Box Bay Model
The one-box model of San Francisco Bay has been used to model PCBs (Davis 2004), PBDEs (Oram et al., 2008), and methylmercury (Yee et al., 2010) in the Bay. This model treats the Bay as a single, well-mixed volume with two compartments representing the water column and the bed (surface) sediments. Conceptually, the model assumes that exchange between water, sediment, and air is more important than exchange between the various geographic subregions of the Bay. Atmospheric exchanges have been incorporated by estimating a deposition rate (in the case of PBDEs, estimates were based on assuming air concentrations were half gaseous and half particulate). Losses through volatilization was also included. The relative PBDE loads into the Bay in 2005 were estimated to come from municipal wastewater (~20%), atmospheric deposition (~1%), local watersheds (~20%), and Delta inflows (~9%) (Werme et al., 2007; Oram, et al. 2008).

For modeling organophosphates, appropriate chemical parameters need to be used. Deposition from the atmosphere may be an important pathway for loads into receiving waters (Rodgers et al., in prep). Therefore, it may be important to incorporate an ambient air compartment within the Bay box model to improve our understanding of atmospheric pathways. Adding an air compartment to the box model requires a mass balance for the air compartment, including pathways entering and leaving the air compartment, and mass transfer processes and chemical degradation within the air compartment. The One-Box Bay model has previously included the water and sediment compartment, but parameters needed to represent organophosphates will need to be developed.

PBDE loads entering the Bay were estimated as part of the mass balance calculation used in the conceptual and steady-state model for PBDEs. The relative PBDE loads entering the Bay in 2005 were estimated to come from municipal wastewater (~20%), atmospheric deposition (~1%), local watersheds (~20%), and Delta inflows (~9%) (Oram et al., 2008; Werme et al., 2007). The model was also used to estimate Bay recovery rates if PBDE loads were reduced or eliminated (Oram et al., 2008). While conceptually this model may be used as a starting point for evaluating organophosphates, the organophosphate load from each pathway is expected to be very different relative to PBDEs due to the high water solubility and more volatile nature of organophosphates (Li et al., 2017).

Multimedia Urban Model (MUM)

The Multimedia Urban Model (MUM with polyparameter linear free energy relationships update) is another steady-state model that has been developed to estimate the fate of semivolatile organic compounds in urban areas. This model includes seven bulk compartments: upper air, lower air, water, soil, sediment, vegetation, and organic film on impervious surface (Priemer and Diamond, 2002). MUM includes an additional compartment for ambient air relative to the current one-box Bay model, and incorporates additional mass transfer processes (e.g., distribution between gas and particulate phase) and chemical degradation in the bulk air phase.

MUM has been used to predict the fate of PCBs and PBDEs in urban environments in peer-reviewed studies (Priemer and Diamond, 2002; Sommerfreund et al., 2010). MUM has recently been modified to incorporate chemical parameterization of organophosphates through the use of polyparameter linear free energy relationships (ppLFERS). Essentially, ppLFERs use more than a single parameter (such as K_d for sediment-water partitioning) to describe chemical partitioning. MUM has been used to estimate the fate and transport of organophosphates in Toronto (Rodgers et al., in prep). Results of this modeling study found that the concentrations of organophosphates measured in Toronto air and air-water mass transfer processes could explain concentrations observed in local streams.

San Francisco Bay Hydrodynamic Model

The San Francisco Bay hydrodynamic model simulates hydrodynamic processes in the Bay, but currently does not include chemical mass transfer and transformation processes. The model has been developed to support transport and dilution studies. This physics-based model incorporates data for tides, Delta outflow, stormwater flows (derived from the Bay Area Hydrological Model described below), local winds, and regional wastewater and refinery dischargers. Further details on the configuration and the water year 2013 validation of the model are available in the Interim Model Validation Report (Holleman et al., 2017).

Recently, a simplified spreadsheet version of the Bay hydrodynamic model has been developed to estimate ambient aqueous concentrations based on dilution of concentrations entering the Bay. This hydrodynamic spreadsheet model was developed by running the hydrodynamic transport model from October 2012 to September 2013. During this period, numerical “dyes” were added to modeled discharges, and the model predicted concentrations of these dyes throughout the Bay.

The model results were condensed into a series of spreadsheets that summarize the relationship between concentrations in load streams (i.e., concentration in stormwater and in individual wastewater or refinery discharges) and ambient concentrations in the Bay for each subembayment. Using this spreadsheet requires specifying concentrations for each of the 42 discharges (37 from wastewater treatment plants and five from refineries) and a representative concentration for stormwater. The spreadsheet then calculates, for each region of the Bay, the sum of contributions from all discharges, providing a baseline estimate for ambient contaminant concentrations. The regions follow RMP subembayment delineations: Lower South Bay, South Bay, Central Bay, San Pablo Bay, and Suisun Bay.

The hydrodynamic spreadsheet model only simulates water concentrations and does not include the sediment or air compartments. Chemical processes such as degradation, sorption to sediment, and atmospheric exchange are currently not included in the model. Since organophosphates are known to degrade and to partition among sediment, water, and air matrices, using this model to simulate organophosphate transport does not seem appropriate. Future model development may add these processes.

Watershed Models - RWSM and BAHM

The Regional Watershed Spreadsheet Model (RWSM) has been developed as a planning level tool for estimating total annual average flow and PCB and mercury loads from small tributaries surrounding the Bay. The model provided estimates of regional and sub-regional scale loads and regionally averaged coefficients for selected land use/source area categories (McKee et al., 2014).

The Bay Area Hydrological Model (BAHM) is a continuous simulation model that was developed to estimate flow and pollutant loads from Bay Area watersheds. The model is built upon HSPF (Hydrological Simulation Program--Fortran), a comprehensive package for simulation of watershed hydrology and water quality for pollutants. The model uses continuous rainfall and other meteorologic records to compute streamflow hydrographs and pollutographs across multiple pollutant sources, spatial scales, and time steps. Currently, the BAHM divides the entire Bay Area into 63 individual watersheds. The model simulation is from 1999 to 2016.

The BAHM can be used to estimate stormwater contaminant loads from individual watersheds in the region in two ways. One is to simply multiply modeled flow by measured stormwater contaminant concentrations. Another more sophisticated approach is to use the BAHM to directly simulate the fate and transport of contaminants in stormwater. Since this is a continuous simulation model, the result of this simulation is a time course of runoff flow rate and contaminant concentrations, making it possible to detect interannual variability of contaminant loads and how they change over time (trend). Based on the load estimates, the watersheds that contribute disproportionately high contaminant loads can be targeted for further investigation. The data gaps identified during model development and implementation can also be used to guide future monitoring efforts.

Either RWSM or BAHM can be used to estimate stormwater loads. Since current stormwater measurements are limited to samples from just two watersheds during two storm events (n=8), stormwater loads can initially be estimated based on multiplying modeled flows with measured concentrations using either model. A key advantage of BAHM over RWSM is that spatial and temporal output of stormwater loads can be fed into the Bay Hydrodynamic Model to predict spatial and temporal changes in ambient Bay water concentrations.

Available Data and Models: Strengths and Weaknesses for Understanding Organophosphate Transport and Fate in Stormwater and the Bay (Task D)

A conceptual and quantitative model is needed to understand the loading and fate of organophosphates in San Francisco Bay. A model is especially needed to answer prioritized management questions:

- What are relative contributions of contaminant loads from air deposition, stormwater, and wastewater effluent?
- Do these loads explain ambient concentrations? Identify key processes or missing processes in conceptual model.

Unlike PBDEs, organophosphates are generally water soluble, and were widely detected in all Bay sample matrices. In the most recent study of Bay matrices (Sutton et al. in prep), median organophosphate concentrations were two orders of magnitude greater than total PBDE concentrations in ambient water, and one order of magnitude greater in stormwater. Bay sediment concentrations of organophosphates were an order of magnitude greater than total PBDE concentrations. While there have not been any studies of air concentrations of organophosphates in the Bay, global studies indicate that organophosphate concentrations in air are at least an order of magnitude higher than PBDEs (Rauert et al., 2018). The higher concentrations of organophosphates in all three environmental matrices points to the need for a multi-media model to simulate the fate and transport of organophosphates in the Bay.

Strength and Weakness of Existing Model Platforms

Three reviewed models that may be used to model organophosphates in the Bay include the Multimedia Urban Model (MUM), the Hydrodynamic Bay Model (hydrodynamic), and the One-Box Bay Model (One-Box Bay). Only MUM has already been developed to simulate the unique physico-chemical properties of organophosphates. This model would need to be updated with parameters to represent the Bay. The MUM model includes additional compartments (e.g., soil, vegetation, and biofilm on impervious surfaces) that need not be included in the development of the model for the Bay.

The hydrodynamic model can be useful for providing more temporally and geographically specific estimates of contaminant levels, but is currently limited in that it assumes contaminants act conservatively, neglecting processes, like degradation, volatilization, or partitioning to sediment, which are important for organophosphates. The One-Box Bay model includes some of these relevant chemical properties, but currently is not developed to include additional chemical parameters for organophosphates and mass transfer processes and chemical degradation in the air phase.

Data Availability for Supporting Model Development

Models are only as good as the data upon which they are built. Previous RMP monitoring has provided some data for organophosphate levels in ambient Bay water and sediment. More limited measurements are available to characterize Bay Area stormwater and wastewater effluent discharges into the Bay.

Ambient Bay concentrations are expected to have significant exchanges with the overlying air. Lack of local air data is prioritized for monitoring because no local air data have been collected. River inflows and ocean exchanges represent important bulk water inflows and outflows into the Bay. River inflow and ocean exchanges are given lower priority because a few samples have been collected, and analytical results are forthcoming; prioritization of these pathways will be evaluated after results are available. A literature review of air concentrations, river inflows, and ocean concentrations is summarized below.

Air

Currently, there are no published data on outdoor air concentrations of organophosphates in the San Francisco Bay Area. There are limited studies reporting concentrations in other urban cities, such as Toronto, Chicago, and Tokyo. Reported concentrations of TCEP vary between 1-2,000 pg/m^3, with recent Toronto average concentrations measuring in the middle of that range (800 pg/m^3). Monitoring of background atmospheric concentrations of persistent organic pollutants by the Global Atmospheric Passive Sampling (GAPS) Network at 48 sites around the world found that PBDE concentrations have not decreased from previous 2005 measurements, and total organophosphate concentrations were at least an order of magnitude higher than PBDE levels, ranging between 69-7,770 pg/m^3 (Rauert et al., 2018). Data for the 18 organophosphates measured at all sites are summarized by Rauert et al. (2018). The most frequently detected organophosphates in 2014 were TCEP, TCPP, TPhP, and TBEP. Point Reyes was the only background California site measured in this GAPS study, which had detections of TCPP and TDCPP above detection limit at concentrations of 7 and 2 pg/m^3. If air deposition is an important loading to the San Francisco Bay, then air concentrations may represent an important data gap, since potential concentrations vary multiple orders of magnitude.

Many consumer products are thought to contribute to the presence of organophosphates in air in urban areas. A review by (Rauert et al., 2014) summarizes studies of flame retardant emissions measured from products using chamber experiments. Organophosphate emissions are reported for a variety of building and insulation materials, polyurethane and upholstery foam, wallpaper materials, printed circuit board electronics, computer systems, and monitors. Additionally, organophosphates are known to be used in plastics, textiles, paints and coatings. While many of these products are used indoors, contamination is expected to move into the outdoor environment. Subsequent deposition to stormwater and the Bay during rain events is anticipated.

Delta Outflow

Currently, the best available data on Delta outflow is a single grab sample from Suisun Bay, which is strongly influenced by flow from the Sacramento and San Joaquin river. During the 2017 Status and Trends water cruise, a single grab sample was collected from RMP historic sites BG20 and BG30, located at the mouths of the Sacramento and San Joaquin rivers; organophosphate analytical results are forthcoming.

Recently, non-targeted analysis by (Moschet et al., 2017) of 51 samples collected during rain events in the winter of 2016 in the Cache Slough Complex of the Delta detected several phosphate flame retardants, including TCEP, TCPP, TDCPP, TEP, and TPhP. TDCPP and TCPP were detected in almost all of the 51 samples. Only maximum concentrations were quantified, and TDCPP and TCPP maximum concentrations were approximately 900 ng/L. These maximum concentrations are comparable to stormwater concentrations measured in local tributaries (Sutton et al., in prep), suggesting that Delta outflow may be an important loading. Flows through the Delta represent approximately 96% of annual freshwater inflows into the Bay, while local tributaries draining urban and agricultural land uses surrounding the Bay represent the remaining 4% of freshwater inputs.

Pacific Ocean Tidal Exchanges

The Bay is a tidally-influenced ecosystem, and previous efforts have estimated water flow losses to the ocean through the Golden Gate Bridge as 3.75 times the freshwater inflow. We will have one measurement of organophosphate concentrations just outside the Golden Gate Bridge based on a grab sample collected by the RMP during the 2017 Status and Trends Water Cruise. This sample represents a mixture of Bay and Pacific Ocean water. Results from this analysis are forthcoming.

There are few published reports of open ocean concentrations of organophosphates that can be used to estimate influx from the Pacific Ocean into San Francisco Bay. Li et al. (2017) measured organophosphates in seawater along a transect from the North Sea to the Arctic, and found a general decreasing trend of organophosphate concentrations moving away from land. The median of the sum of eight organophosphates measured was 3 ng/L. The concentrations in the relatively remote Arctic were 2-3 orders of magnitude lower than seawater near urban areas, which have been measured in the hundred ng/L range (Li et al., 2017). In Southern California, TCPP was also detected in seawater near wastewater effluent discharges at maximum concentrations near detection limits of 50 ng/L (Vidal-Dorsch et al., 2012).

Recommendations

In summary, a modeling effort is recommended to answer management questions about ambient concentrations, estimated loadings, and fate of organophosphates. The model can be used to evaluate the sensitivity associated with different variables, and to assess whether all significant pathways have been incorporated. Based on the limited availability of data, a simple, steady-state model that incorporates multi-media partitioning behavior of organophosphates would be most appropriate. A 2019 RMP Special Study proposal summarizes a plan to develop this model and measure Bay Area air concentrations to fill the most urgent data gap.

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Special Study Proposal: Fipronil and Fipronil Degradates in the Bay Food Web

Summary: Fipronil is a broad-spectrum urban insecticide that is currently classified as a Moderate Concern in the RMP tiered risk framework. In recent years, fipronil use has been increasing in California, and fipronil and its degradates have been detected at levels of concern in Bay sediment, watersheds, and wastewater effluent. A recent study in Southern California also found fipronil and fipronil degradates in several species of fish in locations downstream of urban watersheds and wastewater effluent discharges. This study would provide a screening of fipronil and fipronil degradates in sediment, prey fish, sport fish and harbor seals. Results will be used to evaluate the bioaccumulation and biomagnification potential of these compounds in the Bay food web, and potential human and wildlife exposures.

Estimated Cost: $80,000

Oversight Group: Emerging Contaminant Workgroup

Proposed by: Jennifer Sun, Rebecca Sutton, SFEI

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	***Due Date***
Task 1. Field collection of fish samples	Summer – Fall 2019
Task 2. Laboratory analysis of samples	Fall 2019 – Winter 2020
Task 3. Review of data	Spring 2020
Task 4. Draft technical report	Fall 2020
Task 5. Final technical report	Winter 2020

Background

Fipronil is a broad-spectrum phenylpyrazole insecticide that is widely used in urban environments and households to control ants, termites, fleas, and ticks. In the environment, fipronil is commonly found alongside several stable degradation products, including fipronil sulfide, fipronil sulfone, and fipronil desulfinyl. Fipronil use has increased in recent years, as it has become an alternative to organophosphate or pyrethroid pesticides (CDPR 2017). Ambient Bay sediment monitoring conducted by the RMP has detected significant concentrations of fipronil and its degradates, including multiple detections of fipronil sulfone at levels comparable to an EC_{50} threshold for freshwater invertebrates (Maul et al. 2008). Fipronil and fipronil degradates are currently classified in the RMP tiered risk framework as a likely increasing Moderate Concern for the Bay, based on measured sediment concentrations and increasing use trends.

Recent efforts to monitor and manage fipronil use in California have also increased, following several studies showing high concentrations in watersheds and wastewater effluent. Fipronil concentrations measured in Bay Area watersheds have exceeded the USEPA aquatic life benchmark for chronic invertebrate toxicity, a threshold that was updated in 2016 and calculated based on data from acute toxicity studies (Ensminger et al. 2013; USEPA 2018). Spurred in part by these and similar findings throughout California (Budd et al. 2015), the California Department of Pesticide Regulation (DPR) established restrictions on professional outdoor applications of fipronil in 2017. Additionally, a recent RMP study found that fipronil and fipronil degradates were also ubiquitous in treated wastewater effluent from both secondary and tertiary treatment wastewater facilities (Sadaria et al. 2016). The major source of these compounds to wastewater is thought to be pet flea "spot-on" treatment products (Teerlink et al. 2017). Bay sediment concentrations are notably higher near urban stormwater and wastewater pathways in Lower South Bay as well as nearshore urban areas in South and Central Bay.

Little is known about the presence, fate and effects of these compounds in the Bay food web. Limited environmental monitoring and toxicity data are available in the literature, particularly for fipronil degradates. A recent screening study of CECs in Southern California found fipronil and fipronil degradates in several species of fish sampled in the Los Angeles/Long Beach Harbor (downstream of a highly urbanized watershed) and Santa Clara River watershed (at several locations downstream of wastewater effluent discharges) (Maruya et al. 2016). In this study, fipronil sulfone and fipronil desulfinyl were more commonly detected at higher concentrations than fipronil or fipronil sulfide; previous work has shown that fipronil and fipronil sulfide rapidly degrade to predominantly fipronil sulfone in fish (Konwick et al. 2006; Baird et al. 2012). Concentrations of fipronil were low (ND to 0.21 ng/g ww), but concentrations of fipronil sulfone were orders of magnitude higher (ND to 11 ng/g ww).

USEPA has calculated a bioconcentration factor for fipronil of 321 in whole fish and 164 for edible tissue, but biomagnification has not been assessed (USEPA 2000, Bower & Tjeerdema 2016). The log K_{ow} of fipronil (~4.0) suggests that it could be bioavailable in aquatic food webs, particularly in high-lipid species (CDPR 2017, Bower & Tjeerdema 2016), although studies have shown that fipronil is metabolized quickly to fipronil sulfone (Konwick et al. 2006). Less is known about fipronil sulfone and other degradates, although they are often found at higher concentrations than fipronil in Bay sediments, and both fipronil sulfone and fipronil desulfinyl have been shown to be more stable than fipronil in tissue (Hainzl et al. 1996, Konwick et al. 2006). Both fipronil sulfone and fipronil desufinyl are considered more toxic to fish than fipronil based on EPA aquatic life benchmarks (USEPA 2018). Concurrent monitoring of fipronil and fipronil degradates in sediment and across multiple species and trophic levels in the Bay food web would provide valuable data to fill these gaps in our understanding of the fate of fipronil in the food web.

Data on fipronil and degradates in Bay sport fish can also be used to evaluate the potential for human exposure through consumption of fish. The statewide Sediment Quality Assessment Framework for human health effects currently addresses only PCBs and organochlorine pesticides, but there is interest in potentially expanding it to include CECs; data from this study could be used to assess that need for fipronil and fipronil degradates

(Bay et al. 2017). Additionally, DPR is currently in the process of conducting a human health risk assessment for fipronil, which was triggered in part by low NOELs for acute, subchronic, and chronic exposures in animal toxicity studies. The conceptual model of major fipronil exposure pathways presented in the DPR draft problem formulation document currently does not include seafood consumption as an exposure pathway. Data on exposure risks from this pathway in the Bay would help test the assumption that fipronil and fipronil degradate exposure risk from seafood consumption is negligible. While the USEPA chronic reference dose of 0.0002 mg/kg/day for fipronil is not likely to be exceeded through fish consumption based on the values measured by Maruya et al. (2016), reference doses have not been established for fipronil degradates.

This proposal outlines a study to monitor fipronil, fipronil sulfone, fipronil sulfide, and fipronil desulfinyl in Bay sediment, fish, and harbor seals collected from margin areas that are highly impacted by urban runoff and wastewater effluent. The results from this study will be used to evaluate the bioaccumulation and biomagnification potential of these compounds in the Bay food web, and subsequently assess potential human and wildlife exposures. This information can be used to inform ongoing monitoring of this Moderate Concern chemical and its degradates, as well as DPR's human health risk assessment.

Study Objectives and Applicable RMP Management Questions

The purpose of this study is to conduct a screening of fipronil and fipronil degradates in Bay sediment, fish, and harbor seals to assess the potential for food web biomagnification and human exposure.

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Characterize levels of fipronil and fipronil degradates in the Bay sediment and wildlife tissues.	Characterizing levels of fipronil and fipronil degradates across different species will inform the DPR human health risk assessment for fipronil. Sediment results can be compared to published invertebrate toxicity thresholds to assess toxicity risks. Results can also inform the need to develop additional ecotoxicity or human health toxicity thresholds for both fipronil and its degradates.
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?		

3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	Compare concentrations of fipronil and fipronil degradates in sediment and across aquatic species that occupy different trophic levels and exhibit different life history and feeding strategies.	Biomagnification factors and biota-sediment accumulation factors can be calculated. Comparisons of concentrations across species (i.e., benthic vs. pelagic; detritivore vs. piscivore) may provide insight into fipronil exposure and fate in the Bay food web.
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?		Observed concentrations can be compared to those collected in the future, after recent and/or additional fipronil use mitigation practices have been implemented.
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?		
6) What are the effects of management actions?		Observed concentrations can be compared to those collected in the future, after recent and/or additional fipronil use mitigation practices have been implemented.

Approach

Sample Collection

The objectives of this study are to (1) evaluate bioaccumulation and biomagnification in the aquatic food web, and to (2) characterize potential for human exposure through fish consumption. To address these objectives, fipronil and fipronil degradates will be analyzed in sediment, several fish species that span multiple trophic levels, and harbor seals. Sampling will focus on two sites that are expected to be hot spots for exposure to fipronil and fipronil degradates in the food web (i.e., near wastewater effluent and urban runoff sites).

To address objective #1, sediment, prey fish, sport fish and harbor seal tissue will be collected from two sites, one in Central Bay and one in South Bay. In Central Bay, sediment and fish samples will be collected as part of a planned PCB monitoring study in the Emeryville Crescent priority margin unit (a proposal for this PCB study will be reviewed by the PCB workgroup). In the South Bay, prey and sport fish samples will be collected in the Artesian Slough as part of the 2019 RMP Status and Trends sampling (through Moss Landing Marine Laboratories and a collaboration planned with the City of San Jose). Sediment samples will be collected from the same region as part of regular monthly sampling conducted by the City of San Jose, or taken from archived samples from the 2017 Bay Margins study.

Sediment samples will be collected as subsamples of large surface sediment composites (5 cm depth). Prey fish sampling will target silverside, or topsmelt when silverside are not available; both are high-lipid species commonly found in near-shore regions, and commonly preyed upon by birds and other fish species. Maruya et al. (2016) did not analyze topsmelt in Southern California, and found the highest concentrations of fipronil and fipronil degradates in silverside. Sport fish will include shiner surfperch, another high-lipid, lower-trophic level species that is a benthic feeder, exhibits high site fidelity, and is popularly consumed by anglers at urban fishing locations. These fish samples will be analyzed as 20-fish composites; prey fish will be analyzed as "whole body" tissue, while shiner surfperch will be analyzed whole but with the head, tail, and guts removed. Harbor seal blubber samples will be obtained from Marine Mammal Center archives, and will target individuals sampled at similar locations in Central and South Bay.

To further address objective #2, fish samples from additional species will be collected in the Artesian Slough, which directly receives wastewater effluent from one of the largest wastewater dischargers in the Lower South Bay, as well as local stormwater discharges. Sampling will focus on a) benthic species (i.e., carp, staghorn sculpin) that might be expected to accumulate some of the highest concentrations of fipronil and fipronil degradates due to the partitioning of these compounds to sediment, as well as b) the most popular sport fish species consumed in the Bay (i.e., striped bass). Samples of these additional fish species will be processed and composited according to methods established for RMP Status and Trends studies.

Three samples will be collected for each fish species and sediment at each site (27 samples between two sites). One sediment field duplicate will be collected. Adult harbor seal blubber samples will be taken from archives that may be more widely distributed across similar locations in Central and South Bay (up to 8 samples total). One fish tissue and one harbor seal blubber duplicate sample will be analyzed as well, as a second subsample of a composite or individual seal blubber sample.

Laboratory Analytical Methods

Sediment and fish tissue samples will be processed and subsampled for fipronil analyses by the San Jose State University Research Foundation (Moss Landing Marine Laboratories), together with subsamples processed for the RMP Status and Trends and PCB priority margin unit studies. Archived harbor seal samples will be obtained from the Marine Mammal Center.

Processed samples will be sent to the Southern California Coastal Water Research Project for laboratory analysis. Sediment samples will be analyzed for percent moisture, and tissue samples will be analyzed for percent moisture and percent lipid. Sediment samples will not be analyzed for total organic carbon or grain size, as these will be analyzed in equivalent samples collected for the PCB priority margin units study, or will have been analyzed in previous samples from similar sites via the margins study. Sediment, fish tissue, and harbor seal blubber samples will be analyzed for fipronil and three fipronil degradates (fipronil sulfone, fipronil desulfinyl, and fipronil sulfide) by gas chromatography/electron capture negative ion mass spectrometry (GC/ECNI-MS; Maruya et al. 2016). The target reporting limit is 1 ng/g for a 5 g sample, although reporting limits that are 1-2 orders of magnitude lower are regularly achieved.

Laboratory blanks will be analyzed at a rate of 1 per 20 samples. Laboratory duplicates, and matrix spikes will be analyzed at a rate of 1 per matrix (1 per 6 sediment field samples, and 1 per 30 tissue samples).

Data Interpretation
This study represents an initial screening of fipronil and fipronil degradates. To address objective #1, biomagnification factors will be calculated by comparing fipronil and fipronil degradate concentrations among matrices and trophic positions. To address objective #2, fish tissue concentrations will be used to calculate potential human exposure via consumption, based on consumption rates and frequencies following OEHHA guidelines (Klasing & Brodberg 2008). Concentrations will also be compared across fish species and sites influenced by different contaminant pathways. Data analyses and interpretation will be conducted in consultation with bioaccumulation and risk assessment experts in the EEWG workgroup and at the Office of Environmental Health Hazard Assessment.

Budget

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

Table 2. Proposed Budget.

Expense	**Estimated Cost ($)**
Labor	***57,000***
Fieldwork Planning & Coordination	$10,000
Data Management	$17,000
Reporting	$30,000
Subcontracts	***$21,000***
SCCWRP - up to 42 samples @ $600/sample	$21,000
Direct Costs	***$2,000***
Equipment	$500

Travel	$500
Shipping	$1,000
Grand Total	**$80,000**

Budget Justification

Labor – Fieldwork Planning & Coordination
Fieldwork planning & coordination includes developing of the sampling design, coordinating with two field crews to conduct sediment and fish monitoring (one in Emeryville Crescent and one in Artesian Slough), coordinating harbor seal archive retrieval, and coordinating sample processing and shipments.

Field sampling and equipment costs will be minimized by taking advantage of existing RMP sampling opportunities. The majority of samples will be collected as part of the 2019 RMP Status and Trends monitoring event, or as part of a proposed 2019 RMP PCB workgroup special study that includes fish sampling in Emeryville Crescent.

Labor – Data Management
Data services will include collection and processing of field data and quality assurance for three data sets (sediment, fish tissue, and seal blubber). Sediment data will be uploaded to CEDEN; tissue data will not be uploaded to CEDEN but will be maintained internally and available upon request. Tissue data can be uploaded to CEDEN at an additional $5k cost.

Labor – Reporting
Results will be analyzed and published in a technical report by RMP staff.

Laboratory
Laboratory analytical costs will include analysis of up to 40 environmental samples ($500 per sample) and 4 QA/QC samples (2 laboratory duplicates and 2 CRMs). Laboratory blanks and matrix spikes will be included in the sample cost.

Direct Costs
Equipment costs will cover sampling containers for Artesian Slough sampling and contributions to the PCB sampling effort in Emeryville Crescent. Travel will include visits to each sampling site, as needed. Sample shipping will cover sediment and fish sample shipment from the field crew to SGS AXYS (Emeryville Crescent) or Moss Landing Marine Laboratories (Artesian Slough) for sample analysis, and from these labs to SCCWRP for sample analysis, as well as harbor seal blubber shipment from the Marine Mammal Center to SCCWRP for sample analysis.

Reporting

The primary deliverable will be a technical report. The draft report will be prepared by Fall 2020, and the final report will be prepared by Winter 2020. Data will be reported to SFEI in CEDEN format and reviewed using standard RMP QA/QC procedures. Sediment results will be made publicly available through the RDC on CD3 and CEDEN.

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Special Study Proposal: Sunscreens in Water and Fish

Summary: Ultraviolet (UV) radiation filters (sunscreens) are widely used in sunscreen lotions and other products such as cosmetics, paints, and plastics. In humans, it has been shown that many of these chemicals can be quickly absorbed through skin and circulated throughout the body. For aquatic organisms, the main exposure route is through direct wash-off into surface waters during recreational activities or indirect discharge of these chemicals from wastewater treatment facilities to surface waters. Several sunscreens have been shown to cause adverse effects such as endocrine disruption in fish, and are responsible for significant coral reef bleaching. The City of San Francisco is considering a resolution to examine the occurrence and potential impacts of some of these compounds; to date there have been no studies assessing whether UV sunscreens are detected in Bay fish and water. This study will address that data gap.

Estimated Cost: $127,400

Oversight Group: Emerging Contaminant Workgroup

Proposed by: William Mitch and Djordje Vuckovic (Stanford University), Meg Sedlak and Diana Lin (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	***Due Date***
Task 1. Field collection of fish and water samples	Summer 2019
Task 2. Laboratory analysis of samples	Fall/Winter 2019
Task 3. Review of data	Spring 2020
Task 4. Draft manuscript and management-oriented summary	Summer 2020
Task 5. Final manuscript and management-oriented summary	Fall 2020

Background

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

At present, the US Food and Drug Administration has approved 16 chemicals for sunscreen protection. UV sunscreen chemicals in over-the-counter sunscreen products typically vary between 5 and 20% of the product (Balmer et al. 2005). UV filter sunscreens are also additives to plastic at concentrations of 0.05-2%. These chemicals are widely detected in the environment, and some may biomagnify (Gago-Ferrero et al. 2018). These chemicals are potential endocrine disruptors (Balazs et al. 2016), and there is increasing concern about ecotoxicity (Kunz et al.2006; Balmer et al. 2005; Downs et al. 2016).

Oxybenzone (also known as benzophenone-3 or BP-3) is of high concern due to its wide use in the U.S., detection in the environment, and its potential for endocrine disruption. In a recent study of personal care products, oxybenzone was detected in over 80 percent of the products analyzed (Liao and Kannan 2014); oxybenzone is a High Production Volume Chemical that is manufactured or imported into the U.S. in amounts great than one million pounds per year. Oxybenzone has been detected in surface water, treated wastewater, invertebrates, fish, bird eggs, and coral tissue (Liao and Kannan 2014). It has been identified as an endocrine disruptor in fish, causing a significant increase in testosterone and a corresponding decrease in 17-beta estradiol, with a significant reduction in egg production (Kim et al. 2014). In a laboratory study of zebrafish, a significant skewing of the sex ratio and gonad maturation was observed (Kinneberg et al. 2015). Exposure to oxybenzone in another laboratory study of zebrafish caused mortality, unsuccessful hatching, and structural malformations such as deformed tails, impaired development of the jaw, and lack of swim bladder inflation (Balazs et al 2016).

Due in part to the potential for endocrine disruption and other deleterious effects in fish, and the ability for these compounds to cause coral bleaching, there is currently regulatory interest in restricting their use. A bill was recently introduced in Hawaii that would have banned oxybenzone due to exceedances of an ecological toxicity threshold for coral in water; however, the bill did not pass. The City of San Francisco is considering a resolution stating concerns about sunscreen chemicals oxybenzone, octinoxate, and butylparaben (a preservative) that are implicated in coral reef die-offs and potential endocrine disruption. City officials are interested in knowing whether these chemicals are detected in the Bay; this project would address this question.

We are proposing to analyze Bay surface water and sport and prey fish for sunscreens including oxybenzone, octinoxate, and butylparaben. We will target a variety of fish collected primarily from the Lower South Bay and South Bay. We are focusing on the South Bay as pollutant concentrations tend to be higher due to the limited flushing that occurs in this area.

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

Study Objectives and Applicable RMP Management Questions

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	To identify whether sunscreens are detected in Bay water and fish.	Identifying the presence of sunscreens in the Bay will be important for determining whether there is a potential problem and for assessing the need for management actions.
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	This study will assess whether discharge of effluent is a possible source of sunscreen chemicals to fish.	The study will provide information to help assess the need for pollution prevention activities.
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?	Stanford researchers are evaluating the mechanism of toxicity; the outcome of this independent project can inform interpretation of an RMP study.	This information may be useful for pollution prevention purposes.
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?		This study will provide baseline information that can be used to determine whether sunscreens may be an issue of concern to Bay organisms.
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?		
6) What are the effects of management actions?		This study will provide a baseline to evaluate future management actions.

Approach

Sport Fish Sample Collection

We are proposing to collect sport fish as part of the RMP 2019 sport fish summer collection event. We will primarily focus on the southern portion of the estuary (e.g., Alviso Slough, and Lower South Bay) due to the limited circulation and the tendency to observe higher concentrations of anthropogenic contaminants in fish from this area. We will choose one site in the Central Bay in close proximity to a prey fish site.

The RMP targets approximately 16 species of sport fish; however, not every species is present at every site. Several species, such as striped bass and shiner surfperch, are collected at most sites. In addition to these species, if possible, we will collect white croaker, jack smelt, sculpin, carp, and anchovies. These fish represent a variety of trophic levels, habitat (near shore vs. pelagic), site fidelity and foraging behaviors. We will analyze approximately 30 sport fish composites.

Prey Fish Sample Collection

We will conduct fish seining at three recreational beaches and one wastewater influenced site to collect small prey fish. Sites will be selected to examine the impacts of direct washoff of sunscreens (recreational beaches) and exposure to effluent (wastewater-influenced site). We will collect 3 composites of 10 fish at each of these sites (i.e., 4 sites; 3 composites; 12 samples). We will target a pelagic species such as topsmelt and a more benthic species such as Bay gobies.

Water and Wastewater Sample Collection

Wastewater effluent is a known pathway for these chemicals; in addition, sunscreens may be directly washed off through recreational activities. We will collocate water samples with the sport fish and prey fish sampling sites and will collect 12 water samples at the following locations: three near effluent discharge locations in Lower South Bay (e.g., Alviso Slough, Palo Alto, and a South Bay location TBD); three near popular recreations beaches (e.g. China Camp, Marin; Crowne Beach, Alameda; and Aquatic Park, San Francisco); and six in the South Bay / Lower South Bay near the sportfish collection sites. Collocated water samples will be collected as part of the sport fish/ prey fish collection events. SFEI staff will collect the surface water samples near effluent discharge locations. We will collect unfiltered water samples.

In addition, we intend to analyze wastewater effluent directly for sunscreens prior to conducting field events to determine whether the concentrations in effluent are sufficient to detect sunscreens in the Bay. We anticipate analyzing effluent from two facilities.

Sample Analysis

The target analyte list will at a minimum include: oxybenzone, octinoxate, and butylparaben. At present, the laboratory is confirming the analyte list (Table 2). Oxybenzone is the priority analyte because it is one of the most widely used sunscreens and has significant ecotoxicity concerns. Moisture and lipid content for sport fish and prey fish will be determined based on data available from the RMP sportfish analyses.

Data Analysis

We will compare the surface water and fish tissue concentrations to literature values to determine whether the levels are of concern. In addition, we will calculate bioaccumulation factors based on concentrations observed in surface water and fish.

Table 2. Potential Target Analytes

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

Budget Justification

Table 3. Proposed Budget.

Personnel	SFEI	Stanford/ MLML
Sample design, coordination, and assistance with SAP	$15,000	
Fieldwork (fish, water, effluent)	$10,600	$16,200
Laboratory Analyses (Stanford)		$35,400
Reporting (manuscript and summary)	$22,000	$10,000
Data Technical Services	$17,000	
Direct costs (shipping, field supplies, travel)	$1,200	
Total	**$127,400**	

Field Costs
Field costs will be leveraged through the RMP Status and Trends sport fish work. SFEI staff will collect the effluent and some of the water samples. Small fish and some water samples will be collected by Moss Landing Marine Laboratories (MLML).

Reporting Costs
Preparation of a draft manuscript for publication in a peer-reviewed journal will be the responsibility of the analytical partners with assistance from RMP staff. We have allocated $10,000 to the analytical partners for the preparation of a manuscript. After the manuscript is complete, RMP staff will produce a management oriented summary to describe the results and their implications for RMP stakeholders and the general public.

Laboratory Costs
The laboratory costs are a fixed budget of $35,400 for the analysis of the 30 sport fish, 12 prey fish, 12 water, and 2 effluent samples plus 12 QA samples (e.g., field blanks and duplicates).

Data Management Costs
Data management and upload to CEDEN will be conducted for fish and water samples.

Reporting

Deliverables will include: a) a draft manuscript that serves as an RMP technical report due Fall 2020; b) a management-oriented summary describing the results and their implications due Fall 2020; and c) additions to other RMP publications such as the Pulse.

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Special Study Proposal: Assessing Novel Persistent and Bioaccumulative Contaminants in San Francisco Bay: Implication for Human and Wildlife Exposure

Summary: To leverage RMP funds, we have sought external support for a non-targeted analysis of Bay tissue samples, originally planned for 2020 according to the RMP's approved Multi-Year Plan. We have outlined a three-year project and are requesting $250,000 from Sea Grant; matching funding of $75,000 over three years is requested from the RMP. The proposed study will employ a novel non-targeted analytical approach to examine samples of Bay sport fish to identify a broad array of persistent and bioaccumulative contaminants of emerging concern (CECs). Analysis of cormorant eggs and harbor seals will be used to assess the potential for biomagnification of these CECs in the food web. Comparison of the contaminant profiles of fish species with different feeding habits and collected from different sites in the Bay will be used to identify pollution hotspots. Insights about the potential sources and pathways of these CECs may be obtained through comparison with findings from an ongoing RMP study of near-shore sediment samples collected from San Francisco Bay. Results will be presented to the RMP's ECWG, EEWG, and Sport Fish Strategy team. Potential outcomes may include the development of fish consumption advisory tissue levels for newly identified contaminants, follow-up research from the scientific community to fill targeted data gaps, and pollution prevention activities.

Estimated Cost: RMP match $75,000 over three years ($25,000 per year)
Cal Sea Grant Proposal $250,000 over three years

Oversight Group: ECWG

Proposed by: Eunha Hoh and Nate Dodder (San Diego State)
Rebecca Sutton and Meg Sedlak (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Field collection of samples	Summer 2019
Task 2. Laboratory analysis of samples	Fall – Winter 2019
Task 3. Review data and prepare preliminary report of findings	Spring 2020
Task 4. Present findings to ECWG, EEWG, and Sport Fish Strategy Team and solicit feedback	Spring 2020
Task 5. Additional contaminant review based on expert feedback	Summer – Fall 2020
Task 6. Draft manuscript and fact sheet	Spring 2021
Task 7. Final manuscript and fact sheet	Fall 2021

Background

The Principal Investigators have submitted a three-page pre-proposal, "Assessing Novel Persistent and Bioaccumulative Contaminants in San Francisco Bay: Implication for Human and Wildlife Exposure" (attached), to USC Sea Grant in response to the Ocean Protection Council Prop 84: USC Competitive Grants Program call. Pre-proposals are undergoing review now, and the program will announce its decision as to which should be developed into full proposals in June. Full proposals will be due August 1, 2018, and those selected for funding will be announced by November. Funding is awarded in December.

According to the Multi-Year Plan for the ECWG, a non-targeted analysis of Bay tissue samples is scheduled for the year 2020. To best leverage precious RMP funds, we have sought external funds for this element of the strategy. We have outlined a three-year project and are requesting $250,000 from Sea Grant to conduct non-targeted analyses of Bay samples (see attached pre-prepoposal for details). However, State funding does not fully cover our costs due to the low multiplier so we are requesting matching funds of $75,000 over three years from the RMP, for a total project budget of $325,000.

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?	Identify unexpected contaminants in Bay sport fish, cormorant egg, and harbor seal blubber, and review available toxicity information in the scientific literature. Evaluate future monitoring needs and toxicity data gaps.	Which newly identified contaminants merit further monitoring? Which merit management actions to prevent pollution or reduce risk (e.g., development of risk-based thresholds such as advisory tissue levels)?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Determine whether hot spots of contamination exist. Compare tissue contaminants to those present in the RMP's 2018 special study of margin sediment, to see if inferences can be made about potential sources or pathways.	What are the key pathways that impact concentrations and potential risk of emerging contaminants? Does influence of these pathways explain any hot spots observed in the samples?
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?	Determine whether any of the newly identified contaminants biomagnify in the Bay food web.	Do contaminants that biomagnify in the Bay food web merit examination with respect to human exposure and health concerns?

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

Budget

Budget Justification (Table 2)

Leveraged Funding Opportunity
If we are successful in obtaining a Sea Grant for $250,000, we will have been able to substantial leverage the amount of funding we are requesting from the RMP. At present, we are asking the RMP to help enhance the project deliverables as well as cover the shortfall from the low multiplier that the State requires.

Field Costs
Field costs are minimized by leveraging the RMP 2019 sport fish and 2018 (archived) cormorant egg sampling efforts. Experienced contractors will be employed for harbor seal blubber (Moss Landing) and reference Tomales Bay sediment (Coastal Conservation & Research) sample collection. The budget includes staff hours to aid in drafting the sport fish sampling and analysis plan and to assist in the harbor seal and reference sediment sample collection events.

Laboratory Costs
The RMP will benefit from prior negotiations to reduce the indirect costs charged by San Diego State, from 50.5% to 25%. The RMP is funding margin sediment non-targeted analysis through a 2018 special study; the information generated in this project can inform interpretation of the findings generated by the proposed project.

Reporting Costs
Preliminary data will be presented to three separate RMP advisory groups, the ECWG, the EEWG, and the Sport Fish Strategy Team. A single, preliminary report will be prepared; this report is anticipated to require more extensive analysis than a report prepared for a single advisory group. RMP staff also anticipate significant participation in writing of the manuscript, and will lead the preparation of the fact sheet.

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

Table 2. Estimated costs for a three-year project to analyze Bay tissue samples for persistent and bioaccumulative contaminants using non-targeted analysis.

Expense	Estimated Hours	Estimated Cost
Labor		
Project Staff	690	117,200
Senior Management Review	40	9,000
Project Management	40	6,800
Contract Management	20	3,800
Data Technical Services		0
GIS Services	18	2,000
Creative Services	60	7,500
IT Services		0
Communications	32	6,000
Operations		0
Subcontracts		
Name of contractor		
Moss Landing Marine Lab (harbor seal capture)		25,000
Coastal Conservation & Research (reference sediment)		15,000
San Diego State - Non-targeted analysis		120,000
Additional peer review		4,000
Direct Costs		
Equipment		2,000
Travel		3,200
Printing		500
Shipping		3,000
Other		0
Grand Total		325,000

Reporting

Preliminary findings will be reported to the ECWG, the EEWG, and the Sport Fish Strategy Team. Final deliverables include a journal manuscript and a fact sheet. Findings from the project may also be summarized in other RMP documents, such as the Pulse of the Bay.

Attachment

The following attachment is a three-page pre-proposal, "Assessing Novel Persistent and Bioaccumulative Contaminants in San Francisco Bay: Implication for Human and Wildlife Exposure," submitted on March 15^{th} to USC eSeaGrant in response to the Ocean Protection Council Prop 84: USC Competitive Grants Program call.

Pre-proposal submitted to USC Sea Grant on March 15, 2018

1. Project Summary or Abstract

Sport fish in the San Francisco Bay are exposed to pollution derived from the surrounding urban landscape, and are consumed by people, particularly in low-income and immigrant communities, as well as by apex predators like cormorants and harbor seals. Routine sport fish contaminant monitoring and human health fishing advisories focus on just eight contaminants; investigations of wildlife collected from highly urbanized coastal southern California sites indicate that these regularly monitored contaminants make up a small fraction of the total number of bioaccumulative contaminants present in tissue. The proposed study will employ a novel non-targeted analytical approach to examine samples of Bay sport fish to identify a broad array of persistent and bioaccumulative contaminants of emerging concern (CECs). Analysis of cormorant eggs and harbor seals will be used to assess the potential for biomagnification of these CECs within the foodweb. Comparison of the contaminant profiles of fish species with different behavior and feeding habits and collected from different sites in the Bay will be used to identify pollution hotspots. Information about the potential sources and pathways of these CECs will be obtained through comparison with findings from the PIs' ongoing study of near-shore sediment samples collected from San Francisco Bay. Results will be presented to established committees of international experts and local stakeholders with expertise in CECs, ecotoxicology, and sport fish monitoring and consumption risks. Potential outcomes may include the development of fish consumption advisory tissue levels for newly identified contaminants, follow-up research from the scientific community to fill targeted data gaps, and/or pollution prevention activities. A successful demonstration for the San Francisco Bay could lead to later use of this general approach across the state.

2. Background

As the largest estuary on the western coast of the Americas, San Francisco Bay provides habitat for numerous populations of fish and wildlife living in the midst of an urban area supporting seven million people. The Bay receives continuous inputs of pollutants including CECs from the surrounding urban environment, trapping persistent chemicals and potentially exposing inhabitants to increased risks. Some Bay Area residents, particularly from low-income and immigrant communities, regularly consume sport fish caught from the Bay; this important protein source can expose them to contaminants. State and local entities take steps to reduce human health risks relating to eight contaminants in sport fish, including posting of fish advisories at popular fishing sites. Regular Bay sport fish monitoring for these advisories is conducted by the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP), a collaboration among the Regional Water Quality Control Board, the regulated discharger community, and independent scientists of San Francisco Estuary Institute. The RMP also monitors the Bay for CECs; studies of Bay sport fish have detected persistent and bioaccumulative halogenated organic compounds (HOCs), including polybrominated diphenyl ethers [1], perfluoroalkyl substances [2], and polyhalogenated carbazoles [3]. People who regularly eat Bay sport fish are likely exposed to these, as are apex predators such as cormorants and harbor seals. Are other, as yet unidentified HOCs accumulating in Bay sport fish consumed by humans and wildlife? Which of these HOCs might pose the greatest risk to human and non-human populations? Are there hotspots of contamination within the Bay? Our recent study of bottlenose dolphin blubber from coastal Southern California, habitat with a similarly strong urban influence, identified more than 300 HOCs, excluding regularly monitored legacy contaminants like DDTs and PCBs [4]. Eighty-six percent of the HOCs, including 133 anthropogenic chemicals and 41 natural products, are not regularly monitored [4]. We expect that there are many similarly unmonitored HOCs in San Francisco Bay. Because regularly monitored contaminants represent a small subset of full contaminant exposure, many unknown or unrecognized contaminants with the potential to cause physiological harm fall outside routine ecosystem monitoring efforts.

3. Project Goals and Objectives

The goal of this study is to use an innovative non-targeted analytical approach to identify the presence of unexpected HOCs typically not monitored in San Francisco Bay sport fish, cormorants and harbor seals and to assess the potential for human and wildlife exposures.

Objective 1: Identify typically unmonitored HOCs in sport fish in San Francisco Bay.

Objective 2: Evaluate their biomagnification potential through food chains in San Francisco Bay.

Objective 3: Test if there are distinguishable differences in the HOC profiles among sport fish with different diets and habits (feeding in benthic vs. pelagic zones; species with high site fidelity vs. those with wide-ranging, ocean-migrating habits).

Objective 4: Determine spatial difference of HOC profiles (South, Central, and North San Francisco Bay, as well as Tomales Bay) to identify hotspots of pollution.

Objective 5: Determine potential sources and pathways of HOCs by comparison with those identified in ongoing collaboration among the PIs to analyze sediment from San Francisco Bay.

4. Methods

<u>Sample Collection</u>

Samples include sport fish, cormorant eggs, harbor seal blubber, and sediment (Table 1). Sport fish samples will be obtained by leveraging the RMP's 2019 sport fish sample collection effort. Three species will be targeted: Shiner surfperch (*Cymatogaster aggregata*), an abundant and popular benthic-feeding sport fish that exhibits high site fidelity, useful for assessing regional differences; striped bass (*Morone saxatilis*), a popular sport fish that provides an integrated signal for higher trophic predators due to its wide-foraging behavior and opportunistic consumption of prey fish; and northern anchovy (*Engraulis mordax*), an abundant sport fish that is prey for larger fish and predators. Samples will be collected at up to three popular fishing sites within the Bay (Figure 1). Additional samples will be collected at a reference site with relatively low urban influence, Tomales Bay (Figure 1).

Cormorant (*Phalacrocorax auritus*) egg samples will be obtained by leveraging the RMP's 2018 sample collection effort. Samples will be obtained from three regularly monitored sites (Figure 1): Richmond Bridge (Central Bay), Wheeler Island (Suisun Bay/Delta), and Don Edwards Wildlife Refuge (South Bay). Harbor seal (*Phoca vitulina*) blubber samples will be collected during capture events in two locations (Figure 1), a seal colony in the South Bay (Corkscrew Slough), and a reference site (Tomales Bay). Finally, an ongoing study funded by the RMP, to identify CECs in sediment collected from near-shore sites in the southern Bay, will be supplemented through analysis of samples collected at the reference site, Tomales Bay (Figure 1).

Chemical Analysis

Analysis of HOCs will be performed using previously developed and successfully implemented extraction, cleanup, and non-targeted instrumental methods [4-9]. Final extracts will be analyzed using a LECO Pegasus 4D comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC/TOF-MS) system. The non-targeted analysis generates large datasets with thousands of mass spectra per sample. Therefore, we recently developed and optimized a filtering algorithm to isolate HOCs from the thousands of other chromatographic peaks and associated mass spectra (Figure 2). The filtration reduces the dataset size to approximately 5% of the original (Figure 3) and substantially reduces the time required for manual validation of the mass spectra identities. Contaminant loads and profiles will be analyzed via statistical comparisons (hierarchical clustering, K-means clustering, and principal components analysis).

5. Project Outcomes (to science, specific communities, regulators or the general public)

HOCs identified will be prioritized based on the level of confidence in the identification as well as the frequency and intensity of contaminant signals, and will be reviewed by three RMP advisory panels including leading international experts. The RMP's Emerging Contaminants Workgroup uses a risk-based framework to classify CECs in the Bay and recommend monitoring and management actions [10]. The RMP's Exposure and Effects Workgroup focuses on the biological impacts observed in the Bay, and is informed by top ecotoxicologists. The RMP's Sport Fish Strategy Team guides targeted contaminant monitoring in fish in coordination with the California Office of Environmental Health Hazard Assessment (OEHHA), the agency charged with developing risk-based fish consumption guidance and advisories. By bringing the diverse, independent expertise of these established RMP groups to bear, a risk-based review of the newly identified Bay contaminants would allow for prioritization of those suspected of the greatest potential for harm to people or wildlife. Should a contaminant identified in the proposed study be a human health risk with an established oral reference dose, OEHHA could establish an advisory tissue level that would be used in advisories about the safety of consuming different species of fish. For HOCs with major data gaps, significant detections in San Francisco Bay would be likely to spur additional, independent research within the scientific community.

A successful demonstration for the San Francisco Bay could lead to later use of this general approach across the state. By focusing on sport fish, we target a matrix with direct impacts to both people and wildlife who consume Bay fish. In the Bay Area, residents who regularly eat these fish include members of low income and immigrant communities; assuring the safety of these fish is important for the health of these vulnerable populations, and is essential to protecting fishing as a beneficial use of the Bay. Findings from this study will be disseminated to: 1) state agencies and programs involved in pollution prevention, including California's unique Safer Consumer Products Program; 2) the RMP stakeholder community of over 1,000 local decision-makers, including water quality managers within the regulatory and regulated communities; and 3) the general public. Where detected CECs can be linked to potential sources or uses, pollution prevention efforts may be possible, with consumer education or regulatory activities undertaken by informed entities.

Pre-proposal submitted to USC Sea Grant on March 15, 2018

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Table 1. Proposed samples: species, tissue type, sampling location, number of samples, and composite or not for contaminant analysis. *Tail, head, and viscera removed.

Matrix	Species	Tissue type	Site Locations	Number of Samples/Site	Composite
Fish	Shiner surfperch (popular sportfish)	Whole fish*	South Bay	5	Yes
			San Leandro Bay	5	
			Tomales (reference)	3	
	Striped bass (popular sportfish)	Fillets (skin off)	South Bay	5	Yes
			San Leandro Bay	5	
			Oakland/ SF Waterfront	5	
			Tomales (reference)	3	
	Anchovy (prey fish, also popular sportfish)	Whole fish*	South Bay	5	Yes
			San Leandro Bay	5	
			Tomales	3	
Pinnepeds	Harbor seal	Blubber	South Bay	10	No
			Tomales (reference)	3	
Birds	Cormorant	Egg	South Bay	2	Yes
			Central Bay	2	
			Delta	2	
Sediment		Sediment	South Bay margins	35	No
			Tomales (reference)	3	

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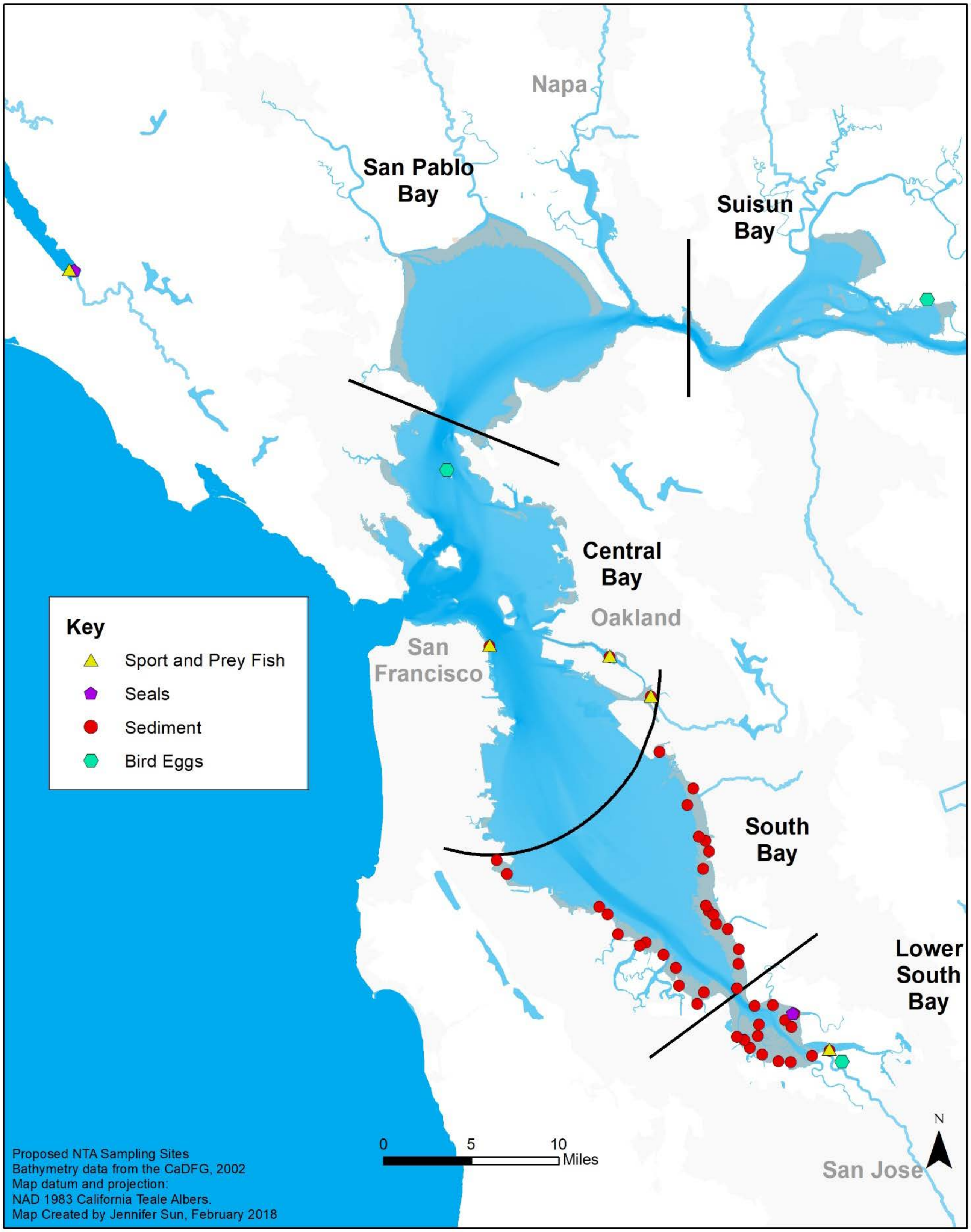

Figure 1. Proposed sampling sites in San Francisco Bay.

Pre-proposal submitted to USC Sea Grant on March 15, 2018

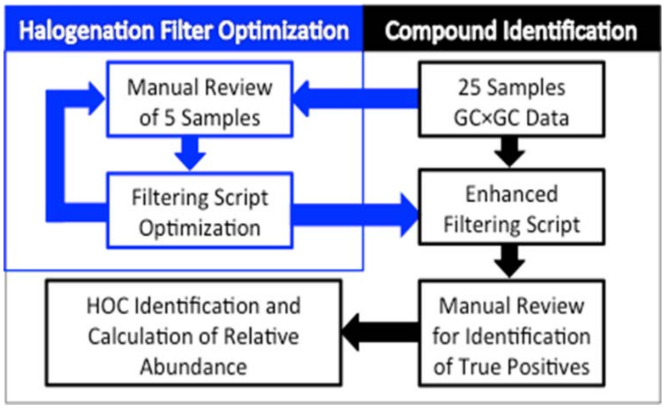

Figure 2. GC×GC/TOF-MS data analysis scheme implemented with the filtering script to automatically select mass spectra of HOCs.

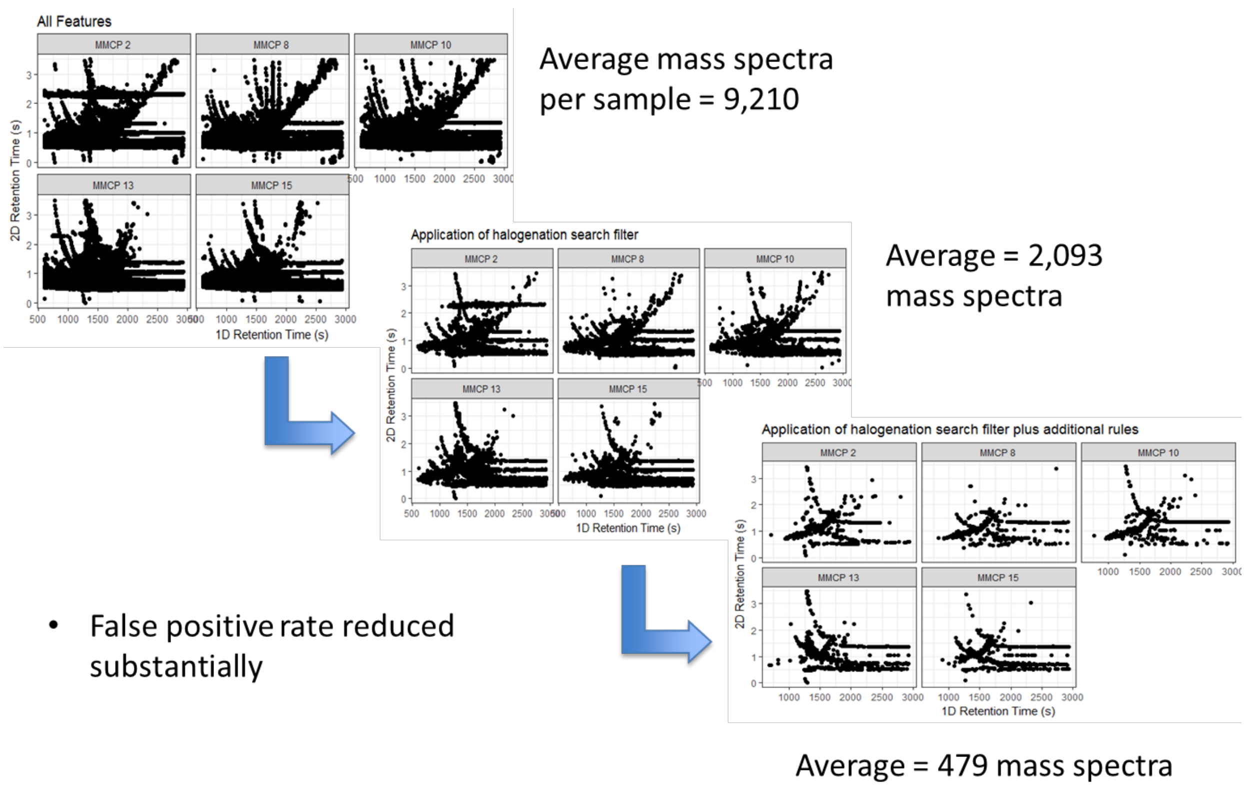

Figure 3. Data reduction of mass spectra by the filtering script. The script isolates compounds containing halogens.