RMP Emerging Contaminants Workgroup Meeting

April 23-24, 2020
10:00 AM – 1:00 PM

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DAY 1 AGENDA - April 23rd

1.	**Introductions and Goals for This Meeting** The goals for this meeting: ● Provide updates on recent and ongoing ECWG activities (today) ● Obtain feedback on draft 2020 CEC Strategy Update, including discussion of persistence as a secondary factor in assigning CECs to tiers within the risk-based framework (today) ● Discuss potential strategy to use predictive toxicology in evaluating the risk of data-poor CECs, and develop a consensus for next steps (today) ● Discuss program review of Status and Trends monitoring (tomorrow) ● Recommend which special study proposals should be funded in 2021 and provide advice to enhance those proposals (tomorrow) Meeting materials: 2019 ECWG Meeting Summary pages 5-20	10:00 Melissa Foley

2.	**Discussion: CEC Strategy Update** (Attachment) • Review of current RMP and related activities (20 min) • Discuss persistence as a secondary factor in assigning CECs to tiers within the risk-based framework (40 min) Desired Outcome: Feedback on the draft 2020 CEC Strategy Update, including consensus on whether to consider persistence as a secondary factor Deadline for comments on draft Update: May 29, 2020 Meeting materials: Draft 2020 CEC Strategy Update	10:15 Rebecca Sutton
3.	**Discussion: CEC Toxicology Strategy** (Attachment) A potential strategy to use predictive toxicology in evaluating the risk of data-poor CECs is presented in the draft 2020 CEC Strategy Update. Potential refinements to the proposed strategy and next steps will be discussed after the break (Item 3b). Desired Outcome: Feedback on the toxicology strategy, consensus on next steps Deadline for comments on draft Update: May 29, 2020 Meeting materials: Draft 2020 CEC Strategy Update; RMP webinar materials https://www.sfei.org/events/sf-bay-rmp-webinar-introduction-predictive-toxicology	11:15 Ezra Miller
	Short Break	11:30
3.	**Discussion: CEC Toxicology Strategy** (Attachment) A potential strategy to use predictive toxicology in evaluating the risk of data-poor CECs is presented in the draft 2020 CEC Strategy Update. Potential refinements to the proposed strategy and next steps will be discussed. Desired Outcome: Feedback on the toxicology strategy, consensus on next steps Deadline for comments on draft Update: May 29, 2020 Meeting materials: Draft 2020 CEC Strategy Update; RMP webinar materials https://www.sfei.org/events/sf-bay-rmp-webinar-introduction-predictive-toxicology	11:45 Ezra Miller
4.	**Discussion: Update on Monitoring of CECs in Urban Stormwater** Review of pilot year study findings, including adjustments to study design as a result of initial results. A major focus will be the preliminary findings on per- and polyfluoroalkyl substances (PFAS). Desired outcome: Informed Workgroup	12:20 Rebecca Sutton
	Adjourn	1:00

DAY 2 AGENDA - April 24th

5.	**Summary of Yesterday and Goals for Today** The goals for today's meeting: ● Brief recap of yesterday's discussions and outcomes ● Discuss potential changes to Status and Trends monitoring ● Recommend which special study proposals should be funded in 2021 and provide advice to enhance those proposals	10:00 Melissa Foley
6.	**Information: Status and Trends Monitoring Review** The RMP will be reviewing its Status and Trends study design, in part motivated by the anticipation of increased prioritization of CECs monitoring as part of Status and Trends activities. CEC-specific considerations to inform study design are needed. Desired Outcome: Informed Workgroup	10:10 Melissa Foley
7.	**Summary of Proposed ECWG Studies for 2021** 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. 2021 Special Study Proposals include: ● CECs in stormwater (year 3 of 3) ● PFAS in Bay water ● Seasonal influence on concentrations of bisphenols and organophosphate esters in Bay water ● Toxicology strategy followup ● PFAS in North Bay margin sediment (archived samples; lower priority) ● Azo dyes in South Bay margin sediment (archived samples; lower priority) ● Non-targeted analysis of harbor seal tissues for perfluorinated and nonpolar contaminants (archived samples; lower priority) Meeting materials: ECWG 2021 Special Studies Proposals, pages 21-52	10:20 Rebecca Sutton, Miguel Mendez, Ezra Miller, Diana Lin
	Short Break	11:20
8.	**Discussion of Recommended Studies for 2021 - 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.	11:30 Melissa Foley
9.	**Discussion of Recommended Studies for 2021 - Prioritization** The workgroup will consider the studies as a group, ask questions of the Principal Investigators, and begin the process of prioritization by stakeholders.	12:15 Melissa Foley

10.	**Closed Session - Decision: Recommendations for 2021 Special Studies Funding** RMP Special Studies are identified and funded through a three-step process. Workgroups recommend studies for funding to the Technical Review Committee (TRC). The TRC weighs input from all the workgroups and then recommends a slate of studies to the Steering Committee (SC). The SC makes the final funding decision. For this agenda item, the ECWG is expected to decide (by consensus) on a prioritized list of studies to recommend to the TRC. To avoid an actual or perceived conflict of interest, the Principal Investigators for proposed special studies are expected to leave the meeting during this agenda item. Desired Outcome: Recommendations from the ECWG to the TRC regarding which special studies should be funded in 2021 and their order of priority.	12:30 Karin North
11.	**Report out on Recommendations**	12:50 Karin North
	Adjourn	1:00

FINAL

RMP Emerging Contaminants Workgroup Meeting

April 11-12, 2019
San Francisco Estuary Institute
4911 Central Avenue, Richmond, CA

Meeting Summary

Science Advisors	Affiliation	Present
Lee Ferguson	Duke University	Yes
Kelly Moran	TDC Environmental	Yes
Derek Muir	Environment and Climate Change Canada	Remote (phone)
Heather Stapleton	Duke University	Yes
Bill Arnold	University of Minnesota	Yes
Miriam Diamond	University of Toronto	Yes

Attendees

Robert Wilson (City of Petaluma)
Abigail Noble (DTSC)
Anne Cooper Doherty (DTSC)
Eunha Hoh (San Diego State University)
Erica Kalve (SFBRWQCB)
Heather Bischel (UC Davis)
Mary Lou Esparza (CCSD, Central San)
Simret Yigzaw (City of San Jose)
Holly Wyer (CA Ocean Protection Council)
Luisa Valiela (EPA, Region 9)
Karin North (City of Palo Alto)
Tum Mumley (SFBRWQCB)
Shoba Iyer (OEHHA)
Jennifer Teerlink (CA DPR)
Lorien Fono (BACWA)
Artem Dyachenko (EBMUD)
Terry Grim (Cambridge Isotope Laboratories)
Heather Peterson (SFPUC)
Charles Wong (University of Winnipeg)
Keith Maruya (SCCWRP)
Anne Hansen (City of San Jose)
Dawit Tadesse (SWRCB)
Maggie Monahan (SFBRWQCB)
June-Soo Park (DTSC)
Miaomiao Wang (DTSC)
Richard Looker (SFBRWQCB)
Eric Dunlavey (City of San Jose)
Reid Bogert (San Mateo Pollution Prevention)
Bill Mitch (Stanford University)
Dave Williams (BACWA)
Jay Davis (SFEI)
Alicia Gilbreath (SFEI)
Melissa Foley (SFEI)
Rebecca Sutton (SFEI)
Liz Miller (SFEI)
Don Yee (SFEI)
Ila Shimabuku (SFEI)
Diana Lin (SFEI)
Nina Buzby (SFEI)

Remote Attendees:
Simona Balan (DTSC)
Chris Sommers (BASMAA)

Remote Attendees (contd.)
Denise Greig (California Academy of Sciences)
Greg LeFevre (University of Iowa)
Ed Kolodziej (University of Washington)
Richard Grace (SGS AXYS)
Lisa Sabin (Santa Clara Stormwater; BASMAA) Scott Coffin (SWRCB)

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

DAY ONE - April 11

1. Information: Introduction and Goals

Melissa Foley began the meeting with a brief background on the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) by outlining the program's goals, history, management questions, and monitoring structure. Melissa then gave a quick introduction of the Workgroup advisors, and allowed time for everyone in the room to introduce themselves.

Melissa's presentation outlined the goals of the meeting and noted the financial context behind special studies funding. The current Multi-Year Plan includes studies that amount to 150% of the available budget. The meeting participants were advised that only the top ~70% of prioritized studies will likely receive RMP core funds. Melissa then gave a short overview of the ECWG daily agendas and related each item to the overarching meeting goals.

2. Discussion: CEC Strategy Update

Rebecca Sutton gave an update on CEC efforts and strategy, including an overview of current activities, monitoring priorities for Low and Possible Concern contaminants, as well as future plans. Additionally, meeting attendees welcomed a new ECWG team member: Liz Miller.

Rebecca's outline of current CEC activities categorized efforts into three strategic elements: (1) targeted monitoring work, (2) learning from others/sharing expertise, and (3) non-targeted analysis (NTA) monitoring. Multiple projects were noted for each element. As an example of targeted monitoring work, the meeting participants were presented with preliminary data from the 2019 pilot stormwater monitoring. Rebecca also noted a few deliverables that would be finalized in the near future, such as the NTA factsheet describing the 2016 RMP study on Bay water and wastewater.

The tiered risk framework is less prescriptive regarding follow-up monitoring recommendations for contaminants in the Low and Possible Concern categories. Meeting participants were asked to react to SFEI's rationale to deprioritize or continue to periodically monitor specific contaminants. All such recommendations were posed in a strategy memo circulated to the workgroup prior to the meeting.

For both the Low and Possible Concern monitoring rationale tables, attendees suggested adding a column that outlines possible management outcomes that would be aided by continued monitoring. Additionally, there was discussion that some chemical classes (e.g., personal care and cleaning products, PFAS) may be too broad. Suggestions included: 1) adding CAS (Chemical Abstracts Service) registration numbers specific to individual chemicals within the classes; 2) creating more explicit subcategories; 3) creating two sets of tables, one that includes more technical chemical names and another with communication-friendly descriptions; and/or 4) adding explanatory footnotes to the existing tiered risk framework.

Comments that differed from the rationale SFEI presented to deprioritize or continue to periodically monitor specific contaminant are as follows. Meeting participants agreed with the suggestion to off-ramp pyrethroid monitoring in the Bay, with a note that they still are a concern in tributaries; possibly continuing PBDD/F monitoring given recent wildfires; and not deprioritizing paraffin monitoring. Meeting attendees arrived at this final suggestion because only short-chain paraffins have been targeted for analysis in the Bay and medium- and long-chain chlorinated paraffins are used in large volumes globally.

In the discussion of Possible Concern contaminants, Miriam Diamond questioned the efficacy of targeted analysis of compounds given the large number of contaminant degradates and emerging replacements, giving the example of the PFAS class. She noted that it might be worth investigating analytical methods that allow species group detection, e.g., total organic halogens (TOX). The TOP assay for PFAS and total organic fluorine measurements (TOF) were suggested examples. Lee Ferguson suggested the following two analytical techniques were some of the best current options if these by-class analyses were to be pursued: (1) a jump in sensitivity using a cryoprobe with high-field nuclear magnetic resonance to quantify PFAS at a ng or lower level; and (2) coupling fluorine mass-defect-based detection against a superset database generated from annotating PubChem to identify PFAS that are lacking existing chemical standards, i.e., GenX ether compounds. This discussion ended with the idea that such efforts will be dependent on how chemical classes are defined and what level of specificity is needed to accurately support management actions.

The lists of Low and Possible Concern contaminants include many contaminants without proposed monitoring actions, pending new data specifically related to toxicity. Rebecca Sutton noted that looking into predictive toxicology resources would be beneficial for filling these gaps and informing future contaminant listing suggestions. Rebecca highlighted two existing methods - ECOSAR and in vitro high-throughput screening assays - that could be helpful. Additionally, Rebecca suggested holding a webinar on predictive toxicology with top experts to inform workgroup members, and help establish next steps. Meeting attendees were supportive of this idea and suggested including the following toxicity tools: the EPA Chemistry and ToxCast Dashboards, Chemical Hazard Data Commons, and the ToxEVAL R-package (Derek Muir suggested ToxPi GUI via email). Tom Mumley was in support of the webinar, but noted that it should be treated as a stepping stone to developing a more robust toxicology strategy.

Discussion around study prioritization led the group to deliberate on the trade-off between prioritizing moderate concern contaminant monitoring and having less resources for exploratory work. The group decided that contaminant persistence, toxicity, and relevance to management action are important factors to consider during prioritization. Miriam Diamond suggested considering persistence as a key parameter (Derek Muir also noted this approach via email).

3. Information: Bisphenols (BPs) and Organophosphate Esters (OPEs; Flame Retardants) in Bay Water

Ila Shimabuku presented recent results on organophosphate esters (OPEs) and bisphenols from the 2017 RMP Status and Trends Water Cruise. Members of both these contaminant classes are endocrine disrupting, high production volume chemicals that are included on California's Prop 65 list and used in a wide variety of applications. OPE and bisphenol (specifically BPA and BPS) compounds were detected in open bay waters. Data were considered semi-quantitative due to field replicate discrepancies.

A member of each of the classes (TDCPP and BPA) was detected at levels comparable to or exceeding existing protective thresholds. She recommended that given these results, in addition to the lack of knowledge concerning toxic effects and environmental fates as well as expected increases in use trends, both OPEs and bisphenols merit classification as moderate concern. Anne Cooper Doherty noted that DTSC has management categories that include bisphenols due to the human health concerns associated with the compounds. The group discussed knowledge gaps in the domestic production and commerce of bisphenols. There was also discussion on long-term trends and other monitoring results for OPEs. Lee Ferguson and Derek Muir noted that TCPP and TPhP have been detected in drinking water and out in the open ocean, respectively. Heather mentioned that OPE use is increasing, which supports monitoring as moderate concern contaminants. The group mentioned TDCPP is being phased out of furniture, while TCPP is used in housing insulation. Meeting participants and workgroup members supported the listing of both compound classes as moderate concern.

4. Information: Neonicotinoids and Degradates in Bay Water

Nina Buzby presented the 2017 monitoring results for neonicotinoids in Open Bay and South Bay Margins water samples. Imidacloprid was introduced in 1991 and continues to be the most widely used of the class. There are no neonicotinoid toxicity thresholds for marine settings, so freshwater-related thresholds were used as a point of reference.

Results showed one detection of imidacloprid in the Open Bay as well as three imidacloprid detections in margins samples. All detections were in Lower South Bay and were comparable to or exceeded freshwater toxicity thresholds for imidacloprid. The potential sources of imidacloprid were presented visually as a conceptual model. Hydrodynamic modeling using existing stormwater and wastewater monitoring data predicted similar levels in Lower South Bay during the dry season to those observed. The model also showed that concentrations in Lower South Bay are likely to be higher during the wet season. Nina suggested listing imidacloprid as a contaminant of moderate concern, while keeping the rest of the chemical class as Possible Concern compounds.

Workgroup members supported the proposed listing. Tom Mumley initially suggested noting that imidacloprid is a moderate concern in the LSB, and not to the whole Bay, so as not to overstate the concern for the contaminant class. However, others argued that because imidacloprid management action is currently underway *and* on a statewide scale, listing imidacloprid as moderate concern only in the LSB as opposed to Bay-wide would not affect any management actions and would be an unnecessary complication. Moreover, listing for the whole Bay would retain consistency with other classified contaminants as several contaminants are elevated in or only present in the LSB. Additionally, imidacloprid may be present in more than just the Upper and Lower South Bays during the wet season. This discussion led Tom to withdraw this suggestion. Jennifer Teerlink noted that these pesticides are already a focus at DPR and that a concerted monitoring effort from the RMP may not be as necessary. Lee mentioned that imidacloprid guanidine was detected in previous NTA analysis from Coyote Creek samples, but not Napa River samples. The meeting participants also commented on the benefits associated with the hydrodynamic modeling efforts, noting that similar approaches could be used in future work to help identify and prioritize monitoring strategies.

5. Information: Quaternary Ammonium Compounds (QACs) and Antibiotics in Bay Sediment

Bill Arnold, an ECWG advisor from the University of Minnesota, presented preliminary pro-bono analyses of RMP sediment samples for antibiotics and QACs. Bill highlighted the major classes of compounds identified in the sediment: sulfonamides, fluoroquinolones, tetracyclines, macrolides, BACs, DADAMACs, and ATMACs. Similar detections were observed in wastewater effluent and lake sediment samples in Minnesota.

Bill highlighted that detections are not necessarily cause for concern, given the high toxicity levels and sorption coefficients of these compounds, as well as their tendency to bio- or photodegrade. Miriam Diamond agreed with this sentiment, but noted that impacts may be greater for organisms that ingest particles with sorbed chemicals.

6. Information: Triclosan and Methyl Triclosan in Prey Fish

Diana Lin presented on levels of triclosan and methyl triclosan in small fish collected in 2017 from the Lower South Bay. There is concern surrounding the ubiquitous use of triclosan given the ability of the parent and its methylated transformation product to disrupt endocrine systems, and harm aquatic organisms. Since the previous 2011 RMP work to identify triclosan-related data gaps, new protective thresholds have come out, and evidence has emerged of bioaccumulation in fish via water and dietary exposures. Results showed that methyl triclosan concentrations were higher than triclosan. It is unknown whether triclosan is methylated prior to accumulation within fish, or whether methylation occurs in fish tissues. Diana showed that concentrations of triclosan and methyl triclosan measured in small prey fish suggested bioaccumulation through the food web, showed a clear spatial pattern with concentrations decreasing with distance from the San Jose outfall, and could be used to back calculate and estimate equivalent “water” exposure concentrations that could be compared to water-based toxicity thresholds.

Diana suggested that periodic monitoring should be considered, as levels of the chemicals may not decrease as initially expected and, instead, increase. Meeting participants noted that the FDA is phasing out the use of such compounds in antibacterial hand soaps for consumers, but that triclosan has other applications (e.g., plastics), as well as exceptions for use in hospitals and restaurants. Diana commented that monitoring for these compounds could be added to future pharmaceutical monitoring efforts. A proposal will be presented on Day 2 for this type of add-on sampling.

7. Information: Preliminary Results of Non-targeted Analysis of North Bay Fire-impacted Stormwater

Rebecca Sutton introduced the item as a preliminary look at the findings coming from the 2017 North Bay wildfires. Two groups - the Department of Toxic Substances Control (DTSC) and San Diego State University (SDSU) - conducted NTA on stormwater samples for polar and non-polar species, respectively. The monitoring occurred during two storms in Sonoma and Napa, and during one storm in Santa Rosa.

Miaomiao Wang presented the initial findings from DTSC, organizing the results into negative and positive ion clustering and summary information. After a brief explanation of the workflow, Miaomiao outlined various interpretation techniques such as evaluating the number of shared features between sites and clustering data by storm event. Pesticides, consumer products, phenols, phosphates, and surfactants were more abundant in the first storm compared to the second. Additionally, preliminary data revealed significant chemical profile changes between burnt and unburnt sites, as well as between storm events. Four PFAS were observed with high detection frequency: PFOS, PFHxS, PFBS, and PFOA.

Discussion after the initial presentation brought up further details about the storm sampling events. SFEI staff noted that the first storm was actually the first storm to hit the area after the fires (November 2017) but did not have the heaviest rainfall. The second storm, comparably, was not the second storm experienced (January 2018), but it was a large storm.

Eunha Hoh from SDSU then presented on her laboratory’s non-polar NTA work. Eunha clarified that all identifications were tentative and reference site levels from Sonoma and Napa were used to allow for comparison in Santa Rosa. Interpretations of the preliminary results showed that there was a low number of compounds shared between sites in each storm event. Eunha also highlighted compounds of interest at each monitoring location. Particularly, Napa and Santa Rosa showed many compounds that contain carbonyl groups and oxygen, suggesting evidence of combustion products. In general, a majority of the compounds identified contained oxygen; a majority were cyclic/aromatic; some compounds contained nitrogen; some are known combustion products; others are thought to be industrial in origin.

The discussion following Eunha's presentation brought up interest in the conditions of both the fires and storm events. Miriam Diamond noted that the extreme variance in temperature (i.e., the heat from the fire or cold from a storm) could have a unique influence on chemical compositions. Rebecca Sutton also noted that the rainfall pattern following the wildfires could have affected water quality. If the first storm event had been larger , it is possible that more chemicals at greater quantities could have been washed off the landscape.

DAY TWO - April 12

1. Summary of Yesterday and Goals for Today

Melissa Foley reminded meeting participants of what occurred during the previous day's meeting and allowed time for a second round of introductions. Melissa then informed the meeting participants that the current day's meeting would focus on a modeling strategy, recommendations for status and trends monitoring, and a review and prioritization of special studies proposals.

2. Discussion: CEC Modeling Strategy

Diana Lin outlined the short and long-term modeling goals for CECs. The proposed long-term modeling goal would involve developing a framework to assess and forecast sources, loads, concentrations, and temporal trends. In the short term, plans would focus on modular steps to integrate existing tools, such as conceptual models, box models, and spreadsheet models, into future projects.

Rebecca Sutton provided further details on these goals by identifying current and future examples of leveraging existing tools and efforts to identify relevant factors, data gaps, and temporal trends. Related to future ideas, Rebecca noted that it would be useful to refine tools and add capabilities that would make them better suited to CEC work. For example, altering the bay hydrodynamic spreadsheet model to include multiple inputs for stormwater, instead of just one, similar to how the model is currently set up to deal with wastewater treatment plants.

Rebecca then asked for comments from workgroup members, either at the meeting or in the form of later communication by email or phone. Miriam Diamond suggested entering OPE data into the hydrodynamic spreadsheet model, similar to what was done with neonicotinoids. Kelly Moran identified that the biggest gap in CEC modeling is the uncertainty in quantifying the amount of chemicals released by products. Kelly identified the benefit of drawing from DPR models as they are doing the bulk of such work for pesticides. Tom Mumley also noted the possible resource in SFEI's Nutrient Management Strategy modeling work and the importance of leveraging all available models and not just those previously used by SFEI.

Meeting attendees also discussed the importance of toxicological and conceptual models, both in the context of management actions, as well as for education and outreach tools. Miriam suggested creating a conceptual model for each chemical or class and mapping this information onto a more generalized model that will help build upon knowledge of general processes. Tom recommended that an optimal level of effort (range of low to high effort) should be applied for each contaminant conceptual model, and that, as part of the CEC strategy, the CECs team should build, maintain, and develop the best conceptual models as more information is collected. Chris Sommers was in agreement with this idea, but noted that in order to truly inform monitoring strategies the models may need more detail. Tom also recommending considering use of empirical models because mechanistic models can be very challenging to develop and use.

3. Discussion: Status and Trends Monitoring Recommendations

Following the previous day's discussion of contaminants newly classified as Moderate Concern, i.e., bisphenols, OPEs, and imidacloprid, Rebecca Sutton presented recommendations for Status and Trends monitoring to the workgroup.

Because no strong regional trend was identified, suggested monitoring of OPEs and bisphenols would likely be Bay-wide. Discussion on these compounds focused on optimizing the analyte list to include a smaller subset of chemicals (i.e., TDCPP, BPA, BPS, BPF) if substantial savings could be made, and adding these to RMP Status and Trends water monitoring in both the open Bay and margins. The workgroup decided not to monitor imidacloprid in status and trends work, given the amount of work being done by other entities like DPR.

4. Information: Ongoing CEC Trend Monitoring by POTWs

Lorien Fono from Bay Area Clean Water Agencies (BACWA) presented on the group's efforts to develop a strategy to monitor CEC trends at POTWs. This work would include a database of treatment plant and service area characteristics as well as a plan for ongoing monitoring to capture trends. Both aspects would be beneficial given the ad-hoc aspect to WWTP selection/volunteering for current CEC studies. The intention would be to enlist RMP support for laboratory communication and data management, as well as to integrate the efforts within the CEC strategy, given RMP experience and past work with CECs in wastewater.

Lorien suggested that any POTWs interested in contributing to the monitoring strategy should contact her. Karin North noted that the entire ECWG should be given the opportunity to review the final monitoring strategy.

The discussion then moved to ancillary topics including POTW anonymity and possible crossover or intersection with microplastics work. The latter of these topics prompted a suggestion to have any ECWG participants contact SFEI if they have interest in receiving Microplastic Workgroup communications.

Diana Lin had a final note for the group during this item, asking for volunteers to participate in the RMP study of ethoxylated surfactants in wastewater and other matrices. The study was funded last year and Lee Ferguson, the analytical partner for the work, noted that it would be helpful to have greater diversity in treatment types.

5. Summary of Proposed ECWG Studies for 2020

SFEI staff outlined the five proposed special studies in order to provide context to the workgroup members and aid the upcoming prioritization discussion.

Rebecca Sutton informed the workgroup on the details related to the Emerging Contaminant Strategy proposal. Previous discussions related to incorporating toxicology and more modeling efforts suggested that the budget for this work may need to be increased. Tom Mumley noted that funds would likely need to be added to the 2019 strategy budget to begin work on a toxicology strategy.

Rebecca also informed the workgroup on the stormwater CECs proposal that would fund the second year of a multi-year study. Rebecca reminded the meeting attendees that the deliverables and significant data management for this work would come in the third year of this work, and dropping funding for the project now would result in a near-wasted year one effort.

Diana Lin presented a proposal on pharmaceutical monitoring in Bay water, wastewater effluent, and sediment samples. The work would build upon the 2017 study on pharmaceuticals in wastewater and include additional analytes. Diana noted that the bulk of the study's budget resulted from high analytical cost, but could be scaled up or down. An add-on possibility that was mentioned on Day 1 would be to screen for triclosan. The study would be somewhat time sensitive, in order to have enhanced comparability with the 2017 work. There was initial discussion as to whether study objectives should investigate differences in removal efficiencies from different wastewater treatment processes in order to inform management actions related to treatment. However, the group instead prioritized evaluating whether pharmaceuticals are of concern in the Bay, and discussion focused on study design and evaluating in-Bay temporal and spatial variation as well as possible leveraging opportunities. Because of the high budget, meeting participants suggested thinking about a modular organization in anticipation of a smaller funding amount.

Ila Shimabuku outlined the monitoring proposal for bisphenols in sport fish tissue as part of the 2019 RMP Sport Fish monitoring. The motivations for such work included a lack of understanding of the environmental fates of bisphenols. The objectives of the study were to determine which bisphenols are present, if levels are of concern, and where to prioritize future efforts. The work would also determine if fish consumption is a pathway for human exposure. Meeting participants brought up concerns that sport fish tissue is not the highest-priority matrix, and that bioaccumulation and resultant risk may not be significant.

Diana Lin informed the workgroup of a proposal that was originally proposed by Meg Sedlak at the 2018 workgroup meeting. The study would aim to quantify concentrations of UV sunscreen compounds like oxybenzone in wastewater effluent. Sampling events would occur during the summer and winter to identify seasonal trends related to predicted use patterns. There was some discussion about the reason for monitoring effluent, and meeting attendees were reminded that the initial proposal included other matrices, though last year's discussion reframed the scope of work to include only effluent.

6. Information: Characterizing the Mechanism of Toxicity of the Sunscreen Oxybenzone to Sea Anemones

Bill Mitch from Stanford University presented his work investigating the toxicity mechanism of oxybenzone to sea anemones. Sunscreens have been a hot topic recently because these compounds cause coral bleaching (expelling of symbiotic algae from coral polyps) and are toxic to coral larvae. Dr. Mitch explained that the toxicity mechanism of oxybenzone and its metabolites stems from their role as a photosensitizer; this results in the creation of free radicals. Bill's current work is focused on developing a method to quantify levels of oxybenzone and biometabolites, as well as attempting to synthesize biometabolites so they can be dosed directly to anemones. Takeaways from the work show that replacement sunscreen materials have similar structures to the metabolites of concern in Dr. Mitch's research.

Meeting attendees asked various technical questions, including impacts of mineral-based sunscreens. Bill Mitch noted that it's difficult to get information from manufacturers on what is actually used in the products, and therefore hard to make predictions of impacts.

7. Discussion of Recommended Studies for 2020 - General Q&A

Melissa Foley outlined the steps associated with special study prioritization. All RMP workgroups have been tasked with prioritization recommendations, which will be brought to the Technical Review Committee (TRC). The TRC will then determine what studies should be funded using the available budget. The RMP Steering Committee will then have the final say on what funding gets approved for 2020 work. Any remaining studies that are not approved may be eligible to go onto the Supplemental Environmental Project (SEP) list for future consideration. Tom Mumley also reminded the workgroup that there is $270K available in Alternative Monitoring Requirement (AMR) funds that generally go to CEC projects.

Meeting attendees then took the time to ask any remaining questions while proposal PIs were still in the room. There was little discussion surrounding the strategy and stormwater proposals given the proposals' necessity and/or multi-year approach.

<u>Pharmaceuticals</u>

When discussing the pharmaceutical study, there were multiple suggestions for scaling the study by focusing on wastewater in order to make the budget more amenable to partial funding. There was also discussion on the possibility of utilizing NTA efforts or existing data. Because Lee Ferguson's lab is already handling a lot of RMP analytical work, it was suggested that SFEI look into other possible options for NTA work focused on pharmaceuticals.

Kelly Moran brought up the point that it would be tricky to inform any management response because there are few options related to managing pharmaceutical sources. Erica Kalve added to this, noting that the decision would be more focused on wastewater treatment investments, so any guidance would likely be more useful to POTW infrastructure decisions. Karin North and Diana Lin suggested that the impacts of standard wastewater treatment processes on the relative persistence or susceptibility to degradation for some pharmaceuticals have already been investigated in the literature.

Bisphenols

The discussion concerning the bisphenol proposal continued to focus on topics brought up during Ila's initial presentation, including whether fish tissue is the best monitoring matrix for 2020 and that archiving tissue should be considered. There was general agreement that the proposal should be refocused on stormwater and effluent monitoring and take advantage of archived sediment; sport fish tissue could be archived for later analysis, as needed.

Sunscreens

There were additional comments that highlighted the data gap concerning direct bay exposure from human swimming and beach activities.

To scale down on cost, the workgroup suggested conducting only one sampling event during the summer to get an idea of the worst case scenario. This topic also led into a side discussion on the rationale for how many plants would ideally participate. Such comments reinforced the importance of BACWA's POTW strategy development, and also highlighted the opportunity for leveraging RMP studies. The workgroup recommended this study be recrafted as an add-on to the bisphenols proposal.

8. Discussion of Recommended Studies for 2020 - Prioritization

Tom Mumley solicited the group for any proposal ideas that hadn't yet been brought up at the meeting, and reminded everyone that costs for a predictive toxicology webinar would be added into the current 2019 CEC Strategy budget. Lee Ferguson brought up the idea of using the ChemTox tool to compare stormwater samples as something to implement down the line. Miriam Diamond proposed that this idea be a separate study with associated critical analysis and be brought forward in future years.

Karin North then summarized the last item's discussions, specifically the changes to the proposed studies that would need to be taken into account during prioritization. These included:

- Increasing the CEC strategy budget to include enough funds to cover conceptual modeling and toxicity work
- Request toxicology funds from the Steering Committee to be added to the current 2019 CEC strategy budget
- Add bisphenols to the list of analytes monitored in stormwater
- Focus pharmaceutical sampling to just Bay water and POTW effluent
- Alter bisphenol sampling to cover stormwater, LSB margins sediment archives, and wastewater effluent
- Tack sunscreen monitoring onto bisphenol wastewater effluent work and only conduct sampling during the summer

Any meeting participants that had presented a special study proposal to the workgroup were then asked to leave the meeting room.

9. Closed Session - Decision: Recommendations for 2020 Special Studies Funding

Following extensive discussion, studies were prioritized via a closed-door session. Studies are listed in order of priority with comments on how to alter and improve the studies summarized in the final column of the following table.

https://docs.google.com/document/d/15c1MvQpfMC6m8rtLZFD8agUwAn8Xs-LPEJUugv6PgSQ/edit#

10. Report out on Recommendations

After the closed door session proposal authors were invited back to the meeting to hear the final prioritization decisions. Karin North and Melissa Foley provided a brief summation of the suggestions discussed by the group to make proposals more modular and leverage efforts from other studies (i.e., conduct both bisphenol and sunscreen effluent monitoring together).

Adjourn

About the RMP

RMP ORIGIN AND PURPOSE

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

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

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

RMP PLANNING

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

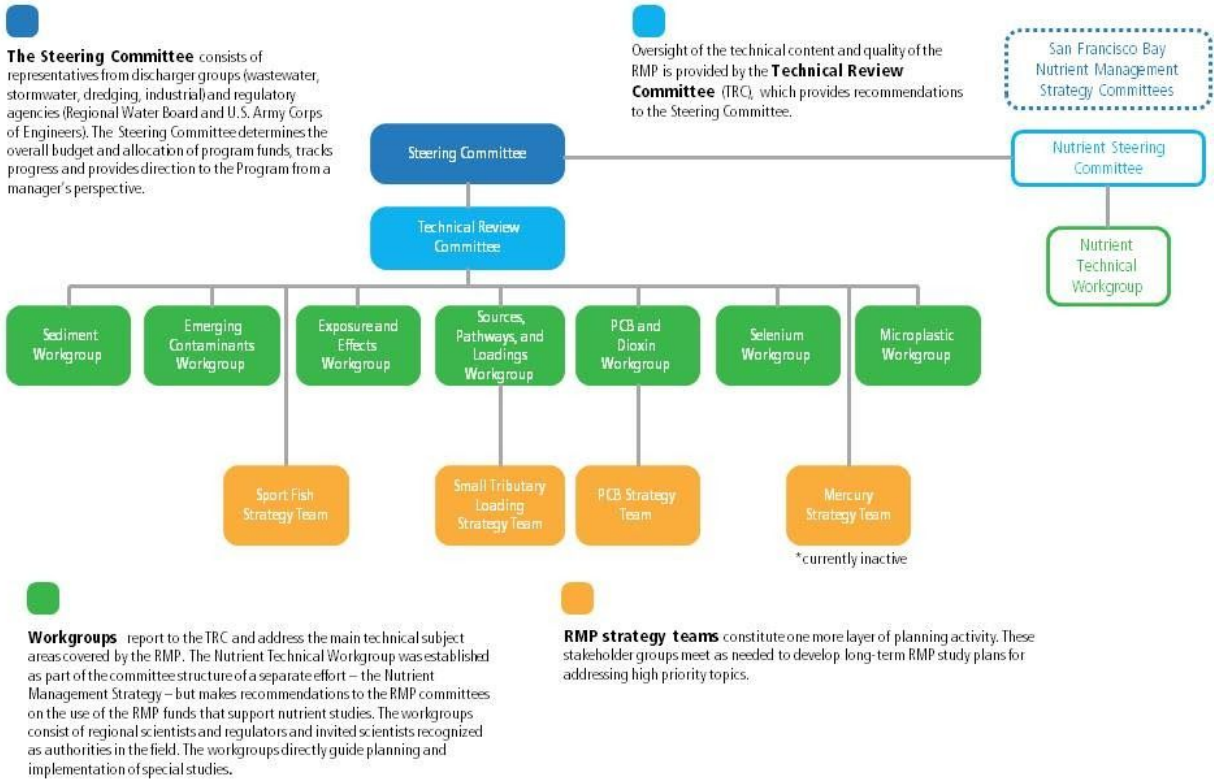
The annual planning cycle begins with a workshop in October in which the Steering Committee articulates general priorities among the information needs on water quality topics of concern. In the second quarter of the following year the workgroups and strategy teams forward recommendations for study plans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

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

PURPOSE OF THIS DOCUMENT

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

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



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

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

As scoped in the present proposal, Year 3 would be the final year of funding, and would support activities including further site selection, sample collection, and analysis for a greater number of samples for this Bay Area-wide screening study, as well as laboratory analysis, data management, and preparation of scientific manuscripts and a summary of results to inform water quality managers.

Due to the disrupted field season in Year 2, fewer samples and sites will be characterized in the overall, three-year study than was originally intended, and the resulting Year 3 funding request is reduced relative to the estimation in the ECWG multi-year plan. Another option is to extend the study for a fourth year, in order to provide a more robust dataset for this pioneering examination of CECs in urban stormwater.

Estimated Cost: $148,000 for Year 3 (Year 1 $132,000; Year 2 $181,000)
Oversight Group: ECWG and SPLWG
Proposed by: Rebecca Sutton (SFEI), Ed Kolodziej (University of Washington), Chris Higgins (Colorado School of Mines), Da Chen (Jinan University), Lee Ferguson (Duke University)
Time Sensitive: Yes (multi-year study already underway)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable (Year 3)	Due Date
Task 1. Site selection and reconnaissance, in coordination with SFEI stormwater and STLS teams; refinement of pilot sampling protocol	Summer 2020
Task 2. Field collection of stormwater samples	Fall 2020 – Spring 2021
Task 3. Laboratory analysis of samples	Spring – Summer 2021
Task 4. Draft manuscripts and management summary	Spring 2022
Task 5. Final manuscripts and management summary	July 2022

Background

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

Findings from this study indicated that water samples from the stormwater-influenced site, San Leandro Bay, contained a broad array of unique contaminants with strong signals suggesting higher concentrations (Ferguson et al. in prep; Sun et al. in prep). One example of a contaminant identified with high confidence is 1,3-diphenylguanidine (DPG), a rubber vulcanization agent derived from vehicle tires. The European Chemicals Agency established predicted no effect concentrations (PNEC) for DPG of 30 µg/L in freshwater and 3 µg/L in marine waters (ECHA 2018). While the non-targeted analysis provides only qualitative data, the high relative strength of the DPG signal 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 contributing to 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 the Bay. Furthermore, CEC investigations to date in the RMP and elsewhere have focused primarily on wastewater, and CECs in stormwater have received relatively little attention.

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 experience acute toxicity and 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 monitored pesticides, metals, or polycyclic aromatic hydrocarbons (Scholz et al. 2011).

In an effort to identify the potential cause of this acute toxicity in the Puget Sound area, non-targeted analysis of stormwater and tissues from runoff-exposed fish were conducted and 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 approaching 10 µg/L (Peter et al. 2018). More recent research indicates that aqueous leachates from automobile tires can induce acute toxicity in coho salmon (Peter et al. 2018), 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 in Puget Sound was the development, by Dr. Kolodziej, of a list of target analytes consisting of contaminants of concern that are characteristic of urban stormwater. While there are a number of targeted CEC lists designed around the influence of wastewater (e.g., focused on pharmaceuticals and other compounds typically disposed of down the drain), this is the first concerted analytical effort to develop a CEC list targeting the influence of urban runoff in aquatic habitats. While the endangered coho salmon, the focus of the Puget Sound research effort, are now absent from tributaries discharging to the Bay, steelhead (*Oncorhynchus mykiss*), a threatened species, are observed in some Bay streams (e.g., Guadalupe River, Alameda Creek) and may also be susceptible to these contaminants.

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

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

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

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

<u>Ethoxylated surfactants</u> – Ethoxylated surfactants include alkylphenol ethoxylates (classified as Moderate Concerns for the Bay), as well as alcohol ethoxylates and others. A conceptual model of sources of ethoxylated surfactants to stormwater includes outdoor use as automotive cleaners, lubricants and other fluids, as well as pesticides, plastics, paints, and many other products. The non-targeted analysis of San Francisco Bay sites described previously also identified a number of ethoxylated surfactants with strong signals in the stormwater-influenced site, San Leandro Bay (Ferguson et al. in prep; Sun et al. in prep). The RMP funded a 2019 special study to screen Bay

water, sediment, and wastewater for ethoxylated surfactants; results from the two studies will be complementary.

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

This proposal is structured to indicate that Year 3 will be the final year for funding. Another option would be to extend this multi-year proposal through Year 4 to allow for additional monitoring to make up for the limited fieldwork possible in Year 2. Adding a fourth year would require additional financial support from the RMP.

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 CECs? Is a need for management actions indicated?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Compare concentrations observed at different sites in the Bay Area to glean possible insights regarding the influence of sources or land use types. Compare Bay Area concentrations to other measurements of other urban areas.	What are the key sources or land uses that are associated with individual CECs or CEC classes in stormwater?
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	N/A	
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	Compare concentrations with previous monitoring data for a limited number of analytes.	The data from this study can establish baseline data for stormwater CECs in the Bay Area. Instructive comparisons

		are possible for a subset of analytes previously examined in Bay Area stormwater, though robust trends cannot be inferred due to data limitations.
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	N/A	
6) What are the effects of management actions?	N/A	

Approach

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

Up to 20 samples (including field blank and duplicate samples) will be collected as part of Year 3 sample collection. Samples will consist of grabs or composites. Composites collected using an ISCO pump are preferred for the new stormwater CECs analyte list developed by Dr. Kolodziej. For the other types of contaminants, the ISCO pump may lead to procedural contamination. For these contaminants, one or more grab samples will be collected at each site, and may be combined in the field or in the analytical laboratory to produce a composite.

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

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

Stormwater CECs: Unfiltered samples will be analyzed by the Kolodziej Laboratory (University of Washington) with a newly developed, targeted analytical method using multi-residue solid phase extraction (SPE) and liquid chromatography with tandem mass spectroscopy (LC-MS/MS). 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.

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

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

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

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

Ethoxylated surfactants: Stormwater samples will be analyzed for ethoxylated surfactants by the Ferguson Laboratory (Duke University), using a method in development. The matrix is expected to be total water, and the analyte list is expected to include the following surfactant families: nonylphenol ethoxylates, octylphenol ethoxylates, and C12, C14, and C16 alcohol ethoxylates. Analytes for each family will include compounds with a broad range of ethoxylate chains. Isotopically labeled standards are only available for a few of these analytes; however, the uncertainty associated with quantitation was deemed acceptable by the ECWG for screening purposes.

<u>Data Interpretation</u>

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

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

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

Budget

Budget Justification

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

With the proposed scope, fewer samples and sites will be characterized in the overall, three-year study than was originally intended, and the resulting Year 3 funding request ($148,000) is slightly reduced relative to the estimation for 2021 in the ECWG multi-year plan ($186,000, split among the 5 classes of analytes).

Another option is to extend the study for a fourth year, with monitoring through water year 2022, to provide the more robust dataset originally intended for this pioneering examination of CECs in urban stormwater. It is important to note that the overall cost of the multi-year study is likely to increase somewhat if this option is selected, due to an expected reduction in opportunities to leverage stormwater sample collection via other RMP efforts in water year 2022 (reduced legacy contaminant reconnaissance monitoring is planned).

Table 2. 2021 CECs in Stormwater budget (Year 3 only)

Expense	Estimated Hours	Estimated Cost
Labor - Year 3		
Study Design, Stakeholder Engagement	20	$2,800
Stormwater Sample Collection	200	$28,000
Data Technical Services		$40,000
Analysis and Reporting	130	$18,000
Subcontracts - Year 3		
Stormwater CECs: Kolodziej, U. Washington		$12,000
PFASs: Higgins, Colorado School of Mines		$15,800

Organophosphate Esters: Chen, Jinan U.	$7,000
Bisphenols: Chen, Jinan U.	$4,000
Ethoxylated Surfactants: Ferguson, Duke U.	$5,500
Direct Costs - Year 3	
Equipment	$2,500
Travel	$1,400
Shipping	$11,000
Grand Total	**$148,000**

Planning and Stakeholder Engagement Costs
In consultation with RMP and STLS stormwater experts, we will establish a Year 3 study design that specifies site selection. Study design discussions and preliminary data reports will require regular participation in monthly calls with the STLS team. Year 2 funds for coordination have not been depleted and will be carried over to Year 3.

Field Costs
The Year 3 budget includes $28,000 devoted to stormwater sample collection; the Year 2 budget for this element of the study is not yet exhausted, and will supplement this allocation. Every effort will be made to minimize field costs by leveraging existing stormwater monitoring activities of the RMP. Based on the pilot year sampling experience, we anticipate that two-thirds of the sites visited in Year 3 will leverage RMP monitoring of legacy contaminants, while one-third of the sites will be specific to CECs.

Data Management Costs
Preliminary data management activities have occurred during Years 1 and 2, with the bulk of data management to be funded via the Year 3 budget. Data services will include quality assurance review and upload to CEDEN.

Analysis and Reporting Costs
Preparation of draft manuscripts for publication in a peer-reviewed journal (stormwater-themed special issue) would occur following Year 3 sampling and analysis, and generally be led by the analytical partners. RMP scientists may be lead authors of one of the manuscripts, and coauthors of others. After the manuscripts are complete, RMP staff will produce a summary document for stakeholders, which describes the results and their implications for water quality management. Year 2 funds for analysis and reporting ($18,000) remain and will be carried over to Year 3 activities.

Laboratory Costs
Each laboratory is allocated funds sufficient to analyze up to 10 samples via the Year 3 budget; the Year 2 budget is expected to cover an additional 10 samples. Laboratory QA/QC samples will be analyzed at no charge, while field blanks and field duplicates will be considered part of the 20 samples charged to the RMP.

Reporting

Deliverables will include: a) draft manuscripts[1] that serve as RMP technical reports, due July 2022; b) a summary for managers describing the results and their implications, due July 2022; and c) additions to other RMP publications such as the Pulse.

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

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Special Study Proposal: Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Bay Water

Summary: Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are fluorine-rich, chemically stable compounds widely used in consumer, commercial, and industrial applications, and are ubiquitous in the environment. The RMP has found PFAS in biota, water, and sediment as well as stormwater and wastewater. Two of the most studied PFAS, perfluorooctanoic sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are considered highly toxic, and other members of the class are predicted to have similar toxicity. The ECWG classified PFOS, PFOA, and other long-chain perfluoroalkyl carboxylates as Moderate Concern in the RMP tiered risk-based framework due to concentrations in Bay biota linked to potential risks. However, the most recent Bay water monitoring occurred in 2009, and included just 13 PFAS. Since that time, several new members of the PFAS class have been identified in environmental matrices elsewhere, and standardized analytical methods have been expanded to include a broader suite of analytes. We propose a study to assess the concentrations of 33 PFAS in Bay water to characterize newly identified PFAS and begin to assess trends in those previously observed PFAS.

Estimated Cost: $66,000
Oversight Group: ECWG
Proposed by: Miguel Mendez and Rebecca Sutton (SFEI)
Time Sensitive: Yes, leverages Status and Trends 2021 water cruise

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Example Due Date
Task 1. Develop sampling plan	May 2021
Task 2. Field sampling – Bay water	August 2021
Task 3. Lab analysis	November 2021
Task 4. QA/QC and data management	January 2022
Task 5. Presentation at ECWG	April 2022
Task 6. Draft Report	June 2022
Task 7. Final Report	September 2022

Background

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a class of thermally and chemically stable compounds that are ubiquitous in the environment. The widespread use of PFAS in consumer, commercial, and industrial products means they readily end up in waste streams that are ultimately discharged into the environment. Their highly persistent and recalcitrant nature, due to their strong carbon-fluorine bonds, combined with bioaccumulation risks, raise concerns regarding potential negative impacts on human and wildlife health. Perfluorooctanoic sulfonate (PFOS) and perfluorooctanoic acid (PFOA), the best studied compounds within the class, have been identified as highly toxic. Investigations of PFOS and PFOA exposure in laboratory animals and human populations have provided evidence for classification as multi-system and developmental toxicants (DeWitt, 2015). PFOS and PFOA have been linked to liver damage, adverse developmental effects, suppression of the immune system, and carcinogenicity in studies of various species (Lau et al., 2007; Sunderland et al., 2019; Wang et al., 2017).

The RMP has conducted a series of monitoring studies to evaluate PFAS in the Bay, detecting them in biota, water, and sediment (Sedlak et al., 2018). In particular, PFAS were ubiquitous in Bay biota including fish, bird eggs, and harbor seals. Concentrations of PFOS in Bay harbor seals and bird eggs in 2004 and 2006 were some of the highest detected globally (Sedlak et al., 2018, 2017). PFOS concentrations in South Bay bird eggs have shown decreasing levels since the mid-2000s, though, based on available toxicity data, current concentrations may still pose a risk to hatching success. Based on these findings, PFOS has been identified as Moderate Concern within the RMP tiered risk-based framework for emerging contaminants (Sedlak et al., 2018). Continued detection of PFOA and other long-chain carboxylate perfluoroalkyl substances at consistent levels over time in biota, as well as updated toxicology information, has supported the classification of Moderate Concern in the Bay (Sedlak et al., 2018).

The RMP has also synthesized the findings of studies on Bay Area stormwater and wastewater, which found detectable levels of PFAS (Sedlak et al., 2018). Multiple years of data showed wastewater concentration trends were consistent with manufacturing and use trends, with average levels of short-chain perfluoroalkyl substances increasing (statistically significant), and average levels of PFOS and PFOA trending downwards (not statistically significant). Additional data on wastewater is likely to be generated as part of a State Water Board statewide assessment to determine the scope of PFAS contamination in water systems and groundwater; sampling will include discharges from wastewater treatment facilities. Stormwater has been monitored less frequently, with the most recent Bay Area studies, completed in 2010-2011, finding detectable levels of PFAS, especially in more urbanized areas (Sedlak et al., 2018). To fill this data gap, PFAS have been included as one of five classes of analytes in the RMP's ongoing screening study of CECs in urban stormwater.

The RMP recently participated in a pro bono project to develop a multi-box mass balance model to predict the long-term distribution and concentrations of PFAS in water and sediment (Sánchez-Soberón et al., 2020). The model was based on similar, one-box models developed previously by the RMP for other contaminants (Davis, 2004; Greenfield and Davis, 2005; Oram et al., 2008; Yee et al., 2011), and included rate constants as well as time-varying external inputs, meant to capture the expected continuing declines in discharge due to the US phase-outs. The multi-box model estimated levels of these compounds for each subregion, allowing for a more spatially differentiated assessment of risks. As noted previously, PFOS and PFOA are generally observed at higher levels in South and Lower South Bays, and wildlife exposures in these subembayments have been the focus of risk evaluation in the Bay.

The base case scenario for the model describes conditions in 2009, as this is the year for which the majority of ambient Bay water and sediment PFAS monitoring data are available. Model predictions for recent years could only be compared to sediment concentrations, as Bay water has not been monitored for PFAS since 2009. The model predicts nearly stable PFOA concentrations would be reached after 50 years, while PFOS needed close to 500 years to stabilize. Concentrations stabilize between 4 and 23 pg/g in sediment and between 0.02 and 44 pg/L in water, depending on compound and region. South Bay had the greatest final concentrations of pollutants, regardless of compartment. In general, the model advanced our understanding of PFAS in the Bay, while identifying some major monitoring data gaps.

To build on previous RMP work and address one of the gaps in the model, we propose a study to monitor PFAS in Bay water. Bay water concentrations can be compared to data from previous monitoring of PFOS, PFOA, and other PFAS in 2009 as an initial assessment of temporal trends. Measured concentrations can also be compared to model predictions for PFOS and PFOA in different subregions of the Bay. In addition, this study would provide a first look at a range of other PFAS, particularly polyfluorinated alkyl substances such as GenX, which are now part of improved, standardized analytical methods. Results will allow characterization of risks posed by a broader array of PFAS in the Bay. Findings will also inform the State Water Board's statewide investigation of PFAS.

Study Objectives and Applicable RMP Management Questions

The purpose of this study is to assess the concentrations of PFAS in Bay waters to improve our understanding of risks to wildlife and people. Comparisons to concentrations measured in 2009 will provide information on trends over the past decade. Additionally, we will compare levels of PFAS in different embayments to monitor potential spatial patterns of contamination, which may be compared to model predictions. This new study will expand on the 13 previously tested contaminants to evaluate the presence of at least 33 total PFAS, including those of newly identified concern.

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Monitor at least 33 PFAS in Bay water. Develop baseline concentrations of PFAS and compare to aquatic toxicity thresholds, where available.	Do PFAS in the Bay have the potential to cause impacts to aquatic life? Which PFAS compounds are of greatest concern?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?		
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 in different embayments.	Do specific embayments or regions appear to have greater levels of contamination?
4) Have the concentrations of individual CECs or groups of CECs increased or decreased?	Compare current concentrations to those assessed previously (2009).	Do concentrations of different PFAS compounds appear to be trending toward an increase or decrease?

5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	Compare monitored concentrations to predictions via multi-box Bay model for PFOS and PFOA.	Evaluation of model predictions.
6) What are the effects of management actions?		Do current concentrations suggest phase-outs of PFOS and PFOA have reduced contamination? Are newly identified replacement compounds present in the Bay?

Approach

Bay Water Sampling
Sample collection of Bay Water will be coordinated with the RMP Status and Trends water monitoring cruise in the summer of 2021. Grab samples of ambient Bay water (500 mL, HDPE) will be collected from all 22 Bay Status and Trends sites; two field duplicates and three field blanks will also be collected. Exposure to teflon will be avoided during sample collection. Samples will be shipped overnight to SGS AXYS, where they will be frozen to extend hold time to 90 days.

Analytical Methods
Samples will be analyzed by SGS AXYS (Sidney, BC, Canada) using SGS AXYS method MLA-110 to quantify at least 33 different PFAS using liquid chromatography tandem mass spectrometry (LC-MS/MS; Table 2). Briefly, samples (total water) are spiked with isotopically labeled surrogate standards samples, extracted and cleaned up by Solid Phase Extraction (SPE), then analyzed via LC-MS/MS. Final sample concentrations are determined by isotope dilution/internal standard quantification. Detection limits range from 0.8 ng/L for perfluoroalkyl carboxylates and many sulfonates, as well as perfluorooctane sulfonamides and sulfonamidoacetic acids, to 8 ng/L for perfluorooctane sulfonamide ethanols.

Table 2. 33 PFAS in list MLA-110 (SGS AXYS)

Abbreviation	PFAS	MDLs by Class (ng/L)
PFBA	Perfluorobutanoic acid	Perfluoroalkyl carboxylates 0.8-3.2
PFPeA	Perfluoropentanoic acid	
PFHxA	Perfluorohexanoic acid	
PFHpA	Perfluoroheptanoic acid	
PFOA	Perfluorooctanoic acid	
PFNA	Perfluorononanoic acid	
PFDA	Perfluorodecanoic acid	
PFUnA	Perfluoroundecanoic acid	
PFDoA	Perfluorododecanoic acid	
PFTrDA	Perfluorotridecanoic acid	
PFTeDA	Perfluorotetradecanoic acid	

PFBS	Perfluorobutanesulfonic acid	Perfluoroalkyl sulfonates 0.8
PFPeS	Perfluoropentanesulfonic acid	
PFHxS	Perfluorohexanesulfonic acid	
PFHpS	Perfluoroheptanesulfonic acid	
PFOS	Perfluorooctanesulfonic acid	
PFNS	Perfluorononanesulfonic acid	
PFDS	Perfluorodecanesulfonic acid	
PFDoS	Perfluorododecanesulfonic acid	
4:2 FTS	1H, 1H, 2H, 2H-perfluorohexane sulfonic acid	Fluorotelomer sulfonates 3.2
6:2 FTS	1H, 1H, 2H, 2H-perfluorooctane sulfonic acid	
8:2 FTS	1H, 1H, 2H, 2H-perfluorodecane sulfonic acid	
PFOSA	Perfluorooctanesulfonamide	Perfluorooctane Sulfonates 0.8
N-MeFOSA	N-Methylperfluorooctanesulfonamide	
N-EtFOSA	N-Ethylperfluorooctanesulfonamide	
N-MeFOSAA	N-Methylperfluoro-1-octanesulfonamidoacetic acid	Perfluorooctane sulfonamidoacetic acids 0.8
N-EtFOSAA	N-Ethylperfluoro-1-octanesulfonamidoacetic acid	
N-MeFOSE	N-Methylperfluoro-1-octanesulfonamidoethanol	Perfluorooctane sulfonamidethanols 8
N-EtFOSE	N-Ethylperfluoro-1-octanesulfonamidoethanol	
HFPO-DA, GenX	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3 -heptafluoro-propoxy)propionic acid	Ether carboxylates 3.2
ADONA	Decafluoro-3H-4,8-dioxanonoate	
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	Ether sulfonates 3.2
11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	

Budget

Table 3. Proposed Budget

Expense	Estimated Hours	Estimated Cost
Labor		
Study Design	10	$12,000
Sample Collection	32	$3,200
Data Technical Services		$5,500
Analysis and Reporting	200	$30,000
Subcontracts		
SGS AXYS		$11,745
PFAS consultants (review)		$2,000

Direct Costs	
Travel	$200
Shipping	$1,355
Grand Total	$66,000

<u>Budget Justification</u>

SFEI Labor
Labor hours are estimated for SFEI staff to manage the project, develop the study design, support sample collection, analyze data, review toxicological risks, present findings, and write a report. The PFAS class is complex and detections of individual compounds will require review of likely sources, identification of precursors and expected degradates, and available ecotoxicity data.

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

Sample Collection
Costs are minimized through leveraging sample collection during the RMP 2021 Status and Trends water sampling cruise.

Laboratory Costs (SGS AXYS)
Analytical costs per sample are estimated to be $435. For 27 samples, including two duplicates and three field blanks, the total analytical cost is $11,745.

PFAS Consultant
Given the complexities associated with the PFAS class, additional honoraria are recommended to fund a detailed review of our findings. Previously, this role has been filled by PFAS experts Jen Field (Oregon State) and Erika Houtz (Arcadis).

Reporting

Results will be presented to the ECWG at the spring 2022 meeting; a draft report will be prepared by 6/30/22, which will be reviewed by the ECWG and TRC. Comments will be incorporated into the final report, published by 9/30/22.

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Special Study Proposal: Organophosphate Esters and Bisphenols in Bay Water during Wet and Dry Seasons

Summary: Widely used as plastic and polymer additives, organophosphate esters (OPEs) and bisphenols are compounds detected ubiquitously in many environmental matrices. The RMP just completed a study on bisphenols in Bay water, with studies in stormwater, wastewater, and sediment ongoing. The RMP has measured OPEs in Bay water, sediment, and tissue, as well as Bay Area stormwater and wastewater. Within each class, well-studied compounds have been identified as toxic, including potential for carcinogenic (OPEs) and reproductive (bisphenols) effects. The RMP classified OPEs and bisphenols as Moderate Concern in the RMP tiered risk-based framework due primarily to concentrations in Bay water in the range of or above current toxicity thresholds. As Moderate Concern contaminants, both classes could be proposed as analytes that merit routine monitoring via the RMP Status and Trends water cruise; however, their expected presence in both stormwater and wastewater pathways suggests that the current sampling design of the Status and Trends water cruise, which occurs in the summer and therefore minimizes the influence of stormwater flows, may not adequately characterize contaminant concentrations in the Bay. We propose a study to assess the concentrations of 13 OPEs and 6 bisphenols in South and Lower South Bay waters during wet and dry seasons.

Estimated Cost: $115,000
Oversight Group: ECWG
Proposed by: Miguel Mendez and Rebecca Sutton (SFEI)
Time Sensitive: Yes, to inform RMP Status and Trends sampling design review

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Develop sampling plan	September 2020
Task 2. Field sampling – Bay water	November 2020 - August 2021
Task 3. Lab analysis	November 2021
Task 4. QA/QC and data management	December 2021
Task 5. Draft Report	March 2022
Task 6. Final Report	June 2022

Background

Organophosphate esters (OPEs) and bisphenols are classes of mobile, endocrine-disrupting chemicals found widely in the environment. Predominantly used as plastic and polymer additives, these compounds are manufactured and used at high volumes globally (US EPA, 2016). OPEs have also emerged as a new generation of flame retardants due to the phase-out of polybrominated diphenyl ethers (PBDEs). OPEs and bisphenols enter the environment through different pathways, notably wastewater and stormwater. The two classes share unique chemical properties, including hydrophilicity that make them difficult to remove via traditional wastewater treatment processes and high mobility in the environment. Though their toxicity is not well understood, OPEs have been linked to endocrine-disrupting effects, neurotoxicity, adverse fertility effects, and cancer, with three OPEs — tris(2-chloroethyl) phosphate (TCEP), tris(2,3-dibromopropyl)phosphate (TDBPP), tris(1,3-dichloro2-propyl) phosphate (TDCPP) — listed as carcinogens on California's Proposition 65 List (OEHHA [Office of Environmental Health Hazard Assessment], 2019; Wei et al., 2015). BPA, the best studied of the bisphenols, has been shown to cause adverse estrogenic effects and linked to multiple negative effects, notably listed on California's Proposition 65 List for developmental toxicity and female reproductive toxicity (Bjornsdotter, 2017, OEHHA, 2019).

In 2017, the RMP biennial Status and Trends water cruise included analysis of 22 OPEs and 16 bisphenols in samples collected from 22 sites throughout the Bay during the dry season (Shimabuku et al., 2020). Fifteen of 22 OPEs were detected, with six found in 100% of samples. The sum of all OPEs ranged from 35-290 ng/L (median 100 ng/L) across all Bay sites. In particular, concentrations of TDCPP ranged from 2.8-23 ng/L, in the range or above marine PNEC of 20 ng/L at many Bay sites. These detections were consistent with a previous screening study of flame retardants in surface water, sediment, bivalves, and harbor seal blubber conducted in 2013, which reported exceedances of toxicity thresholds for both TDCPP and TPhP (Sutton et al., 2019).

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

Several studies have identified wastewater treatment plant effluent and stormwater as important pathways to study further. Bisphenol A has been observed in both pathways, indicating potentially significant migration from products into waterways and a need for further study of bisphenols not previously examined (Björnsdotter et al., 2017; Boyd et al., 2004; Fairbairn et al., 2018; Jackson and Sutton, 2008; Vidal-Dorsch et al., 2012). Screening of bisphenols in stormwater is underway to better understand the importance of this pathway to Bay contamination. OPEs have previously been detected in Bay Area wastewater effluent and stormwater (Sutton et al., 2019). Screening of OPEs in stormwater is also now underway to fill a major gap identified in the RMP synthesis and strategy report on OPEs (Lin and Sutton, 2018).

As Moderate Concern contaminants, bisphenols and OPEs could be added to routine monitoring via the RMP Status and Trends water cruise. However, the current Status and Trends monitoring design only includes dry season sampling, which may not provide representative concentration data for contaminants discharged via both wastewater and stormwater. The RMP will be reviewing its Status and Trends sampling design in 2020 and 2021, in part motivated by the need for a greater focus on CECs in Status and Trends monitoring.

We propose a study to monitor 13 OPEs and 6 bisphenols in Bay water collected in the South and Lower South Bay during summer and winter months. This region of the Bay tends to have higher concentrations of these contaminants, and is visited monthly in support of nutrients monitoring. Summer and winter concentrations can be compared to understand the relative influence of wastewater and stormwater pathways to the Bay for these contaminants. Results from this study will inform the discussion of appropriate study designs for the RMP Status and Trends program.

Study Objectives and Applicable RMP Management Questions

The purpose of this study is to determine and compare concentrations of bisphenols and OPEs in Bay surface water during wet and dry seasons. At present, Bay water monitoring occurs only in the summer, which is biased towards the influence of wastewater effluent discharges. Monitoring during the winter will provide a better characterization of stormwater as a pathway for these contaminants.

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

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Monitor bisphenols and OPEs in Bay water.	Do monitored bisphenols and OPEs have the potential to cause impacts to aquatic life?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Compare Bay water concentrations by season to better understand the influence of seasonally discharged stormwater as a pathway of bisphenols and OPEs to the Bay.	Assess the relative influence of two primary pathways (wastewater and stormwater) on OPEs and bisphenols concentrations in Bay Water.
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?	Compare current summer concentrations to those assessed previously in the same regions of the Bay.	Note trends of bisphenols and OPEs over the period of record.
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?		Are there seasonal patterns for any individual contaminants that might suggest specific management actions could have an impact on loadings to the Bay?

Approach

Bay Water Sampling
Collection of water samples will be coordinated with monthly monitoring activities conducted on behalf of the Nutrient Management Strategy at moored sensor sites in South and Lower South Bays. Grab samples of Bay surface water (two, 1L samples in amber glass per site) will be collected from six sites. Samples will be collected during three wet season months and three dry season months; one to two field duplicates and two field blanks will also be collected during each round of sampling. Samples will be shipped overnight to SGS AXYS, where they will be extracted within one (bisphenols) or two (OPEs) weeks, or frozen to extend hold time to 90 days of extraction.

Analytical Methods
Samples will be analyzed by SGS AXYS (Sidney, BC, Canada) using SGS AXYS methods MLA-098 (OPEs) and MLA-113 (bisphenols) to quantify 13 OPEs and 6 bisphenols using liquid chromatography tandem mass spectrometry (LC-MS/MS; Table 2). The chosen analytes are some of the most commonly detected within each class. Briefly, samples (total water) are spiked with isotopically labeled surrogate standards, extracted and cleaned up by Solid Phase Extraction (SPE), then analyzed via LC-MS/MS. Final sample concentrations are determined by isotope dilution/internal standard quantification. Detection limits for bisphenols range from 1.3 (BPS) to 5 ng/L (bisphenol E), while for OPEs the range is from 0.1 (tripropyl phosphate) up to 360 ng/L for tris(2-butoxyethyl) phosphate.

Table 2. 13 OPEs and 6 bisphenols in methods MLA-098 and MLA-113 (SGS AXYS)

Abbreviations	Target Analytes	Method	MDLs (ng/L)
TEP	Triethyl phosphate	MLA-098 OPEs	0.1
TCEP	Tris(2-chloroethyl) phosphate		1
TPrP	Tripropyl phosphate		0.1
TCPP	Tris(2-chloroisopropyl) phosphate		0.5
V6	Tetrakis(2-chloroethyl)dichloroisopentyldiphosphate		0.5
TDCPP	Tris(1,3-dichloro-2-propyl) phosphate		5
TPP	Triphenyl phosphate		0.5
TDBPP	Tris(2,3-dibromopropyl) phosphate		3
TBP	Tributyl phosphate		Up to 24
TBEP	Tris(2-butoxyethyl) phosphate		Up to 360
TCrP	Tricresyl phosphate		0.2
EHDPP	2-Ethylhexyl-diphenyl phosphate		5
TEHP	Tris(2-ethylhexyl) phosphate		0.2
BPA	Bisphenol A	MLA-113 Bisphenols	2
BPAF	Bisphenol AF		2
BPB	Bisphenol B		2
BPE	Bisphenol E		5

BPF	Bisphenol F	MLA-113 Bisphenols	5
BPS	Bisphenol S		2.5

Budget

Table 3. Proposed Budget

Expense	Estimated Hours	Estimated Cost
Labor		
Study Design	24	$3,200
Sample Collection	40	$4,000
Data Technical Services		$16,600
Analysis and Reporting	140	$21,500
Subcontracts		
SGS AXYS bisphenols		$27,600
SGS AXYS OPEs		$36,600
Direct Costs		
Travel		$500
Shipping		$5,000
Grand Total		$115,000

Budget Justification

SFEI Labor

Labor hours are estimated for SFEI staff to manage the project, develop the study design, support sample collection, analyze data, present findings, and write the draft and final reports.

Data Technical Services

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

Sample Collection

Costs are minimized through leveraging sample collection as part of monthly nutrients monitoring activities.

Laboratory Costs (SGS AXYS)

Analytical costs per sample are estimated to be $460 and $610 for bisphenols and OPEs, respectively. For 60 field samples, the total analytical cost is $27600 for bisphenols and $36600 for OPEs.

Reporting

A draft report will be prepared by spring 2022, which will be presented to the ECWG and reviewed by the ECWG and TRC. Comments will be incorporated into the final report, published in summer 2022.

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Special Study Proposal:
Toxicological Thresholds for Emerging Contaminants

Summary: The RMP uses a risk-based framework for prioritizing monitoring of contaminants of emerging concern (CECs). Environmental toxicity threshold values are variable in availability and quality, and inappropriate thresholds may easily be used by researchers without toxicology knowledge. Past identification of toxicity thresholds for the Bay RMP has been on a study-by-study basis. This study proposes synthesizing and assessing the quality of the available thresholds for CECs detected in the Bay in the past ten years, calculating or estimating thresholds for data-poor contaminants using EU guidance and predictive toxicology methods, and risk screening for the Bay using a risk characterization ratio approach. This project will result in a "living document" of CEC ecotoxicity thresholds and their quality, and will inform design of future monitoring. The estimation and compilation of toxicity thresholds may support recategorization of some contaminants currently classified as Possible Concern due to insufficient toxicity data.

Estimated Cost: $60,000
Oversight Group: ECWG
Proposed by: Ezra Miller (SFEI)
Time Sensitive: Yes, intended to inform future study priorities

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Synthesize and assess quality of available CEC toxicity thresholds; identify toxicity threshold knowledge gaps	April 2021
Task 2. Calculate thresholds to fill knowledge gaps	August 2021
Task 3. Compare measured concentrations and updated thresholds to assess placement of Possible Concern contaminants within the tiered risk-based framework and identify priorities for future work	February 2022
Task 4. Draft technical report; presentation to the ECWG	April 2022
Task 5. Final technical report and "living document" synthesis of thresholds	July 2022

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, strives to stay ahead of the curve by identifying problem pollutants *before* they can harm aquatic life. Prioritizing CECs that may pose a risk, and therefore merit use of limited resources for further study and monitoring, is currently based on occurrence data and the probability of effects on Bay wildlife. This information is used to rank CECs within the RMP tiered risk-based framework.

Prioritization of many CECs, which are currently listed in the Possible Concern category, is hindered by a lack of toxicological data and toxicity thresholds. The Emerging Contaminants Workgroup (ECWG) discussed using predictive toxicological tools to inform risk-based prioritization at the April 2019 meeting, and decided it was an urgent priority for the focus area. For 2020, the ECWG also recommended increased resources to accommodate further development and refinement of a toxicology strategy designed to inform prioritization of monitoring and science relating to data-poor (Possible Concern) contaminants.

There are many available tools for assessing the possible risks of single compounds known to be present in the Bay that do not have adequate toxicological data. Available predictive toxicological tools were discussed during the April 2019 ECWG meeting and elaborated on at the March 10, 2020, RMP webinar *Introduction to Predictive Toxicology* (https://www.sfei.org/events/sf-bay-rmp-webinar-introduction-predictive-toxicology). Available predictive tools include both *in silico* (i.e., computer) and *in vitro* (i.e., test tube) models to predict how a chemical will interact with biological systems and what types of adverse effects may result.

Identifying and prioritizing CECs that may pose a risk is also complicated by the huge number of anthropogenic chemicals entering the environment. Requirements for toxicity information for anthropogenic chemicals on the market are variable, and abundance, quality, and reporting of toxicological data are therefore variable. Identifying toxicological thresholds thus requires querying multiple sources, and interpretation and assessment of identified thresholds often requires specialized knowledge. Interpreting ecotoxicity data often requires an understanding of the study context, including the species tested, toxic endpoint, exposure route, and exposure length. There are a variety of different types of data, from predicted no effect concentrations (PNECs) for whole ecosystems, which may be calculated using a variety of different methods requiring varying amounts of data, to concentrations derived from a study of a specific effect to one test species (e.g., no observed effect concentration or NOEC). While the resulting thresholds from these approaches can be very different, it may not be clear to someone without toxicological training which threshold is most appropriate to use when comparing them to measured concentrations in the environment and assessing risk.

To date, the RMP has identified ecotoxicity thresholds for comparison with measured concentrations of CECs on a study-by-study basis, giving preference to the lowest available thresholds under the assumption that these will be most protective. However, this approach is inefficient and may not always result in using the most appropriate threshold value.

The purpose of this project is to synthesize available environmental toxicity thresholds and identify toxicity knowledge gaps for CECs known to be present in the Bay, calculate thresholds using predictive toxicology methods for the CECs without good literature thresholds, and establish a process for identifying ecotoxicological thresholds for future RMP studies. In addition, we propose to evaluate measured CEC concentrations compared with newly identified protective thresholds to prioritize CECs and areas of concern in San

Francisco Bay for future monitoring. Results may identify data gaps for contaminants currently designated as Possible Concern in the RMP tiered risk-based framework that could be the subject of RMP-funded ecotoxicity studies. These results may also guide the design of future toxicological high-throughput screening studies in 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 toxicity information reported in the scientific literature. Evaluate toxicity data gaps. Inform risk evaluation of data-poor (Possible Concern) chemicals and prioritization of followup work.	Does the latest science suggest a reprioritization of chemicals? Which CECs and environmental compartments are highest priority for 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?		
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 in the Bay?		
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 work addresses question 1 by assuring use of the best toxicity threshold information to evaluate the relative risk of CECs to Bay aquatic life. For example, calculation of a toxicity threshold for a contaminant that did not previously have a threshold might suggest it should be moved from the Possible Concern risk tier to the Low, Moderate, or High Concern tier.

Approach

CECs detected in the Bay and the toxicological thresholds used for comparison will be compiled from RMP-funded CECs studies from the past ten years (2009–2019). For all identified CECs, available toxicological thresholds will be obtained from the literature by querying multiple toxicity databases and conducting a literature review.

Cited and newly obtained thresholds will be evaluated for quality based on their source, using a tiered quality scale developed as part of the literature review. An example of possible quality rankings is shown in Table 2.

Table 2. Example toxicity threshold quality criteria.

Quality Score	Description
0: n/a	No threshold
1: prediction only	Threshold based on QSAR or read-across predictions only, with no experimental data
2: poor	Single endpoint (e.g., EC50, LOEC, or NOEC) from a single study
3: acceptable	PNEC based on limited experimental data (3 or fewer toxicity tests)
4: good	Marine PNEC estimated from freshwater PNEC based on adequate experimental data from multiple freshwater species
5: excellent	Estuarine or marine-specific PNEC or equivalent based on adequate experimental data from multiple marine or estuarine species

For all CECs with available toxicological thresholds with low quality scores (e.g., of 0, 1, or 2 in the example scoring system shown above), PNECs will be calculated from available experimental data and then scored in the same manner as literature thresholds. Derivation of PNECs will follow EU guidance (European Chemicals Agency, 2008), and methods will depend on the available experimental data. For example, sensitivity distribution methods are based on statistical calculations and require experimentally determined NOEC values for a number of species from different taxonomic groups, whereas assessment factor methods involve division of the lowest available toxicity value with an assessment factor that varies based on the sparseness of available data.

In the absence of any available experimental data, toxicity thresholds will be predicted using tools developed by the Toxicology in the 21st Century (Tox21) program, a joint initiative of the US Environmental Protection Agency (EPA), National Toxicology Program (NTP) headquartered at the National Institute of Environmental Health Sciences (NIEHS), National Center for Advancing Translational Sciences (NCATS), and Food and Drug Administration (FDA), as outlined in the 2020 Draft CEC Strategy Update (Miller et al., 2020). For example, EPA's Ecological Structure Activity Relationships (ECOSAR) Class Program is a computerized predictive system that estimates aquatic toxicity. The program estimates a chemical's acute (short-term) toxicity and chronic (long-term or delayed) toxicity to fish, aquatic invertebrates (daphnids), and aquatic plants (US EPA, 2015). Predicted thresholds will be scored using the same criteria as literature and calculated thresholds. Predicted thresholds will not necessarily be scored as acceptable even though the data used to derive them were from poor or prediction-only studies; in the cases of data poor compounds, the goal is to have a threshold for comparison with monitoring data and to identify which Possible Concern contaminants could be the subject of RMP-funded ecotoxicity studies.

All identified and calculated threshold values will be updated regularly (i.e., when new contaminants are studied and as part of future CEC strategy updates) so that future RMP studies have a streamlined system for identifying and reporting ecotoxicity thresholds.

Risk characterization ratios (PEC/PNEC ratios) for all detected CECs will be calculated by environmental compartment (i.e., sediment, water), where appropriate (e.g., a water ratio would not be calculated for a contaminant only measured in sediment). The risk characterization ratio is the ratio of the predicted exposure concentration (PEC) to the PNEC. PEC values will be estimated as the 90th percentile detected concentration in the Bay as a conservative protective approach; the highest detected concentrations may be outliers and not representative of Bay exposures, but a mean or median value would not be protective of areas near pathways that may have higher concentrations. Higher ratio values indicate more potential risk, with a ratio exceeding 1 indicating elevated concern. These results will be used to inform the design of future monitoring.

Budget

Expense	Estimated Hours	Estimated Cost
Labor		
Literature Review	100	$12,000
Threshold Calculations	200	$26,000
Senior Scientist Review	60	$12,000
Data Technical Services	50	$10,000
Direct Costs		
Equipment		0
Travel		0
Shipping		0
Grand Total		$60,000

<u>Budget Justification</u>

This budget would support approximately 300 hours of work by SFEI environmental analysts and the SFEI toxicologist, Dr. Ezra Miller, as well as 60 hours of work by senior scientists providing guidance and feedback and 50 hours of assistance from SFEI Data Technical Services compiling past RMP data.

Reporting

The methods and initially identified and calculated ecotoxicity threshold values and their quality scores will be compiled in a technical report. They will also be the start of a living document available to RMP staff and stakeholders that can be updated when new CECs are detected in the Bay and as part of future strategy updates. Results will be documented in RMP CEC Strategy documents and presented at the 2021 and 2022 ECWG meetings for discussion.

References

European Chemicals Agency, 2008. Guidance on information requirements and chemical safety assessment Chapter R.10: Characterisation of dose [concentration]-response for environment.

Miller, E., Shimabuku, I., Mendez, M., Buzby, N., Sutton, R., 2020. DRAFT Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations.

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Monitoring for Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in North Bay Margin Sediments

Study Budget, Total: $40,000 - $125,000

SFEI Contacts:

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Study Description

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a class of fluorine-rich, thermally and chemically stable compounds that are ubiquitous in the environment. More than 4,700 PFAS are used in consumer, commercial, and industrial applications, and widespread use of PFAS means they readily end up in waste streams that are ultimately discharged into the environment. Their highly persistent and recalcitrant nature, combined with bioaccumulation risks, raise concerns regarding potential negative impacts on human and wildlife health. Perfluorooctanoic sulfonate (PFOS) and perfluorooctanoic acid (PFOA), the best studied compounds within the class, have been identified as highly toxic with potential for multi-system and developmental effects. PFOS, PFOA, and other PFAS have been previously detected in San Francisco Bay biota, sediment, and water, and identified as Moderate Concerns within the RMP tiered risk-based framework.

To improve our understanding of the occurrence and risks associated with PFAS in the Bay, this study aims to assess North Bay margin sediment samples for PFAS. North Bay margin sediments are of particular interest given the presence of oil refineries and fuel storage facilities that are expected to store and/or use PFAS-containing foams for fire suppression. Through the RMP Status and Trends program, sampling of North Bay margin sites is planned for summer 2020; archived sediment samples can be examined upon funding of this proposal. Depending on available funding, the scope of this study may be limited to a subset of North Bay sites (n=15), or may be expanded to include analysis of all North Bay sites, as well as analysis of archived South Bay margin sediments collected in summer 2017 to inform a regional comparison. Higher levels of funding would permit analysis of both targeted PFAS using tandem liquid chromatography/mass spectrometry (LC-MS/MS) and precursors using the total oxidizable precursors (TOP) assay.

Monitoring for Halogenated Azo Dyes in Bay Sediments

Study Budget, Total: $65,000 – $95,000

SFEI Contacts:
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Analytical Laboratory Partner: Hui Peng, University of Toronto

Study Description

More than 10,000 dyes are used in textile manufacturing, and azo dyes account for >70% of the global industrial demand. These dyes are not only used in textiles, but also in lacquers and varnishes, printing inks, plastics, and to color cosmetics, waxes (e.g., candles), soaps, leather, and paper. In addition to their environmental release as part of industry waste, azo dyes may also be released to the environment via the use (e.g., laundering) and disposal of products containing them. Brominated and chlorinated azo dyes are structurally diverse, and therefore have diverse environmental fates and toxicities, but many are mutagenic, genotoxic, or carcinogenic. Despite their potential risk to aquatic food webs, environmental monitoring of these dyes remains relatively rare. However, recent studies revealed brominated azo dyes to be the most commonly detected and abundant contaminant in indoor dust (Dhungana et al., 2019; Peng et al., 2016). Other recent studies have implicated halogenated azo dyes in the mutagenicity of urban river water and sediment samples (de Aragão Umbuzeiro et al., 2005; Palma de Oliveira et al., 2006; Vacchi et al., 2017).

Halogenated azo dyes have not been previously monitored in San Francisco Bay; monitoring is needed to assess whether and to what extent these contaminants are present in the Bay. The goal of this study is to assess Bay sediment samples for brominated and chlorinated azo dyes using high-resolution mass spectrometry. This project would use archived margin sediment samples from Lower South Bay. As an add-on option, this project could also include analysis of archived North Bay margin sediment, to be collected in 2020, in order to begin to assess spatial distribution of azo dyes within the Bay. Concentrations in Bay sediment would be compared to available toxicity thresholds to assign detected chemicals to a tier in the RMP tiered risk-based framework for CECs and determine whether follow up study is needed.

References

de Aragão Umbuzeiro, G., Freeman, H.S., Warren, S.H., de Oliveira, D.P., Terao, Y., Watanabe, T., Claxton, L.D., 2005. The contribution of azo dyes to the mutagenic activity of the Cristais River. Chemosphere 60, 55–64. https://doi.org/10.1016/j.chemosphere.2004.11.100

Dhungana, B., Peng, H., Kutarna, S., Umbuzeiro, G., Shrestha, S., Liu, J., Jones, P.D., Subedi, B., Giesy, J.P., Cobb, G.P., 2019. Abundances and concentrations of brominated azo dyes detected in indoor dust. Environmental Pollution 252, 784–793. https://doi.org/10.1016/j.envpol.2019.05.153

Palma de Oliveira, D., Kuhlmann, M.L., de Aragão Umbuzeiro, G., 2006. Evaluation of the Presence of Mutagenic Dyes in Sediments from Cristais River. Soil and Sediment Contamination: An International Journal 15, 455–462. https://doi.org/10.1080/15320380600846882

Peng, H., Saunders, D.M.V., Sun, J., Jones, P.D., Wong, C.K.C., Liu, H., Giesy, J.P., 2016. Mutagenic Azo Dyes, Rather Than Flame Retardants, Are the Predominant Brominated Compounds in House Dust. Environmental Science & Technology 50, 12669–12677. https://doi.org/10.1021/acs.est.6b03954

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Non-targeted analysis in South Bay harbor seals

Study Budget, Total: $75,000 – $250,000

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Analytical Laboratory Partner: Heather Bischel, University of California at Davis

Study Description

Non-targeted analysis is a powerful and rapidly evolving new tool in environmental investigations that allows researchers to screen samples for thousands of chemicals to identify new contaminants that may have been missed by traditional targeted methods. The purpose of this study is to screen for a wide range of contaminants in archived Bay harbor seal tissues using non-targeted and related suspect screening analytical approaches. Harbor seals are apex predators in the Bay, which means contaminants that biomagnify tend to be present in their tissues at higher concentrations compared to species lower in the food web.

Previous RMP investigations have indicated that South Bay harbor seals are exposed to high levels of per- and polyfluorinated alkyl substances (PFAS), a broad class of fluorine-rich contaminants that are of growing environmental concern because they are ubiquitous, extremely persistent, and several have been shown to be highly toxic and bioaccumulative. However, only a few different PFAS were examined in these previous studies. A recent study of marine mammals collected across the northern hemisphere identified an additional 33 PFAS that have not been examined in Bay species (Spaan et al., 2019).

In addition to PFAS, harbor seals tend to bioaccumulate hydrophobic and persistent chlorinated and brominated organic contaminants. The RMP funded a non-targeted analysis of San Francisco Bay seals nearly a decade ago, which identified chlorinated and brominated organics including legacy pollutants and a few additional contaminants that had not been previously monitored (Sutton and Kucklick, 2015). Methods have improved significantly in recent years; an examination of Bay samples using improved methods may reveal new insights.

PFAS bind to proteins and tend to accumulate in the blood and liver, while chlorinated and brominated organics tend to accumulate in fatty tissue. Samples of harbor seal liver and blubber archived from animals found in the South Bay will be analyzed to screen for a wide range of contaminants. The number of samples analyzed will depend on the level of funding. Higher levels of funding would permit a comparison of contaminants in samples collected recently and in previous time periods to identify temporal trends. Results may indicate the presence of PFAS and other contaminants accumulating in Bay wildlife that are not typically analyzed in targeted monitoring studies. Alternatively, should results reveal most compounds are already included in targeted monitoring studies, this will help confirm that current Bay monitoring sufficiently captures priority contaminants.

References

Spaan, K., van Noordenburg, C., Plassmann, M., Schultes, L., Shaw, S.D., Berger, M., Heide-Jørgensen, M.P., Rosing-Asvid, A., Granquist, S., Dietz, R., Sonne, C., Rigét, F., Roos, A., Benskin, J., 2019. Fluorine Mass Balance and Suspect Screening in Marine Mammals from the Northern Hemisphere (preprint).

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