# RMP Emerging Contaminants Workgroup Meeting

**March 30, 2017**  
**9:00 AM – 4:30 PM**

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

## Agenda

|   | Introductions and Goals for Today’s Meeting (Attachment) | 9:00  
|   | Phil Trowbridge |
|---|--------------------------------------------------------|---|
| 1. | The goals for today: |  |
|   | ● Provide updates on recent and ongoing ECWG activities  
|   | ● Feedback on Revised CEC Strategy document  
|   | ● Recommend which special study proposals should be funded in 2018 and provide advice to enhance those proposals |  |
|   | Meeting materials: 2016 ECWG minutes (See pages 3-14) |  |
| 2. | Discussion: Revised CEC Strategy (Attachment) | 9:10  
|   | Rebecca Sutton |
|   | Review of recent RMP activities and Revised CEC Strategy document; discussion of major changes embedded within the draft revision. |  |
|   | Desired Outcome: Feedback on Revised CEC Strategy (draft); additional feedback may be provided during a follow-up call, to be scheduled during the ECWG meeting |  |
|   | Meeting materials: Revised CEC Strategy - Draft (attached separately) |  |
|   | Short Break | 11:20  
|   | Lunch (provided) | 12:20  
| 3. | Information: Non-targeted Analysis of Polar Compounds in San Francisco Bay Water and Effluent | 11:30  
|   | Lee Ferguson |
|   | Review preliminary findings from non-targeted analysis of ambient Bay water and wastewater effluent. Contaminants identified as part of this analysis may be suitable for follow-up quantitative monitoring in the Bay. |  |
|   | Desired outcome: Workgroup insights to refine analysis of data |  |
4. **Summary of Special Study 2018 Proposals** (Attachments)

   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.

   Special Study 2018 Proposals include:
   
   - CEC Strategy
   - Characterizing Unknown PFAS in Seals and Margin Sediment
   - Non-targeted Analysis of Margin Sediment and Related Studies
   - Nonylphenol Ethoxylates in Margin Sediment
   - Pesticides and Wastewater Contaminants in Margin Sediment and Water
   - Non-targeted Analysis of RO Concentrate
   - Pharmaceuticals in Effluent Report

   Meeting materials: ECWG 2018 Special Studies Proposals (See pages 15-79)

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<thead>
<tr>
<th>Time</th>
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<tr>
<td>1:00</td>
<td>Rebecca Sutton, Diana Lin, Meg Sedlak, Jennifer Sun</td>
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5. **Discussion of Recommended Studies for 2018**

   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.

   **Short Break**

   3:50

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

   RMP Special Studies are identified and funded through a three-step process. Workgroups recommend studies for funding to the Technical Review Committee (TRC). The TRC weighs input from all the workgroups and then recommends a slate of studies to the Steering Committee. The Steering Committee makes the final funding decision. For this agenda item, the ECWG is expected to decide (by consensus) on a prioritized list of which studies to recommend to the TRC. To avoid an actual or perceived conflict of interest, the Principal Investigators for proposed special studies are expected to leave the room during this agenda item.

   Desired Outcome: Recommendations from the ECWG to the TRC regarding which special studies should be funded in 2018 and their order of priority.

   **Report out on Recommendations**

   4:20 Karin North

7. **Adjourn**

   4:30
# RMP Emerging Contaminants Workgroup Meeting

## April 15, 2016

San Francisco Estuary Institute

## Meeting Summary

### Attendees

<table>
<thead>
<tr>
<th>Science Advisor</th>
<th>Affiliation</th>
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<tr>
<td>Lee Ferguson</td>
<td>Duke University</td>
<td>Yes</td>
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<td>Philip Gschwend</td>
<td>MIT</td>
<td>Yes</td>
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<td>Kelly Moran</td>
<td>TDC Environmental</td>
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<td>Derek Muir</td>
<td>Environment Canada</td>
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<td>Heather Stapleton</td>
<td>Duke University</td>
<td>Yes</td>
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<tr>
<td>Bill Arnold</td>
<td>University of Minnesota</td>
<td>Yes</td>
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### Others Present

- Rebecca Sutton (SFEI)
- Phil Trowbridge (SFEI)
- Jay Davis (SFEI)
- Meg Sedlak (SFEI)
- Don Yee (SFEI)
- Jennifer Sun (SFEI)
- Tom Mumley (SFBRWQCB)
- Dawit Tadesse (SWRCB)
- Luisa Valiela (USEPA) - phone
- Gail Kroweche (OEHHA)
- June-So Park (DTSC)
- Anne Cooper Doherty (DTSC)
- Eileen Sheehan (DTSC)
- Sabrina Crispo-Smith (DTSC)
- Miaomiao Wang (DTSC)
- Jennifer Teerlink (DPR)
- Keith Maruya (SCCWRP)
- Nathan Dodder (SCCWRP)
- Erika Houtz (Arcadis)
- Karin North (City of Palo Alto)
- Eric Dunlavey (City of San Jose)
- Simret Yigzaw (City of San Jose)
- Nadia Borisova (EBMUD)
- Heather Peterson (City of San Francisco)
- Jennifer Jackson (City of San Francisco) - phone
- Miriam Diamond (University of Toronto)
- Mike Elliott (AXYS)
- Terry Grimm (Cambridge Isotope Labs)
- Tri Nguyen (CCCSD)
- Melody LaBella (CCCSD) - phone
- Martice Vasquez (CDFW) - phone
- Robert Wilson (City of Petaluma) - phone
- Andria Ventura (Clean Water Action) - phone
1. Introductions, Approval of Minutes, and Goals for the Meeting
The Emerging Contaminants Workgroup has a planning budget of $234k out of the total RMP planning budget of $1,556k, although expected Special Studies funding is expected to be approximately $1,073k. Karin North indicated that the distribution of budget across workgroups is based in part on permit monitoring requirements.

Rebecca Sutton introduced the Emerging Contaminants Workgroup’s two new science advisors: Heather Stapleton (Duke University), an expert on environmental chemistry and health; and Bill Arnold (University of Minnesota), an expert on transformation processes, reaction mechanisms and reaction rates.

2. Information: Update on CEC Strategy
Rebecca Sutton presented an overview of the Emerging Contaminants Strategy, including a review of the tiered chemical classification scheme and a proposal to add new management questions to the strategy.

Tiered Classification Scheme
- Tier 3 (moderate concern)
  - PFOS (present but below the Minnesota threshold for PFOS in fish)
  - Fipronil
  - Nonylphenol (reviewed SNUR comment letters -- actually many potential uses aside from detergent)
  - PBDEs (monitoring recovery)
- Tier 2 (low concern)
  - Pharmaceuticals
  - Triclosan
- Tier 1 (possible concern)
  - Microplastics
  - Bisphenols and other plasticizers
  - Other pesticides
  - Other fluorinated chemicals
  - Alternative flame retardants
  - Many others

Management Questions
Rebecca proposed three new management questions:
1. What emerging contaminants have the potential to adversely impact beneficial uses of the Bay? [current management question]
2. What are sources and pathways of emerging contaminants?
3. Are the sources and pathways controllable, and if so, what are known or potential management actions?
4. Are management actions effective?

Key comments are highlighted below:

- Several group members agreed that the management questions should explicitly include an evaluation of trends rather than just thresholds, and include a method for reevaluating the classification of contaminants within the tiered risk framework.
- Management Question 4 should be reformulated to be more open ended, asking “What effects are management actions having?” which will also encompass a review of alternative and substitute chemicals. Management actions can have both positive and negative impacts.
- Miriam Diamond noted that the evaluation of trends should include consideration of secondary stressors like climate change that could impact expected trends.
- Phil Gschwend emphasized the need for mass-balance modeling to understand the causes of the trends being observed, and thus the expected impact of planned management actions.

Lee noted that all compounds in the “moderate concern” category are currently being addressed except nonylphenol, which is planned for future study in the multi-year plan. Lee highlighted the need to collect current data to monitor detergent phase-out related trends. He also suggested monitoring both nonylphenol ethoxylates, which will indicate whether sources are primarily wastewater or stormwater, as the SNUR has shown many non-wastewater uses for nonylphenol. Water and possibly sediment would be the ideal monitoring matrices. A finer resolution of ratios of nonylphenols to octylphenols could help to identify sources. Jennifer Teerlink suggested possible split sampling of these compounds in urban stormwater, as they might be ingredients in pesticide formulations. Miriam noted that nonylphenols were included on the Great Lakes candidate list for contaminants of emerging concern.

Rebecca then asked for feedback on formal inclusion of a class-based approach in the CEC strategy, including chemical class (ie. chemicals with similar toxic impacts) and functional class (ie. chemicals used for similar applications). Chemical classes would be constrained in part by analytical laboratory classifications and capabilities. Lee suggested grouping chemicals in a more systematic way, and described his current effort to use text data mining of scientific publications to calculate similarities between compounds based on text descriptors. Derek Muir pointed out that this level of rigor may be beyond the scope of the RMP, which focuses primarily on the universe of known and previously studied chemicals with toxicity thresholds. Phil Gschwend suggested looking at functional groups to help identify emerging contaminants developed as alternatives to known chemicals.

Tom Mumley noted that the program has not yet begun more extensive, proactive examinations of sources or use trends as a means of identifying potential emerging contaminant issues in the Bay, although some additional effort to do so could better inform expectations and interpretations of ambient Bay results. Tom and other stakeholders and science advisors agreed...
that it would be desirable for the group to meet twice a year -- once in the fall to discuss the strategy, and once in the spring to discuss specific proposals.

3. Information: Update on Effluent Pesticide Monitoring: Fipronil and Imidacloprid

Rebecca presented results from a recent study on fipronil and imidacloprid in wastewater influent, effluent, and biosolids (LC-ESI-MS/MS in aqueous and solid phase). The analyses were conducted using the newest isotope labeled standards by Akash Sadaria in Dr. Rolf Halden’s lab at Arizona State University. Fipronil and imidacloprid were widely detected in wastewater, in many cases at concentrations exceeding toxicity thresholds. Wastewater treatment appeared to have little impact on concentrations of these compounds, and imidacloprid concentrations in both influent and effluent concentrations were significantly higher than the nationwide average (not normalized by population size). Fipronil, but not imidacloprid, was detected in sewage sludge.

Rebecca also presented Kelly Moran’s conceptual model showing sources and pathways of imidacloprid into surface water bodies, which highlights pet treatments as a source. Other sources include indoor, outdoor and underground pest treatments.

Kelly Moran noted that based on per capita effluent concentration calculations, fipronil and imidacloprid use seems to be associated with population size, suggesting household applications as a dominant source. Bill Arnold noted that in Minnesota imidacloprid is used on nursery plants, resulting in a seasonal use pattern. The variation in wastewater effluent concentrations is narrow, suggesting a more constant and ubiquitous source. Concentrations in pet treatments and predicted wash off are much higher than other potential sources, suggesting a focus on pet treatments would be appropriate for source control efforts.

Jennifer Teerlink and Kelly Moran explained that it is difficult to get source information about fipronil and imidacloprid sales; current pounds of sale data are two years old and have in the past been severely underreported, and data on sales of individual products are proprietary. Lee noted that imidacloprid and fipronil are not always combined in production; imidacloprid is also often produced with methoprene.

Derek Muir asked whether the RMP should be studying neonicotinoids more broadly. Jennifer Teerlink indicated that imidacloprid is the most significant neonicotinoid of concern to the DPR. Kelly also pointed out that the current wastewater study focuses on indoor use, rather than broader outdoor or agricultural applications, in which other compounds may also be of interest.

Phil Gschwend suggested that the final report include a structural diagram of the target compounds (including fipronil degradates). Phil also questioned the chemical properties listed from the compounds, which were drawn from regulatory documents.
4. Information: Occurrence and Fate of PFASs in SFO Industrial Treatment Plant During Annual AFFF Testing

Erika Houtz presented results from her recent study of PFASs in the effluent of the San Francisco Airport’s industrial treatment plant. USEPA recently finalized health advisories on PFOA and PFOS in drinking water, which combined should be lower than 70 ng/L. This is nearly an order of magnitude lower than the provisional health advisories. The objective of this study was to investigate PFAS fate and transport during AFFF testing at SFO, including sources, transformation rates and products, and mass loading to the Bay. Although SFO does not conduct fire training with AFFF, the FAA requires that all trucks and AFFF stock are tested annually; the spent foam is discharged to their industrial wastewater treatment plant. Historically, 3M’s AFFF has been used in fire fighting foams, and is a major source of PFOS. Airport records indicate that SFO is currently using Ansulite 3% AFFF, which does not contain PFOS, although photos taken at SFO showed that the current fire fighting material used is National Foam Aero-o-water, which also does not contain PFOS but does contain other polyfluorinated compounds of concern, such as 6:2 fluorotelomer compounds.

Influent, effluent, and mid-treatment samples were collected in November and December 2015 when the airport was testing their stock of foams and discharging them to the industrial treatment plant. Samples were analyzed by LC-MS/MS for PFAS compounds, as well as a total oxidizable precursor (TOP) assay to measure total PFAS and LC-QTOF-MS for identification of PFAS without standards. Both PFOS and 6:2 FtS matched AFFF use peaks, although PFOS-containing 3M AFFF has not been used for many years; residual on equipment may be contributing to concentrations in discharge. Background concentrations at SFO are orders of magnitude higher than in other locations, suggesting residual concentrations within the aging wastewater treatment plant itself. Over 95% of the PFAS mass added from testing of AFFF stocks and equipment was removed from the wastewater treatment plant over 12 days; some of these compounds may be filtered out but some may also be adhering to the walls of the treatment equipment.

95-98% of the total PFAS mass was not directly measured by the target analyte list, indicating that traditional analytical methods are missing large masses of polyfluorinated compounds that are beginning to be used in new AFFF formulations.

Erika noted that although AFFF contains other compounds, these other chemicals break down more readily under aerobic conditions. The formulations are reported to contain about 1-2% fluorinated content.

5. Information: Management Update

Tom Mumley presented an overview of the region’s current strategy for managing Contaminants of Emerging Concern. The Water Board is working to avoid direct regulatory actions, and instead emphasizes the need to focus efforts on source identification and control. This includes both RMP pathways monitoring as well as work farther upstream, such as tracking product use.
and market trends. This type of management will also require a focus on public education and industry cooperation.

Tom provided an overview of current management efforts on chemicals in the tier 3 moderate concern category. The Water Board has developed CEC Action Plans for these compounds:

- **PBDEs** - currently the main action is monitoring recovery, as well as tracking and evaluating flame retardant alternatives. California is revisiting its flammability standards, which may reduce use of toxic alternatives.
- **Nonylphenol and nonylphenol ethoxylates** - following 2006-2016 phase-outs, currently the main management action is monitoring recovery.
- **PFOS** - following phase-outs in the early 2000s, the main management action is also monitoring recovery. Related activities including tracking and evaluating precursor compounds.
- **Fipronil** - management efforts include DPR’s current review and evaluation of fipronil uses and mitigation methods; the EPA Office of Pesticides Programs fipronil reregistration review; and the Water Board’s statewide urban pesticide reduction project, which focuses primarily on urban runoff and creeks. The Water Board would like to avoid developing a TMDL but instead will work with DPR and EPA to track these efforts and increase focus on fipronil in estuaries and estuary pathways.

Tom then listed some additional compounds that are candidates for CEC Action Plans:

- Pyrethroids and other pesticides
- Alternative flame retardants
- PFASs
- Pharmaceuticals
- Personal Care Products, such as triclosan
- Microplastics

### 6. Special Study 2017: PFAS Synthesis and Strategy

Meg Sedlak presented a proposal to synthesize toxicity information and existing data collected by the RMP, Stanford, UC Berkeley, SCCWRP, AXYS, DTSC and other agencies on PFAS in ambient Bay water, sediment, biota and pathways, and develop a strategy for ongoing monitoring. While PFOS is considered a tier 3 moderate concern compound in the RMP’s CEC risk framework, other members of the PFAS family are less well studied.

PFAS concentrations in the Bay are particularly high in seals compared to concentrations measured elsewhere, but concentrations in effluent and ambient water are comparable. Terry Grimms suggested focusing the synthesis on areas where we expect to see higher concentrations relative to other locations. Lee Ferguson and Derek Muir pointed out that out of several thousand possible PFAS chemicals, only a few dozen have been identified in any environmental matrix; Phil Gschwend suggested that future monitoring include methods to identify some unknown precursors and/or measure concentrations of total perfluorinated
compounds (TOP). Erika indicated that TOP methods can become quite sensitive even in dilute matrices (ug/L or lower), depending in part on the detection limits of known analytes.

Derek Muir suggested that extracting organofluorines could be a good method for measuring the bioavailable fraction; however, Erika indicated that the new shorter-chain alternative compounds are very mobile and not as bioaccumulative, and are only able to be captured using reverse osmosis or nanofiltration. Shorter chain alternatives easily break through GAC, which is being used to treat PFOS and PFOA in some treatment systems.

Heather Stapleton suggested using methods to look at C-6 perfluorinated compounds. Heather’s previous work has found C-6 telomer alcohols and others at ug/g levels in indoor dust samples, which can be a source for compounds in wastewater effluent. Derek suggested a future monitoring target known as F53B, recently identified in environmental samples.

7. Special Study 2017: Phosphate Flame Retardants in Water
Rebecca Sutton presented a proposal for monitoring phosphate flame retardants in ambient Bay water as part of the 2017 Status and Trends Water Cruise. Past ambient Bay monitoring, focused largely on South Bay, showed the presence of numerous phosphate flame retardants, some of which were at concentrations approaching toxicity thresholds. This study would support a stronger classification of these compounds through Bay-wide monitoring, include new compounds that were not previously monitored.

Heather Stapleton indicated that through her work studying these compounds in furniture, it appears that TDCPP is being phased out, but non-halogenated aryl phosphate mixtures are of concern and should be added to the proposed analysis list. Heather indicated that although she doesn’t have standards for the dominant isomers in some of the popular commercial mixtures, she does have the commercial mixture formulas for comparison.

Derek Muir noted that some high production volume phosphate flame retardants may not have been studied yet, and may be good candidates to include in this monitoring. Rebecca responded that an initial investigation of USEPA high production volume lists suggested the existing list of analytes was appropriate, but a more thorough check is warranted.

The science advisors expressed strong support for this study, particularly as these compounds are highly mobile and thus are likely to be increasingly studied internationally. Furthermore, many of these compounds are also used as antioxidants or ingredients in plastic, and thus may be introduced through sources other than flame retardants.

8. Special Study 2017: Imidacloprid in Water
Rebecca presented a proposal for monitoring imidacloprid in ambient Bay water during the 2017 Status and Trends Water Cruise. Imidacloprid is a widely used neonicotinoid insecticide that has
been shown to be present in wastewater effluent at concentrations exceeding an established aquatic toxicity threshold.

Lee suggested measuring imidacloprid transformation products as well, particularly if aquatic toxicity information is available and imidacloprid concentrations are expected to be high. 6-CNA is a major transformation product that is not as toxic as imidacloprid but still has some aquatic toxicity. Kelly Moran suggested monitoring for other neonicotinoids as well, which may be delivered in non-agricultural discharges. Kelly was uncertain as to the potential environmental relevance of imidacloprid degradates. EPA's upcoming review will look at the toxicity of degradates. In the absence of experimental data, potential toxicity can be identified using ECOSAR (Ecological Structure Activity Relationships predictive model, which predicts aquatic toxicity for uncharacterized compounds based on structural similarities to compounds with known toxicity data, and can be updated with new data).

Kelly indicated that the reporting timeline should be accelerated. The EPA is currently conducting its risk assessment for imidacloprid, which is expected to be released in early 2017. The final reregistration decision is typically proposed one year, in early 2018, so data should be written up and reported prior to 2018.

Tom Mumley expressed support for this proposal, but expressed concern that concentrations would not be high enough throughout the Bay to warrant whole-Bay sampling. Rebecca noted that use of a conservative tracer model seeded with the effluent concentrations from the RMP study reported earlier in the day suggests concentrations in the South and Lower South Bays suggest levels could exceed toxicity thresholds. Kelly indicated that imidacloprid concentrations are high in both urban runoff and agriculture, and it is unlikely that monitoring would occur when these sources are diluted by stormwater. Imidacloprid is used in outdoor structural pest control and is retailed widely; furthermore, it has been detected in areas with no record of application, suggesting that it is mobile and easily transferred. Although Scotts and Lowes are no longer selling products with imidacloprid, the large retailer Bayer is continuing to sell the product. Ambient Bay water sampling would occur during the summer, when use volumes are high.

9. Special Study 2017: Bisphenols in Water

Jennifer Sun presented a proposal for monitoring 16 bisphenol compounds in ambient Bay water and pathways, including stormwater and wastewater effluent. Bisphenols are a class of widely used endocrine disrupting chemicals for which new methods are available to analyze a broader range of chemicals with lower detection limits than previously possible. A new toxicity threshold was established in 2011 that is below the detection limit for the bisphenol A method previously used to monitor bisphenol A (as part of a larger pharmaceutical compound scan) in ambient Bay water. This data will enable a stronger risk classification for the broader bisphenol class of compounds.

Lee suggested analyzing chlorinated bisphenols in effluent, which are a likely transformation product during water treatment and are more estrogenic than non-chlorinated bisphenol
compounds. Tom expressed concern about the stormwater monitoring design, which may be limited to only a few urban watersheds based on the STLS monitoring design. Although a major source of bisphenols in stormwater is likely to be trash, some members indicated that sources of bisphenols in stormwater are likely more widespread (i.e., wash-off from paints and metal coatings on outdoor structures), such that monitoring should not only focus on trash-heavy locations.

10. Special Study 2017: Triclosan in Small Fish
Rebecca Sutton presented a proposal for monitoring triclosan in small fish. Samples would be collected in collaboration with existing small fish collection efforts, including those occurring in the Lower South Bay and the North Bay. Triclosan has previously been monitored in ambient Bay water and sediment and found at levels indicating low concern (Tier 2) for the Bay. A single surface water sample collected more recently in the Lower South Bay suggests concentrations may now be higher. In addition, a recent study in Puget Sound showed that triclosan can bioaccumulate and be found at levels of concern in biota even when concentrations are below levels of concern in ambient water.

Lee confirmed that the proposed study would include other compounds on the AXYS pharmaceuticals list 3, including triclocarban. Miriam Diamond indicated that the analysis should include methyl triclosan, a triclosan metabolite, which would require a different method.

Phil Gschwend suggested that fish concentrations simply be calculated based on ambient Bay water concentrations. Although this might be possible, Rebecca and Derek Muir expressed concern this method of determining triclosan exposure risk in biota would not be sufficient to direct management or regulatory action. There is no currently available tissue-based toxicity threshold for triclosan, but chronic toxicity studies showed aggressive behaviors after about a month.

Karin North noted that triclosan will already be monitored in some wastewater treatment plant outfalls as part of the voluntary RMP pharmaceuticals in wastewater study occurring this summer. Bill Arnold asked where the small fish are typically collected, and Eric Dunlavey and other stakeholders indicated that they are often caught near wastewater outfalls. In order to reduce cost and focus sampling in areas likely to be most impacted by triclosan, Becky suggested an alternate scope of study including both water and small fish sampling in Lower South Bay.

Phil Gschwend and Miriam suggested studying algal toxicity and antibacterial resistance as well. Kelly Moran indicated that the EPA has cited a green algae EC-50 of 750 ng/L, which is within the same range of the expected effect on fish. Claudia Gunsch (Duke University) and researchers at Marquette University are currently studying triclosan impacts on bacteria. However, Karin North and Eric Dunlavey indicated that antibiotic resistance does not seem to be a current issue, as their wastewater facilities are not experiencing any issues with their biological treatment systems.
11. Special Study 2017: CEC Strategy Support
Rebecca Sutton presented the proposal for support the Contaminants of Emerging Concern strategy. These funds are required to support the management and development of this program, including work to track new contaminant occurrence and toxicity science and regulatory, assisting the Water Board with emerging contaminants action plans, coordinating pro-bono studies, and updating the CEC Strategy.

Karin North and other stakeholders expressed concern that the proposed $40k will not be sufficient to cover true program costs, including crucial networking efforts. Phil Trowbridge indicated that Rebecca currently uses other RMP program management funds to support her work developing the Contaminants of Emerging Concern program, and that the proposed $40k does not fully cover her program management costs.

12. Discussion of Recommended Studies for 2017
The total budget for all proposed studies is $315k, while the planning budget is $234k.

Karin North suggested supporting all proposed studies by phasing the studies over a two year period, funding sample collection and analysis in 2017 and data analysis and reporting in 2018. Discussion highlights about relative study priorities and recommendations for future CEC studies and strategy are summarized below.

Regulatory and Management Priorities
- Jennifer Teerlink indicated that imidacloprid monitoring would complement DPR’s current efforts, which do not currently include saltwater monitoring and management. It is unlikely that DPR will currently be able to provide funding for these studies, though Jennifer, Rebecca, and Kelly will continue this discussion with other DPR staff.
- Anne Cooper Doherty indicated that DTSC’s Safer Consumer Products program cannot prioritize work on imidacloprid because it is a pesticide and pesticides are excluded from DTSC’s authorities. DTSC can address any chemicals on their Candidate Chemical List used in consumer products as described in the Safer Consumer Product statutes and regulations.
- Anne Cooper Doherty indicated that in cases in which compounds were previously not detected as a function of high detection limits, additional monitoring is a high priority to clarify the true toxicity risk. All studies are relevant to the safer consumer products work.

Passive Sampling
Phil Gschwend and Lee Ferguson suggested that the RMP consider passive sampling in place of or in addition to grab sampling for many of these water samples. Phil Gschwend has used passive sampling in Richmond Harbor to identify a previously unknown source of DDT - groundwater. Phil suggested using POCIS with C-13 labeled internal standards that can be used to calculate transfer in and out of the sampler, enabling quantitative sampling. Additional
work could be done to mine data on sources and use simple mass-balance models to estimate concentrations expected in water samples. Lee has used this method to successfully predict nonylphenol concentrations within a factor of two.

Derek Muir indicated that the European AQUA-GAPS program, though poorly funded, is developing a monitoring program using silicone passive samplers, which Derek suggested may be preferable to more common polyethylene samplers. Passive samplers are also being used in the Great Lakes to monitor PCBs, PBDEs and PAHs (by Rainer Lohmann, one of Phil’s former postdocs). However, because passive samplers are not fully measuring colloid-bound contaminants, concentrations estimated using passive samplers have been measured at 100 x lower concentrations, and are thus not easily comparable to historically measured compounds and should not replace important measurements for long-term time trends.

Passive sampling techniques are better developed for hydrophobic compounds, although the majority of proposed studies target hydrophilic compounds. Lee suggested testing passive sampling on bisphenols or phosphate flame retardants and not imidacloprid, although he indicated that he has detected imidacloprid on passive samplers previously. Jennifer Teerlink indicated the DPR has previously done some passive sampling for hydrophobic but not hydrophilic compounds. Both passive and grab samples could be taken in parallel as methods for quantitative sampling of desired target compounds are developed.

Multiple stakeholders, including DPR and wastewater representatives, expressed concern that agencies (including pesticide registrants) would not be comfortable with accepting calculated concentrations measured using passive samplers for use in a regulatory context. However, Tom Mumley agreed that the group should begin investigating the use of passive samplers. The group agreed to hold a brown bag webinar in the fall to introduce passive sampling methods and applications to stakeholders and explore potential applications in the RMP.

Comments on Specific Studies

- Although the triclosan study is not time-sensitive, it is taking advantage of existing small fish surveys that are already occurring. Eric Dunlavey suggested phasing this study by collecting the fish in 2017 and conducting analyses in future years, particularly if adding methyl triclosan analysis will significantly increase costs.
- Imidacloprid monitoring is a high priority as it has the potential to influence regulatory decisions; for this reason, it should not be studied using passive samplers as easily understood and defensible numbers are needed to support regulatory decisions.
- Bisphenols and phosphate flame retardants span a broad range of chemical characteristics and could be of interest in either sediment or water, and possibly passive samplers.
- Tom Mumley, Kelly Moran, and others advocated for adding simple modeling to the CEC strategy, including the collection of source data.
- Phil Gschwend argued that PFAS and bisphenols are relatively high study priorities because they have been poorly studied in the past and information about new “versions”
of these compounds offers the opportunity to influence upstream management actions earlier in the cycle before they become major concerns.

13. Closed Session - Decision: Recommendations for 2017 Special Studies Funding

14. Report out on Recommendations

The group agreed on the following study prioritization and proposal revisions:

1. CEC strategy - increase budget to include simple modeling and a webinar on passive sampling methods
2. Imidacloprid in Ambient Bay Water - add imidacloprid degradates and other neonicotinoids
3. PFAS Synthesis & Strategy
4. Phosphate flame retardants in Ambient Bay Water - broaden the analyte list to at minimum include compounds recently detected in furniture foam and any additional compounds identified as high production volume
5. Bisphenols in Ambient Bay Water - monitoring ambient Bay water only, eliminating pathways characterization, and consider concurrent exploration with passive sampling
6. Triclosan in Small Fish - include methyl triclosan in the analysis, and limit the sampling to small fish in the Lower South Bay
<table>
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<tr>
<th>Study Name</th>
<th>Budget</th>
<th>Summary</th>
<th>RMP Tier</th>
<th>Critical Drivers</th>
<th>Deliverables</th>
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<tr>
<td>Emerging Contaminants Strategy</td>
<td>$65,000</td>
<td>Annual update of CEC Strategy, including tracking new information, updating the Tiered Framework and Multi-Year Plan. Increasing needs for stakeholder support, coordination of pro bono studies, and development and use of CEC transport model.</td>
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<td>Essential to coordinate studies relevant to management actions. Inform policy actions at local, state, federal levels. Funding request ~20% of planning budget.</td>
<td>Technical assistance to stakeholders; Update and share CEC strategy; Continue development of Bay contaminant transport model.</td>
<td>19 - 24</td>
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<tr>
<td>Characterizing Unknown PFASs in SF Bay Seal Blood and Sediment</td>
<td>$78,000</td>
<td>This study will use new methods to identify a more complete list of PFASs in harbor seal blood and sediment. This is important to identify the PFAS alternatives as manufacturers phase out PFOS and perfluorooctanoic acid (PFOA).</td>
<td>III and I</td>
<td><strong>Scientific driver</strong>: PFAS are highly persistent; high concentrations have been measured in Bay seals; Early recommendation arising from ongoing PFAS synthesis/strategy (2017 special study). <strong>Management driver</strong>: Inform regional CEC Action Plan, DTSC Safer Consumer Products program. <strong>Cost savings</strong>: Leverages 2017 margin sediment sample collection, RMP sediment and TMMC harbor seal archives.</td>
<td>Fact Sheet, Manuscript: Jan 2019. Key PFAS analytes uploaded to CEDEN.</td>
<td>25 - 32</td>
</tr>
<tr>
<td>Study Name</td>
<td>Budget</td>
<td>Summary</td>
<td>RMP Tier</td>
<td>Critical Drivers</td>
<td>Deliverables</td>
<td>Page #</td>
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| Non-targeted Analysis of Sediment and Related Studies | $117,550 | Non-targeted analysis (NTA) will identify nonpolar and polar contaminants in Bay sediment, a matrix not yet screened. NTA helps assure focus on contaminants with greatest potential for concern, by seeking to remove a “knowledge bias” on previously identified contaminants. This study will also screen for nonpolar compounds in previously collected passive sampler samples. Margin sediment will also be analyzed for mutagenic dyes and dye-related compounds. | I        | **Scientific driver:** NTA is a key element in the RMP CEC Strategy, and can identify unanticipated contaminants that can lead to targeted chemical monitoring or toxicity evaluations.  
**Management driver:** Additional screening of a new class of contaminants, dyes, can inform DTSC’s Safer Consumer Products program.  
**Cost savings:** Leverages 2017 margin sediment sample collection, previously collected 2016 POCIS samples. | Fact Sheet, Manuscript: Spring 2019.  
Dye data will be transcribed to CEDEN formats; later upload may be possible. | 33 - 45 |
| Nonylphenol Ethoxylates in Margin Sediments      | $53,840 | This study will analyze a broad suite of NPEs and related compounds in margin sediment. Recent non-targeted analysis indicates that there are many more ethoxylated NPEs that have never been targeted for analysis. Monitoring will help determine whether NPEs should be classified as Tier III contaminants, and provide insights about the influence of effluent and runoff. | III      | **Scientific driver:** NPEs are classified as a moderate concern, yet no recent Bay data exist; with this study, we can evaluate a suite of potential analytes to determine which merit further attention.  
**Management driver:** Inform DTSC Safer Consumer Products program and regional CEC Action Plans.  
**Cost savings:** Leverages 2017 margin sediment collection. | Report March 2019; presentation at spring 2019 ECWG meeting.  
Data uploaded to CEDEN. | 46 - 51 |
## 2018 Emerging Contaminants Special Studies Proposal Abstracts

<table>
<thead>
<tr>
<th>Study Name</th>
<th>Budget</th>
<th>Summary</th>
<th>RMP Tier</th>
<th>Critical Drivers</th>
<th>Deliverables</th>
<th>Page #</th>
</tr>
</thead>
</table>
| Current Use Pesticides and Wastewater Contaminants in Margin Sediment and Water | $125,746| This study will analyze of two current use pesticides and key fragrance ingredients (and other wastewater contaminants) in margin sediment and water. This data collection fills key monitoring data gaps for current use pesticides, fragrance ingredients, and other wastewater contaminants prioritized by state agencies (DPR, State Water Board), and complements a larger USGS study of freshwater streams. | I        | **Scientific driver**: Target analytes selected based on prioritizations from state agencies. Bay data will complement larger USGS study on freshwater streams.  
**Management driver**: Inform DPR and DTSC Safer Consumer Products program actions.  
Data uploaded to CEDEN. | 52 - 59 |
| Pharmaceuticals in Wastewater Data Analysis & Reporting                   | $30,000 | In 2016, six Bay Area wastewater treatment agencies conducted a study of pharmaceutical compounds in wastewater, including samples of influent, effluent, partially treated effluent, recycled water, and reverse osmosis concentrate. This dataset is the most comprehensive analysis of pharmaceuticals in wastewater in this region. The proposed study includes quality assurance/quality control review, data analyses and reporting of this data. This synthesis will assist participating agencies while maximizing use of these data to inform future pharmaceutical monitoring strategy, management and source reduction efforts. | II and I | **Scientific driver**: Improved analytical methods; data will inform future monitoring strategies and risk prioritization.  
**Management driver**: Increasing populations, pharmaceutical use, and policy focus on drug take-back programs indicate a need to reassess levels of pharmaceutical compounds in wastewater  
**Cost savings**: Leverages $77,500 from WWTPs and combines QA/QC and data analysis across agencies for cost efficiency.  
**Time constraint**: 75% of the data is already available and analysis will be most useful for WWTPs if conducted this year                                                                 | Technical Report: Fall 2018  
Data uploaded anonymously to the Regional Data Center; NOT uploaded to CD3 or CEDEN | 60 - 70 |
### 2018 Emerging Contaminants Special Studies Proposal Abstracts

<table>
<thead>
<tr>
<th>Study Name</th>
<th>Budget</th>
<th>Summary</th>
<th>RMP Tier</th>
<th>Critical Drivers</th>
<th>Deliverables</th>
<th>Page #</th>
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</thead>
<tbody>
<tr>
<td>Non-Targeted Analysis of Reverse Osmosis Concentrate</td>
<td>$59,000</td>
<td>The objective of this study is to provide broader insight into the degradation processes occurring during advanced oxidative pre-treatment and open-water engineered wetland treatment. The study is designed to qualitatively track the degradation and removal of broad chemical classes present in ROC, before and after treatment in an open-water engineered treatment cell, and with and without advanced oxidative pre-treatment. Novel non-targeted analysis methods will be used to provide insights into the fate of broad chemical classes that are not currently monitored in ROC.</td>
<td>I</td>
<td><strong>Management driver:</strong> This study will inform management decisions concerning expanded production of recycled water throughout the Bay region. Disposal of ROC, which contains ~six times the contaminant concentration typically found in pre-treatment wastewater effluent, presents a barrier to wider adoption of RO treatment. <strong>Logistical constraint:</strong> This study would add-on to a one-time pilot ROC treatment project (May 2017-October 2018), and will leverage the engineering and technical resources of the project team, including UC Berkeley, Stanford, Santa Clara Valley Water District, and GHD.</td>
<td>Technical Report (draft manuscript): Winter 2018&lt;br&gt;Non-technical 2-page Report: Spring 2019&lt;br&gt;Data will not be stored in an RMP database</td>
<td>71 - 79</td>
</tr>
</tbody>
</table>
Special Study Proposal: Emerging Contaminants Strategy

Summary: Increasing interest in emerging contaminants issues by the San Francisco Bay Regional Water Board, RMP stakeholders, and the general public is reflected in headline news as well as policy actions at local, state, and federal levels. The amount of effort needed to manage the RMP Emerging Contaminants Strategy has increased significantly in recent years. Core deliverables have been tracking new information regarding contaminant occurrence and toxicity and updating the RMP’s Tiered Risk and Management Action Framework. New requests for information include assisting the Water Board with emerging contaminants action plans. Coordination of pro bono analyses by partners, such as BACWA and universities, is another rapidly expanding component of strategy implementation. A recently improved Bay-specific contaminant transport model will also be tested to assess its utility in improving understanding of the role of pathways, in response to a need for improved modeling capabilities identified by stakeholders and experts. For these reasons, this proposal requests a $15,000 (30%) increase in funding for managing the RMP Emerging Contaminants Strategy. This represents less than 20% of the overall RMP CECs planning budget ($350,000).

Estimated Cost: $65,000

Oversight Group: ECWG

Proposed by: Rebecca Sutton (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

<table>
<thead>
<tr>
<th>Deliverable</th>
<th>Due Date</th>
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<tbody>
<tr>
<td>Task 1. Information gathering from a variety of sources throughout the year, including presentations at scientific conferences</td>
<td>Year-round</td>
</tr>
<tr>
<td>Task 2. Assist Water Board and other stakeholders with science summaries relating to policy including emerging contaminants action plans and comment letters regarding proposed actions of other agencies</td>
<td>Year-round</td>
</tr>
<tr>
<td>Task 3. Present an update of emerging contaminants strategy, ongoing or completed special and pro bono studies, and new studies to the Steering Committee</td>
<td>Summer 2018</td>
</tr>
<tr>
<td>Task 4. Review tiered monitoring and management risk framework</td>
<td>Summer 2018</td>
</tr>
<tr>
<td>Task 5. Update the RMP CEC Strategy document with revised tiered framework tables and multi-year plan; include discussion of role of improved Bay contaminant transport model in informing understanding of fate and transport of emerging contaminants in the Bay</td>
<td>Fall 2018</td>
</tr>
</tbody>
</table>
Background

The science and management of contaminants of emerging concern (CECs) is an area of dynamic recent development. In 2016, Congress made major changes to the Toxic Substances Control Act, the primary legislation governing production and use of chemicals in the U.S. While the full impacts of this action are not yet certain, passage of legislation designed to modify a law that has been unchanged for 40 years is a clear sign of the growing concern surrounding the widespread introduction of thousands of chemicals into commerce without significant testing to establish safety for humans or wildlife. The general public has also become increasingly engaged on issues of chemical safety and potential ecological harm, informed by headlines in major newspapers across the country.

The RMP, a global leader on contaminants of emerging concern (CECs), stays ahead of the curve by identifying problem pollutants before they can harm wildlife. The RMP completed a strategy document outlining a comprehensive, forward-looking approach to addressing CECs in San Francisco Bay (Sutton et al. 2013). A major revision to this document (Sutton et al. 2017) will be discussed at the March 2017 ECWG meeting. The RMP’s CECs strategy consists of three major elements. First, for contaminants known to occur in the Bay, the RMP evaluates relative risk using a Tiered Risk and Management Action Framework. This risk-based framework guides future monitoring proposals for each of these contaminants. The second element of the strategy involves review of scientific literature and other aquatic monitoring programs to identify new contaminants for which no Bay data yet exist. Finally, the third element of the strategy consists of non-targeted monitoring, including broadscan analyses and development of bioanalytical tools.

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

In 2017, the RMP Steering Committee approved $50,000 for this strategy support task. Also beginning in 2017, the RMP directed significantly increased resources for monitoring and special studies relating to emerging contaminants, the result of an optional reduced monitoring schedule for municipal wastewater discharges to the Bay in exchange for increased payments to the RMP. With the potential for a similar level of resources directed towards emerging contaminants in 2018, and the addition of specific deliverables regarding modeling, the recommended budget needed for managing the RMP CEC Strategy is $60,000. Additional budget details are provided in the following sections.


## Study Objectives and Applicable RMP Management Questions

<table>
<thead>
<tr>
<th>Management Question</th>
<th>Study Objective</th>
<th>Example Information Application</th>
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</thead>
<tbody>
<tr>
<td>1) Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?</td>
<td>Compare existing occurrence data with new toxicity information reported in the scientific literature.</td>
<td>Does the latest science suggest a reprioritization of chemicals as we learn more about them? Is newly identified contaminants merit further monitoring?</td>
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<td></td>
<td>Evaluate future monitoring needs and toxicity data gaps.</td>
<td></td>
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<tr>
<td>2) What are the concentrations and masses of contaminants in the Estuary and its segments? 2.1 Are there particular regions of concern?</td>
<td>Does new knowledge including recently published toxicity data and/or source/pathway information suggest different relative risks for any of the five subembayments?</td>
<td>What are the key regional influences on different subembayments that impact concentrations, masses, and potential risk of emerging contaminants?</td>
</tr>
<tr>
<td>3) What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary? 3.1. Which sources, pathways, etc. contribute most to impacts?</td>
<td>Evaluate improvements in modeling capabilities through by comparing predictions to monitoring results. Does new research in other regions provide insight as to key sources, pathways, loadings, and processes that affect impacts of emerging contaminants?</td>
<td>Are relative levels of contaminants in different matrices or subembayments consistent with our expectations for various contaminated processes?</td>
</tr>
<tr>
<td>4) Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased? 4.1. What are the effects of management actions on concentrations and mass?</td>
<td>Does trend data from other regions suggest likely trends in the Bay? Which new management actions are likely to impact contaminant levels?</td>
<td>Are additional or different actions needed to reduce levels below aquatic toxicity thresholds?</td>
</tr>
<tr>
<td>5) What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?</td>
<td>Do data on production, use, and source trends in the scientific and trade literature provide a means of prioritizing relative risk of Bay contaminants?</td>
<td>Do production, use, and source trends suggest likely changes in the relative risk of specific emerging contaminants?</td>
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Emerging contaminants strategy work most directly addresses questions 1, 3, and 5, by assuring that all manner of relevant new information is brought to bear in evaluating the relative risk of emerging contaminants to Bay wildlife. For example, a new study identifying a lower toxicity threshold for a particular contaminant might suggest that the risk tier in which that contaminant had been placed should be revised.
In addition, the study will address emerging contaminants priority questions:

- Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?
- What are the sources, pathways, loadings, and processes leading to CEC pollution in the Bay? (proposed)
- Have the concentrations of CECs in the Bay increased or decreased? (proposed)
- Which management actions may be effective in reducing CEC levels? (proposed)

**Approach**

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

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

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

- Numerous presentations, briefings, and stakeholder interactions
- Scientific assistance to the Water Board as the agency prepares emerging contaminant action plans
- Scientific assistance to stakeholders engaged in emerging contaminants policy
- Coordination of pro bono analyses
- Improved modeling capabilities: In 2017, the San Francisco Bay transport model will be updated with major improvements regarding stormwater and runoff sources. In 2018, the model can then be used to predict the stormwater and wastewater contributions of water-soluble contaminants (e.g., imidacloprid, phosphate flame retardants) to Bay waters, using existing data on concentrations in each of these pathways. These predictions can be compared to values measured in ambient Bay water samples collected in 2017, allowing an assessment of the transport model’s functionality and as well as the conceptual models relevant to each contaminant.

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

The following budget represents estimated costs for 2018 Emerging Contaminants Strategy.

**Table 2. 2018 Emerging Contaminants Strategy budget**

<table>
<thead>
<tr>
<th>Deliverables</th>
<th>Budget</th>
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<tbody>
<tr>
<td>Tasks 1-5: Information gathering from a variety of sources throughout the year, including presentations at scientific conferences; Assist Water Board and other stakeholders with science summaries relating to policy including emerging contaminants action plans and comment letters regarding proposed actions of other agencies; Present an update of emerging contaminants strategy, ongoing or completed special and pro bono studies, and new studies to the Steering Committee; Review tiered monitoring and management risk framework; Update the RMP CEC Strategy document with revised tiered framework tables and multi-year plan; include discussion of role of improved Bay contaminant transport model in informing understanding of fate and transport of emerging contaminants in the Bay.</td>
<td>$65,000</td>
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**Budget Justification**

Significant increases in RMP resources dedicated to CEC special studies, beginning in 2017 and expected to continue in 2018, require greater levels of engagement, outreach, and coordination to assure strategic use of available funds.

Funding for managing the CEC Strategy in 2017 ($50,000) covers updates to the Tiered Risk and Management Framework (element one of the RMP CEC strategy), review of the state of the science concerning CECs and interaction with other monitoring groups (element two), and interpretation of the findings of non-targeted analysis (element three) to determine new monitoring priorities. It also covers scientific assistance to stakeholders, including the first RMP webinar, on passive and alternative monitoring techniques, held in January 2017. Finally, a portion of funding is being used to leverage in-house modeling capabilities to improve the understanding of the fate and transport of emerging contaminants in San Francisco Bay.

With the recent increase in the overall RMP planning budget for CECs, a corresponding increase in strategy is needed to maximize programmatic impact. In 2018, we anticipate increased engagement with stakeholders, including scientific advisory support for the Water Board and others concerning relevant policy proposals and actions at the local, state, and federal levels. We also anticipate increasing coordination of pro bono analyses that leverage RMP funds. Finally, the development and use of contaminant transport modeling as a tool for understanding and predicting the fate and transport of emerging contaminants will require resources. To provide cost-effective expertise to address these demands, this proposal requests an additional $15,000 of funding for 2018.

By providing funding for the emerging contaminants strategy, the RMP can be assured it is getting “the most bang for its buck,” targeting the highest priority contaminants among the
many thousands in commerce and potentially discharged to the Bay. The RMP is a global leader in CEC monitoring, yet it must be efficient and pragmatic in the face of finite resources. An increase in funding for this task will allow for strategic thinking using the latest science, so that the RMP can continue to generate the information water managers need to effectively address emerging contaminants in the Bay. This represents less than 20% of the overall RMP CECs planning budget ($350,000); historically, CEC strategy funding has often represented 20% of the planning budget.

**Reporting**

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

**References**


Special Study Proposal: Characterizing Unknown Perfluoroalkyl and Polyfluoroalkyl Substances in SF Bay Seal Blood and Sediment

Summary: Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are an important class of chemicals that are widely used in industrial, commercial and residential applications. They are of concern because they are highly persistent and many are associated with a myriad of health effects. Some of the highest concentrations in the world of perfluorooctane sulfonate (PFOS) have been observed in Bay seals and cormorants. The RMP routinely monitors for about a dozen of the ~3,000 PFASs in use today. This study will use recently developed methods to provide a more comprehensive picture of the complete suite of PFASs in harbor seal blood and sediment. This is of critical importance as manufacturers phase out the use of PFOS and perfluorooctanoic acid (PFOA) in favor of alternative PFASs. Very little is known about these alternatives – both in terms of chemical structure and production volumes. Hence this study will produce a unique dataset for identifying the presence of these alternatives. Use of this novel method will be critical for tracking the use of this very pervasive and toxic class of compounds.

Estimated Cost: $78,000

Oversight Group: Emerging Contaminant Workgroup

Proposed by: Chris Higgins (Colorado School of Mines) and Meg Sedlak (SFEI)

<table>
<thead>
<tr>
<th>PROPOSED DELIVERABLES AND TIMELINE</th>
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<tbody>
<tr>
<td>Deliverable</td>
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<tr>
<td>Task 1. Field collection of margin sediment and seal samples</td>
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<tr>
<td>Task 2. Laboratory analysis of sediment and archived blood samples</td>
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<tr>
<td>Task 3. Update to ECWG on preliminary results</td>
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<tr>
<td>Task 3. Review of data</td>
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<tr>
<td>Task 4. Draft factsheet and manuscript</td>
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<tr>
<td>Task 5. Final factsheet and manuscript</td>
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</table>

Background
Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are an important class of chemicals that are widely used in industrial, commercial and residential applications. They are of concern because they are highly persistent and many are associated with a myriad of health effects. Historically, PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid) have been widely used in such diverse applications as the manufacture of fluoropolymers (e.g., Teflon), stain/water repellant coatings for textiles and food packaging, and fire-fighting foams.
Due to the widespread detection of PFOS in human blood, the production and use of PFOS in the US was phased out in early 2000. Similar concerns over the widespread detection of PFOA in humans and in the environment resulted in eight major manufacturers phasing out the production of PFOA by 2015, replacing it with shorter chained compounds such as C6 (PFHxA) and C4 (PFBA) that are thought to be less bioaccumulative and toxic. Perfluoroalkyl ether carboxylic acids have also been identified as alternatives. However, these alternatives are being detected in the environment. One of the more well-known compounds, GenX (perfluoro-2-propoxypropanoic acid [PFPrOPrA]), a PFOA replacement, was recently detected in a watershed downstream of a PFAS manufacturer at very high concentrations (up to 630 ng/L) (Sun et al. 2016). In addition, although the use of PFOA and PFOS in the US is restricted, they continue to be identified in many products used in the US (Schaider et al. 2017).

A second concern is the transformation of polyfluorinated substances to the problematic perfluoroalkyl substances such as PFOS and PFOA. These polyfluorinated substances are often referred to as precursors and include the polyfluoroalkyl phosphate esters (PAPs), fluorotelomer acrylate polymers, and fluorotelomer sulfonamide-based substances.

The RMP has routinely analyzed sport fish, bird eggs, and seals for approximately 13 PFASs. PFOS is most frequently detected, and is found at elevated concentrations in harbor seal blood. This is of concern as they are apex predators and appear to bioaccumulate PFOS. The most recent seal monitoring suggests a possible decline of PFOS in seal blood from approximately 700 ppb (2011) to 180 ppb (2014). There are few studies of the toxicological effects of perfluorinated compounds on marine mammals; however, PFOS studies in other mammals suggest that these concentrations may be of concern. It will be important to confirm that concentrations of PFOS are continuing to decline.

The RMP has recently begun focusing on the concentrations of pollutants in the margins of the Bay as this has been a geographical area in the past that has been under-sampled. This area is an important habitat for Bay wildlife to forage for food, to breed, and to raise young of the year. At the same time, it is recognized as an area that typically contains higher concentrations of pollutants due to its proximity to sources. As a result, it is important to monitor margin sediments for a suite of PFASs. Prior work suggests that the margins can have elevated concentrations of the precursors such as di-PAPs.

One of the formidable challenges about PFASs is the large number of compounds in use, upwards of 3,000 individual chemicals; the RMP only routinely monitors a handful of these. A second challenge is the dearth of information regarding the structure and use of these 3,000 compounds. Given these challenges, one approach is to monitor using broad analytical techniques such as the total oxidizable precursor (TOP) method (Houtz and Sedlak 2012) or nontargeted techniques. Using more broad scale analytical techniques would be consistent with recent state and federal approaches, which are moving towards monitoring/regulating the whole class of compounds. For example, the State of Washington has introduced a bill (HB 1744) that will prohibit the sale and distribution of food packaging materials that contain any amount of PFASs.

In the Bay Area, wastewater effluent was recently characterized using the TOP method (Houtz et al. 2016). Similarly, University of California Berkeley researchers applied this
technique to stormwater collected in the winter of 2010/2011 (Houtz and Sedlak 2012). In both instances, greater than 60% of the PFAS load was attributed to unidentified precursors. While the TOP method alone is able to identify the fraction of precursors that can degrade to perfluoroalkyl substances such as PFOA, it is not suitable for identifying the specific structures of these unknown precursors nor some of the suspected replacement PFASs.

In this project, both the TOP assay as well as liquid chromatography coupled with high-resolution mass spectrometer (quadrupole time-of-flight mass spectrometry (LC-QToF-MS)) will be used to identify a much broader suite of PFASs, including potential precursors. This approach successfully identified 40 new classes of PFASs in groundwater contaminated by aqueous film-forming foam (AFFF; Barzen-Hanson et al. 2017). In total, 240 individual PFAS were identified in AFFF and AFFF-contaminated groundwater. More relevant to the work proposed here, a study of firefighters in Australia found several new PFOS-like PFASs in human serum (Rotander et al. 2015).

As part of this work, we will not only quantify the standard list of PFAAs (including PFOS and PFOA), but we will use the LC-qToF-MS mass spectral library developed as a result of the work of Barzen-Hanson et al. (2017) and Rotander et al. (2015) to examine the potential presence of a broader suite of PFASs. This will include not only AFFF-derived PFASs, but also PFASs more common in consumer products such as polyfluoroalkyl phosphate mono/di-esters (monoPAPs/diPAPs) and various other perfluoroalkyl sulfonamide-based chemicals.

The information derived from this project will be important for the following reasons.

- The data will provide information to assess trends of the more routinely monitored PFASs such as PFOS and PFOA in seals and sediments. This will be important for establishing whether there is a continued decline in PFOS in seals and to assess whether concentrations of PFOS in sediment indicate any trends.
- The data will show whether the declines in PFOS/PFOA are consistent across the class of compounds or whether there is merely a substitution from one type of subclass such as PFOS/PFOA to another.
- This project will help to elucidate the unknown precursors that have been identified as part of previous Bay Area stormwater and effluent studies. Without knowing what the precursors are, it will be impossible to mitigate or manage the impact of the use of these chemicals.

**Study Objectives and Applicable RMP Management Questions**
The purpose of this study is to monitor well-studied PFASs and identify previously unknown chemicals in seals and sediment.
<table>
<thead>
<tr>
<th>Management Question</th>
<th>Study Objective</th>
<th>Example Information</th>
</tr>
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<tbody>
<tr>
<td>1) Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?</td>
<td>Are PFOS and PFAS at levels of concern in Bay seals and margin sediment? Are there significant concentrations of previously unidentified PFASs in sediment and seal blood?</td>
<td>Identifying a more complete array of PFASs present in the Bay will be important for understanding the magnitude of the problem and for assessing the impact of management actions.</td>
</tr>
<tr>
<td>2) What are the concentrations and masses of contaminants in the Estuary and its segments?</td>
<td>This study will only focus on the South Bay. It could be expanded to evaluate PFASs in other embayments.</td>
<td></td>
</tr>
<tr>
<td>3) What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary?</td>
<td>The study objective is to better characterize the PFASs in sediment and seals to understand possible sources.</td>
<td>This information may be useful for source identification such as AFFF or novel replacements for C8 chemicals.</td>
</tr>
<tr>
<td>4) Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased?</td>
<td>Evaluate temporal trends in biota.</td>
<td>Conduct statistical evaluations using prior data.</td>
</tr>
<tr>
<td>5) What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?</td>
<td>Understanding the suite of PFASs in sediment will help us better assess the concentration and mass in the Lower South Bay.</td>
<td>Projections may inform classification in Tiers.</td>
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</table>

**Approach**

This project will characterize PFASs in margin sediment and harbor seal blood (serum) from the Lower South Bay. Archived sediment and seal samples will be analyzed and compared to current sediment and seal concentrations. Archived seal blood (~2010) from five seals residing in a colony located in the Lower South Bay will be analyzed for PFASs. The same seal colony site will be targeted for collection of blood from five seals in 2017. RMP staff will work with seal researchers from Moss Landing Marine Labs to capture and collect seal blood. As part of the RMP Status and Trends margin sediment cruise, five sites in close proximity to the seal colony will be sampled for surface sediments. Archived sediment samples (~2010) will also be submitted for analyses. It is likely that these samples will be
located more in the center of the Lower South Bay; however, samples that are near the seal colony will be targeted.

The sediment and seal samples will be sent to Colorado School of Mines for PFAS analyses using LC-Q-ToF-MS. Seal serum will be prepared for LC-QToF-MS analysis using established protocols (Reiner et al., 2009; Kato et al., 2011). Briefly, after the addition of appropriate quantities of the mass-labeled internal standards, formic acid (0.1M) will be added to denature proteins, which will then be precipitated via addition of cold acetonitrile. Following vortexing and centrifugation, the samples will then be diluted, as appropriate, for LC-QToF-MS analysis. Sediment samples will be extracted and cleaned up using established protocols for the analysis of PFASs in soils and sediments (McGuire et al., 2014; Barzen-Hanson et al., in prep). After extraction, each sample will be split, with one aliquot being subjected to the TOP assay (oxidation followed by LC-QToF-MS; Houtz and Sedlak, 2012) and the other aliquot being directly analyzed by LC-QToF-MS.

Serum and sediment extracts will be injected and separated on a C18 column prior to analysis by both ESI+ and ESI- LC-QToF-MS using chromatographic conditions previously established for characterizing PFASs in AFFF formulations (Barzen-Hanson et al., 2017). Quantitative analysis will be enabled through the use of matrix-matched calibration standards containing known quantities of PFASs for which analytical standards are available. For the novel PFASs, HRMS spectra and LC-retention time data will be compared against AFFF-spiked matrix matched samples and mass spectral libraries developed in Dr. Higgins’ laboratory from previous work (Barzen-Hanson et al., 2017); only features matching both retention time and MS/MS fragmentation spectra to known PFASs will be confirmed as present. For these PFASs, semi-quantitative analysis will be performed using peak intensities and equimolar MS response factor assumptions for the most closely related structural analog.

Finally, HRMS data generated will also be queried using R scripts (Loos, 2015), in addition to mass defect screening approaches, to enable the identification of new metabolites of the PFASs present in the AFFF dosing solution. For example, data will be specifically queried for the presence of GenX (Sun et al. 2016) and other highly fluorinated PFOA replacement chemicals. This approach successfully identified new PFASs present in environmental samples (i.e., groundwater) that are presumably derived from microbial metabolism of PFASs in AFFF (Barzen-Hanson et al., 2017).

**Budget**

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

<table>
<thead>
<tr>
<th>Personnel</th>
<th>Budget</th>
</tr>
</thead>
<tbody>
<tr>
<td>Project Staff (SFEI)</td>
<td>$24,500</td>
</tr>
<tr>
<td>Laboratory Analyses (CSM)</td>
<td>$30,000</td>
</tr>
<tr>
<td>Seal capture and blood collection (MLML)</td>
<td>$11,000</td>
</tr>
<tr>
<td>Contract Management</td>
<td>NA</td>
</tr>
<tr>
<td>Data Technical Services</td>
<td>$11,500</td>
</tr>
<tr>
<td>Direct cost (shipping)</td>
<td>$1,000</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>$78,000</strong></td>
</tr>
</tbody>
</table>

**Budget Justification**

**Field Costs**
Field costs are minimized through by leveraging the sample collection during the RMP’s margin sediment cruises and the use of archive samples (blood and sediment). The main cost is associated with the seal capture event.

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

**Laboratory Costs**
The laboratory costs are on a fixed budget for the analysis of the 20 samples. Data interpretation to identify new analytes is quite time intensive.

**Data Management Costs**
Data management and upload to CEDEN is suggested only for the standard 13 PFAS analytes that have been identified in the past (e.g. PFOS, PFOA, etc.). Other tentatively identified compounds will be maintained in excel spreadsheets and included as supplemental material in a manuscript.

**Reporting**
Deliverables will include: a) a draft manuscript that serves as an RMP technical report due Fall 2018; b) a plain language RMP fact sheet describing the results and their implications due January 2019; and c) additions to other RMP publications such as the Pulse.
References


Special Study Proposal: Non-targeted Analysis of Sediment and Related Studies

Summary: Non-targeted analysis, a key element of the RMP’s CEC strategy and recent state CEC guidance, can help to provide a measure of assurance that the RMP is not missing unexpected yet potentially harmful contaminants simply because of failures to predict their occurrence based on use or exposure prioritization criteria. The RMP has recently conducted non-targeted analysis of nonpolar, fat-soluble compounds in bivalve tissue and seal blubber, and polar, more water-soluble compounds in water and effluent. This new proposed study would use non-targeted techniques from two different labs to examine both nonpolar and polar contaminants in Bay sediment, a matrix that has not yet been screened. This type of non-targeted study will lay the foundation for future targeted CEC monitoring by helping to identify new potential contaminants of concern without *a priori* knowledge of their occurrence.

In addition to the non-targeted sediment study, two related study components are also proposed to leverage other monitoring efforts. The first would screen extracts of passive samplers deployed in 2016 for the presence of nonpolar compounds using non-targeted analysis, a direct complement to the ongoing screening for more polar compounds. The second would quantitatively assess margin sediment samples for a dozen mutagenic dyes and dye-related compounds. This targeted chemical analysis would provide first-ever information on this widely used class of compounds in the California ambient environment, which may have particular relevance to the State’s green chemistry effort.

Estimated Cost: $117,550

Oversight Group: ECWG

Proposed by: Rebecca Sutton (SFEI), Lee Ferguson (Duke University), Eunha Hoh (San Diego State University)

**PROPOSED DELIVERABLES AND TIMELINE**

<table>
<thead>
<tr>
<th>Deliverable</th>
<th>Due Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1. Project Management (manage subcontracts, track budgets)</td>
<td>Summer 2017 – 2019</td>
</tr>
<tr>
<td>Task 2. Develop detailed sampling plan</td>
<td>Summer 2017</td>
</tr>
<tr>
<td>Task 3. Field Sampling (Margin Sediment)</td>
<td>Summer 2017</td>
</tr>
<tr>
<td>Task 4. Lab analysis</td>
<td>Fall 2017</td>
</tr>
<tr>
<td>Task 5. QA/QC and contaminant risk review</td>
<td>Winter 2017</td>
</tr>
<tr>
<td>Task 6. Field Sampling (Ambient Bay Sediment)</td>
<td>Spring-Summer 2018</td>
</tr>
<tr>
<td>Task 7. Lab analysis</td>
<td>Fall 2018</td>
</tr>
<tr>
<td>Task 8. QA/QC and contaminant risk review</td>
<td>Winter 2018</td>
</tr>
<tr>
<td>Task 6. Draft report and fact sheet</td>
<td>Spring 2019 (ECWG mtg)</td>
</tr>
<tr>
<td>Task 7. Final report and fact sheet</td>
<td>Summer 2019</td>
</tr>
</tbody>
</table>
Background

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

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

One class of non-targeted method highlighted by the state guidance includes those “designed to screen for new or unexpected contaminants; i.e., unknown CECs” (pg 29, Dodder et al. 2015). The RMP, in collaboration with the National Institute of Standards and Technology (NIST), recently completed a non-targeted analysis of Bay harbor seal blubber and mussel tissues, which focused on persistent, fat-soluble (nonpolar), chlorine and bromine-rich chemicals (Sutton and Kucklick 2015). This investigation brought to light five contaminants not previously identified in Bay wildlife, and for which toxicity is largely unknown. However, most of the Bay chemical contamination was from high priority contaminants that the RMP already monitors, or closely related compounds.

A second non-targeted analysis focusing on more polar, water-soluble organic compounds in ambient Bay water and effluent samples was initiated in 2016. Bay water samples were collected via passive samplers (Polar Organic Chemical Integrative Sampler; POCIS), with accompanying grab samples on deployment and retrieval. Initial findings will be presented and discussed at the 2017 ECWG meeting.

Sediment is an important Bay matrix that has not yet been characterized via non-targeted analysis. Sediment can harbor both polar and nonpolar contaminants, and transfer them to the food web particularly via exposure of lower trophic level benthic organisms. The RMP has conducted targeted chemical monitoring of ambient Bay sediment for decades. Recent efforts to similarly monitor near-shore, “margin” sediment for contaminants have just begun. Near-shore sites are more likely to be depositional sediment environments influenced by current uses of chemicals.

This proposal is primarily focused on non-targeted analysis of sediment, using two different techniques designed to probe a wide range of contaminants (nonpolar and polar). Components that leverage other valuable monitoring efforts are also included. The first is additional non-targeted analysis of passive sampler extracts from 2016, using a
complementary technique to probe nonpolar compounds. Adding a small number of these already-collected samples to this sediment study would be an efficient means of gaining valuable insights regarding the presence of nonpolar compounds in ambient Bay waters.

The second add-on study involves targeted analysis of the same sediment samples for some commonly used azobenzene-based disperse dyes and their breakdown products, a recently developed method from one of our academic partners. Azo dyes have been identified as potential candidate chemicals in multiple product categories in California’s Safer Consumer Products Priority Product Work Plan. There is a notable dearth of data on environmental levels of these compounds.

**Study Objectives and Applicable RMP Management Questions**

Given the increased burden on the RMP from multiple areas of interest to stakeholders, it is essential that the RMP focus on those CECs that are the highest priority. Traditional, targeted contaminant monitoring focuses on specific lists of chemicals already identified as potentially problematic through either expert judgement, anticipation of high toxicity, use-based prioritization, or other *a priori* methods. Through non-targeted monitoring, we can provide a measure of assurance that the RMP is not missing unexpected, potentially harmful contaminants in the Bay water simply because of failures to predict their occurrence based on use or exposure prioritization criteria.

Non-targeted analysis is an essential element of the RMP’s CEC Strategy (Sutton et al. 2017). The current proposal is to use two types of non-targeted analysis to scan for a wide range of organic contaminants in Bay sediment. This special study would provide data on contaminants in an important Bay matrix that has not yet been explored with this set of techniques, essentially filling a major data gap in characterizing possible contaminant chemistries in the Bay. It would also take advantage of considerable advances in identifying nonpolar contaminants via non-targeted analysis relative to the previous RMP study on tissue samples, initiated in 2010.

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

In contrast, because of the comprehensive nature of the non-targeted methods proposed herein, should few unexpected contaminants be identified, the RMP would then have considerable evidence that existing CEC monitoring is already focusing on the highest priority contaminants for the Bay.

This proposal also provides for a small number of additional non-targeted analyses on Bay passive sampler extracts to assess the presence of contaminants in Bay waters using gas chromatography, which can be especially useful for detecting nonpolar compounds. This additional analysis would close the loop on the non-targeted chemical characterization using liquid chromatography and focusing more on polar compounds, a study funded in 2016.
leveraging the previous monitoring effort. Nonpolar compounds are likely to be present in Bay samples due to sorption on suspended particulates or co-solvation with natural organic matter.

Finally, this proposal would also provide for a targeted chemical analysis of dyes on the same sediment samples examined via non-targeted analysis. The Ferguson Lab at Duke University has recently developed a method that covers a range of selected azobenzene-based disperse dye compounds, partly in response to recent detections of dyes as contaminants in household dust (Peng et al. 2016). Dr. Ferguson has found these dyes at high ppb concentrations in house dust, similar to levels measured for ubiquitous brominated flame retardants. Despite ubiquitous use in consumer products, there is little information regarding the presence of disperse dyes in the environment. Of note, some of these dye compounds and their breakdown products have mutagenic properties (Peng et al. 2016), suggesting ecotoxicity concerns.

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

<table>
<thead>
<tr>
<th>Management Question</th>
<th>Study Objective</th>
<th>Example Information Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?</td>
<td>Identify (i) polar and nonpolar sediment contaminants and (ii) nonpolar water contaminants not yet characterized by targeted monitoring efforts. Evaluate future monitoring needs and toxicity data gaps. Measure (iii) dyes and dye breakdown products in sediment.</td>
<td>Have previous targeted monitoring efforts focused on contaminants with the highest relative risk to the Bay? Which newly identified contaminants merit further monitoring? Do findings suggest dyes should be classified as moderate, low, or possible concern emerging contaminant within the RMP’s tiered risk framework? Do data indicate a need for management actions?</td>
</tr>
<tr>
<td>2) What are the concentrations and masses of contaminants in the Estuary and its segments? 2.1 Are there particular regions of concern?</td>
<td>Comparison of margin vs. ambient Bay sediment with respect to (i) non-targeted detections and (ii) dyes. Initial comparison of sites influenced by different pathways (agriculture-dominated river, stormwater, wastewater) with respect to (ii) passive sampler water detections.</td>
<td>Do margin sediments have different contaminants than ambient Bay sediments? Are there regional or pathway-related differences in the presence of newly identified contaminants?</td>
</tr>
</tbody>
</table>
### 3) What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary?

#### 3.1 Which sources, pathways, etc. contribute most to impacts?

Investigate the influence of different pathways based on sample locations (e.g., near stormwater vs. wastewater discharges) for both sediment and water contaminants.

Do sites influenced by different pathways show different patterns of contamination?

Do differences in detection suggest persistence, degradation, or additional pathways for specific contaminants?

### 4) Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased?

#### 4.1 What are the effects of management actions on concentrations and mass?

Establish a baseline for future studies.

Identify sources of newly identified contaminants to evaluate effects of current management actions on potential discharges and project trends with likely changes in use and treatment technology.

Are relevant management actions having the intended effect?

Will newly identified contaminants suggest the need for additional or different management actions?

This monitoring effort would most directly address questions 1, 2, and 3, identifying water-soluble contaminants not yet characterized by targeted monitoring efforts, and providing information useful to initial comparisons with respect to contaminants in sites influenced by different pathways. This proposal does not include an examination of potential sources of newly identified contaminants. Such a study could be completed in future years and would provide information useful in addressing questions 4 and 5, concerning likely past and future trends.

In addition, the study will directly and explicitly address the established emerging contaminants priority question: What emerging contaminants have the potential to adversely impact beneficial uses of the Bay?

It will also address proposed emerging contaminants priority question #2, What are the sources, pathways, loadings, and processes leading to CEC pollution in the Bay?

**Approach**

**Margin and Ambient Bay Sediment Sampling**

Sample collection will occur in conjunction with RMP margin and ambient Bay sediment sampling cruises, scheduled for Summer 2017 and 2018, respectively. Approximately 15 samples of margin sediment will be collected, and 5 samples of ambient Bay sediment. Sites will be selected in consultation with RMP staff; some sites will be selected based on likely
influence of wastewater discharges. Ancillary data collected by the RMP efforts, including DOC and grain size distribution, will be provided to analytical partners.

Sediment samples will be collected shipboard using a Van Veen sediment grab. A metal scoop and bucket will be used to remove and composite sediment; exposure to plastic will be avoided. Two samples of approximately 50 g will be collected at each site and placed into certified pre-cleaned amber glass jars, stored and shipped on ice to Duke University and San Diego State University, respectively. Three field blanks will also be collected for analysis.

**Ambient Bay Water Sampling**

In 2016, Bay water sampling was conducted using passive sampling devices called Polar Organic Chemical Integrative Samplers (POCIS; Environmental Sampling Technologies, St. Joseph, MO) containing a solid phase sorbent (Waters Oasis HLB). Remaining extracts from this previous effort will be analyzed for nonpolar compounds.

During the summer of 2016, POCIS canisters were deployed for around three weeks at each of three sites: 1) a site within the tidally influenced portion of the Napa River, probing potential agricultural and pesticide influences (spring 2016); 2) San Leandro Bay, a site influenced by stormwater discharges (winter 2016); and 3) a site in the Lower South Bay influenced by WWTP discharges (summer 2016). A single blank was also collected.

POCIS were shipped (on ice) to Dr. Ferguson’s laboratory at Duke University (NC) after collection for immediate extraction and analysis, as described below. Remaining extract will be subjected to non-targeted analysis focused on nonpolar compounds.

**Analytical Methods**

**Polar Compounds:**

Non-targeted analysis of 23 sediment samples will be conducted by Dr. Ferguson’s Lab (Duke University) using Orbitrap liquid chromatography high resolution mass spectrometry (LC-HRMS). Sediment samples (shipped directly from SFEI to Duke University) will be processed by Soxhlet extraction with 1:1 acetone hexane, followed by cleanup using gel-permeation chromatography and (where necessary) silica gel chromatography prior to concentration and solvent exchange to 50:50 acetonitrile:water.

Extracts will be separated using UHPLC (Thermo Hypersil Gold column, 1.9 µm particle size, 2.1 x 100 cm) over a 70 minute gradient prior to introduction into the mass spectrometer. The LTQ-Orbitrap MS/MS will be operated at 100,000 resolution to achieve < 2 ppm mass accuracy across the mass range of interest. Sample extracts will be spiked with internal mass calibration/quantitation standards (chosen from a set of stable-isotope labeled compounds available in the PI’s laboratory) immediately prior to injection. Ionization will be performed by either electrospray in either positive or negative polarity mode, depending on the analyte. High resolution detection of analytes in MS mode will be performed by the Orbitrap analyzer, while simultaneous data-dependent MS/MS will be performed in the...
LTQ Velos module before the Orbitrap. Ions for MS/MS analysis (10 per Orbitrap scan) will be dynamically chosen on a per-scan basis, with priority given to accurate mass values corresponding to compounds in compiled “suspect” lists (already compiled based on production volume, toxicity, and/or literature reports), with secondary priority given to “non-target” analytes in order of decreasing intensity. These MS/MS data will provide important information to aid in identification of non-target analytes.

Data generated through these approaches will be applied to both commercially-available (ThermoFisher Scientific TraceFinder, Compound Discoverer, and MassFrontier) and custom-written processing software designed to aid in identifying polar organic compounds based on HRMS/MS data. Final validation of tentative identities will be made based on authentic standard match wherever possible.

The Ferguson laboratory has extensive experience in use of accurate mass MS and MS/MS for identifying non-target compounds in complex mixtures (Benotti et al. 2003; Eichhorn et al. 2005; Cui et al. 2009; Stapleton et al. 2011), and this strategy has proved successful for identifying emerging contaminants in wastewater, as well as in coastal surface waters impacted by water reuse activities (e.g., on Kiawah Island, SC). These new identifications include several micropollutants that have not, to our knowledge, been previously reported to occur in environmental media such as wastewater or surface water. Dr. Ferguson’s laboratory was chosen for this work because it is uniquely qualified and experienced to undertake the experiments described.

Nonpolar Compounds:
Non-targeted analysis of 23 sediment samples and 4 POCIS extracts (3 samples and 1 blank) for non-polar compounds will be conducted by Dr. Hoh’s laboratory (San Diego State University) using a novel instrument, and a method known as comprehensive two-dimensional gas chromatograph coupled to time-of-flight mass spectrometry (GC×GC/TOF-MS). Sediment samples will first be processed by modifying QuEChERS (Quick Easy Cheap Effective Rugged and Safe; Anastassiades et al., 2003; Payá et al., 2007). Extraction will be done by ethyl acetate by partitioning with pure water and salts. And then, extracts will be minimally cleaned with QuEChERS dispersive solid phase extraction with C18, PSA and anhydrous MgSO₄. At the beginning of extraction, a known amount of internal standard mixture (isotope labeled compounds) will be spiked to each sediment sample. Due to the GC×GC’s high separation power, minimal clean-up is acceptable.

GC×GC/TOF-MS has an enhanced ability to identify compounds (Dalluge et al. 2002). GC×GC is a powerful separation mechanism and is able to resolve compounds that would otherwise co-elute on a conventional single-dimension GC system. In GC×GC, an additional degree of separation is provided by a secondary GC column with different retention properties compared to the primary column. In addition to providing enhanced resolving power, the GC×GC system narrows chromatographic peak widths, resulting in up to 100 times higher sensitivity compared to single column GC systems.

As chromatographic peaks elute from the second GC column, they are ionized and analyzed by the TOF-MS. The TOF-MS continuously collects full scan mass spectra for the length of the run. The mass spectra then undergo spectral deconvolution, which mathematically
resolves closely eluting spectra and eliminates background noise. The deconvoluted spectra, in conjunction with the retention times, are used for compound identification.

Because a mass spectrum is collected from every peak that elutes from the GC×GC system, this analytical method is non-targeted, and prior hypotheses regarding the presence of particular compounds are not required to detect their presence in the sample. The deconvoluted mass spectra are searched against mass spectral databases to make tentative compound identifications. An advantage of non-targeted analysis based on GC×GC/TOF-MS is that the standard NIST EI mass spectral library (which contains over 240K chemical compounds) can be used as a searchable mass spectral database.

The framework of overall data processing is briefly summarized here: 1) use of the “Statistical Compare” software tool to isolate differentiating chemicals present in sediment extracts and POCIS extracts; 2) manual review to finalize a list of “truly detected compounds”; 3) manual review of compounds identified through searches against the NIST EI mass spectral library; 4) further confirmation with authentic standards if available in Hoh’s laboratory; and categorization of the identification uncertainty for compounds without authentic standards; and 5) creation of a custom mass spectral library of all truly detected compounds, including both identified and unidentified compounds. The custom library will also include the compounds’ chromatographic information (GC×GC retention times), spectral match score to the standard spectra, and other ancillary information. It stores the complete set of evidence used for each identification, and also documents the spectra for which identifications were not possible.

The Hoh laboratory has extensive experience in use of GC×GC/TOF-MS for identifying non-target compounds in biological tissues (Hoh et al., 2009; Hoh et al., 2012; Shaul et al., 2015; Millow et al., 2015; Mackintosh et al., 2016; Alonso et al., 2017), and has successfully implemented non-targeted analysis to identify emerging contaminants in sediment, soil, and dust (currently working on projects sponsored from Orange County Water District, Southern California Coastal Water Research Projects, US EPA, and CA Tobacco Related Disease Research Program). Dr. Hoh’s laboratory was chosen for this work because of the group’s strong qualification and successful records in similar projects.

Disperse Dyes:
Aliquots of margin sediment extracts prepared for non-targeted LC-HRMS analysis as described above will also be prepared for disperse dye analysis. These extracts will be purified by florisil adsorption chromatography and then analyzed by LC-MS/MS using a triple-quadrupole mass spectrometer, operated in multiple-reaction-monitoring mode. The dyes to be monitored represent those that have been measured to be most abundant in house dust samples (Table 2).

Ambient Bay sediment will not be subjected to this analysis. 15 margin sediment samples, one blank and one field duplicate will be analyzed, for a total of 17 samples.
Table 2: Disperse Dyes to be analyzed in sediments

<table>
<thead>
<tr>
<th>Name</th>
<th>CAS #</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disperse Orange 25 (DO 25)</td>
<td>31482-56-1</td>
<td>C_{17}H_{17}N_{5}O_{2}</td>
</tr>
<tr>
<td>Disperse Orange 37 (DO37)</td>
<td>13301-61-6</td>
<td>C_{17}H_{15}ClN_{5}O_{2}</td>
</tr>
<tr>
<td>Disperse Orange 61 (DO61)</td>
<td>55281-26-0</td>
<td>C_{10}H_{13}BrN_{5}O_{2}</td>
</tr>
<tr>
<td>Disperse Orange 30 (DO 30)</td>
<td>5261-31-4</td>
<td>C_{10}H_{12}ClN_{5}O_{4}</td>
</tr>
<tr>
<td>Disperse Orange 44 (DO 44)</td>
<td>4058-30-4</td>
<td>C_{18}H_{15}ClN_{5}O_{2}</td>
</tr>
<tr>
<td>Disperse Blue 373 (DB373)</td>
<td>51868-46-3</td>
<td>C_{21}H_{21}BrN_{6}O_{6}</td>
</tr>
<tr>
<td>Disperse Blue 183:1 (DB 183:1)</td>
<td>2537-62-4</td>
<td>C_{19}H_{19}BrN_{6}O_{3}</td>
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<tr>
<td>Disperse Blue 79:1 (DB 79:1)</td>
<td>3618-72-7</td>
<td>C_{23}H_{23}BrN_{6}O_{10}</td>
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<tr>
<td>Disperse Violet 93 (DV 93)</td>
<td>52697-38-8</td>
<td>C_{18}H_{19}BrN_{6}O_{5}</td>
</tr>
<tr>
<td>Disperse Red 167:1 (DR 167:1)</td>
<td>1533-78-4</td>
<td>C_{22}H_{22}ClN_{5}O_{7}</td>
</tr>
<tr>
<td>2-bromo-4,6-dinitroaniline (BDNA)</td>
<td>1817-73-8</td>
<td>C_{6}H_{4}BrN_{2}O_{3}</td>
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<tr>
<td>2,6-dibromo-4-nitroaniline (DBNA)</td>
<td>827-94-1</td>
<td>C_{6}H_{4}Br_{2}N_{2}O_{2}</td>
</tr>
</tbody>
</table>

In addition to the ten targeted disperse dye compounds listed, two azo dye transformation products will be analyzed: 2-bromo-4,6-dinitroaniline (BDNA) and 2,6-dibromo-4-nitroaniline (DBNA) are examples of products formed after reductive cleavage of the azo functional group of disperse dyes in sediments. In the case of the disperse dyes listed in Table 2, DO 61 will yield DBNA, while DB 373, DB 183:1, DB 79:1, and DV 93 are expected to form BDNA under reducing conditions. Results from house dust analysis indicate that sensitivities of approximately 1 ng/g for each analyte should be achievable in sediments.

Budget

The following budget represents estimated costs for this proposal. Efforts and costs can be adjusted by changing the number of samples or adjusting add-on studies (i.e., nonpolar analysis of POCIS samples or quantitative dye analysis).
Table 3. Budget summary.

<table>
<thead>
<tr>
<th>Expense</th>
<th>Estimated Hours</th>
<th>Estimated Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Labor</strong></td>
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<td>Project Staff</td>
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<td>Senior Management Review</td>
<td>6</td>
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<td>Project Management</td>
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<td>Contract Management</td>
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<tr>
<td>Data Technical Services</td>
<td></td>
<td>5,700**</td>
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<tr>
<td>GIS Services</td>
<td>8</td>
<td>800</td>
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<tr>
<td>Creative Services</td>
<td>20</td>
<td>1,700</td>
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<tr>
<td>IT Services</td>
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<td>0</td>
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<tr>
<td>Communications</td>
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<tr>
<td>Operations</td>
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</table>

**Subcontracts**

Name of contractor
- Duke - sediment NTA: 29,900
- SD State - sediment NTA: 29,900
- SD State - archived passives NTA: 5,200
- Duke - dyes in sediment: 11,050

**Direct Costs**

- Equipment: 200
- Travel: 200
- Printing: 50
- Shipping: 2,000
- Other: 0

**Grand Total**: 117,550

*Not needed because core RMP funding provides this service.
**Data services apply to quantitative analysis of dyes only.
Budget Justification

Field Costs
Field costs are minimized by leveraging the sample collection during the RMP’s margin and ambient Bay sediment cruises, as well as use of POCIS samples collected and extracted in 2016. Only a small amount of planning hours are included in this budget.

Reporting Costs
Preparation of a draft manuscript for publication in a peer-reviewed journal would be the responsibility of the analytical partners (Lee Ferguson at Duke and Eunha Hoh at San Diego State University), and will require relatively little RMP staff time. After the manuscripts are complete, RMP staff will produce a 2-page fact sheet to describe the results and their implications for RMP stakeholders and the general public. This fact sheet would be a companion to one recently completed for non-targeted analysis of fat-soluble compounds (Sutton and Kucklick 2015).

Laboratory Costs
Both types of non-targeted analysis cost $1,300 per sample; the quantitative dye analysis costs $650 per sample. The RMP will benefit from prior negotiations to reduce the indirect costs charged by both universities below standard rates. These indirect costs (10% for Duke University, negotiated from 58%, and 25% for San Diego State University, negotiated from 50.5%) are embedded in the per sample analytical costs provided and amount to a cost-share of over $25,000.

Data Management Costs
Data management is suggested only for the quantitative analysis of dyes; data services are not needed for non-targeted analysis components of this project. Dye data will be transcribed into CEDEN templates, and upload may be possible later.

Reporting
Deliverables will include: a) a draft manuscript\(^1\) that serves as an RMP technical report, due spring 2019; b) a plain language RMP fact sheet describing the results and their implications, due spring 2019; 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.
References


Sutton R, Kucklick J. 2015. A Broad Scan of Bay Contaminants: Cutting edge analysis identifies low levels of five unmonitored compounds in wildlife of San Francisco Bay. SFEI Contribution 748. San Francisco Estuary Institute, Richmond, CA.

Special Study Proposal: Nonylphenol Ethoxylates in Margin Sediments

Summary: Nonylphenol ethoxylates (NPEs) and related compounds are nonionic surfactants that were once widely used in industrial and household laundry detergents; key NPEs are ubiquitously detected in Bay water, sediment, and bivalve samples. Currently, these compounds are classified as Moderate Concern (Tier III) compounds, and it has been suggested that concentrations of these compounds may be decreasing from voluntary phase-out of NPEs from laundry detergents. However, there are many other potential sources of NPEs. Moreover, preliminary results from a 2016 RMP special study suggest that Bay samples contain a broad, complex mixture of NPEs and related compounds, including more ethoxylated NPEs that have not been targeted for monitoring in the Bay. This proposed study will analyze a broad suite of NPEs and related compounds in sediments collected in the Lower South Bay margin areas. These margin sites receive considerable wastewater and stormwater discharges, and are more likely to reflect contamination of current uses of chemicals. This study would provide information to help determine whether NPEs should continue to be classified as Tier III contaminants, and additional information about the influence of ongoing sources of contamination, including effluent and runoff. This study will also provide a more complete baseline of a suite of NPEs to evaluate the effectiveness of management decisions in reducing concentration of NPEs in the Bay.

Estimated Cost: $53,840

Oversight Group: ECWG

Proposed by: Diana Lin and Rebecca Sutton (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

<table>
<thead>
<tr>
<th>Deliverable</th>
<th>Due Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1. Project Management (manage subcontracts, track budgets)</td>
<td>Summer 2017 – Spring 2019</td>
</tr>
<tr>
<td>Task 2. Field Sampling</td>
<td>Summer 2017</td>
</tr>
<tr>
<td>Task 3. Lab analysis</td>
<td>Spring 2018</td>
</tr>
<tr>
<td>Task 4. QA/QC and data management</td>
<td>Summer 2018</td>
</tr>
<tr>
<td>Task 5. Draft report</td>
<td>December 2018</td>
</tr>
<tr>
<td>Task 6. Final report and presentation to ECWG</td>
<td>March 2019</td>
</tr>
</tbody>
</table>
Background

Nonylphenol ethoxylates (NPEs) are nonionic surfactants with a wide range of potential consumer and industrial applications. NPEs were once widely used in industrial and household laundry detergents, though voluntary phase-outs may have reduced this particular use significantly (Maruya 2015, EPA 2010). NPEs are manufactured by reacting nonylphenols (NPs) with ethylene oxide. Longer-chain nonylphenol ethoxylates can degrade to shorter products like nonylphenol monoethoxylates (NP1EO), nonylphenol diethoxylates (NP2EO), and nonylphenol (NP). Nonylphenols are persistent in the aquatic environment, moderately bioaccumulative, and extremely toxic to aquatic organisms (USEPA 2010). A small set of NPE and NP compounds, specifically 4-NP, 4-NP1EO, 4-NP2EO, have been analyzed in Bay surface water, sediments, bivalves, small fish, and aquatic bird eggs (Klosterhaus et al. 2013).

Currently, these compounds are classified as Moderate Concern (Tier III) compounds. Although concentrations in the Bay are well below most toxicity thresholds, previously measured concentrations in the surface water were above concentrations that impacted barnacle settlement in a laboratory study (Billinghurst et al. 1998). Other studies have shown the potential for synergistic effect of NP and NPEs in combination with other contaminants such as pesticides, which could elicit estrogenic effects on fish (Schlenk et al. 2012) at concentrations measured in the Bay.

It has been suggested that use of NPs and NPEs, and associated environmental contamination, may have declined significantly following voluntary phase-outs among laundry manufacturers. A single study of archived bivalve tissue from San Francisco Bay showed declining levels of NP and NP1EO from 1994 to 2009 (Maruya et al. 2015). However, laundry detergent is just one use of these compounds. Comment letters in response to a recently proposed USEPA Significant New Use Rule (SNUR) indicate a number of other current uses for NPEs, including: adhesives, agricultural use for animals, antioxidant, catalyst, caulk, cleaning surfactant, coatings, colorant or ink component, corrosion inhibitor, defoamer, emulsifier, epoxy catalyst, food additives, food contact adhesives and coatings, fuel additive, hardener, lubricant, paints, paint primer, paint stripper, pesticide ingredient, plastic and polymer additive, printing ribbon component, processing aid, resins, rheology modifier, sealants, and wetting agent. Current environmental data are needed to assess whether this class of contaminants continues to merit classification as a moderate concern for the Bay.

Also of interest are many members of the NPE family that have not been examined in the Bay. Recent non-targeted analysis of Bay water and effluent samples, a 2016 RMP Special Study, detected the presence of a complex suite of NPEs and related octylphenol ethoxylates (OPEs), including longer chain NPEs with 3-11 ethoxylate groups (L. Ferguson, personal communication). This means that there are many additional NPEs present in Bay water that have never been the subject of targeted monitoring in the Bay. The qualitative data from this non-targeted analysis suggests that residential wastewater effluent may not be the only source of NPEs to the Bay, and that stormwater discharges may also be a source of NP and NPEs. For example, relatively few detections were observed in effluent samples, while many, more intense detections were observed in samples obtained from San Leandro Bay, a site
Nonylphenol Ethoxylate in Margin Sediments

heavily influenced by stormwater discharges. Since NPEs were used as an additive in a variety of industrial and consumer products, NPEs may enter the environment through a variety of sources and pathways. A model of NPE sources in an urban catchment area in Sweden estimated that biggest source of NPEs came from vehicles from the wear and tear of car products that contained NPEs (Bjorklund 2007).

Given the potentially wide range of sources of NPEs, analysis of a broad set of NPEs in Bay samples would provide information to determine whether NPEs should continue to be classified as Tier III contaminants.

This proposal will analyze a broad suite of nonylphenols and nonylphenol ethoxylates and related compounds in sediments collected in the Lower South Bay margins. Margin sites are more likely to be depositional and reflect contamination of current uses of chemicals. The Lower South Bay receives considerable wastewater and stormwater discharges, and is less readily diluted by waters of the Pacific Ocean and the San Joaquin and Sacramento rivers.

**Study Objectives and Applicable RMP Management Questions**

This study will provide data essential to understanding the distribution of NPEs and related compounds in the SF Bay.

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

<table>
<thead>
<tr>
<th>Management Question</th>
<th>Study Objective</th>
<th>Example Information Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?</td>
<td>Measure contaminants in sediments not previously characterized by previous NPE monitoring efforts. Evaluate future monitoring needs and toxicity data gaps.</td>
<td>Which newly identified contaminants merit further monitoring? Do findings suggest NPEs should be classified as high, moderate, or low emerging contaminant within the RMP’s tiered framework?</td>
</tr>
<tr>
<td>2) What are the concentrations and masses of contaminants in the Estuary and its segments? 2.1 Are there particular regions of concern?</td>
<td>This study will only focus on the South Bay and Lower South Bay.</td>
<td></td>
</tr>
<tr>
<td>3) What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary? 3.1. Which sources, pathways, etc. contribute most to impacts?</td>
<td>Investigate the influence of different pathways based on sample locations (e.g., near stormwater vs. wastewater discharges) for sediment contaminants.</td>
<td>Do sites influenced by different pathways show different patterns of contamination? Do differences in detection suggest persistence, degradation, or additional pathways for specific contaminants?</td>
</tr>
</tbody>
</table>
4) Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased?  
4.1. What are the effects of management actions on concentrations and mass?  
5) What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?  

<table>
<thead>
<tr>
<th></th>
<th>Establish a baseline for future studies.</th>
<th>Measure changes in historic concentrations in the sediment.</th>
<th>Newly measured contaminants may suggest information about sources or effects of current management actions on current and future discharges.</th>
<th>Are relevant management actions having the intended effect?</th>
<th>Will newly measured contaminants suggest the need for additional or different management actions?</th>
</tr>
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<tbody>
<tr>
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</table>

### Approach

Sample collection will occur in conjunction with the proposed RMP margin sediment sampling cruise in South Bay and Lower South Bay, scheduled for Summer 2017. Approximately 20 samples of margin sediment will be collected. Sites will be selected in consultation with RMP staff; some sites will be selected based on likely influence of wastewater discharges. Sediment samples will be collected using a Van Veen sediment grab. A field blank and two duplicates will also be collected.

SGS AXYS has previously developed a method to analyze a broad array of NPEs and related compounds, and are likely to bring this method back online in 2018. A number of academic laboratories can also provide similar services. Samples may be archived at -20°C until SGS AXYS or a comparable analytical laboratory is available to run the desired analyses.

The measured concentrations of a broad suite of NPEs and related compounds will be used to determine which compounds merit further monitoring. This study may identify new NPE-related compounds that have not been targeted for analysis in the Bay. Identification of compounds and comparison to published toxicity thresholds will help determine whether NPEs should continue to be classified as Tier III, or if the data warrants reclassification to a different tier. This study would establish a baseline for NPE-related compounds in sediment to assess future measurements and test for trends.

Sampling will be focused on the South Bay and Lower South Bay, where greater anthropogenic influence leads us to expect higher concentrations in this region. Therefore, this study will indicate whether NPE-related compound concentrations in sediment are at levels of concern. This study will also reveal what NPEs are dominant in sediments and whether compositions of NPEs are different between sites influenced predominantly by wastewater effluent or stormwater runoff. Understanding the sources and pathways of NPEs will also support determining what management decisions will be effective in reducing future concentrations. For example, major sources of NPEs to runoff may come from car products and concrete, while sources of NPEs to effluent may be from textiles and related products (Bjorklund 2007, Mansson 2008). Composition of NPEs may also shed light on...
Nonylphenol Ethoxylate in Margin Sediments

degradation kinetics and pathways. If some long-chain NPEs do not degrade to more toxic NP, then they may have a lower level of concern.

Moreover, the Department of Toxic Substance Control’s (DTSC) Safer Consumer Products program has identified NPEs and the degradation product nonylphenol as chemicals that warrant further research, and DTSC is currently gathering data about their presence and toxicity in the aquatic environment. Data from this study may provide useful findings to support DTSC’s evaluation of these chemicals.

Budget

The following budget represents estimated costs for this proposed special study (Table 2). Efforts and costs can be scaled back by reducing the number of sites sampled.

<table>
<thead>
<tr>
<th>Expense</th>
<th>Estimated Hours</th>
<th>Estimated Cost</th>
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<td>Contract Management</td>
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<td>GIS Services</td>
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<td>Creative Services</td>
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<td>IT Services</td>
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<tr>
<td>Communications</td>
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<td>0</td>
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<tr>
<td>Operations</td>
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<td>0</td>
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<tr>
<td><strong>Subcontracts</strong></td>
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<tr>
<td>Name of contractor</td>
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<tr>
<td>SGS AXYS/comparable lab</td>
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<td><strong>Direct Costs</strong></td>
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<tr>
<td>Shipping</td>
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<tr>
<td>Other</td>
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</tr>
<tr>
<td><strong>Grand Total</strong></td>
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<td>53,840</td>
</tr>
</tbody>
</table>
Budget Justification

Field Costs
Field costs are minimized through sample collection during the RMP’s margin sediment cruise. Only a small amount of field planning hours are included in this budget.

Laboratory Costs
Analytical costs are expected to be around $900/sample. A total of 23 samples, including blank and field duplicates, are planned.

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

Reporting

The primary deliverable will be a presentation of study findings at the ECWG meeting and a technical report due in spring 2019 (3/31/19).

References


U.S. Environmental Protection Agency (EPA). 2010. Nonylphenol (NP) and Nonylphenol Ethoxylates (NPEs) Action Plan [RIN 2070-ZA09]
Special Study Proposal: Current Use Pesticides and Wastewater Contaminants in Margin Sediment and Water

Summary: To leverage an existing RMP effort to collect samples of margin sediment in the South and Lower South Bays this summer, monitoring of two sets of analytes in margin water and sediment is proposed. First, a screening study to assess concentrations of current use pesticides is recommended. Current use pesticides are currently listed as Possible Concerns (Tier I) for the Bay; many pesticides widely used in urban settings have not been the subject of Bay monitoring studies. Current use pesticides may also be responsible for some of the unexplained sediment toxicity in the Bay. By employing analytical methods developed by USGS California Water Science Center (CAWSC; Sacramento, CA), over 150 pesticides can be monitored, including several pesticides that the California Department of Pesticide Regulation has identified via recent prioritization modeling and marketplace surveys as high priorities for the southern Bay region, and for which limited to no Bay data are available.

A second screening analysis performed by USGS National Water Quality Laboratory (NWQL; Denver, CO) scientists can measure the polycyclic musk fragrance ingredient galaxolide (or HHCB) and a number of other fragrance ingredients. The State Water Board has recently prioritized monitoring for galaxolide in water as part of a pilot study design for CECs because laboratory studies indicate aquatic toxicity at low levels; previous monitoring the RMP has conducted on this contaminant was in bivalves and bird eggs collected in 2002-2004. Analysis of Bay samples would complement an upcoming USGS National Water Quality Assessment Program study of northern and central California, part of a series of studies taking place in regions across the nation, which will monitor both pesticides and wastewater contaminant in freshwater streams, but not the Bay. Monitoring water and sediment samples in southern portions of the Bay for these wastewater contaminant will also provide concentrations that may be compared conservatively to available aquatic toxicity thresholds, as this portion of the Bay experiences longer hydraulic residence times relative to other embayments.

Estimated Cost: $125,746

Oversight Group: ECWG

Proposed by: Rebecca Sutton (SFEI), Michelle Hladik (USGS CAWSC), Ed Furlong (USGS NWQL), Jennifer Sun (SFEI), Diana Lin (SFEI)
PROPOSED DELIVERABLES AND TIMELINE

<table>
<thead>
<tr>
<th>Deliverable</th>
<th>Due Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1. Project Management (write and manage sub-contracts, track budgets)</td>
<td>Summer 2017 – Fall 2018</td>
</tr>
<tr>
<td>Task 2. Field Sampling</td>
<td>Summer 2017</td>
</tr>
<tr>
<td>Task 3. Lab analysis</td>
<td>Winter 2017</td>
</tr>
<tr>
<td>Task 4. QA/QC and contaminant risk review</td>
<td>Spring 2018</td>
</tr>
<tr>
<td>Task 5. Draft report</td>
<td>Summer 2018</td>
</tr>
<tr>
<td>Task 6. Final report</td>
<td>Fall 2018</td>
</tr>
</tbody>
</table>

Background

The RMP has recently begun to focus on better characterization of contaminants in near-shore “margin” areas of San Francisco Bay, an area that previously was not included in the study design for Status and Trends. The margins directly receive discharges of stormwater and wastewater, and are more contaminated by some types of urban pollution than the ambient Bay. The margins are more likely to be a depositional sediment environment relative to the ambient Bay, so sediment-bound contaminants may build up in these areas. In the summer of 2017, the RMP is collecting samples of margin sediment in the South and Lower South Bays, embayments with higher ambient levels of urban contaminants, due to higher wastewater and stormwater discharges and lower levels of dilution.

This proposal outlines study of two classes of contaminants in the margins, current use pesticides and wastewater contaminants including key fragrance ingredients. Consultation with DPR scientists suggests the need for Bay data on several pesticides in current use. DPR uses two methods to prioritize pesticides for study. The first is a Surface Water Protection Program (SWPP) Surface Water Monitoring Prioritization Model (cdpr.ca.gov/docs/emon/surfwtr/sw_models.htm), which uses pesticide application data from the Pesticide Use Reporting (PUR) database and pesticide chemical toxicity benchmarks from USEPA to run a watershed-specific pesticide prioritization algorithm. Because the PUR database does not include information on use of pesticides marketed to consumers, DPR uses a second method, a marketplace survey to assess relative availability of different active ingredients, to supplement the model-based prioritization.

A synthesis of these exercises specific to the South and Lower South Bay region suggests the need to monitor a number of current use pesticides in margin sediment, including eight pyrethroids, fipronil (and degradates), pyriproxyfen (a hormone mimic), etofenprox (a pyrethroid ether), and oxyfluorfen and pendimethalin, both herbicides. Pesticides identified as priorities for water monitoring include nine pyrethroids, fipronil (and degradates), pyriproxyfen, organophosphate insecticides (dichlorvos, malathion, diazinon, naled, chlorpyrifos), imidacloprid, atrazine (herbicide), mancozeb (fungicide, degradate ethylene thiourea), diquat dibromide (herbicide), oxyfluorfen, sulfometuron-methyl (herbicide), diuron (herbicide), pendimethalin, flumioxazin (herbicide), and etofenprox. Screening studies focused on these priority pesticides will provide information useful to Bay water quality managers as well as DPR.
Of note, previous RMP monitoring of several pyrethroids in Bay sediment found concentrations well below levels of concern, leading to the designation of this pesticide class as Low Concern (Tier II) contaminants for the Bay. However, the samples tested were collected in the ambient Bay, generally removed from stormwater and wastewater discharges. If there are problematic concentrations of pyrethroids in the Bay, they are more likely to be found in the margins. Current use pesticides may also be responsible for some of the unexplained sediment toxicity in the Bay.

Monitoring for a second set of analytes, using a USGS method for a diverse set of wastewater contaminants, is also proposed. Of key importance to water quality managers is the inclusion of a number of compounds used in fragrances added to personal care and household products, in particular the polycyclic musk, galaxolide. The State Water Board considers galaxolide to be a priority emerging contaminant for monitoring in aquatic ecosystems due to toxicity concerns, specifically a NOEC (no observed effect concentration) of 7 micrograms per liter in a study that evaluated the impacts of subchronic exposure on larval development of the marine copepod *Nitocra spinipes* (Breitholtz et al. 2003). A recent study of effluent-dominated rivers in southern California reported average galaxolide levels of 2 micrograms per liter (Sengupta et al. 2014). These compounds have also been detected in sediment cores from the Great Lakes (Peck et al. 2006).

Other contaminants covered in the screening that are of interest to the RMP include nonylphenol and octylphenol and their mono- and diethoxylates (but not the broader array of ethoxylated compounds recommended for study in another proposal), five phosphate flame retardants, bisphenol A, triclosan, phthalates (DEP, DEHP), and several pesticides (atrazine, bromacil, carbazole, chlorpyrifos, diazinon, metalazyl, metalochlor, DEET, pentachlorophenol, prometon).

Existing monitoring of these contaminants by state and federal agencies does not include San Francisco Bay. DPR conducts targeted monitoring studies of pesticides in freshwater ecosystems, but does not monitor estuarine or marine systems. Likewise, an upcoming USGS National Water Quality Assessment (NAWQA; https://water.usgs.gov/nawqa/) Program study of northern and central California, part of a series of studies taking place in regions across the nation (https://txpub.usgs.gov/RSQA/), will monitor both pesticides and wastewater contaminants in freshwater streams, but not the Bay. Because the scope of current state and federal monitoring efforts specifically excludes the Bay environment, the RMP has the opportunity to fill this important data gap while gaining additional insights from independent monitoring being conducted on Bay Area streams.

**Study Objectives and Applicable RMP Management Questions**

This study will focus on analytes prioritized by California regulatory agencies, and fill key monitoring data gaps for current use pesticides, fragrance ingredients, and other wastewater contaminants in water and sediment in southern stretches of the near-shore Bay environment. The southern Bay margins are likely to be strongly influenced by wastewater and stormwater discharges, and these waters experience longer residence times relative to other embayments. As a result many urban contaminants have been found to be especially concentrated in this portion of the Bay, making the region something of a worst case
scenario. Concentrations can be compared to available toxicity thresholds, allowing contaminants to be classified within the RMP’s tiered risk framework.

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

<table>
<thead>
<tr>
<th>Management Question</th>
<th>Study Objective</th>
<th>Example Information Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?</td>
<td>Compare levels of current use pesticides, fragrance compounds, and other wastewater contaminants to toxicity thresholds, where available.</td>
<td>Are any target analytes at levels of potential concern for the Bay?</td>
</tr>
<tr>
<td>2) What are the concentrations and masses of contaminants in the Estuary and its segments? 2.1 Are there particular regions of concern?</td>
<td>This study is focused on South and Lower South Bays. Levels measured here may represent a worst case scenario for the Bay as a whole.</td>
<td>Does the DPR model accurately predict the presence of current use pesticides of concern in the region? If not, why not?</td>
</tr>
<tr>
<td>3) What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary? 3.1 Which sources, pathways, etc. contribute most to impacts?</td>
<td>Investigate the influence of different pathways based on sample locations (e.g., near stormwater vs. wastewater discharges) for both sediment and water contaminants.</td>
<td>Do sites influenced by different pathways show different patterns of contamination? Do differences in detection suggest persistence, degradation, or additional pathways for specific contaminants?</td>
</tr>
<tr>
<td>4) Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased? 4.1 What are the effects of management actions on concentrations and mass?</td>
<td>Establish a baseline for future studies.</td>
<td>Are management actions associated with observed contaminant trends in water and sediment?</td>
</tr>
<tr>
<td>5) What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?</td>
<td>Identify sources of contaminants to evaluate effects of current management actions on potential discharges and project trends with likely changes in use and treatment technology.</td>
<td>Are relevant management actions having the intended effect? Do detections suggest the need for additional or different management actions?</td>
</tr>
</tbody>
</table>

This monitoring effort will address questions 1 and 2, by monitoring chemicals in southern portions of the Bay margins. In addition, the study will directly and explicitly address the established emerging contaminants priority question: What emerging contaminants have the potential to adversely impact beneficial uses of the Bay?
Approach

Margin Bay Sediment and Water Sampling

Sample collection will occur in conjunction with the RMP Bay margin sediment sampling cruise in South and Lower South Bay, scheduled for Summer 2017. Approximately 12 co-located samples of margin water and sediment will be collected. Sites will be selected in consultation with RMP staff; some sites will be selected based on likely influence of wastewater and stormwater discharges, respectively.

Water will be collected as surface grab samples. Sediment samples will be collected using a Van Veen sediment grab. Both types of samples will be collected into certified pre-cleaned amber glass jars, stored and shipped on ice to USGS laboratories in Sacramento and Denver, respectively. At least one field blank, field replicate, and matrix spike/duplicate sample will also be collected for analysis.

Analytical Methods

Pesticides:
USGS Sacramento has developed multiple broad screening analyses for pesticides in water and sediment. Water samples will be analyzed via gas chromatography-mass spectrometry (GC-MS; water and suspended sediment; Hladik et al., 2008; Hladik et al., 2009) and liquid chromatography-tandem mass spectrometry (LC-MS/MS; water only; Hladik and Calhoun, 2012). Using these methods, the laboratory can analyze at least 18 of the 25 DPR priorities for water monitoring. Ongoing refinements to the method make it possible that 3 more of the prioritized pesticides may be included.

Sediment samples will be analyzed by GC-MS (Hladik and McWayne 2012). With this method, 12 of 13 DPR priorities for sediment monitoring can be analyzed; the final pesticide (pyriproxyfen) may be added to this broad screen.

Galaxolide and Other Fragrances Ingredients and Wastewater Contaminants:
USGS Denver has developed GC-MS methods for total water and sediment screenings of galaxolide and other contaminants (Burkhardt et al. 2007; Zaugg et al. 2007). Wastewater compounds in whole-water samples are extracted using continuous liquid–liquid extractors and methylene chloride solvent, and then determined by capillary-column GC-MS.

Sediment and soil samples are extracted using a pressurized solvent extraction system. The compounds of interest are extracted from interfering matrix components by high-pressure water/isopropyl alcohol extraction, then isolated using disposable solid-phase extraction (SPE) cartridges containing chemically modified polystyrene-divinylbenzene resin. The cartridges are dried with nitrogen gas, and then sorbed compounds are eluted with methylene chloride (80 percent)-diethyl ether (20 percent) through Florisil/sodium sulfate SPE cartridge, and then determined by capillary-column GC-MS.
Data Interpretation

Pesticide and wastewater contaminant concentrations will be compared to available toxicity thresholds. Results will be evaluated quantitatively and qualitatively (e.g., presence/absence) to determine whether contamination patterns are different between sites influenced predominantly by wastewater effluent or stormwater runoff. Comparison of detected pesticides to the pesticides prioritized for monitoring via DPR’s model may suggest further insight as to pesticide use, fate and transport in the region. Comparison with USGS monitoring efforts in nearby freshwater ecosystems will also provide further insight as to sources, persistence and degradation, and other relevant environmental processes.

Budget

The following budget represents estimated costs for this proposal. Efforts and costs can be adjusted by changing the number of samples (n=12, with 3 additional QA/QC samples), the matrices of interest (water and sediment), or the analyses of interest (pesticides and galaxolide and other wastewater contaminants).

Budget Justification

Field Costs
Field costs are minimized through sample collection during the RMP’s margin sediment cruise. Only a small amount of planning hours are included in this budget.

Laboratory Costs
Per sample costs are as follows: Pesticides in water (and suspended sediment, in the case of GC-MS) $2150; pesticides in sediment $1820; wastewater contaminants in water $655.20; wastewater contaminants in sediment $795.20. USGS may be able to offer a match of up to 10% for USGS CAWSC labor costs associated with this project.

The USGS Sacramento pesticide analyte list shows the broadest correspondence to DPR priorities in water and sediment relative to a number of other analytical laboratories evaluated. The USGS Denver wastewater contaminants analysis is recommended because it includes galaxolide, and because the same contaminants will be examined in a number of freshwater streams in the region as part of a large USGS study starting in spring 2017; data from this independent monitoring effort will be useful in placing Bay findings in context.

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

Reporting

The primary deliverable will be a report; a draft is due in the summer of 2018, and the final report is due in the fall of 2018.
Table 3. Budget summary.

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<thead>
<tr>
<th>Expense</th>
<th>Estimated Hours</th>
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*Not needed because core RMP funding provides this service.
References


Pharmaceuticals in Wastewater: Data Analysis and Reporting

Summary: In 2016, six Bay Area wastewater treatment agencies contributed a total of $77,500 towards a voluntary study of pharmaceutical compounds in wastewater. This RMP-coordinated study represents the most comprehensive analysis of pharmaceuticals in wastewater to date in this region. The data from this study include the first information available about pharmaceutical compounds in influent and effluent from secondary treatment plants, and includes measurements in influent, partially treated effluent (tertiary treatment facilities only), final effluent, recycled water, and reverse osmosis concentrate. Synthesis of the data would be an opportunity to evaluate the current level of concern associated with pharmaceutical compounds in the Bay following recent policy developments surrounding pharmaceutical stewardship. This proposal is for funding to perform quality assurance/quality control review, data analysis, and reporting for the pharmaceuticals dataset. Proposed work would leverage the investment made by the wastewater agencies to collect the data and would maximize the use of these data to inform regional efforts to monitor pharmaceuticals and manage contaminant treatment and source reduction.

Estimated Cost: $30,000

Oversight Group: ECWG

Proposed by: Jennifer Sun and Rebecca Sutton (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

<table>
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<td>Task 1. Data Management, including Quality Assurance / Quality Control</td>
<td>Winter 2017</td>
</tr>
<tr>
<td>Task 2. Draft report</td>
<td>Summer 2018</td>
</tr>
<tr>
<td>Task 4. Final report</td>
<td>Fall 2018</td>
</tr>
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</table>

Background

Pharmaceuticals are detected frequently in U.S. waterways, creating concern for their potential to impact wildlife as well as humans. Laboratory studies indicate fish exposed to antidepressant medications at environmentally relevant doses exhibit behavioral changes that affect survival and reproduction (e.g., Weinberger and Klaper 2014; Brodin et al. 2013). Antibiotic medications, designed specifically to kill organisms, may disrupt bacterial communities and essential ecosystem functions (e.g., Näslund et al. 2008), impart broader antibiotic resistance (e.g., Rizzo et al. 2013), and are often toxic to algal species (e.g., Ferrari et al. 2004). Other pharmaceutical compounds have significant endocrine disrupting effects on aquatic species (e.g., Kolodziej et al. 2013). Pharmaceuticals typically enter the wastestream through excretion and flushing of unused medicines,
suggesting that the primary pathway for Bay contamination is treated wastewater. Increasing support for developing recycled water as a local drinking water source also elevates the concern for the detection of these pharmaceutically active compounds in effluent.

In 2016, the RMP coordinated a study of pharmaceutical compounds in wastewater. Six wastewater facilities located throughout the Bay Area voluntarily participated in this study, contributing a total of $77,550 to analyze 104 pharmaceutical compounds in a total of 39 samples. These combined results provide the most comprehensive analysis of pharmaceuticals in wastewater in the Bay Area to date. Prior to this study, few studies of pharmaceuticals in wastewater in the Bay Area have been conducted, including an RMP study of influent and effluent collected in 2006 from the City of Palo Alto wastewater treatment plant and the San Jose-Santa Clara Regional Wastewater Facility (SJSCRWF), a study of reverse osmosis treatment in 2008-2009 by the City of Palo Alto wastewater treatment plant, and a more comprehensive study of influent and effluent conducted by SJSCRWF in the summer of 2010 (Harrold et al. 2009; Reinhard et al. 2010; Dunlavey et al. 2010).

This voluntary study generated a wealth of data that will fill several gaps in the current understanding of pharmaceutical compound removal by wastewater treatment processes and concentrations in final, discharged effluent. This study included measurements of pharmaceuticals in the final effluent of facilities that employ only secondary treatment, as well as measurements at multiple points along the treatment process in facilities that use tertiary treatment processes. Participating agencies included those discharging to Lower South, South, Central and North Bays. In addition to wastewater influent and final effluent in both secondary and tertiary treatment facilities, this study also included samples of partially treated effluent (prior to tertiary treatment), recycled water, and reverse osmosis concentrate, matrices that have not previously been tested for pharmaceuticals in this region. Twenty-nine samples were collected during the dry season in early October 2016, when stormwater infiltration is expected to be negligible, particularly after a prolonged drought, and the influence of wastewater is greatest in the Bay. An additional 5 samples will be collected at a single agency in both spring and summer 2017.

Previous Bay Area wastewater studies showed significant removal for many pharmaceutical compounds detected in effluent, but focused only on tertiary treatment facilities. This study covers a broader list of contaminants and will provide a better estimate of the final effluent concentrations that should be expected at facilities that do not use tertiary treatment processes.

In addition to the previous wastewater data, pharmaceuticals data were collected in ambient Bay water from Lower South Bay in conjunction with the 2006 wastewater study (Harrold et al. 2009), and in ambient Bay water, sediment, and mussel tissue throughout the Bay in 2009-2010 (Klosterhaus et al. 2013a, 2013b). Though these studies showed that concentrations in the Bay are generally below toxicity thresholds, some pharmaceutical compounds were found at levels approaching thresholds of concern, indicating they may be candidates for further monitoring both in the Bay and in pathways. Key compounds include sulfamethoxazole (intermittently detected above a water PNEC) and erythromycin (intermittently detected above the algal PNEC). High
concentrations of these and other compounds in final wastewater effluent may suggest that further monitoring of these compounds in the Bay is warranted.

A growing policy focus on pharmaceuticals also supports an updated review of current levels of pharmaceuticals in wastewater to reevaluate the level of concern that should be associated with these compounds. Seven of the nine Bay Area counties (Alameda, San Francisco, San Mateo, Santa Clara, Marin, Sonoma, and Contra Costa Counties) currently have drug take-back ordinances in effect, five of which have gone into effect within the past two years. Meanwhile, changes to federal regulations may make voluntary collection projects easier to implement. The 2016 San Francisco Estuary Blueprint calls for additional pharmaceutical CECs reduction efforts (SFEP 2016), which could be informed by the levels of pharmaceuticals in wastewater influent and effluent found in this study. Findings from this study could suggest the need for additional management actions to address pharmaceutical water pollution, as well as additional Bay monitoring.

An initial survey of project participants has indicated support for RMP ECWG staff to analyze and interpret the data. The Bay RMP will contribute significant expertise in evaluating pharmaceuticals in wastewater and other matrices, including experience with similar data sets and reviews of recent scientific and policy developments (Harrold et al. 2009, Klosterhaus et al. 2013a, 2013b; SFEI 2013). Multiple agencies have requested assistance for analyses such as identifying compounds at potential levels of concern based on comparisons of concentrations to thresholds of concern, and evaluating removal efficiencies. The study will also include broader data synthesis, such as comparisons with other data collected both regionally and nationally, and including historical data when available. Simple modeling calculations will also be performed to estimate ambient Bay water concentrations based on concentrations measured in final effluent. All six of the participating agencies have given the RMP permission to analyze and publish their results anonymously in a technical report.

With these funds, the RMP will be able to leverage the existing work completed by six participating agencies and maximize the use of these data to not only identify compounds of concern but also inform regional efforts to monitor pharmaceuticals and manage contaminant treatment and source reduction. Furthermore, substantial cost savings can be realized by combining quality assurance/quality control review across the agencies, as well as data analyses such as comparisons of concentrations to thresholds and other studies.

**Study Objectives and Applicable RMP Management Questions**

This study will provide information that will help to determine the level of concern associated with pharmaceutical pollution in the Bay. Currently available data on pharmaceuticals in the Bay suggests the class is of low concern (Tier II contaminants) (Sutton & Sedlak 2015). However, the rapidly growing Bay Area population and associated rise in pharmaceutical use indicates periodic monitoring of these widely used compounds is appropriate. In addition, analytical advances allow for characterization of a broader array of target compounds among the approximately 3,000 pharmaceuticals available in the U.S. (Howard and Muir 2011).
This study will also address RMP management questions, shown in Table 1 below.

**Table 1.** Study objectives and outcomes related to the RMP Management Questions

<table>
<thead>
<tr>
<th>Management Question</th>
<th>Study Objective</th>
<th>Example Information Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?</td>
<td>Identify pharmaceutical compounds found at concentrations in dischargeable final effluent that could potentially cause adverse impacts upon dilution in receiving waters.</td>
<td>Which pharmaceutical compounds are present at high enough concentrations in wastewater effluent to cause potential concerns and warrant additional monitoring in San Francisco Bay?</td>
</tr>
<tr>
<td>2) What are the concentrations and masses of contaminants in the Estuary and its segments?</td>
<td>N/A (see MQ #5)</td>
<td>N/A (see MQ #5)</td>
</tr>
<tr>
<td>3) What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary? 3.1. Which sources, pathways, etc. contribute most to impacts?</td>
<td>Characterize range of pharmaceutical concentrations observed in the wastewater pathway.</td>
<td>What wastewater treatment processes are most effective at removing pharmaceutical compounds, and which ones? How do final effluent concentrations and removal rates vary with treatment type, size, or operation?</td>
</tr>
<tr>
<td>4) Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased? 4.1. What are the effects of management actions on concentrations and mass?</td>
<td>Compare new wastewater pharmaceutical data alongside available data from previous studies.</td>
<td>Have concentrations of pharmaceuticals in the wastewater pathway increased or decreased? How effective are secondary and tertiary wastewater treatment processes in removing pharmaceutical compounds?</td>
</tr>
<tr>
<td>5) What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?</td>
<td>Evaluate per capita concentrations of pharmaceuticals, to support predictions</td>
<td>Which pharmaceuticals may reach levels of concern in the next decade based on increasing population?</td>
</tr>
</tbody>
</table>
This study will also address the current and proposed RMP CEC Management Questions:

1. Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?
2. What are the sources, pathways, loadings, and processes leading to CEC pollution in the Bay? (proposed question)
3. Have the concentrations of CECs in the Bay increased or decreased? (proposed question)
4. What are the effects of management actions? (proposed question)

Approach

Wastewater Sampling & Analytical Methods

Twenty-nine samples were collected by six participating agencies in October 2016. Five additional samples were collected at one of the participating agencies in February 2017, and a third round of 5 samples are planned to be collected in summer 2017. Because this work was voluntary, the sampling design and collection method differed among agencies. The majority of samples were collected as 24-hour flow-weighted composites, but some were collected as grab samples at peak flow.

Samples will be analyzed by SGS-AXYS (formerly AXYS Analytical, Inc.) Analytical Services Ltd. (Sidney, BC, Canada) for 104 pharmaceutical compounds in Lists 1, 3, 4 and 5 (AXYS Method MLA-075; Table 3) using liquid chromatography tandem mass spectrometry (LC-MS/MS). SGS-AXYS conducted analyses in all matrices for prior RMP pharmaceutical studies as well as the 2010 SJSCRWF study (Harrold et al. 2009; Dunlavey et al. 2010; Klosterhaus et al. 2013b).

The target analytes are listed in Table 3, along with information as on the extraction and LC-MS/MS mode used. The 29 samples already analyzed were run in two lab batches. One field blank and one duplicate sample was included, and will be included, with each lab batch.

Data Analysis

Data will be compiled from the agencies and QA/QC reviewed by RMP staff. Data analyses will include summary statistics calculated for concentrations measured across matrices and facility types, evaluation of removal of pharmaceutical compounds by different treatment methods and facilities, estimated calculations of per capita pharmaceutical concentrations, and model estimations of corresponding diluted concentrations in ambient Bay water. Data will be reported in the context of available thresholds of concern, including monitoring guidelines and published toxicity thresholds, as well as published data available regionally and nationally. In addition, the results will be synthesized in visually attractive graphics that can be used by the facilities to easily explain the results to management, interested parties or the public.
The technical report will also include data synthesis and recommendations that will inform the RMP and broader regional strategy for monitoring and managing pharmaceutical compounds. For example, the report will address topics such as:

- Confirming the categorization of pharmaceuticals in the RMP tiered risk framework or flagging compounds for further monitoring to verify their categorization. The data may continue to support the categorization of pharmaceuticals as chemicals of low concern (Tier II), or it may indicate that particular compounds are present in wastewater at levels that could potentially cause concern in the Bay.
- Providing recommendations for future RMP pharmaceuticals monitoring. This may include identifying compounds of concern that may be candidates for monitoring in the Bay and identifying remaining data gaps.

### Budget

#### Table 2. Budget Summary

<table>
<thead>
<tr>
<th>Expense</th>
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<tr>
<td>Data Management</td>
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<td>Data Analysis &amp; Report Writing</td>
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<td><strong>Grand Total</strong></td>
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</table>

**Budget Justification**

Field collections and laboratory analysis have already been largely completed. This study will leverage the $77,500 in laboratory analytical funds and in-kind labor provided by the six wastewater agencies that participated in the voluntary study by providing an overall synthesis of the data, statistical evaluations, and placing the data in context. RMP staff will bring to this project significant expertise in the area of pharmaceuticals, and the ability to broadly synthesize these data to inform future monitoring strategies. Significant cost-savings will be realized by utilizing RMP staff expertise, and combining QA/QC and data analyses across agencies.

Labor costs include data management and QA/QC, literature review, data analysis, and preparation of a technical report. Data management and QA/QC tasks include $8,500 in labor costs. Data analysis and report writing will cost an additional $22,500. The technical report will undergo multiple rounds of review, including an initial review by the ECWG and participating BACWA agencies, followed by a review by the Technical Review Committee.
**Reporting**

Standard RMP data management formatting and QA/QC procedures will be used. Data will be uploaded to the local regional data center for internal record but will not be published to CD3 or CEDEN in order to maintain data anonymity.

A draft technical report will be completed by Summer 2018. A final technical report will be completed by Fall 2018. The report will be reviewed by the ECWG, TRC, and participating BACWA members.

**References**


Table 3. Pharmaceutical Compounds in Lists 1, 3, 4 and 5 (EPA 1694, AXYS MLA-075). Superscripts indicate analytes for which only estimates of concentration are available.

<table>
<thead>
<tr>
<th>List 1 – Acid Extraction in Positive Ionization</th>
<th>List 3 – Acid Extraction in Negative Ionization</th>
<th>List 4 – Basic Extraction in Positive Ionization</th>
<th>List 5 – Acid Extraction in Positive Ionization</th>
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<td>Sulfanilamide</td>
<td>Virginiamycin</td>
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Non-Targeted Analysis of Reverse Osmosis Concentrate

Summary: Concerns over water supply and water scarcity have led to a growing interest among regional water managers to develop local water supplies, including increased recycled water use. However, the advanced treatment methods needed to purify wastewater effluent for reuse produce concentrated waste streams. Reverse osmosis concentrate (ROC), the concentrated waste stream produced when wastewater is treated by reverse osmosis, has levels of salts and contaminants about six times higher than typical wastewater effluent. Safe, cost-effective disposal of this concentrate currently represents a significant barrier to the wider adoption of this technology.

This proposed study would evaluate the effects of ROC treatment processes on a wide range of chemicals using non-targeted analysis techniques. The Santa Clara Valley Water District has funded a project to develop a Reverse Osmosis Concentrate Management Plan. One component of this project is a pilot study of an advanced oxidation process unit and engineered open-water treatment cells for the removal of contaminants in ROC. We are proposing to add novel non-targeted analyses to the pilot study to screen for the occurrence and transformation of a broad range of chemical classes before and after these treatment processes. Results of the study will provide valuable information about the chemical processes occurring during these treatment processes and the fate of compound classes that are not being monitored for the original study.

Estimated Cost: $59,000

Oversight Group: ECWG

Proposed By: Rebecca Sutton (SFEI), Lee Ferguson (Duke), and Jennifer Sun (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

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<th>Due Date</th>
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<td>Task 1. Samples Collected</td>
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</tr>
<tr>
<td>Task 2. Laboratory Analyses</td>
<td>Fall 2017-Fall 2018</td>
</tr>
<tr>
<td>Task 3. Draft report(^1) and non-technical project summary</td>
<td>Winter 2018</td>
</tr>
<tr>
<td>Task 4. Final report</td>
<td>2019(^2)</td>
</tr>
<tr>
<td>Task 5. Final Non-Technical Project Summary</td>
<td>Spring 2019</td>
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\(^1\) – The draft report will be distributed by email, not published on the website, so as to not jeopardize publication of manuscripts in a peer-reviewed journal.

\(^2\) – Publication of the final report as a manuscript will be dependent on the journal submission process.
Background

Reverse osmosis concentrate (ROC), or the concentrated waste stream produced by wastewater effluent treatment by reverse osmosis, represents an unusually concentrated pathway for contaminants to enter the Bay. Interest in reverse osmosis treatment technologies has grown rapidly as wastewater facilities work towards increasing local water supplies and wastewater reuse. However, the treatment and disposal of the ROC, which contains metals, nutrients, emerging contaminants, and salts at about six times the concentration typically found in the pre-treatment wastewater effluent, presents a barrier to the adoption and expansion of this technology.

To address these issues, the Santa Clara Valley Water District (SCVWD) recently funded a project to develop a ROC Management Plan. Current production of recycled water in the South Bay region is 8 MGD, at the Silicon Valley Advanced Water Purification Center. However, the SCVWD has plans to produce up to 40 MGD by 2025 (Santa Clara Valley Water News, 2016). ROC is currently mixed with tertiary treated water before being discharged into the Bay, but at higher production volumes further treatment beyond dilution will likely be needed to reduce contaminant concentrations to acceptable levels for in-Bay discharge.

A primary component of the SCVWD project includes pilot-scale testing of an advanced oxidation process unit and engineered open-water wetland treatment cells for the removal of contaminants in ROC. The pilot scale study, which will be conducted in collaboration with researchers at UC Berkeley and Stanford, and engineers at the GHD Group, will monitor general water quality parameters, nutrients, major anions, metals, and selected trace organics. However, wastewater effluent and ROC are complex matrices that contain hundreds of trace organic compounds, including pharmaceuticals and personal care products as well as pesticides. This proposed study would be an opportunity to leverage the engineering and technical advisory resources of the SCVWD pilot study and use novel non-targeted analyses to screen for the occurrence and transformation of a much larger range of broad chemical classes that are not currently being monitored.

This study will also build upon previous laboratory, microcosm, and pilot field studies that have shown that non-vegetated, shallow, open-water unit treatment cells are effective at removing several pharmaceutical compounds in wastewater effluent through a combination of phototransformation and microbiological transformations that occur near and within a biomat that colonizes the bottom of the treatment wetland (Jasper et al. 2013; Jasper et al. 2014; Prasse et al. 2015). The waste stream in this study will be about six times as concentrated as previous studies of regular wastewater effluent, which could potentially require different, currently uncharacterized transformation processes. The current study will also evaluate the effect of advanced oxidative pre-treatment on degradation in the wetland. This pre-treatment has the potential to increase the efficiency of the open-water treatment, by partially degrading recalcitrant organic compounds, rendering them more

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susceptible to further biological degradation, and by increasing the UV/visible light transmittance, aiding photodegradation.

Novel non-targeted analysis methods will be used to provide insights into the fate of broad chemical classes that are not currently monitored. In contrast to previous RMP studies using non-targeted analysis, the focus of this study will not be on the identification of specific new chemicals of concern, nor the evaluation of potential adverse impacts. Due to the complex nature of ROC, treatment processes are likely to cause the formation of previously uncharacterized and difficult-to-predict transformation products, leading to greater challenges in definitively identifying many compounds. For the subset of “known” compounds (e.g., present in databases), a high degree of success in structural identification is expected.

However, profiling of molecular formulas will be generally achievable, as will classification by chemical functionalization (e.g. alcohol, acid, amine-containing molecules) using a common-fragment approach with tandem mass spectrometry. By observing the signals of these broad chemical classes at different points of treatment, we can observe chemical transformations and declines for clusters of related compounds, providing greater predictive insight as to the impact of these treatment processes on contaminants not commonly monitored.

**Study Objectives and Applicable RMP Management Questions**

The goal of this add-on study is to inform the management of ROC via treatment and disposal. ROC management has been identified as a new focus area to be developed within the RMP. The larger $500,000 SCVWD project presents a unique opportunity to use novel non-targeted analysis methods to expand understanding of the effectiveness of this proposed treatment system, by gathering broad information about its ability to remove contaminants. Broader knowledge concerning the efficacy of this treatment technology will also be relevant to management decisions concerning expanded production of recycled water throughout the Bay region.

By evaluating ROC as a potential new pathway and informing ROC management, this study will address key RMP Management Questions about sources, pathways and processes leading to pollution in the Bay:

**RMP Management Questions**

3. What are the sources, pathways, loadings, and processes leading to contaminant-related impacts to the Estuary?

**Proposed RMP CEC Management Questions**

2. What are the sources, pathways, loadings, and processes leading to CEC pollution in the Bay?

4. What are the effects of management actions?
The objective of this study is to provide broader insight into the degradation processes occurring during advanced oxidative pre-treatment and open-water engineered wetland treatment. The study is designed to qualitatively track the degradation and removal of broad chemical classes present in ROC, before and after treatment in an open-water engineered treatment cell, and with and without advanced oxidative pre-treatment. Through this design, this RMP special study will address the following guiding questions established in the SCVWD project workplan.

- Can the open-water treatment system remove significant amounts of contaminants from ROC? (Results will be semi-quantitative)
- Does pre-treatment with advanced oxidation processes improve contaminant removal by the treatment system?

To answer these guiding questions, specific monitoring objectives include:

- Characterizing broad classes of chemical pollutants present in a new CEC pathway, reverse osmosis concentrate, before and after treatment.
- Characterizing the degradation processes occurring during the ROC treatment processes and their influence on organic compound classes remaining in treated ROC.
- Exploring the seasonal effectiveness of the wetland treatment processes on degrading organic pollutants.

**Approach**

**SCVWD Pilot Project Design**

The pilot-scale treatment system will consist of a flow-through oxidative treatment system and an open water unit process system. There will be two parallel cells: one receiving untreated ROC and one that has received oxidative pre-treatment to compare these scenarios side-by-side.

Laboratory tests will inform the type of advanced oxidative pre-treatment (e.g., ozonation) and the level that will be evaluated. Batch experiments conducted with the biomat will inform design decisions with respect to hydraulic residence times needed to achieve adequate treatment in the wetland cells. Laboratory tests are expected to be concluded during the spring of 2017. The pilot-scale treatment wetland is scheduled to be built in spring 2017 and operational by summer 2017. The exact study design will be refined following the completion of these laboratory and microcosm studies, and after the basic operation of the treatment system is assessed during the summer of 2017.
RMP Non-Targeted Study Design

The research team will employ non-targeted analysis to screen for the occurrence and transformation of broad classes of chemicals in ROC before and after oxidative treatment and passage through an open-water treatment wetland. Results of the study will provide insights into the fate of compounds that are not currently monitored. However, the non-targeted analysis is not directly intended to accomplish identification of new contaminants or provide insight into the potential adverse impacts of contaminants in ROC.

Sampling for this study will begin once the biomat is fully formed and the system has reached an equilibrium state (likely two to three months). Sampling will likely begin in August 2017, during a warm season with longer sunlight hours and higher biomat activity. The efficiency of wetland treatment is hypothesized to decline with cooler weather and lower natural sunlight intensity over the following three months. Samples will be collected over 6 sampling rounds, over the course of at least one warm and one cool season.

A minimum of four samples will be collected during each sampling round, including two samples taken along each treatment train. These samples will include (1) untreated ROC, before advanced oxidation or wetland treatment; (2) ROC treated with the selected advanced oxidative pre-treatment, prior to wetland treatment; (3) treated, dischargeable ROC at the end of wetland treatment in the treatment train without advanced oxidative pre-treatment; and (4) treated, dischargeable ROC at the end of wetland treatment in the treatment train with advanced oxidative pre-treatment (Figure 1). One set of replicates (one at each sampling location) and two field blank samples will be collected. Effluent inflow and ROC outflow from the SVWAPC is expected to be relatively homogenous, given the large volumes and multiple sources of wastewater input to the SJSCRWF, and the aggregation of flow during treatment at the SVWAPC. Samples will be collected as grab samples rather than composites, to minimize hold time and thus sample degradation between collection and extraction.

Figure 1. Conceptual diagram of non-targeted sample collection locations within each treatment train.
Laboratory Analytical Methods

Non-targeted analysis of up to 30 samples will be conducted by Dr. Ferguson’s lab (Duke University) using Orbitrap-enabled liquid chromatography high resolution mass spectrometry (LC-HRMS). Water samples will be immediately filtered (< 0.45µm GF/F) for particle removal and processed for solid-phase extraction using an automated SPE system (Dionex Autotrace 280) fitted with custom layered-bed extraction cartridges (containing cation exchange, anion exchange, hydrophobic, and amphiphilic resins) designed for enhanced recovery of polar organic compounds. Extracts will be eluted with sequential basic and acidic methanol/MTBE solvent systems prior to combination and concentration.

Extracts will be separated using UHPLC (Thermo Hypersil Gold column, 1.9 mm particle size, 2.1 x 100 cm) over a 70 minute gradient prior to introduction into the mass spectrometer. The LTQ-Orbitrap MS/MS will be operated at 100,000 resolution to achieve < 2 ppm mass accuracy across the mass range of interest. Sample extracts will be spiked with internal mass calibration/quantitation standards (chosen from a set of stable-isotope labeled compounds available in the PI’s laboratory) immediately prior to injection. Ionization will be performed by either electrospray in both positive and negative polarity mode (separately). High resolution detection of analytes in MS mode will be performed by the Orbitrap analyzer, while simultaneous data-dependent MS/MS will be performed in the LTQ Velos module before the Orbitrap. Ions for MS/MS analysis (10 per Orbitrap scan) will be dynamically chosen on a per-scan basis, with priority given to accurate mass values corresponding to compounds in compiled “suspect” lists, with secondary priority given to “non-target” analytes in order of decreasing intensity. These MS/MS data will provide important information to aid in identification of non-target analytes.

Data Analysis Methods

Data generated through these approaches will be applied to both commercially-available (ThermoFisher Scientific Compound Discoverer and Mass Frontier) and custom-written processing software designed to aid in identifying polar organic compounds based on HRMS/MS data. These tools rely on in silico mass spectral fragment prediction and matching of candidate molecular structures against predicted spectra. In cases where no structural candidates are available (e.g., unknown transformation products), compounds will be identified to the molecular formula level, with additional structural information (e.g., chemical functional groups) provided through automated or manual mass spectral interpretation strategies. Final validation of tentative identities will be made based on authentic standard match wherever possible.

A novel clustering and fate-pattern recognition strategy will be used to prioritize candidate compounds for identification after mass spectrometric analysis. Specifically, this process will be used to focus attention and identification efforts on compounds that are most relevant to the question of removal and/or transformation product production from pollutants present in ROC.
This will be accomplished by profiling occurrence and relative abundance of detected analytical signals for non-targeted compounds at various points along the treatment process (e.g., before and after oxidative treatment and passage through the open-water treatment wetland). An example of this strategy is shown in Figure 2, where non-targeted analysis was coupled with fate-dependent prioritization to classify detected molecular features as persistent transformation products, recalcitrant pollutants, or transient species formed and removed during treatment.

Figure 2. Non-targeted analysis and data-processing strategy applied to prioritize compounds formed, removed, and persistent in wastewater during conventional wastewater treatment processes. The heat map on the left is created during data processing, after molecular feature extraction and before structure determination. Each row represents a unique molecular feature detected (~4,000 total). The colors indicate intensity (red is highest, blue is lowest), centered and scaled by row. The data is organized vertically according to “fate class” (e.g., wastewater derived, recalcitrant; non-wastewater derived; etc.) and horizontally by sample location within the wastewater treatment process. This prioritization tool demonstrates the ability to cluster molecular features by fate process prior to structure determination.
Budget

Table 1. Budget Summary

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<thead>
<tr>
<th>Expense</th>
<th>Estimated Cost ($)</th>
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<tr>
<td>Labor</td>
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<tr>
<td>Project Coordination</td>
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<td>Fact Sheet</td>
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<td>Subcontracts</td>
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<td>Duke University – 30 samples @ 1,300/ sample</td>
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<tr>
<td>Direct Costs</td>
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<tr>
<td>Shipping</td>
<td>1200</td>
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<tr>
<td>Grand Total</td>
<td>59,000</td>
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Budget Justification

This RMP study would be an add-on to the $500,000 SCVWD pilot project conducted by UC Berkeley, Stanford, and SFEI. The study would leverage the extensive engineering and technical resources of the project team, including the unique set-up and operation of a pilot advanced oxidative process unit and open-water treatment wetland system.

The SCVWD project is also guided by BACWA, the City of San Jose, and an independent advisory panel that will be able to provide input from both technical and management perspectives during the development of the project and interpretation of results.

Field Costs

Samples will be collected monthly and shipped immediately to Duke University for analysis. Direct costs will include sampling equipment (i.e., containers) and sample shipping.

Subcontractor Costs - laboratory analysis and reporting

Laboratory analytical costs will include analysis of 28 samples ($1200 per sample). Preparation of a technical report will also be the primary responsibility of the analytical partner, Duke University.

SFEI Costs - project coordination and reporting
RMP staff will coordinate the development of the final study design and implementation of field sampling. Following publication of the technical report, RMP staff will also prepare a 1- or 2-page non-technical project summary to describe the results of this study and their implications for ROC management for RMP stakeholders.

**Reporting and Deliverables**

Data will be generated and analyzed by the analytical partner, Duke University, and reported in a technical report. Data produced through this study will be under publication embargo until data from the primary SCVWD study has been published. The final technical report for the SCVWD study is scheduled to be completed in November 2018.

Data will not be reported to SFEI in a standard data format, and additional data management or QA/QC procedures will not be conducted by SFEI. Results will not be saved or published in a local or public database.

Deliverables will include:
1. Technical Report – draft manuscript (Duke University) – Draft, November 2018; Final, 2019
2. 2-page plain-language fact sheet (SFEI) - Draft, December 2018; Final, March 2019

**References**


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1 The draft report will be distributed by email, not published on the website, so as to not jeopardize publication of manuscripts in a peer-reviewed journal. Publication of the final report as a manuscript will be dependent on the journal submission process.