Special Study Proposal: Perfluorinated and Polyfluorinated (PFAS) Compounds in San Francisco Bay: Synthesis and Strategy

Summary: Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are a class of fluorine-rich chemicals with extremely high persistence. Well-studied members of this family have been shown to be highly toxic, while others have received little to no testing. Concentrations of one PFAS, perfluorooctane sulfonate (PFOS), in Bay Area seals and bird eggs in 2004/2006 were some of the highest detected globally. As a result, PFOS has been identified as moderate concern (Tier III CEC) for San Francisco Bay. Recent monitoring suggests decreases in PFOS concentrations in seals and cormorants, likely as a result of changing use patterns that include a nationwide phaseout in 2002.

However, concentrations of other members of the PFAS family, the commonly monitored carboxylates, have remained relatively constant albeit it at substantially lower levels overall. Meanwhile, a number of "precursors," PFAS that degrade to the more persistent PFOS or PFOA, have been detected in sediments. Recent studies of Bay Area stormwater and wastewater suggest that a significant fraction of these precursors are of unknown chemical composition. All PFAS besides PFOS are considered possible concerns (Tier I CEC) for the Bay, as toxicity data are often incomplete or unavailable.

A comprehensive review of PFAS monitoring and toxicity data is needed to determine whether PFOS is the only member of the family to merit regular surveillance. (The RMP currently monitors for 13 perfluorinated chemicals including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonamide (PFOSA).) The purpose of this study is to synthesize the PFAS monitoring to date, to evaluate the classification of these compounds according to the RMP CEC tiers, and to develop a strategy for monitoring PFASs.

Estimated Cost: $56,300

Oversight Group: ECWG

Proposed by: Meg Sedlak, Adam Wong, and Rebecca Sutton (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	***Due Date***
Task 1. Compile data sets, standardize, conduct statistical evaluations	February 2017
Task 2. Evaluation of data in context of recent literature	Spring 2017
Task 3. Assessment of individual PFASs into Tiers (where sufficient information exists)	Spring 2017
Task 4. Draft report	6/31/2017
Task 5. Final report	9/15/2017

Background

Since their first discovery in the mid-1950s, perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been widely used in almost every sector of the economy in such varied applications as providing grease-protection in food-packaging materials, water and stain-repellency for textiles and carpets (e.g., Scotchgard, Gore Tex), coatings for nonstick applications (polytetrafluoroethylene [PFTE] coatings for cookware [Teflon], aerospace, printed circuit boards, cables etc.), and surfactants in semiconductor, metal-coating industries, and firefighting (e.g., AFFF) (Kissa 2001; Wang et al. 2013).

PFASs are carbon chains that have at least one fully fluorinated carbon atom (Buck et al. 2011). In addition to fluorine, the chains may have functional groups such as alcohols, sulfates, carboxylates, ethers, etc. In the case of perfluoroalkyl substances, all of the hydrogens on the carbon are replaced by fluorine, C_nF_{2n+1}–, to which a functional group (e.g., sulfate or carboxylate) is added. Perfluorooctanic acid (PFOA) is an example of a perfluoroalkyl substance. Polyfluoroalkyl substances are not fully fluorinated; an example of polyfluoroalkyl substances are the fluorotelomer alcohols (e.g., 8:2 FTOH $C_8F_{17}CH_2CH_2OH$, which can degrade to PFOA).

As a result of high volume of production and chemical stability, PFASs have been detected throughout the world, even in relatively remote and pristine areas such as the Arctic. In the mid-2000s, PFOS was detected in the human blood supply and the major US manufacturer of perfluoroalkyl sulfonates phased out the production of longer chained PFASs (greater than 8 carbons) (Wang et al 2013). More recently, the USEPA has identified PFOA in 94 drinking water supplies across the country (EWG 2015) and in some instances the concentrations are significantly above the provisional health advisory of 400 ng/L established in 2009 (see letter to Mayor of Hoosick NY- http://www.epa.gov/sites/production/files/2015-12/documents/hoosickfallsmayorpfoa.pdf).

PFOS and PFOA are associated with a number of adverse health effects. Based on the findings of an independent panel reviewing the scientific literature as part of a class action settlement, exposure to PFOA in humans has been associated with six possible outcomes including: testicular cancer, kidney cancer, ulcerative colitis, thyroid disruption, and pregnancy induced hypertension (see http://www.hpcbd.com/Personal-Injury/DuPont-C8/Science-Panel-Probable-Link-Findings.shtml). In laboratory animals, exposure to PFAS has resulted in a myriad of adverse outcomes including low birth weights, compromised immune systems, and tumor formation (Lau et al. 2007). Very few studies have been conducted on the effects of PFAS of estuarine and marine animals. In a study of California sea otters, a significant correlation between the incidence of disease and PFOS/PFOA concentrations in liver was observed (Kannan et al. 2006).

As a result of the adverse impacts, there has been a shift in Europe and North America to shorter-chained carboxylates and sulfates such as perfluorohexanoic acid (PFHxA), perfluorobutanoic acid (PFBA), perfluorobutanesulfonic acid (PFBS) as potential substitutes (Wang et al. 2013); however, the toxicity of these shorter-chained compounds and the precursors to these compounds are not well understood. In addition, there is some evidence to suggest that some precursors (such as the fluorotelomer alcohols) may be more toxic than the perfluorinated carboxylic acids that they degrade to (Phillips et al. 2007).

PFOS and to a lesser extent PFOA have been detected in birds and seals in the Bay Area at some of the highest concentrations observed globally (Sedlak and Greig 2012; Sedlak et al. in prep). The concentrations of PFOS have declined in recent years but nonetheless remain at levels of concern particularly for birds (Custer et al. 2013). Based on the most recent seal and bird data, the concentrations of carboxylates do not show a similar decrease in concentration that was observed for PFOS. There is some concern that some precursors may be degrading to the carboxylates.

Using the RMP's CEC risk and management action framework, the RMP has classified PFOS as a moderate concern (Tier III) chemical, based on the early Bay data for seals and bird eggs (Sutton et al. 2013; Sutton and Sedlak 2015). Remaining compounds have been categorized as a class as possible concerns (Tier I), due largely to limited toxicity data. It is an appropriate time to re-assess the categorization of PFOS and to see whether there is sufficient information to consider re-classifying any of the other PFASs detected in the Bay.

Study Objectives and Applicable RMP Management Questions

The purpose of this study is threefold. First, the project will synthesize existing San Francisco Bay PFAS data collected by the RMP and other scientists into one document.

Secondly, this project will classify the PFASs detected in the Bay using the RMP's tiered risk framework that guides monitoring and management actions on emerging contaminants in San Francisco Bay (Sutton et al. 2013; Sutton and Sedlak 2015). Currently, PFOS is placed in Tier III (Moderate concern); all other PFASs have been placed in Tier I (Possible concern). This study would review the literature to confirm that the PFOS classification is still appropriate in light of new information and, in the cases where there is sufficient information, to classify other PFASs detected.

Third, this project will propose a monitoring strategy for the RMP for PFAS. At present, only cormorant eggs (triennial) and sportfish (every five years) are routinely monitored under Status and Trends for a subset of PFASs that includes PFOS and PFOA (13 analytes total).

PFAS includes quite a broad class of compounds comprising thousands of chemicals. It is neither logistically nor financially feasible to measure each and every one of these chemicals. Strategic decisions will need to be made about which compounds to monitor, and in which matrices.

In the absence of information regarding which chemicals are currently being used, it may be possible to use more generalized techniques to quantify PFASs. Houtz and Sedlak (2012) developed a method for measuring total PFAS precursors levels without requiring molecular identification of each one. Using this method, Houtz and Sedlak estimated that on average 70 % of Bay Area storm water is composed of unidentified precursors. Techniques such as this will be evaluated as potential additions to the RMP monitoring strategy.

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

Management Question	Study Objective	Example Information Application
1) Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?	Synthesize disparate data sets and evaluate concentrations to recent literature.	This information will be used to classify chemicals in the RMP Tiers.
2) What are the concentrations and masses of contaminants in the Estuary and its segments? 2.1 Are there particular regions of concern?	Evaluate spatial distributions.	South Bay seal and cormorant eggs have higher concentrations of PFOS/PFOA.
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?	Synthesis will include data on stormwater and effluent pathways.	Estimation of loads to the Bay from wastewater treatment facilities and storm water runoff.
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?	Evaluate temporal trends in biota.	Conduct statistical analyses of data to determine potential trends.
5) What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?	Review predicted manufacturing trends as well as available data on degradation of precursors to end-products PFOS/PFOA.	Projections may inform classification in Tiers.

This effort would most directly address questions 1 and 4.

Approach

<u>Synthesis</u>
The synthesis will include the following studies focused on the San Francisco Bay:

- Harbor seals. Blood from harbor seals collected in 2004 through 2014 and analyzed for PFASs (Sedlak and Grieg 2012; Sedlak et al. in prep).
- Cormorant eggs. Since 2006, triennial sampling of cormorant eggs have been analyzed for a subset of PFASs as part of the Status and Trends program. Similar to seals, distinct spatial and temporal patterns are evident (Sedlak and Grieg 2012; Sedlak et al. in prep). Data from 2006, 2009, 2012, and 2016 (assuming it is available in time) will be included.

- Fish. San Francisco Bay Sportfish were collected in 2009 and 2014 as part of the RMP Status and Trends monitoring effort and analyzed for PFAS (Davis et al. 2011). In addition, prey fish were collected in 2009, 2010, 2011, and 2012 and analyzed for PFAS (Sedlak and Grieg 2012; Sedlak et al. in prep).
- Mussels. Bay Mussels were collected in 2009/2010 as part of a special study conducted by NOAA mussel watch and analyzed for PFAS (Dodder et al 2014).
- Water. Ambient Bay water was analyzed in 2009 (Klosterhaus et al. 2013) and an urban creek in the South Bay in 2007 (Plumlee et al. 2008).
- Sediment. Bay sediment samples were collected and analyzed in 2004 for PFAS (Higgins et al. 2005) and in 2012 (Benskin et al. 2013).
- Stormwater. Stormwater samples were collected from 10 Bay Area watersheds and analyzed for PFAS in 2010 and 2011(Houtz and Sedlak 2012).
- Effluent. Effluent has been analyzed for PFAS (Houtz et al. 2016) as well as several of the precursors (Benskin et al. 2013).
- Groundwater. Shallow groundwater was collected from the South Bay in 2007 and analyzed for PFAS (Plumlee et al. 2008).

An outline of the synthesis is presented in the Appendix.

Strategy

As part of the synthesis, a monitoring design for PFAS will be proposed that indicates: the matrix, spatial distribution, frequency, and analytes. We will vet the proposed strategy and classification of compounds with known PFAS experts including Derek Muir and Jennifer Field as well as the ECWG and TRC. We anticipate that the PFAS strategy will be updated in future years as part of the CEC strategy review.

Budget

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

Table 3. Proposed Budget.

Personnel	**Budget**
Project Staff	$44,450
Senior Management Review	$1,930
Contract Management	NA
Data Technical Services	$7,460
GIS Services	$960
Honorarium (J Field)	$1,500
Total	$56,300

Reporting

Results will be provided to the RMP committees in the form of a draft report by 6/31/17. Comments will be incorporated into the final report published by 9/30/17.

References

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Appendix: Outline of the PFAS Synthesis and Strategy Report

1. RMP Monitoring of PFASs in San Francisco Bay
    a. PFASs: Structure and Uses
    b. Growing Concerns: Ubiquitous Contaminant, Hot Spots, Toxicity Studies
    c. PFAS Sources and Pathways
    d. Fate in the Environment: transformation processes and terminal degradation products
    e. Management Actions – brief summary
        1. Voluntary phase out C8; PFOA Stewardship Program
        2. Alternatives – Regrettable substitutions?
2. Summary of PFAS Occurrence and Trends
    a. PFASs in San Francisco Bay: The Abiotic Environment
        i. Water
        ii. Sediment
    b. PFASs in San Francisco Bay: Biota
    c. PFAS in Mussel
    d. PFASs in San Francisco Bay Fish
        i. Prey fish
        ii. Sportfish
    e. PFASs in San Francisco Bay Aquatic Bird Eggs
        i. PFASs in Double-crested Cormorant Egg
            1. Spatial and temporal variation
    f. PFASs in San Francisco Bay Harbor Seals
        1. Spatial and temporal variation
3. PFAS Contamination and Bay Impairment
    a. Risks to Humans: PFAS Levels in Fish Are Safe for Human Consumption
    b. Risks to Wildlife:
        i. PFASs Pose ? Risks to Benthic Organisms
        ii. PFASs Pose ? Risks to Fish
        iii. PFASs Risk to Birds
        iv. PFASs Pose Risks to Harbor Seals
    c. Potential for Impairment: Summary
4. PFAS Pathways and Loads to San Francisco Bay
    a. Pathways of PFASs to the Bay: Stormwater and Large Tributary Inputs
    b. Pathways of PFAS to Bay: Effluent
    c. Pathways to the Bay: Groundwater
    d. Pathways to the Bay: Contaminated sites –Former landfills, Use of AFFF at Spills/ Airports/ Refineries
    e. Loadings of PFASs to the Bay
5. Past and Future Trends in Contamination
    a. Declining Levels of PFOS in San Francisco Bay Biota
    b. Trends in other PFASs
        i. PFOA and other Carboxylates
    c. Trends in PFASs Observed in Wastewater and Sediment
    d. Anticipated Future Trends
        i. ?Fluorotelomer?

        ii. Shorter chain
        iii. Polyfluorinated
        iv. Other markets – BRIC -PFOS?

6. CEC Strategy: PFAS Tiers, Monitoring and Management Strategy
    a. Classification for PFOS
    b. Recommendation for classification PFOA
    c. Recommendation for other PFASs
    d. Monitoring Strategy (Table)
        i. Abiotic
        ii. Biotic
            1. Target organisms

    e. Management Actions
        i. Federal
            1. Voluntary phase out C8 PFOS
            2. PFOA stewardship
            3. SNURs
        ii. State
            1. RWQCB Action Plan
            2. Potential Prop 65