MONITORING ALTERNATIVE FLAME RETARDANTS IN SF BAY WATER, SEDIMENT, AND BIOTA: PATHWAY CHARACTERIZATION - WASTEWATER AND STORMWATER (addendum requested by the RMP Steering Committee)

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ESTIMATED COST: $24,000
OVERSIGHT GROUP: Emerging Contaminants Work Group (ECWG)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Collection of stormwater samples	Fall 2013 – Spring 2014
Task 2. Project Management (write and manage sub-contracts, track budgets)	Jan – Dec 2014
Task 3. Collection of wastewater effluent	Spring 2014
Task 4. Laboratory analysis	Summer 2014
Task 5. QA/QC and data management	Dec 2014
Task 6. Draft and final manuscript	Mar 2015

Background

During the July 17, 2013 RMP Steering Committee meeting, attendees expressed interest in evaluating alternative flame retardants present in Bay exposure pathways of wastewater treatment plant (WWTP) effluent and stormwater, in addition to the other Bay matrices identified in the original proposal. Of note, the California State Water Resources Control Board's CEC Science Advisory Panel report directs agencies to include sampling these contamination pathways when screening for emerging contaminants (Anderson et al. 2012). In addition, by encouraging a collaborative monitoring effort among dischargers, it may be possible to avoid implementing new, costly permit requirements.

This proposal addendum outlines additional monitoring of wastewater and stormwater for alternative flame retardants, as part of the conditionally approved study to monitor the same chemicals in Bay water, sediment, bivalves, and seals. Wastewater in particular may contain significantly greater concentrations of alternative flame retardants as compared to Bay water, suggesting the utility of targeting a broader selection of analytes than previously identified for water sample analysis. Measurements made as part of this study may provide an initial indication of the relative importance of wastewater versus stormwater as contamination pathways for specific alternative flame retardants in San Francisco Bay.

Applicable RMP Objectives and Management Questions

This study will address the following RMP Objectives and Management Questions:

MQ.1 Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?

- A: Which chemicals have the potential to impact humans and aquatic life and should be monitored?

MQ.2 What are the concentrations and masses of contaminants in the Estuary and its segments?

- A: Do pollutant spatial patterns and long-term trends indicate particular regions of concern?

Detailed Outline of Study Objectives

1. Describe the distribution and trends of pollutants concentrations in pathways leading to the Estuary.

- This study will provide some of the first data to determine the distribution of concentrations of non-PBDE flame retardant compounds in contaminant pathways leading to the Estuary, and to place these concentrations in context with concentrations observed in other locations.

2. Project future contaminant status and trends using current understanding of ecosystem processes and human activities.

- The relative significance of different exposure pathways in Bay contamination may suggest potential future trends, particularly in combination with time trends observed in biota.

3. Measure pollution exposure and effects on selected parts of the Estuary ecosystem (including humans).

- Flame retardants are considered a class of emerging contaminants. As such, it is important that we determine their concentrations in contamination pathways leading to the Bay and biota to evaluate whether management actions are needed.

4. Compare monitoring information to relevant benchmarks, such as TMDL targets, tissue screening levels, water quality objectives, and sediment quality objectives.

- The concentrations detected in this study will be compared to known threshold effect levels, where possible.

Relationship of the Study to the ECWG Priority Question and Current RMP List of Emerging Contaminants

The Emerging Contaminants Workgroup is focused on answering the following question: "What emerging contaminants have the greatest potential to adversely impact beneficial uses in the Bay?"

Following management actions to eliminate production and use of PBDEs, manufacturers must use alternative (non-PBDE) flame retardants in many products. Because use of these alternatives is expected to increase, it is essential to identify those flame retardants of highest concern for the Bay and conduct preliminary monitoring studies to assess contamination levels. Alternative flame retardants are included as a priority class of compounds in the ECWG five-year plan. The

California State Water Resources Control Board's CEC Science Advisory Panel has directed agencies to include sampling contamination pathways when screening for emerging contaminants (Anderson et al. 2012).

Approach

As a means of initially assessing the importance of wastewater and stormwater as pathways for Bay contamination, *all* alternative flame retardants assessed in the original, conditionally approved study for *any* matrix (water, sediment, and biota) will be considered analytical targets for these additional matrices (see Figure 1, original proposal). While many flame retardants are hydrophobic and will not be targeted for analysis in Bay water samples due to expected low concentrations, it is anticipated that samples collected from exposure pathways will contain significantly higher levels that may permit quantification.

Analysis of samples will be conducted by Dr. Da Chen of Southern Illinois University. Two analytical techniques will be used. A highly sensitive liquid chromatography–electrospray ionization(+)-triple quadrupole mass spectrometry (LC–ESI(+)-QQQ-MS/MS) based analysis method will measure hydrophilic, phosphate flame retardants (Chen et al. 2012a; Chu et al. 2011). Limits of detection vary with the compound, and range from 0.1 to 0.5 ng/L. In contrast, gas chromatography coupled with electron-capture negative ion mass spectrometry (GC-ECNI-MS) will be used to measure halogenated, hydrophobic flame retardants (Chen et al. 2012b, c). Limits of detection vary with the compound, and range from 0.2 to 1 ng/L.

WWTP Effluent
Grab samples of WWTP effluent voluntarily provided by three Bay Area dischargers will be characterized. A replicate sample will be collected as well, for a total of four WWTP effluent samples. Samples will be analyzed for total suspended solids as well as alternative flame retardants. A grab sample is considered preferable to a 24-hour aggregate sample because the equipment used to aggregate samples would expose sample water to plastic; some phosphate flame retardants are also used as plasticizers, so exposure to plastic is best avoided. At present, no drivers are anticipated to influence the relative levels of flame retardants present in treated wastewater released at different times of day.

Dischargers are not specifically named here, as they will have the option to keep their identities confidential in subsequent reporting of the data. Measurements for each discharger will be reported individually using unique identifiers should dischargers request their identities be withheld. Through cooperative relationships with wastewater dischargers, we can obtain and share data about the extent of alternative flame retardant contamination of effluent without implementing expensive permit requirements.

Initial tests of Bay Area WWTP effluent, as well as ambient samples collected close to discharges, suggest that both hydrophilic and some hydrophobic flame retardants will be detected at quantifiable levels in these samples. Monitoring of WWTP effluent samples collected in southern California has already documented significant concentrations of some hydrophilic flame retardants (TCPP and TCEP; Vidal-Dorsch et al. 2012).

Stormwater
Stormwater will be collected from urban, industrial channels in Richmond and Sunnyvale, both monitored as part of other RMP studies. Two storm events will be characterized at each site, with a preference for storms occurring early in the wet season, when higher levels of alternative flame retardants may be flushed from the watershed. Two samples will be obtained from each storm, during the rising portion of the hydrograph when contaminant levels will likely be higher, particularly for sediment-bound compounds. A replicate sample will be collected as well, for a total of nine stormwater samples. Samples will be analyzed for total suspended solids as well as alternative flame retardants. In addition, they will be filtered to allow analysis of both particulate and dissolved phases.

Reporting

Results of these proposed study elements will be reported in conjunction with those of the conditionally approved study as an RMP Technical Report and/or manuscript in early 2015. Comparisons will be made to past screening efforts in the Bay and in the literature from other locations, as well as to relevant toxicological information on these emerging contaminants available at that time.

Proposed Budget

The budget is presented as separate tasks that can be performed as separate elements or combined.

Task	**Estimated Cost**
Analysis of 2014 WWTP effluent (n=3+1 replicate), data management and reporting	$9,000
Analysis of 2014 stormwater (n=8+1 replicate), data management, and reporting	$15,000
Total	**$24,000**

References

Anderson, P.D., N.D. Denslow, J.E. Drewes, A.W. Olivieri, D. Schlenk, G.I. Scott and S.A. Snyder. 2012. Monitoring Strategies for Chemicals of Emerging Concern (CECs) in California's Aquatic Ecosystems. Costa Mesa, CA.

Chen D, Letcher RJ, Chu S. 2012a. Determination of non-halogenated, chlorinated and brominated organophosphate flame retardants in herring gull eggs based on liquid chromatography – tandem quadrupole mass spectrometry. J Chromatogr A 1220: 169-174.

Chen D, Letcher RJ, Martin P. 2012b. Flame retardants in eggs of American kestrels and European starlings from southern Lake Ontario region (North America). J Environ Monit 14(11): 2870-2876.

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Vidal-Dorsch DE, Bay SM, Maruya K, Snyder SA, Trenholm RA, Vanderford BJ. 2012. Contaminants of emerging concern in municipal wastewater effluents and marine receiving water. Environ Toxicol Chem 31(12): 2674-2682.