Special Study Proposal: Phosphate Flame Retardants in Ambient Bay Water

Summary: California's past implementation of unique flammability standards has resulted in decades of flame retardant additives in consumer goods. RMP-funded monitoring of ambient Bay water in 2013 revealed the presence of numerous phosphate flame retardants. Some South Bay samples exhibited levels of one particular flame retardant, triphenyl phosphate (TPhP), which approached an established marine aquatic toxicity threshold. New furniture testing data also reveal key flame retardants in current use that have yet to be monitored. The proposed study would screen ambient water samples from San Francisco Bay to determine whether levels of TPhP or other widely used phosphate flame retardants commonly exceed aquatic toxicity thresholds. Findings are necessary to determine whether these chemicals have been appropriately classified as "possible concerns" (Tier I) within the RMP's Tiered Risk Framework for contaminants of emerging concern (CECs), and may influence ongoing efforts within state agencies aimed at reducing environmental contamination and ecological impacts of flame retardants.

Estimated Cost: $47,125

Oversight Group: ECWG

Proposed by: Rebecca Sutton (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Project Management (write and manage sub-contracts, track budgets)	2017
Task 2. Develop detailed sampling plan	Spring 2017
Task 3. Field Sampling	Summer 2017
Task 4. Lab analysis	Fall 2017
Task 5. QA/QC and data management	Winter 2017
Task 6. Draft report	5/31/2018
Task 7. Final report	8/31/2018

Background

The state of California has implemented unique flammability standards for consumer products. In response to nationwide phase-outs of polybrominated diphenyl ether (PBDE) flame retardants, manufacturers began to substitute other flame retardant chemicals in their products in order to meet these standards. One particular class of chemicals used as PBDE replacements are phosphate-containing compounds. Some phosphate flame retardants have been in use for decades, while others are new. Some have broader industrial uses, such as additives in plastic. Of greater significance, some exhibit notable aquatic toxicity or endocrine-disrupting properties in laboratory tests. Others have received little study.

The RMP funded a Special Study in 2014 that detected some of these phosphate flame retardants in Bay water, sediment, and biota (Sutton et al. 2014, 2015). Ambient Bay water measurements indicated phosphate flame retardants were widely detected in San Francisco Bay. Tris (2-chloroehtyl) phosphate (TCPP) was typically the most abundant phosphate flame retardant in Bay water samples, followed by tris (2-butoxyethyl) phosphate (TBEP) and TPhP (Table 1).

Phosphate flame retardants were more concentrated in southern parts of the Bay, where surface waters experience the least amount of mixing with non-effluent flow and have the highest hydraulic residence time compared to other segments. The average total concentration of phosphate flame retardants in South and Lower South Bays was four times higher than in the rest of the Bay (Sutton et al. 2014). Averages of all individual phosphates were also higher in southern parts of the Bay (Sutton et al. 2014). San Francisco Bay has higher levels of contamination for most phosphate flame retardants relative to other estuarine or marine regions (Table 1). However, these findings are based on only 10 ambient Bay surface water samples.

Of greater concern than simple detection, some South Bay samples exhibited levels of TPhP approaching the marine aquatic toxicity threshold of 370 ng/L (predicted no effect concentration [PNEC]; ECHA 2014). The RMP's tiered risk and management action framework currently lists alternative (non-PBDE) flame retardants, which includes phosphate flame retardants, as a possible concern (Tier I) for the Bay due to insufficient monitoring and toxicity data. While TPhP was found to exceed a marine toxicity threshold, the limited number of exceedances did not support classification as a moderate concern (Tier III) for the Bay.

Should additional monitoring indicate such levels are common, this flame retardant could be considered to pose potential risks to Bay wildlife, potentially supporting the listing of TPhP as a moderate concern (Tier III) emerging contaminant for San Francisco Bay. The proposed study is designed to fill this critical data gap concerning the frequency of detections at or near a key toxicity threshold. Findings from the proposed study should provide sufficient data for TPhP and other phosphate flame retardants to be listed as either a moderate concern (Tier III), low concern (Tier II), or possible concern (Tier I) for the Bay.

Starting in 2014, changes to California's flammability standards may lessen use of chemical flame retardants in some consumer goods, and therefore possibly reduce contamination in the Bay. Monitoring may provide initial information as to the potential impacts of these actions. Unfortunately, recent foam furniture testing suggests widespread use of newly identified phosphates such as tertbutylphenyl diphenyl phosphate and isopropylphenyl diphenyl phosphate, which have not been examined in the Bay (Heather Stapleton, personal communication). USEPA Chemical Data Reporting from manufacturers in 2012 also suggests use of compounds not yet monitored, such as trixylyl phosphate, resorcinol bisdiphenyl phosphate, isodecyl diphenyl phosphate, di-tert-butylphenyl phenyl phosphate, and isopropylated triphenyl phosphate.

Table 1: Phosphate flame retardants in estuarine or marine environments (ng/L).

Location	Year	TCEP	TCPP	TDCPP	TPhP	TBP	TCrP	TBEP	TEHP	EHDPP	T35DMPP	T2IPPP	Reference
Estuarine / Marine													
San Francisco Bay	2013	6.9 - 300	44 - 2,900	5.3 - 450	13 - 300	3.3 - 39	ND - 5.5	24 - 840	ND - 4.2	ND - 2.3	ND	ND	*this study*
Southern California Bight	2006 - 2007	ND	ND - 56										Vidal-Dorsch et al. 2012
River Elbe Estuary	2010	5 - 20	40 - 250	6 - 30	0.3 - 4	2 - 7.5		ND - 80					Bollmann et al. 2012
North Sea (German Bight)	2010		3 - 28					ND - 6					Bollmann et al. 2012

Abbrev.	**Flame retardant**
Phosphates	
TCEP	Tris (2-chloroethyl) phosphate
TCPP	Tris (1-chloro-2-propyl) phosphate (multiple isomers)
TDCPP	Tris (1,3-dichloro-2-propyl) phosphate
TPhP	Triphenyl phosphate
TBP	Tri-n-butyl phosphate
TCrP	Tricresyl phosphate
TBEP	Tris (2-butoxyethyl) phosphate
TEHP	Tris (2-ethylhexyl) phosphate
EHDPP	2-Ethylhexyl diphenyl phosphate
T35DMPP	Tris (3,5-dimethylphenyl) phosphate
T2IPPP	Tris (2-isopropylphenyl) phosphate

Study Objectives and Applicable RMP Management Questions

This study will provide data essential to determining the placement of a number of phosphate flame retardants in the RMP's tiered risk framework, which guides monitoring and management actions on emerging contaminants in San Francisco Bay (Sutton et al. 2013; Sutton and Sedlak 2015). Previous detections suggest triphenyl phosphate in particular may require additional study (Sutton et al. 2014). Management questions to be addressed by this study are the same as those of the overall RMP program, as shown in Table 2.

Table 2. 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?	Compare measured concentrations to toxicity thresholds.	Do findings suggest specific phosphate flame retardants should be classified as moderate concern, low concern, or possible concern emerging contaminant within the RMP's tiered risk framework? Do data indicate a need for management actions?
2) What are the concentrations and masses of contaminants in the Estuary and its segments? 2.1 Are there particular regions of concern?	Compare levels in different embayments.	Do specific embayments or regions appear to have greater levels of contamination?
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?		
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?	Compare measurements to existing data from 2013.	Are there suggestions of trends in contamination levels, taking into account data limitations and differences in methods?
5) What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?	Review results alongside available projections of use and potential control actions under consideration by state and federal agencies.	Which anticipated changes or actions are likely to have the greatest impact on phosphate flame retardant pollution? Are additional/different actions needed?

This monitoring effort would most directly address question 1, determining whether contaminant levels exceed a toxicity threshold. Inferences regarding regional pollution patterns and temporal trends or future predictions could involve interpretation of the data within the context of Bay Area geography, existing data, and potential changes in use or regulation of flame retardants, all of which may play a role in addressing questions 2, 4, and 5.

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

Approach

Ambient Bay Water Sampling

Bay water sample collection will take place in the summer of 2017 as part of the RMP's regular Status and Trends water monitoring cruise. Grab samples of ambient Bay water (2 L, amber glass, 14 day hold time) will be collected at all Bay sites. Two field replicates and a field blank will also be collected. Some phosphate flame retardants are also used as plasticizers, so exposure to plastics will be avoided.

Analytical Methods

Samples will be analyzed by Dr. Da Chen of Southern Illinois University. Dr. Chen will measure the total suspended solids (TSS) of each sample, then characterize contaminants within the aqueous and solid phases using highly sensitive liquid chromatography–triple quadrupole mass spectrometry (LC–QQQ-MS/MS) based analysis methods (Chen et al. 2012; Chu et al. 2011). Limits of detection are typically in the range of 0.1 ppb.

Dr. Chen has agreed to undertake method development to add newly identified phosphate flame retardants, including tertbutylphenyl diphenyl phosphate and isopropylphenyl diphenyl phosphate, to his already extensive list of target analytes. Analysis is expected to cost around $600 per sample.

Budget

The following budget represents estimated costs for this proposed special study (Table 3). Efforts and costs can be scaled back by reducing the number of sites sampled.

Table 3. Proposed Budget.

Expense	Estimated Hours	Estimated Cost
Labor		
Project Staff	168	24,068
Senior Management Review	6	960
Project Management		NA*
Contract Management		NA*
Data Technical Services		4,500
GIS Services	3	280
Creative Services	4	317
IT Services		0
Communications		0
Operations		0
Subcontracts		
Name of contractor		
Dr. Chen, SIU, or comparable lab		15,000
Direct Costs		
Equipment		0
Travel		0
Printing		0
Shipping		2,000
Other		0
Grand Total		
		47,125

*services included in the base RMP funding

<u>Budget Justification</u>

Field Costs
Field costs are minimized through sample collection during the RMP's 2017 Status and Trends water sampling cruise.

Laboratory Costs
Analytical costs per sample are estimated to be $600. For 25 samples, including two field replicates and a field blank, the total analytical costs will be $15,000.

Data Management Costs
Standard data management procedures and costs will be used for this project. Final quality-assured data will be uploaded to CEDEN and made publicly available through CD3.

Reporting

Results will be provided to the RMP committees in the form of a draft report by 5/31/18, which will be reviewed by ECWG and the TRC. Comments will be incorporated into the final report published by 8/31/18.

References

Bollmann UE, Möller A, Xie Z, Ebinghaus R, Einax JW. 2012. Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. Water Research 46:531-538.

Chen D, Letcher RJ, Chu S. 2012. 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.

Chu S, Chen D, Letcher RJ. 2011. Dicationic ion-pairing of phosphoric acid diesters post-liquid chromatography and subsequent determination by electrospray positive ionization-tandem mass spectrometry. J Chromatogr A 1218(44): 8083-8088.

ECHA (European Chemicals Agency). Registered substances. Retrieved June 15, 2014 from http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances (last updated June 13, 2014).

Sutton R, Sedlak M, Davis J. 2013. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. SFEI Contribution 700. San Francisco Estuary Institute, Richmond, CA.
http://www.sfei.org/documents/contaminants-emerging-concern-san-francisco-bay-strategy-future-investigations

Sutton R, Chen D, Sedlak M. 2014. Alternative flame retardants in San Francisco Bay. SETAC North America 35th Annual Meeting. Vancouver, BC, Canada.

Sutton R, Chen D, Sedlak M. 2015. Alternative flame retardants in San Francisco Bay biota. SETAC North America 36th Annual Meeting. Salt Lake City, Utah, USA.

Sutton, R., Sedlak, M., 2015. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2015 Update. SFEI Contribution No. 761. Regional Monitoring Program for Water Quality in San Francisco Bay, San Francisco Estuary Institute, Richmond, CA.

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. Environmental Toxicology and Chemistry 31:2674-2682.