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Alternative Flame Retardants in San Francisco Bay: Synthesis and Strategy

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Executive Summary

The RMP Small Tributaries Loading Strategy (STLS) Team and the Sources, Pathways and Loadings Workgroup (SPLWG) developed and funded a $13,000 special study in 2018 to review available data and previously developed conceptual models for polybrominated diphenyl ethers (PBDEs) to support a stormwater-related alternative flame retardants conceptual model. This technical report summarizes the results of the study.

Recent RMP monitoring that characterized a wide range of flame retardants has led to the conclusion that among the many categories of alternative flame retardants, organophosphate esters should be prioritized for further investigation. A limited amount of organophosphate ester data has been collected in samples of ambient Bay water (n=12), sediment (n=10), stormwater (n=8), and wastewater effluent (n=3). Monitoring revealed ubiquitous detections of organophosphate esters at concentrations comparable to or greater than PBDEs, with some levels approaching or exceeding predicted no effect concentrations for marine waters, suggesting concerns for aquatic toxicity. Organophosphate esters are used not only as flame retardants, but also as plasticizers, and as such may be found in a wider variety of products.

Key data gaps prioritized for additional monitoring include the stormwater and linked air deposition pathways. A 2019 special study proposal will include screening of organophosphate esters in stormwater. Monitoring of additional organophosphate esters recently identified in consumer products is generally recommended.

As improved estimates of these pathways are developed, a modeling effort is recommended to gain insights regarding the relative importance of these and other pathways by which organophosphate esters enter the Bay. Based on the limited availability of data and wide-ranging multimedia partitioning behavior of organophosphate esters, a simple, steady-state model that incorporates this behavior would be most appropriate. The model can be used to assess the sensitivity of modeled ambient concentrations to different model inputs, including pathway loadings and partitioning in the air, water, and sediment compartments. Knowledge gained from monitoring and modeling can point to the types of sources or management actions that may best address this class of contaminants, and can inform priorities for further monitoring as well.

Introduction

Flame retardants are chemical additives incorporated into a broad array of consumer products to meet industry flammability standards. A wide variety of flame retardants are used in building insulation materials, foams used in furniture and other products, electronics, clothing and textiles, and many other consumer products. Widespread use of PBDEs in response to regulatory flammability standards led to unusually high PBDE exposure in San Francisco residents, as well as contamination of San Francisco Bay and its wildlife (She et al., 2008, 2002). There were three commercial mixtures of PBDEs, each named for the bromination level of its dominant component: "PentaBDE" (dominant congeners are BDE-99, 47, 100; predominantly used in polyurethane foam in furniture), "OctaBDE" (BDE-183, 187, 203; predominantly used in ABS resins), and "DecaBDE" (BDE-209; general use flame retardant used in virtually any polymer, including plastics, textiles, and electronics).

Subsequent state bans and nationwide phase-outs of PBDEs have resulted in declining levels of contamination in the Bay (Sutton et al. 2015). However, PBDEs are being replaced by a diverse array of alternative flame retardants, including brominated, chlorinated, and organophosphate ester compounds. These alternatives are ubiquitously detected in the Bay and around the world, even in remote regions like the Arctic (Li et al., 2017; Sutton et al., 2017, in prep).

Sutton et al. (in prep) concluded that among the many categories of alternative flame retardants, organophosphate esters should be prioritized for further investigation in the Bay because of ubiquitous detections, with some levels exceeding or approaching predicted no effect concentrations for marine waters. Organophosphate concentrations are much higher than PBDE concentrations ever monitored in ambient waters by the RMP. Organophosphate esters are increasingly used as manufacturing additives not only as flame retardants, but also as plasticizers and other applications. Organophosphate esters can be chlorinated or non-chlorinated, and can be manufactured and used in complex mixtures composed of different isomers that are not well described. Organophosphate esters belong to a class of polar, persistent, and mobile organic compounds that have previously been overlooked due to analytical limitations, but are increasingly being investigated because they are very mobile, potentially difficult to remove through water treatment processes, and a threat to water quality for humans and ecosystems (Reemtsma et al., 2016). In 2015, the USEPA released a workplan to assess the potential risks of chlorinated organophosphate esters to aquatic organisms and humans (USEPA, 2015). Some organophosphate esters are acutely toxic to aquatic organisms, and there are concerns with neurotoxicity, carcinogenicity, and endocrine disruption in animal studies.

The Municipal Regional Stormwater NPDES Permit requires local stormwater agencies to investigate or support studies on alternative flame retardants. Motivated in part by this permit requirement, the RMP STLS Team and SPLWG developed a $13,000 special study proposal for 2018 to review available PBDE data and previously developed conceptual models to support a stormwater-related alternative flame retardants conceptual model.

The 2018 proposal, titled "Planning Support for Stormwater Alternative Flame Retardants Conceptual Model," outlines Tasks A through D to be completed by the project and summarized in a technical report. In subsequent STLS meetings, STLS reviewed the workplan to complete these tasks, briefly summarized below.

- Task A: Develop draft management questions and information needs for alternative flame retardants in stormwater and refine questions through STLS.
- Task B: Review existing data: 1) compile and summarize PBDE stormwater data and summarize lessons learned that may be applicable to organophosphate flame retardants conceptual model development, and 2) review and compile relevant RMP alternative flame retardant data.
- Task C: Review modeling platforms that could be used for exploring and predicting alternative flame retardant behavior (e.g., partitioning) in stormwater to fill information gaps. In short, how can these previously developed modeling platforms be used to develop a conceptual model of organophosphate flame retardants to answer RMP and STLS management questions?
- Task D: Report on the strengths and weaknesses of the available data and conceptual models for addressing alternative flame retardant information needs in relation to stormwater, and propose methods for addressing data gaps.

Results of Tasks A, B, and C are summarized in this report. Task D is addressed in this report and a 2019 special study proposal to study contaminants of emerging concern in stormwater, which will include organophosphate esters and address the stormwater data gap.

Management questions for organophosphates developed with STLS input (Task A)

1. What are relative contaminant concentrations/masses in Bay water, sediment and air?
2. What are relative contributions of contaminant loads from air deposition, stormwater, and wastewater effluent?
3. Do these loads explain ambient concentrations?
4. What are the likely true sources of loads?

Summary of Existing Monitoring Data (Task B)

This section briefly summarizes the availability of PBDE and organophosphate esters stormwater data for the Bay Area, as well as data for other Bay matrices.

PBDEs

The RMP began monitoring PBDEs in the Bay in 2002, and following the state ban of two PBDE mixtures a few years later, documented declines of PBDE concentrations in Bay wildlife and sediment (Sutton et al., 2017, 2015, in prep). Detections are now generally below thresholds of potential concern. For example, tern egg concentrations are below a reproductive toxicity threshold, and sport fish concentrations are below protective human health thresholds for fish consumption. Because there is limited information about potential adverse impacts of PBDEs in harbor seals, there is some uncertainty as to the potential impact of PBDEs to seals in the Bay. Recent total water concentrations measured of total PBDEs in ambient water ranged between 0.4 – 18 ng/L, with a median of 2.6 ng/L; ambient sediment concentrations ranged between 0.3 – 4.5 ng/g dw, with a median of 1.7 ng/g dw (Sutton et al., in prep). Maximum sediment concentrations were measured in the Lower South Bay (Sutton et al., in prep).

RMP staff under contract with BASMAA developed a PBDE pollutant profile to support future stormwater model development. PBDEs enter surface waters primarily from stormwater runoff and wastewater treatment plant discharges, as well as in minor amounts from rainfall and direct

atmospheric deposition (McKee et al., 2014). PBDEs in the terrestrial landscape are primarily atmospherically deposited after emissions from production, use, and disposal and recycling. Efforts to monitor stormwater loads including monitoring ten mixed-use watersheds around the Bay Area for PBDEs in stormwater runoff (Table 1). Most of the Bay Area watersheds have only been studied at the screening level, with less than 8 samples collected. Stormwater measurements of sums of PBDEs in total water from these samples ranged between 0.4 - 430 ng/L, with a mean of means of 41 ng/L (McKee et al., 2014). BDE-209 was the dominant PBDE congener (58%), while BDE-47 made up 8% of the stormwater discharge.

A preliminary exploration of how measured stormwater concentrations correlated with land use within those watersheds found strong correlations between median PBDE concentration and combined sum of percent High Density Residential and percent Open Compacted spaces (R^2 = 0.77) (McKee et al., 2014). Also, in terms of water concentrations, PBDEs correlated with total mercury, but not with PCBs. This relationship suggests that PBDEs are not strongly associated with older local industrial sources and source areas, as is the understanding of PCBs. Instead, more ubiquitous urban use and atmospheric deposition may play a stronger role in PBDE concentrations observed in SF Bay Area stormwater, more consistent with our conceptual model of total mercury (McKee et al., 2014). Stormwater measurements in Zone 4 Line A, a 100% urban tributary in Hayward, showed strong correlations with turbidity, and in this watershed an estimate of 99.3% of total PBDE loads was transported during storm flow conditions. Additional data would be needed to see if these correlations hold for organophosphate esters.

Table 1: Mixed-use watersheds sampled for PBDEs in stormwater (McKee et al., 2014)

Borel Creek, San Mateo
San Leandro Creek, San Leandro
Santa Fe Channel, Richmond
Sunnyvale East Channel, Sunnyvale
Lower Penetencia Creek, Milpitas
Lower Marsh Creek, Brentwood
Guadalupe River, San Jose
Coyote Creek, Santa Clara County
Zone 4 Line A, Hayward
Zone 5 Line M, Union City

In WY2014, additional stormwater samples (n=8) were collected from two sites and analyzed for PBDEs and alternative flame retardants, including other brominated flame retardants, dechlorane-based flame retardants, and organophosphate esters (Sutton et al., in prep). Summed PBDE concentrations in total water were between 22 - 180 ng/L; the median BDE-47 and BDE-209 contributions in these samples were 12% and 48%, comparable to the findings in McKee et al. (2014).

PBDEs likely enter the municipal wastewater pathway when products and dust from products containing flame retardants are washed (Schreder et al., 2014). The most recent monitoring data of PBDEs in wastewater effluent from Sutton et al. (in prep) measured total concentrations of the sum of PBDEs between 6.2 – 49 ng/L based on single grab samples from three participating

wastewater treatment facilities in the spring of 2014. This is comparable to wastewater effluent concentrations reported in 2005, which were between 14 – 66 ng/L (Oram et al., 2008).

Organophosphate esters

Current understanding of organophosphate ester concentrations in the Bay is based on monitoring data from 2013 and 2014, and summarized briefly here. For further details, see Sutton et al. (in prep). Bay samples, including ambient sediment and water, stormwater, and wastewater, were analyzed for 13 organophosphate esters, including chlorinated and non-chlorinated types (Table 2). Unlike PBDEs, organophosphate esters are generally water soluble, and were widely detected in ambient Bay water and sediment. Additional organophosphate esters not previously monitored in the Bay have recently been identified as important constituents in common flame retardant mixtures. These include isomers of isopropylated triarylphosphate esters (ITPs) and tert-butylated triarylphosphate esters (TBPPs), which have significant toxicity concerns (Phillips et al., 2017). Inclusion of these analytes is recommended in any future monitoring efforts.

Table 2: Organophosphate esters analyzed in Bay samples (Sutton et al. in prep).

Acronym	**Full Analyte Name**	**CAS No.**
TEP	Triethyl phosphate	78-40-0
TCEP	Tris (2-chloroethyl) phosphate	115-96-8
TCPP	Tris (1-chloro-2-propyl) phosphate (multiple isomers)	13674-84-5
TDCPP	Tris (1,3-dichloro-2-propyl) phosphate (aka “chlorinated tris”)	13674-87-8
TPhP	Triphenyl phosphate	115-86-6
TnBP	Tri-n-butyl phosphate	126-73-8
TCrP	Tricresyl phosphate	1330-78-5
TPrP	Tripropyl phosphate	513-08-6
TBEP	Tris (2-butoxyethyl) phosphate	78-51-3
TEHP	Tris (2-ethylhexyl) phosphate	78-42-2
EHDPP	2-Ethylhexyl diphenyl phosphate	1241-94-7
TDBPP	Tris (2,3-dibromopropyl) phosphate	126-72-7
T2iPPP	Tris (2-isopropylphenyl) phosphate	64532-95-2

<u>Ambient Bay water concentrations</u>

TCPP was typically the most abundant organophosphate ester, with total water concentrations ranging between 46 - 2,900 ng/L (median 140 ng/L, n=12, 2013). TPhP median concentrations were the second highest (90 ng/L), and ranged between 41-360 ng/L, with the highest

concentrations near the predicted no effect concentration of 370 ng/L calculated for marine settings (ECHA, 2018a). Another organophosphate ester, TDCPP (also known as chlorinated tris) was detected in all samples at concentrations ranging between 14 - 450 ng/L (median 33 ng/L); many of these measurements exceeded the predicted no effect concentration of 20 ng/L for marine settings (ECHA, 2018b). The total organophosphate ester concentrations (455 – 51,100 ng/L, median 170 ng/L) were approximately two orders of magnitude higher than total PBDE concentrations (0.4 – 18 ng/L, median 2.6 ng/L). Ambient Bay water concentrations were found to be generally higher than reported for other estuarine and marine settings, such as the Southern California Bight and Maizuru Bay, Japan (Vidal Dorsch et al. 2012, Harino et al. 2014, Sutton et al., in prep). An additional 21 ambient Bay water samples were collected during the 2017 Status & Trends water cruise; analysis will provide more data on ambient Bay water concentrations, as well as concentrations from a site outside the Golden Gate Bridge. Data may indicate a need to re-evaluate the risk tier assignment for this class of contaminants, currently "Possible Concern" for San Francisco Bay.

Ambient Bay sediment concentrations

TEHP was found in the highest concentration, with a median of 8.2 ng/g dw (n=10). For comparison, the long-term average dry season concentration of BDE-209 from 2002-2011 was 5.4 ng/g dw in the Lower South Bay, which was higher than found in other subembayments (Sutton et al., 2014). Ambient Bay sediment organophosphate ester concentrations were generally comparable to those reported for other estuarine and marine settings, such as the Southern California Bight and Scheldt Estuary, Holland (Vidal Dorsch et al. 2012, Brandsma et al. 2015, Sutton et al., in prep).

Stormwater concentrations

Stormwater data are available from two industrial watersheds in Richmond and Sunnyvale, sites selected as part of an initial screening of the urban landscape for identifying high leverage watersheds for PCBs and mercury. These two watersheds were monitored during two separate storm events in WY2014; two samples were collected during the rising hydrograph of each storm (n = 2x2x2 = 8), and both dissolved and total water concentrations were measured. Several organophosphate esters were detected in all samples, and TCPP (150 - 2,100 ng/L, median 935 ng/L) and TBEP (220 - 2,200 ng/L, median 900 ng/L) had the highest median concentrations (Table 2). The organophosphate concentrations measured in stormwater are at least an order of magnitude higher than concentrations that have been measured in stormwater.

Table 2: Comparison of available stormwater measurements of PBDEs and organophosphate esters in total water.

Stormwater	Sum of PBDEs (McKee et al. 2014; Sutton et al., in prep)	Sum of organophosphates (Sutton et al., in prep)
Minimum (ng/L)	0.4	720
Maximum (ng/L)	430	4,900
Mean/Median (ng/L)	41 (mean of means)	2,900 (median)

Wastewater effluent concentrations

Effluent grab samples were collected from three facilities in 2014; TCPP had the highest

concentrations, ranging between 2,500 ng/L - 2,700 ng/L (Sutton et al., in prep). Sums of organophosphate esters were between 3,200 – 8,100 ng/L.

Additional pathways for organophosphate esters to enter the Bay include river outflow from the Sacramento-San Joaquin River Delta and atmospheric deposition. Currently, the RMP has not monitored organophosphate ester concentrations in these pathways, and this section briefly summarizes a brief literature review of organophosphate esters in these pathways.

Delta Outflow

Currently, the best available data on Delta outflow is a single grab sample from Suisun Bay, which is strongly influenced by flow from the Sacramento and San Joaquin river. During the 2017 Status and Trends water cruise, single grab samples were collected from RMP historic sites BG20 and BG30, located at the mouths of the Sacramento and San Joaquin rivers; organophosphate ester analytical results from these samples are forthcoming.

Recently, non-targeted analysis by (Moschet et al., 2017) of 51 samples collected during rain events in the winter of 2016 in the Cache Slough Complex of the Delta detected several phosphate flame retardants, including TCEP, TCPP, TDCPP, TEP, and TPhP. TDCPP and TCPP were detected in almost all of the 51 samples. Only maximum concentrations were quantified, and TDCPP and TCPP maximum concentrations were approximately 900 ng/L. These maximum concentrations are comparable to stormwater concentrations measured in local tributaries (Sutton et al., in prep), suggesting that Delta outflow may be an important loading pathway. Flows through the Delta represent approximately 96% of annual freshwater inflows into the Bay, while local tributaries draining urban and agricultural land uses surrounding the Bay represent the remaining 4% of freshwater inputs.

Air

Currently, there are no published data on outdoor air concentrations of organophosphate esters in the San Francisco Bay Area. There are limited studies reporting concentrations in other urban cities, such as Toronto, Chicago, and Tokyo. Reported concentrations of TCEP vary between 1-2,000 pg/m^3, with recent Toronto average concentrations measuring in the middle of that range (800 pg/m^3).

Monitoring of background atmospheric concentrations of persistent organic pollutants by the Global Atmospheric Passive Sampling (GAPS) Network at 48 sites around the world found that PBDE concentrations have not decreased from previous 2005 measurements, and total organophosphate ester concentrations were at least an order of magnitude higher than PBDE levels, ranging between 69-7,770 pg/m^3 (Rauert et al., 2018). Data for the 18 organophosphate esters measured at all sites are summarized by Rauert et al. (2018). The most frequently detected in 2014 were TCEP, TCPP, TPhP, and TBEP. Point Reyes was the only background California site measured in this GAPS study, which had detections of TCPP and TDCPP above detection limit at concentrations of 7 and 2 pg/m^3.

There are no local measurements of organophosphate esters in precipitation, and very few studies reported globally. One study in a semi-urban city in Germany, reported median TCEP, TCPP, and total organophosphate flame retardants concentrations of 187, 372 ng/L and 605 ng/L

(Mihajlovic and Fries, 2012).

Many consumer products are thought to contribute to the presence of organophosphate esters in air in urban areas. A review by (Rauert et al., 2014) summarizes studies of flame retardant emissions measured from products using chamber experiments. Organophosphate ester emissions are reported for a variety of building and insulation materials, polyurethane and upholstery foam, wallpaper materials, printed circuit board electronics, computer systems, and monitors. Additionally, organophosphate esters are known to be used in plastics, textiles, paints and coatings. While many of these products are used indoors, contamination is expected to move into the outdoor environment. Subsequent deposition to stormwater and the Bay during rain events is anticipated, and may be an important pathway.

Summary of Existing Modeling Platforms (Task C)

This section briefly summarizes modeling platforms that can be used for predicting contaminant behavior in stormwater and the ambient Bay to help guide and prioritize monitoring and management actions. The models summarized are the One-Box Bay Model, Multimedia Urban Model, San Francisco Bay Hydrodynamic Model, Regional Watershed Spreadsheet Model, and Bay Area Hydrological Model.

One-Box Bay Model

The one-box model of San Francisco Bay has been used to model PCBs (Davis 2004), PAHs (Greenfield and Davis, 2005), organochlorine pesticides (Connor et al., 2007), PBDEs (Oram et al., 2008), and methylmercury (Yee et al., 2010) in the Bay. This model treats the Bay as a single, well-mixed volume with two compartments representing the water column and the bed (surface) sediments. Conceptually, the model assumes that exchange between water, sediment, and air is more important than exchange between the various geographic subregions of the Bay. Atmospheric exchanges have been incorporated by estimating a deposition rate (in the case of PBDEs, estimates were based on assuming air concentrations were half gaseous and half particulate). Loss through volatilization was also included.

PBDE loads entering the Bay were estimated as part of the mass balance calculation used in the conceptual and steady-state model for PBDEs. The relative PBDE loads entering the Bay in 2005 were estimated to come from municipal wastewater, local watersheds, Delta inflows, and atmospheric deposition. Predominant loads of BDE-47 were estimated to come from the municipal wastewater pathway, while BDE-209 loads were estimated to come predominantly from local tributaries (Oram et al., 2008; Werme et al., 2007). The model was also used to estimate Bay recovery rates if PBDE loads were reduced or eliminated (Oram et al., 2008). The model suggested that inventory of BDE-47 and BDE-209 in the Bay was highly sensitive to loads entering the Bay, and that inventories were expected to increase or decrease depending on whether higher or lower estimates of annual loadings were used.

While conceptually this model may be used as a starting point for evaluating organophosphate esters, the organophosphate ester load from each pathway is expected to be very different relative to PBDEs due to the high water solubility and more volatile nature of organophosphate esters (Li et al., 2017).

Multimedia Urban Model (MUM)
The Multimedia Urban Model (MUM with polyparameter linear free energy relationships update) is another steady-state model that has been developed to estimate the fate of semivolatile organic compounds in urban areas. This model includes seven bulk compartments: upper air, lower air, water, soil, sediment, vegetation, and organic film on impervious surface (Priemer and Diamond, 2002). MUM includes an additional compartment for ambient air relative to the current one-box Bay model, and incorporates additional mass transfer processes (e.g., distribution between gas and particulate phase) and chemical degradation in the bulk air phase.

MUM has been used to predict the fate of PCBs and PBDEs in urban environments in peer-reviewed studies (Priemer and Diamond, 2002; Sommerfreund et al., 2010). MUM has recently been modified to incorporate chemical parameterization of organophosphate esters through the use of polyparameter linear free energy relationships (ppLFERS). Essentially, ppLFERs use more than a single parameter (such as K_d for sediment-water partitioning) to describe chemical partitioning. MUM has been used to estimate the fate and transport of organophosphates in Toronto (Rodgers et al., in prep). Results indicate high concentrations of organophosphate esters in Toronto, and transfer of organophosphate esters from urban air to urban water through precipitation, could explain concentrations observed in local streams.

San Francisco Bay Hydrodynamic Model
The San Francisco Bay hydrodynamic model simulates hydrodynamic processes in the Bay, but currently does not include chemical mass transfer and transformation processes. The model has been developed to support transport and dilution studies. This physics-based model incorporates data for tides, Delta outflow, stormwater flows (derived from the Bay Area Hydrological Model described below), local winds, and regional wastewater and refinery dischargers. Further details on the configuration and the water year 2013 validation of the model are available in the Interim Model Validation Report (Holleman et al., 2017).

Recently, a simplified spreadsheet version of the Bay hydrodynamic model has been developed to estimate ambient aqueous contaminant concentrations based on dilution of concentrations entering the Bay. This hydrodynamic spreadsheet model was developed by running the hydrodynamic transport model from October 2012 to September 2013. During this period, numerical "dyes" were added to modeled discharges, and the model predicted concentrations of these dyes throughout the Bay. The model results were condensed into a series of spreadsheets that summarize the relationship between concentrations in load streams (i.e., concentration in stormwater and in individual wastewater or refinery discharges) and ambient concentrations in the Bay for each subembayment. Using this spreadsheet requires specifying concentrations for each of the 42 discharges (37 from wastewater treatment plants and five from refineries) and a representative concentration for stormwater. The spreadsheet then calculates, for each region of the Bay, the sum of contributions from all discharges, providing a baseline estimate for ambient contaminant concentrations. The regions follow RMP subembayment delineations: Lower South Bay, South Bay, Central Bay, San Pablo Bay, and Suisun Bay.

The hydrodynamic spreadsheet model only simulates water concentrations and does not include the sediment or air compartments. Chemical processes such as degradation, sorption to sediment,

and atmospheric exchange are currently not included in the model. Since organophosphate esters are known to degrade and to partition among sediment, water, and air matrices, using this model to simulate organophosphate transport does not seem appropriate. Future model development may add these processes.*Watershed Models - RWSM and BAHM*
The Regional Watershed Spreadsheet Model (RWSM) has been developed as a planning level tool for estimating total annual average flow and PCB and mercury loads from small tributaries surrounding the Bay. The model provided estimates of regional and sub-regional scale loads and regionally averaged coefficients for selected land use/source area categories (McKee et al., 2014).

The Bay Area Hydrological Model (BAHM) is a continuous simulation model that was developed to estimate flow and pollutant loads from Bay Area watersheds. The model is built upon HSPF (Hydrological Simulation Program--Fortran), a comprehensive package for simulation of watershed hydrology and water quality for pollutants. The model uses continuous rainfall and other meteorological records to compute streamflow hydrographs and pollutographs across multiple pollutant sources, spatial scales, and time steps. Currently, the BAHM divides the entire Bay Area into 63 individual watersheds. The model simulation is from 1999 to 2016.

The BAHM can be used to estimate stormwater contaminant loads from individual watersheds in the region in two ways. One is to simply multiply modeled flow by measured stormwater contaminant concentrations. Another more sophisticated approach is to use the BAHM to directly simulate the fate and transport of contaminants in stormwater. Since this is a continuous simulation model, the result of this simulation is a time course of runoff flow rate and contaminant concentrations, making it possible to detect interannual variability of contaminant loads and how they change over time (trend). Based on the load estimates, the watersheds that contribute disproportionately high contaminant loads can be targeted for further investigation. The data gaps identified during model development and implementation can also be used to guide future monitoring efforts.

Either RWSM or BAHM can be used to estimate stormwater loads. Since current stormwater organophosphate ester measurements are limited to samples from just two watersheds during two storm events (n=8), stormwater loads can initially be estimated based on multiplying modeled flows with measured concentrations using either model. A key advantage of BAHM over RWSM is that spatial and temporal output of stormwater loads can be fed into the Bay Hydrodynamic Model to predict spatial and temporal changes in ambient Bay water concentrations.

Available Data and Models: Strengths and Weaknesses for Understanding Organophosphate Ester Transport and Fate in Stormwater and the Bay (Task D)
A conceptual and quantitative model is needed to understand the loading and fate of organophosphates esters in San Francisco Bay. A model is especially needed to answer prioritized management questions:

- What are relative contributions of contaminant loads from air deposition, stormwater, and wastewater effluent?
- Do these loads explain ambient concentrations? Identify key processes or missing processes in conceptual model.

Unlike PBDEs, organophosphates esters are generally water soluble, and were widely detected in all Bay sample matrices. In the most recent study of Bay matrices (Sutton et al. in prep), median organophosphate concentrations were two orders of magnitude greater than total PBDE concentrations in ambient water, and one order of magnitude greater in stormwater. Bay sediment concentrations of organophosphate esters were an order of magnitude greater than total PBDE concentrations. While there have not been any studies of air concentrations of organophosphate esters in the Bay, global studies indicate that organophosphate concentrations in air are at least an order of magnitude higher than PBDEs (Rauert et al., 2018). The higher concentrations of organophosphate esters in all three environmental matrices points to the need for a multi-media model to simulate the fate and transport of organophosphate esters in the Bay.

Strength and Weakness of Existing Model Platforms

Three reviewed models that may be used to model organophosphate esters in the Bay include the Multimedia Urban Model (MUM), the Hydrodynamic Bay Model (hydrodynamic), and the One-Box Bay Model (One-Box Bay). Both the One-Box Bay Model and MUM can be used to model the multi-media partitioning properties of organophosphate esters, and both are based on assuming steady-state fugacity between modeled media compartments. The one-box Bay model is simpler, and has the advantage of having been used previously by the RMP to model concentrations of PCBs, PAHs organochlorine pesticides, PBDEs, and methylmercury, and parameter needed to represent the Bay are mostly defined and populated. However, only MUM has already been developed to incorporate the unique physico-chemical properties of organophosphates. MUM would need to be simplified to represent the Bay as a box composing of the air, water, and sediment compartments. MUM has the advantage over the Bay of including the air compartment as a separate compartment, and therefore also includes chemical parameters for organophosphate esters and mass transfer processes and chemical degradation in the air phase. The MUM model includes additional compartments (e.g., soil, vegetation, and biofilm on impervious surfaces) that need not be included in the development of the model for the Bay.

The hydrodynamic model can be useful for providing more temporally and geographically specific estimates of contaminant levels, but is currently limited in that it assumes contaminants act conservatively, neglecting processes, like degradation, volatilization, or partitioning to sediment, which are important for organophosphate esters.

Data Availability for Supporting Model Development

Models are only as good as the data upon which they are built. Previous RMP monitoring has provided some data for organophosphate levels in ambient Bay water and sediment. More limited measurements are available to characterize Bay Area stormwater and wastewater effluent discharges into the Bay.

Several important data gaps are identified, including lack of local air data, river and stormwater inflows, and ocean exchanges. The quality of these estimates will define the quality of the Bay model. A literature review of organophosphate ester concentrations observed in air, stormwater, the Delta, and the ocean is summarized below.

Air

As mentioned above, there is currently no published data on air concentrations of

organophosphate esters in the San Francisco Bay Area. Potential air concentrations vary by three orders of magnitude based on reported concentrations globally (1 – 8,000 pg/m^3 Rauert et al., 2018). Precipitation concentrations in the 400 ng/L range for TCPP have been reported in a semi-urban city in Germany. Wet air deposition via precipitation in the San Francisco Bay watershed may be an important pathway linked to the stormwater pathway.

Stormwater
As mentioned above, only two Bay Area watersheds, in Richmond and Sunnyvale, have been screened for stormwater measurements of organophosphate esters. The total water concentration of organophosphate esters analyzed ranged between 720 – 4,900 ng/L, with a median of 2,900 ng/L, most of which was in the dissolved fraction (fraction of dissolved to total water concentration ranged between 40 – 98%, median 93% out of 8 samples).

Though few studies of stormwater in other regions are available, findings reported to-date suggest Bay Area concentrations are generally comparable to those in urban surface water in Germany and Toronto (Regnery and Püttmann 2010; Rodgers et al., in prep). Additional monitoring data is needed to understand the range of organophosphate ester concentrations in Bay stormwater.

Delta
As described above, analytical results of organophosphate esters collected at the mouth of the Sacramento and San Joaquin rivers by the RMP are forthcoming, and are currently the best available data from the Delta. Non-targeted analysis reported by Moschet et al., 2017 indicate concentrations of organophosphate esters in Delta waters may be high and comparable to stormwater concentrations; maximum concentrations of TCPP were approximately 900 ng/L.

For comparison, previously reported BDE-47 and BDE-209 concentrations from the Delta from WY2005 were 0.2 ng/L and 0.1 ng/L (Oram et al., 2008), and organophosphate ester concentrations are likely one to two orders of magnitude higher based on relative concentrations measured in stormwater.

Pacific Ocean Tidal Exchanges
The Bay is a tidally-influenced ecosystem, and previous efforts have estimated water flow losses to the ocean through the Golden Gate Bridge as 3.75 times the freshwater inflow. We will have one measurement of organophosphate ester concentrations just outside the Golden Gate Bridge based on a grab sample collected by the RMP during the 2017 Status and Trends Water Cruise. This sample represents a mixture of Bay and Pacific Ocean water. Results from this analysis are forthcoming.

There are few published reports of open ocean concentrations of organophosphate esters that can be used to estimate influx from the Pacific Ocean into San Francisco Bay. Li et al. (2017) measured organophosphate esters in seawater along a transect from the North Sea to the Arctic, and found a general decreasing trend of concentrations moving away from land. The median of the sum of eight organophosphate esters measured was 3 ng/L. The concentrations in the relatively remote Arctic were 2-3 orders of magnitude lower than seawater near urban areas, which have been measured in the hundred ng/L range (Li et al., 2017). In Southern California,

TCPP was also detected in seawater near wastewater effluent discharges at maximum concentrations near detection limits of 50 ng/L (Vidal-Dorsch et al., 2012).

Analyte List

As mentioned above, several additional isopropylated and *tert*-butylated triarylphosphate esters (ITP and TBPPs) have been characterized in flame retardant mixtures (Table 3; Phillips et al., 2017). These organophosphate esters have not previously been analyzed in Bay samples, and should be considered for inclusion in target analyte lists for future monitoring efforts. These compounds have also been characterized in house dust standard reference material 2585, which was prepared from dust collected in 1993 and 1994, suggesting that these compounds have been in use long before PBDEs were phased out (Phillips et al., 2017). These compounds are also used as plasticizers in hydraulic fluids. It is important to note that flame retardants can be complex mixtures containing many different components, and there may be many other organophosphate esters in commercial and industrial use that have not been identified and documented in the scientific literature.

Table 3. Isopropylated and *tert*-butylated triarylphosphate esters found to be important components of four flame retardant mixtures studied in Phillips et al., 2017.

Acronym	Full Analyte Name
21PPDP	2-isopropyl phenyl diphenyl phosphate
3IPPDPP	3-isopropyl phenyl diphenyl phosphate
4IPPDPP	4-isopropyl phenyl diphenyl phosphate
24DIPPDPP	2,4-diisopropylphenyl diphenyl phosphate
B2IPPPP	Bis(2-isopropylphenyl) phenyl phosphate
B3IPPPP	Bis(3-isopropylphenyl) phenyl phosphate
B4IPPPP	Bis(4-isopropylphenyl) phenyl phosphate
4tPBDPP	4-tert-butyl phenyl diphenyl phosphate
B4tBPPPP	Bis(4-tert-butyl phenyl) phenyl phosphate
T4tBPP	Tris(4-tert-butylphenyl) phosphate

Recommendations

In summary, additional monitoring and modeling is recommended to answer management questions about ambient concentrations, estimated loads, and the fate of organophosphate esters.

A 2019 special study of contaminants of emerging concern in stormwater includes organophosphate esters in the target analyte list, which will begin to fill the identified data gap on stormwater concentrations. Additionally, air sampling may be an important data gap where there is no local monitoring data.

As key monitoring data are collected, a modeling effort is recommended to gain insights regarding the transport and fate of these contaminants, and evaluate the need for additional data based on the sensitivity of the model to the measured parameters. A simple, steady-state model that incorporates multi-media partitioning behavior of organophosphate esters is recommended. Estimated steady-state concentrations of contaminants in Bay water and sediment can be compared to average concentrations measured in the Bay. A mass balance calculation can allow

comparison of estimated loads from stormwater, wastewater, river inflows, and air deposition, and highlight pathways where additional monitoring would significantly improve these estimates.

Additionally, the model can be used to illustrate the sensitivity of ambient Bay concentrations to changes in loads from different pathways, and gauge the impact of management actions that may affect these loads. Insights gained from the modeling effort may aid in prioritization of management actions designed to address specific sources or pathways relevant to organophosphate esters.

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