ALTERNATIVE FLAME RETARDANTS IN SAN FRANCISCO BAY

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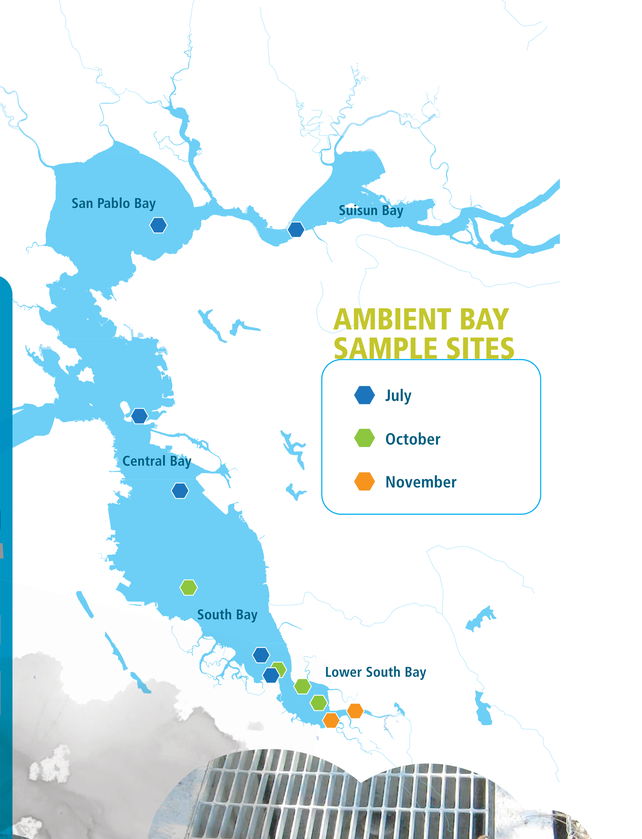
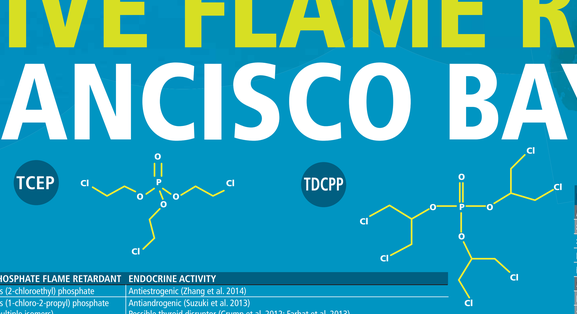
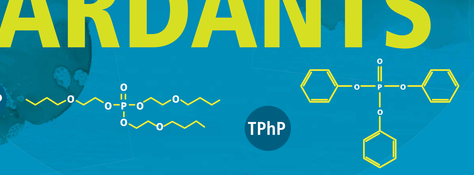
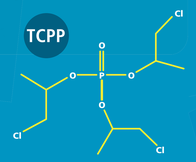


The state of California has implemented unique flammability standards for consumer products and other common goods. In response to nationwide phase-outs of polybrominated diphenyl ether (PBDE) flame retardants, manufacturers began to substitute other flame retardant chemicals in their products. Little is known about many of the diverse array of bromine-, chlorine-, and phosphate-containing compounds that have replaced PBDEs. Some of these chemicals have been in use for decades, while others are new. Many have been shown to have endocrine-disrupting properties. In recent studies, the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has detected some of these alternative flame retardants in samples of Bay water, sediment, and biota. Typically, they are found in lower concentrations than PBDEs. The levels observed have been far below the effects thresholds that exist for a few of these compounds, but for most of these chemicals the potential risks are unknown. Starting in 2014, changes to California's flammability standards may lessen the use of chemical flame retardants and therefore reduce the potential risks in the Bay. Preliminary results from a new survey of alternative flame retardants in Bay water, stormwater, and wastewater treatment plant (WWTP) effluent are presented.







ABBREV.	PHOSPHATE FLAME RETARDANT	ENDOCRINE ACTIVITY
TCEP	Tris (2-chloroethyl) phosphate	Antiestrogenic (Zhang et al. 2014)
TCPP	Tris (1-chloro-2-propyl) phosphate (multiple isomers)	Antiandrogenic (Suzuki et al. 2013) Possible thyroid disruptor (Crump et al. 2012; Farhat et al. 2013)
TDCPP	Tris (1,3-dichloro-2-propyl) phosphate	Estrogenic (Kojima et al. 2013; Liu et al. 2013a; Suzuki et al. 2013; Zhang et al. 2014) Antiandrogenic (Kojima et al. 2013; Liu et al. 2013a,b; Suzuki et al. 2013) Thyroid disruptor (Crump et al. 2012; Wang et al. 2013; Farhat et al. 2013; Meeker et al. 2013)
TPhP	Triphenyl phosphate	Estrogenic (Kojima et al. 2013; Liu et al. 2013a; Suzuki et al. 2013; Zhang et al. 2014) Antiandrogenic (Kojima et al. 2013; Liu et al. 2013a; Suzuki et al. 2013) Thyroid disruptor (Liu et al. 2013b; Meeker et al. 2013)
TBP	Tri-n-butyl phosphate	Estrogenic (Suzuki et al. 2013) Antiandrogenic (Kojima et al. 2013; Suzuki et al. 2013)
TCrP	Tricresyl phosphate	Estrogenic (Suzuki et al. 2013; Zhang et al. 2014) Antiandrogenic (Kojima et al. 2013; Suzuki et al. 2013) Thyroid disruptor (Crump et al. 2014)
TBEP	Tris (2-butoxyethyl) phosphate	
TEHP	Tris (2-ethylhexyl) phosphate	Antiestrogenic (Suzuki et al. 2013; Zhang et al. 2014)

Table 1 Potential Endocrine Activity of Phosphate Flame Retardants

Location	Year	TCEP	TCPP	TDCPP	TPhP	TBP	TCrP	TBEP	TEHP	Reference
Estuarine / Marine										
San Francisco Bay	2013	6.2 - 300	32 - 2,900	5.9 - 450	15 - 300	4.5 - 39	ND - 26	11 - 840	ND - 28	*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
Stormwater										
Richmond, Calif.	2013 - 2014	24 - 370	620 - 1,300	130 - 180	47 - 95	40 - 210	ND - 1.6	710 - 2,400	ND - 1.1	*this study*
Sunnyvale, Calif.	2013 - 2014	21 - 340	55 - 2,700	15 - 77	39 - 100	13 - 150	ND - 56	73 - 1,900	ND - 28	*this study*
Frankfurt, Germany*	2008 - 2009	33 - 275	16 - 5,791	ND - 73		4 - 417		ND - 1,616		Regnery and Puttmann 2010
WWTP Effluent										
SF Bay WWTP 1	2014	180	2,700	180	27	13	1.7	29	ND	*this study*
SF Bay WWTP 2	2014	320	2,500	330	61	88	6.7	69	ND	*this study*
SF Bay WWTP 3	2014	190	1,900	120	85	22	14	2,500	17	*this study*
Oakland, Calif.	2006	ND - 373								Jackson and Sutton 2008
Southern California	2006 - 2007	ND - 1,700	610 - 2,700							Vidal-Dorsch et al. 2012
European Union	2010	up to 2,400	up to 21,000	up to 860	up to 610	up to 1,700	ND - 1.3	up to 43,000	ND	Loos et al. 2013
Norway	2007	1,600 - 2,200	1,700 - 2,100	86 - 740	1,700 - 3,500	270 - 1,300		1,600 - 3,300		Green et al. 2008
Austria	2005	ND - 1,600	270 - 1,400	19 - 1,400	ND - 170	ND - 810	ND - 55	13 - 5,400	ND	Martínez-Carballo et al. 2007

* Samples taken from stormwater holding tank

Table 2 Phosphate Flame Retardants in Estuarine/Marine, Stormwater, and WWTP Effluent Samples (ng/L)

METHODS

Analyses were conducted on 4 L grab samples:

- AMBIENT BAY WATER: Discrete grab samples from 12 locations; eight collected in July (dry season), four collected in October, and two collected in November (beginning of wet season)
- STORMWATER: Two grab samples collected during each of two storm events from two different urban, industrial channels
- WASTEWATER: Discrete grab samples of effluent from three WWTPs

Samples were filtered to allow analysis of both particulate and dissolved phases. Some phosphate flame retardants are also used as plasticizers, so exposure to plastic was avoided.

Samples were analyzed for tri-ester phosphate flame retardants (Table 1) using liquid chromatography-electrospray ionization(+)-triple quadrupole mass spectrometry (LC-ESI(+)-QQQ-MS/MS) (Chen et al. 2012; Chu et al. 2011). Labeled internal standards (including d27-TBP, d15-TPhP, d12-TCEP, and 13C12-TBEP) were used. Limits of detection ranged from 0.1 to 0.3 ng/L.

Results revealed good quality assurance and control performance. Duplicate analysis revealed relative standard deviations less than 8% except for two samples (15% and 16%, respectively). Spiking tests revealed average recoveries of target analytes ranging from 82% to 99%. Internal standard recoveries ranged from 81% to 92%. Only trace levels of contamination (a total of <10 ng/L) were observed in laboratory and field blanks. Lab blank contamination was subtracted from final results.

RESULTS

Phosphate flame retardants were widely detected in San Francisco Bay

- TCPP was typically the most abundant contaminant, followed by TBEP and TPhP. TDCPP, TCEP, and TBP were also widely detected.
- Qualitative data from polar organic chemical integrative samplers (POCIS) deployed in the Bay in 2010 also suggested that TCPP was a relatively abundant contaminant; in contrast, there were few detections of TBEP and TPhP (Klosterhaus et al. 2013). Because POCIS are designed to survey polar compounds, they may not adequately characterize less polar phosphate flame retardants.
- Contaminants were more concentrated in southern parts of the Bay, where surface waters experience the least amount of mixing with non-effluent flow, particularly in the dry season, and have the highest hydraulic residence time compared to other segments. The average total concentration of phosphate flame retardants in the South and Lower South Bays was four times higher than in the rest of the Bay. Averages of all individual phosphates were also higher in southern parts of the Bay.
- San Francisco Bay has higher levels of contamination for most phosphate flame retardants relative to other estuarine or marine regions (Table 2).
- Previous monitoring has detected some of these contaminants in Bay sediment, bivalves, and aquatic bird eggs (Klosterhaus et al. 2013).

Phosphate flame retardants enter the Bay via stormwater and effluent

- TCPP was typically the most abundant contaminant in stormwater, followed by TBEP. TCEP, TDCPP, TPhP, and TBP were also widely detected.
- Bay stormwater contamination is generally similar to that reported in Frankfurt, Germany, with higher levels of TDCPP and lower levels of TBP (Table 2).
- TCPP was typically the most abundant contaminant in WWTP effluent, followed by TBEP. TCEP, TDCPP, TPhP, and TBP were also widely detected.
- Bay WWTP effluent contaminant levels were similar to or less than those reported in other regions (Table 2).

Phosphate flame retardants may pose potential risks to Bay wildlife

- In vitro and in vivo analyses indicate phosphate flame retardants can produce a wide range of endocrine disrupting effects (Table 1).
- Studies in fish show measurable endocrine-related impacts at exposure levels at least 100 times higher than found in San Francisco Bay (Liu et al. 2012, 2013a,b; Wang et al. 2013).
- The potential for impacts caused by exposure to mixtures of these and other endocrine disrupting contaminants must be explored to thoroughly assess risks to wildlife.
- 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).

CONCLUSIONS

- Phosphate flame retardants were present in all parts of San Francisco Bay, with higher levels in the southern region where effluent discharge has a greater influence.
- Detections in WWTP effluent and stormwater suggest these compounds migrate from consumer products and enter the aquatic environment via both pathways.
- The effects of exposure to mixtures of phosphate flame retardants and other endocrine disrupting contaminants have not been examined.
- TPhP concentrations in the Bay are approaching the marine PNEC (ECHA 2014).
- Recent changes to California's flammability standard for foam furniture (TB 117) may reduce use of phosphate flame retardants, potentially leading to lower inputs to the Bay.

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For more information on Emerging Contaminants in the Bay please visit www.sfei.org and download the RMP's 2013 Pulse of the Bay.

For additional information about the RMP please go to www.sfei.org/rmp.