ALTERNATIVE FLAME RETARDANTS IN SAN FRANCISCO BAY

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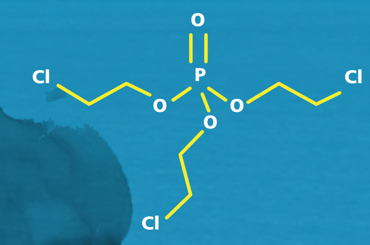
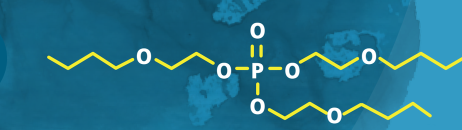
The state of California has implemented unique flammability standards for consumer products. In response to nationwide phase-outs of polybrominated diphenyl ether (PBDE) flame retardants, manufacturers began to substitute other flame retardant chemicals in their products in order to meet these standards. 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. Some exhibit aquatic toxicity or endocrine-disrupting properties in laboratory tests. In recent studies, the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has detected some of these alternative flame retardants in Bay water, sediment, and biota. Typically, they are found in lower concentrations than PBDEs. The levels observed have been 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 in some types of consumer goods, and therefore possibly reduce contamination in the Bay. Presented here are preliminary results from a recent survey of alternative flame retardants in Bay water, stormwater, and wastewater treatment plant (WWTP) effluent, including both dissolved and solid phase analyses.

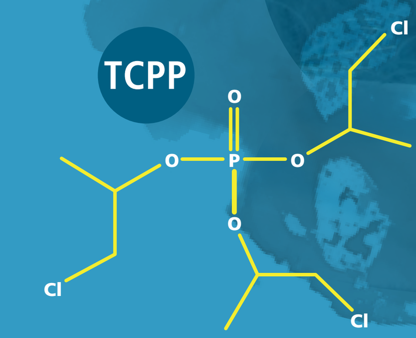
TCEP



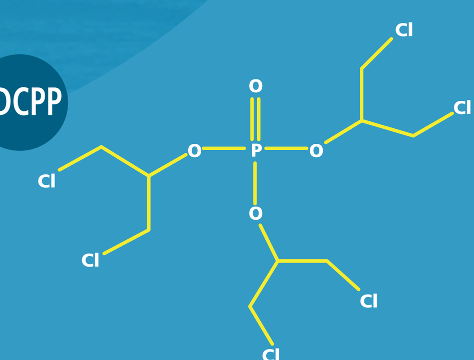
TBEP



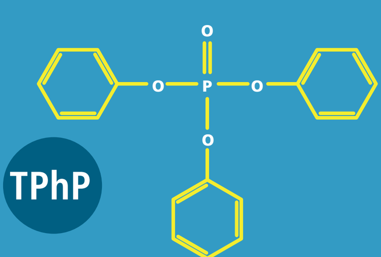
TCPP



TDCPP



TPhP



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 e t 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 - 350	620 - 1,500	130 - 200	47 - 130	40 - 220	ND - 1.7	710 - 2,100	ND - 5.0	ND - 3.1	ND - 9.6	ND - 2.6	this study
Sunnyvale, Calif.	2013 - 2014	21 - 340	55 - 2,700	15 - 76	46 - 100	13 - 150	ND - 56	72 - 1,900	ND - 28	4.5 - 46	ND - 1.8	ND - 1.2	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	ND	ND	ND	this study
SF Bay WWTP 2	2014	320	2,500	330	61	88	6.7	69	ND	ND	ND	ND	this study
SF Bay WWTP 3	2014	400	3,200	410	130	54	12	3,400	15	36	10	7	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	ND - 5,400			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		320 - 710			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 1 Phosphate Flame Retardants in Estuarine/Marine, Stormwater, and WWTP Effluent Samples (ng/L)

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
	Hydrophobic, halogenated
PBBA	Pentabromobenzyl acrylate
PBBZ	Pentabromobenzene
PBBB	Pentabromobenzyl bromide
PBT	Pentabromotoluene
PBEB	Pentabromoethylbenzene
HBBZ	Hexabromobenzene
TBOCT	Tetrabromo-o-chlorotoluene
BB101	Polybrominated biphenyl 101
HCDBCO	Hexachlorocyclopentadienyl-dibromocyclooctane
BTPBE	1,2-bis-(2,4,6-tribromophenoxy)ethane
EHTBB	2-ethylhexyl-2,3,4,5-tetrabromobenzoate
EHTBP	Bis (2-ethyl-1-hexyl)tetrabromophthalate
DBDPE	Decabromodiphenylethane
TBB	1,3,5-Tribromobenzene
HCCP	Hexachlorocyclo-pentadiene
DPMA	Dechlorane plus mono adduct
Cplus	Chlordene plus
DEC-601	Dechlorane-601
DEC-602	Dechlorane-602
DEC-603	Dechlorane-603
DEC-604	Dechlorane-604
DEC-604CB	Dechlorane-604CB
C10-DP	di-dechlorinated dechlorane plus
C11-DP	mono-dechlorinated dechlorane plus
Syn-DP	Syn-dechlorane plus
Anti-DP	Anti-dechlorane plus

List 1 Target Analytes

Figure 1 Phosphate flame retardants detected in suspended solids from samples of ambient Bay water (▲), stormwater (●), and WWTP effluent (■). Concentrations are reported in ng/g dry weight, and displayed on a log scale. Non-detects are not shown.

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 stormwater channels draining to the Bay
- WASTEWATER: Discrete grab samples of final 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 plastics was avoided.

Samples were analyzed for tri-ester phosphate flame retardants using liquid chromatography-electrospray ionization(+)-triple quadrupole mass spectrometry (LC-ESI(+)-QQQ-MS/MS) (Chen et al. 2012a; Chu et al. 2011). Labeled internal standards (including d27-TBP, d15-TPhP, d12-TCEP, d15-TDCPP, and 13C12-TBEP) were used. Limits of detection ranged from 0.1 to 0.3 ng/L for dissolved phase analysis and 0.2 to 0.9 ng/g dw for solid phase analysis.

Samples were analyzed for hydrophobic, halogenated flame retardants using gas chromatography coupled with electron-capture negative ion mass spectrometry (GC-ECNI-MS) (Chen et al. 2012b,c). Labeled and unlabeled internal standards (including F-BDE69, 4-PC-BDE208, BDE156, PCB204, and d18-α-HBCD) were used. Limits of detection ranged from 0.2 to 1 ng/L for dissolved phase analysis and 0.2 to 1.2 ng/g dw for solid phase analysis.

Results revealed good quality assurance and control performance. Duplicate analysis on dissolved phase samples typically revealed relative standard deviations less than 8%. Spiking tests revealed average recoveries of target analytes ranging from 82% to 99% for phosphates and 70% to 90% for hydrophobic, halogenated flame retardants. Internal standard recoveries ranged from 81% to 92% for phosphate analysis and from 69% to 93% for halogenated flame retardant analysis. Only trace levels of contamination (a total of <10 ng/L or <11 ng/g dw for phosphates and <0.3 ng/L or <0.5 ng/g dw for halogenated flame retardants) were observed in laboratory and field blanks. Mean lab blank contamination was subtracted from final results. Sample results were censored if the signal found in the blank was one-third or more of a sample result prior to blank correction.

RESULTS

Phosphate flame retardants were widely detected in San Francisco Bay

- TCPP was typically the most abundant phosphate flame retardant in Bay water samples, followed by TBEP and TPhP (Table 1).
- 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). Previous monitoring has also detected some phosphates in Bay sediment, bivalves, and aquatic bird eggs (Klosterhaus et al. 2013).
- Phosphates 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. Averages of all individual phosphates were also higher in southern parts of the Bay.
- Solid phase concentrations of phosphate flame retardants varied significantly, with some of the highest measurements for TBEP and TPhP (Figure 1).
- San Francisco Bay has higher levels of contamination for most phosphate flame retardants relative to other estuarine or marine regions (Table 1).
- Apart from PBDEs, halogenated, hydrophobic flame retardants were not detected in ambient Bay dissolved phase samples, and rarely detected in solid phase samples.

Flame retardants enter the Bay via stormwater and effluent

- TCPP was typically the most abundant phosphate in both stormwater and WWTP effluent, followed by TBEP (Table 1).
- Stormwater and effluent contamination was generally similar to that reported in other studies (Table 1).
- Apart from PBDEs, halogenated, non-phosphate flame retardants were not detected in dissolved phase stormwater. EHTBB and EHTBP were rarely detected in dissolved phase effluent.
- Solid phase concentrations of phosphates varied significantly, with some of the highest measurements for TBEP (Figure 1). Samples from WWTPs 1 and 2, with advanced secondary treatment, did not contain sufficient solids for analysis.
- Stormwater solids contained detectable levels of hydrophobic, halogenated flame retardants EHTBB, TBOCT, BTPBE, EHTBP, Anti-DP, and Syn-DP. Some samples also contained PBBZ, HBBZ, HCDBCO, DPMA, Cplus, Dec-603, Dec-604CB, and C11-DP.
- WWTP 3 solids contained detectable levels of EHTBB, TBOCT, BTPBE, EHTBP, Anti-DP, and Syn-DP. Levels were generally lower than found in stormwater.

Flame retardants may pose potential risks to Bay 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).
- 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.

CONCLUSIONS

- Phosphate flame retardants were present in all parts of San Francisco Bay, with higher levels in southern regions where effluent discharge has greater influence.
- Detections in WWTP effluent and stormwater suggest these compounds migrate from consumer products and enter the aquatic environment via both pathways.
- TPhP concentrations in the Bay are approaching the marine PNEC (ECHA 2014).
- Frequent detections of both phosphate and halogenated flame retardants in suspended solids indicate sediment is likely to be an important matrix for further study.
- Recent changes to California's flammability standard for foam furniture (TB 117) may reduce use of flame retardants, potentially leading to lower inputs to the Bay.

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ACKNOWLEDGMENTS

We thank local wastewater facilities for providing effluent samples. Poster design by Linda Wanczyk and Joanne Cabling

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