ALTERNATIVE FLAME RETARDANTS IN SAN FRANCISCO BAY

AUTHORS

REBECCA SUTTON[1]
DA CHEN[2]
MEG SEDLAK[1]

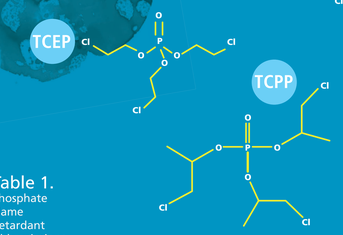
1) San Francisco Estuary Institute, Richmond, CA 94804

2) Southern Illinois University, Carbondale, IL 62901

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. 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.

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
TPrP	Tripropyl phosphate
TBEP	Tris (2-butoxyethyl) phosphate
TEHP	Tris (2-ethylhexyl) phosphate
EHDPP	2-Ethylhexyl-diphenyl phosphate
TDBPP	Tris (2,3-dibromopropyl) phosphate

Table 1.
Phosphate Flame Retardant Abbreviations



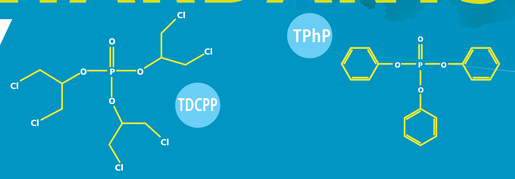
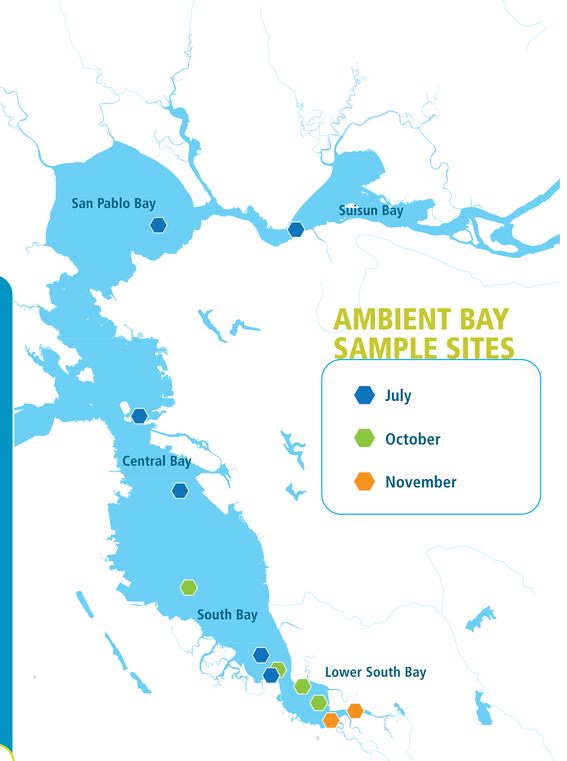


Table 2.
Phosphate Flame Retardants in Estuarine/Marine, Stormwater, and WWTP Effluent Samples (ng/L)

Location	Year	TCEP	TCPP	TDCPP	TPhP	TBP	TCrP	TPrP	TBEP	TEHP	EHDPP	TDBPP	Reference
Estuarine / Marine													
San Francisco Bay	2013	6.2 - 300	32 - 2,000	5.9 - 450	15 - 300	4.5 - 39	ND - 26	ND - 0.2	11 - 840	ND - 28	ND - 20	ND	this study
Southern California Bight	2006 - 2007	ND	NQ - 56										Vidal-Dorsch et al. 2012
River Elbe Estuary	2010	5 - 20	40 - 200	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	ND - 1.2	710 - 2,400	ND - 1.1	ND - 1.4	ND	this study
Sunnyvale, Calif.	2013 - 2014	21 - 340	55 - 2,700	15 - 77	39 - 100	13 - 150	ND - 55	0.1 - 2.0	73 - 1,900	ND - 28	4.5 - 46	ND - 42	this study
Frankfurt, Germany*	2008 - 2009	31 - 275	16 - 5,741	ND - 73		4 - 417			ND - 1,416				Regnery and Puhlmann 2010
WWTP Effluent													
SF Bay WWTP 1	2014	180	2,700	180	27	13	1.7	ND	29	ND	ND	ND	this study
SF Bay WWTP 2	2014	320	2,500	330	61	88	6.7	ND	69	ND	ND	ND	this study
SF Bay WWTP 3	2014	190	1,900	120	85	22	14	ND	2,500	17	27	3.5	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 960	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			Martinez-Carballo et al. 2007

* Samples taken from stormwater holding tank



METHODS

Analyses were conducted on 4 L grab samples:

- AMBIENT BAY WATER: Single 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 samples collected during each of two storm events from two different urban, industrial channels
- WASTEWATER: Single 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 sample exposure to plastic was avoided.

All samples were analyzed for tri-ester organophosphate flame retardants using a highly sensitive liquid chromatography-electrospray ionization(+)-triple quadrupole mass spectrometry (LC-ESI(+)-QQQ-MS/MS) based analysis method (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 for each compound ranged from 0.1 to 0.3 ng/L for all but TDBPP (0.8 ng/L). A single replicate of each matrix was collected at a representative sample site; further replicates were analyzed by subdividing samples in the laboratory.

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 subsequently 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. TCrP, TPrP, TEHP, EHDPP, and TDBPP were detected rarely or not at all.
- 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.
- Comparison to limited data available for other regions indicates 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. TCrP, TPrP, TEHP, EHDPP, and TDBPP were detected at lower levels.
- TDCPP contamination was nearly four times greater at the Richmond site, while TCrP, EHDPP, and TDBPP contamination was more common at the Sunnyvale site.
- 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. TCrP was detected at lower levels, while EHDPP, TEHP, and TDBPP were detected only at WWTP 3. TPrP was not detected.
- Bay WWTP effluent contaminant levels were similar to or less than those reported in other regions (Table 2).
- These snapshots suggest effluent may be an especially important pathway for TCPP and TDCPP, while stormwater may be an especially important pathway for TBP, TCrP, EHDPP, and TDBPP. Both pathways also appear to have the potential to deliver significant TCEP, TBEP, and TPhP to the Bay.

Phosphate flame retardants may pose potential risks to Bay wildlife

- Some South Bay samples exhibited concentrations of TPhP approaching the marine aquatic toxicity threshold of 370 ng/L (predicted no effect concentration [PNEC]; ECHA 2014).
- Concentrations of other phosphate flame retardants were generally an order of magnitude or more below concentrations expected to elicit toxic effects in aquatic organisms (ECHA 2014). However, relatively few toxicity studies are available for many of these compounds. Of note, TDCPP and TCEP have been identified by the state of California as carcinogens. Furthermore, the potential for impacts caused by exposure to environmentally relevant mixtures of flame retardants must be explored to thoroughly assess the risks to wildlife.

CONCLUSIONS

- San Francisco Bay is widely contaminated with phosphate flame retardants, with higher levels measured in the southern region where effluent discharge has a greater influence.
- Detection of phosphate flame retardants in WWTP effluent and stormwater suggests these compounds migrate from consumer products and enter the aquatic environment via both pathways.
- San Francisco Bay monitoring data are a critical addition to the limited number of measurements available for these compounds, especially in estuarine and stormwater matrices.
- TPhP concentrations in the Bay are approaching the marine PNEC; other phosphate flame retardants do not exceed established PNECs (ECHA 2014).
- Lack of ecotoxicity information is a concern, particularly because the effects of long-term exposure to low levels of these contaminants are largely unknown. In addition, the effects of exposure to multiple phosphate flame retardants have not been examined.
- Recent changes to California's flammability standard for foam furniture (TB 117) may reduce the use of some phosphate flame retardants, potentially leading to lower contaminant inputs to the Bay.

SFEI AQUATIC SCIENCE CENTER
SAN FRANCISCO ESTUARY INSTITUTE & THE AQUATIC SCIENCE CENTER
4911 Central Ave, Richmond, CA 94804 p: 510-746-7334 f: 510-746-7300

RMP
REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN THE SAN FRANCISCO ESTUARY

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.

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. Journal of Chromatography 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. Journal of Chromatography A 1218:8083-8088.

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).

Green N, Schlabach M, Bakke T, Brevik EM, Dye C, Herzke D, Huber S, Plosz B, Remberger M, Schlyter H, Uggerud HT, Vogelsang C. 2008. Screening of selected metals and new organic contaminants 2007. NIVA Report 5569-2008, SPFO-report 1014/2008. TA-2367/2008.

Jackson J, Sutton R. 2008. Sources of endocrine-disrupting chemicals in urban wastewater, Oakland, CA. Science of the Total Environment 405:153-160.

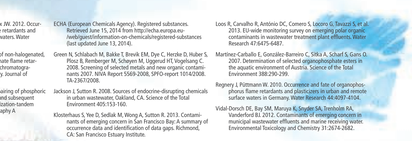
Klosterhaus S, Yee D, Sedlak M, Wong A, Sutton R. 2013. Contaminants of emerging concern in San Francisco Bay: A summary of occurrence data and identification of data gaps. Richmond, CA: San Francisco Estuary Institute.

Loos R, Carvalho R, António DC, Comero S, Locoro G, Tavazzi S, et al. 2013. EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. Water Research 47:6475-6487.

Martínez-Carballo E, González-Barreiro C, Sitka A, Scharf S, Gans O. 2007. Determination of selected organophosphate esters in the aquatic environment of Austria. Science of the Total Environment 388:290-299.

Regnery J, Püttmann W. 2010. Occurrence and fate of organophosphorus flame retardants and plasticizers in urban and remote surface waters in Germany. Water Research 44:4097-4104.

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.



Acknowledgments

We thank local wastewater facilities for providing effluent samples. Poster design by Linda Wanczyk, map by Pete Kauhanen.

Contact Information

Rebecca Sutton, Ph.D. (RebeccaS@sfei.org)