



Characterization of brominated, chlorinated, and phosphate flame retardants in San Francisco Bay, an urban estuary

Rebecca Sutton^a, Da Chen^{b,*}, Jennifer Sun^{a,1}, Denise J. Greig^c, Yan Wu^{d,2}

^a San Francisco Estuary Institute, 4911 Central Avenue, Richmond, CA 94804, USA

^b School of Environment and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou, Guangdong 510632, China

^c California Academy of Sciences, 55 Music Concourse Drive, San Francisco, CA 94118, USA

^d Cooperative Wildlife Research Laboratory and Department of Zoology, Southern Illinois University, Carbondale, IL 62901, USA



HIGHLIGHTS

- Wide range of flame retardants analyzed in urban estuary water, sediment, tissue.
- PBDEs remained dominant among brominated flame retardant contaminants tested.
- Dechlorane Plus and related compounds were detected at low levels or not at all.
- Phosphate compounds were dominant flame retardant contaminants in water, sediment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 25 July 2018

Received in revised form 7 October 2018

Accepted 8 October 2018

Available online 11 October 2018

Editor: Patricia Holden

Keywords:

Contaminants of emerging concern

Water

Sediment

Wastewater

Stormwater

Tissue

ABSTRACT

Flame retardant chemical additives are incorporated into consumer goods to meet flammability standards, and many have been detected in environmental matrices. A uniquely wide-ranging characterization of flame retardants was conducted, including polybrominated diphenyl ethers (PBDEs) and 52 additional brominated, chlorinated, or phosphate analytes, in water, sediment, bivalves, and harbor seal blubber of San Francisco Bay, a highly urbanized estuary once considered a hot spot for PBDE contamination. Among brominated flame retardants, PBDEs remained the dominant contaminants in all matrices, though declines have been observed over the last decade following their phase-out. Hexabromocyclododecane (HBCD) and other hydrophobic, brominated flame retardants were commonly detected at lower levels than PBDEs in sediment and tissue matrices. Dechlorane Plus (DP) and related chlorinated compounds were also detected at lower levels or not at all across all matrices. In contrast, phosphate flame retardants were widely detected in Bay water samples, with highest median concentrations in the order TCPP > TPhP > TBEP > TDCPP > TCEP. Concentrations in Bay water were often higher than in other estuarine and marine environments. Phosphate flame retardants were also widely detected in sediment, in the order TEHP > TCrP > TPhP > TDCPP > TBEP. Several were present in bivalves, with levels of TDCPP comparable to PBDEs. Only four phosphate flame retardants were detected in harbor seal blubber: TCPP, TDCPP, TCEP, and TPhP. Periodic, multi-matrix screening is recommended to track contaminant trends impacted by changes to flammability standards and manufacturing practices, with a particular focus on contaminants like TDCPP and TPhP that were found at levels comparable to thresholds for aquatic toxicity.

© 2018 Elsevier B.V. All rights reserved.

* Corresponding author.

E-mail address: dachen@jnu.edu.cn (D. Chen).

¹ Present address: Harvard John A. Paulson School of Engineering & Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA.

² Present address: School of Public and Environmental Affairs, Indiana University, Bloomington, IN 47405, USA.

1. Introduction

Flame retardant chemical additives have been incorporated into a broad array of consumer products (Chen et al., 2009; Stapleton et al., 2009, 2011, 2012; van Bergen and Stone, 2014; Cooper et al., 2016; Petreas et al., 2016), largely in response to regulatory or voluntary industry flammability standards. Examples of standards include Technical Bulletin 117 (TB 117), a unique regulatory flammability standard promulgated in 1975 that applied to upholstered furniture and infant products sold in California (BHFTI, 2000), and Underwriters' Laboratories 94 (UL 94), adopted by the electronics industry as a flammability standard applicable to plastic materials for parts in devices and appliances (USEPA, 2014). Widespread use of PBDEs in response to standards like these contributed to unusually high PBDE exposure in San Francisco residents (She et al., 2002), as well as contamination of San Francisco Bay ("the Bay") and its wildlife (She et al., 2002, 2008).

Subsequent state bans and nationwide phase-outs of PBDEs have resulted in declining levels of contamination in the Bay (Sutton et al., 2015), but product testing initially indicated that manufacturers shifted from PBDEs to alternative flame retardant additives (Stapleton et al., 2012). While revisions to TB 117 now eliminate the need for these additives in regulated products (BEARHFTI, 2013), studies indicate reduced but continuing use of a variety of flame retardants in upholstered furniture and infant care items (Cooper et al., 2016; Petreas et al., 2016). In addition, regulatory or voluntary flammability standards remain in place for electronics, building and construction materials, and other products (Babrauskas et al., 2012; USEPA, 2014).

For the diverse array of bromine-, chlorine-, and phosphate-containing compounds that have replaced PBDEs, considerable data gaps concerning production and use, environmental occurrence, and toxicity remain (Covaci et al., 2011; van der Veen and de Boer, 2012). Many of these chemicals have been in use for decades, while others are relatively new (de Wit, 2002; Covaci et al., 2011; van der Veen and de Boer, 2012; Cooper et al., 2016). Some (e.g., TCPP and TPhP; acronyms defined in Table S1) are high production volume chemicals (van der Veen and de Boer, 2012). Some (e.g., HBCD and DP) are known to bioaccumulate (Covaci et al., 2011; Wang et al., 2016a), and some (e.g., TDCPP and TPhP) exhibit aquatic toxicity or endocrine-disrupting (e.g., estrogenic and reproductive) properties in laboratory tests (Covaci et al., 2011; Liu et al., 2012, 2013; van der Veen and de Boer, 2012; ECHA, 2018a, 2018b). Some (e.g., PBDEs, HBCD) have been the subject of phase-outs in many countries (Stockholm Convention, 2017), though production and use has not ceased worldwide.

Prompted by the observations of rapid changes in chemical use via product testing, as well as the shifting regulatory landscape, a thorough characterization of current Bay contamination by flame retardants was undertaken. PBDE congeners as well as dozens of brominated, chlorinated, and phosphate-based flame retardants were examined in water, sediment, and tissue; this broad array of analytical targets was intended to "cast a wide net" to detect the presence of alternative flame retardants that may be in greater use in recent years. Observed flame retardant concentrations were compared to: a) concentrations of PBDEs, given concerns relating to historical accumulation in the Bay; b) concentrations of alternative flame retardants found in a previous study of the Bay (Klosterhaus et al., 2012), as well as in other estuarine locations in recent years; and c) available toxicity thresholds.

2. Materials and methods

2.1. Sample collection

Ambient Bay water and sediment were collected as part of routine chemical contaminant monitoring conducted by the Regional Monitoring Program for Water Quality in the San Francisco Bay (RMP; <http://www.sfei.org/rmp>). Sites are shown in Figs. 1 and S1. Surface water grab samples (4 L) were collected directly into amber glass containers

from a total of 12 sites in 2013: six in July (dry season), four in October, and two in November (beginning of wet season). Water samples were stored at 4 °C up to 14 days until extraction, and were filtered with a 0.45 µm Whatman filter to allow measurement of total suspended solids (TSS) and analysis of particulate and dissolved phases. Surface sediment samples were collected from 10 sites in July of 2014. Sediment (0 to 5 cm depth) was collected from two or more grabs using a Young-modified Van Veen sampler with a surface area of 0.1 m² and was composited by mixing with a stainless steel spoon. Sediment samples were kept at -20 °C prior to chemical analyses.

Two stormwater grab samples (4 L each) were collected from two urban, industrial channels during the rising limb of each of two storm events in the winter of 2013–2014 ($n = 8$). Single grab samples of final effluent (4 L) were collected from three urban wastewater treatment plants in the spring of 2014. Additional details on sampling and analytical measurements for stormwater and wastewater samples can be found in Supplementary Information.

Transplanted bivalves (*Mytilus californianus*) were deployed at six stations in the Bay for 90 days during the summer. Bivalves were retrieved whole, wrapped in foil, and frozen at -20 °C prior to compositing using clean techniques. Generally, 30–40 bivalves were retrieved from each site; each sample was divided into two subsamples and composited and analyzed separately. Bivalves from Bodega Bay, a reference site with minimal urban impacts located outside of San Francisco Bay (and source of the transplanted bivalves), was also collected and analyzed.

Blubber was collected in June of 2014 from seven seals captured at a major haul-out site in the South Bay, Corkscrew Slough (37.5242°N, 122.2171°W). Samples of blubber were obtained from each animal using a sterile 8 mm dermal biopsy punch (Millex, Inc., York, PA) after shaving the area, administering lidocaine, and disinfecting with alcohol. The skin was cut from the blubber with a solvent rinsed stainless steel scalpel blade, and the blubber placed into a solvent rinsed glass jar and then into a cooler with ice packs. Blubber was shipped overnight on ice, then stored frozen at -80 °C. The sex, age class, length and mass of these seals are provided in Supplementary Information, along with the lipid content of the samples (Table S2).

For all samples, exposure to plastic, a potential source of phosphate compounds, was avoided during collection and processing.

2.2. Sample treatments

Detailed information on standards and reagents is provided in Supplementary Information. Filtered water samples (approximately 1000 mL) were adjusted to approximately pH 3, spiked with surrogate standards, and then treated via liquid-liquid extraction with dichloromethane (DCM) three times (50, 25, and 25 mL each). The water-DCM mixture was hand shaken for approximately 15 min. The extracts were combined, concentrated, and divided into two halves. One half was concentrated and solvent exchanged to a final volume of approximately 200 µL and spiked with internal standard (FBDE-154), and analyzed on a gas chromatography – mass spectrometer (GC-MS) for the determination of hydrophobic, halogenated flame retardants. The other half was cleaned through a solid phase extraction (SPE) cartridge packed with 1 g of ammonium silica (Biotage, Charlotte, NC), which was pre-cleaned in sequence with 15 mL each of methanol, DCM, and hexane (HEX). After sample loading, the SPE cartridge was cleaned with 2 mL of a mixture of HEX:DCM (20:80, v/v) and the target phosphate flame retardants were then eluted out with 4 mL of 20:80 (v/v) HEX:DCM and 8 mL of DCM. The final extract (approximately 200 µL) was spiked with internal standard (coumaphos-d₁₀) for the determination of phosphate analytes on a liquid chromatography – tandem mass spectrometer (LC-MS/MS).

Dried solid phase portions of the water samples (on the filter), sediment (sieved through a 100 µm stainless cloth sieve), or bivalve tissues and wet harbor seal blubber were spiked with surrogate standards and

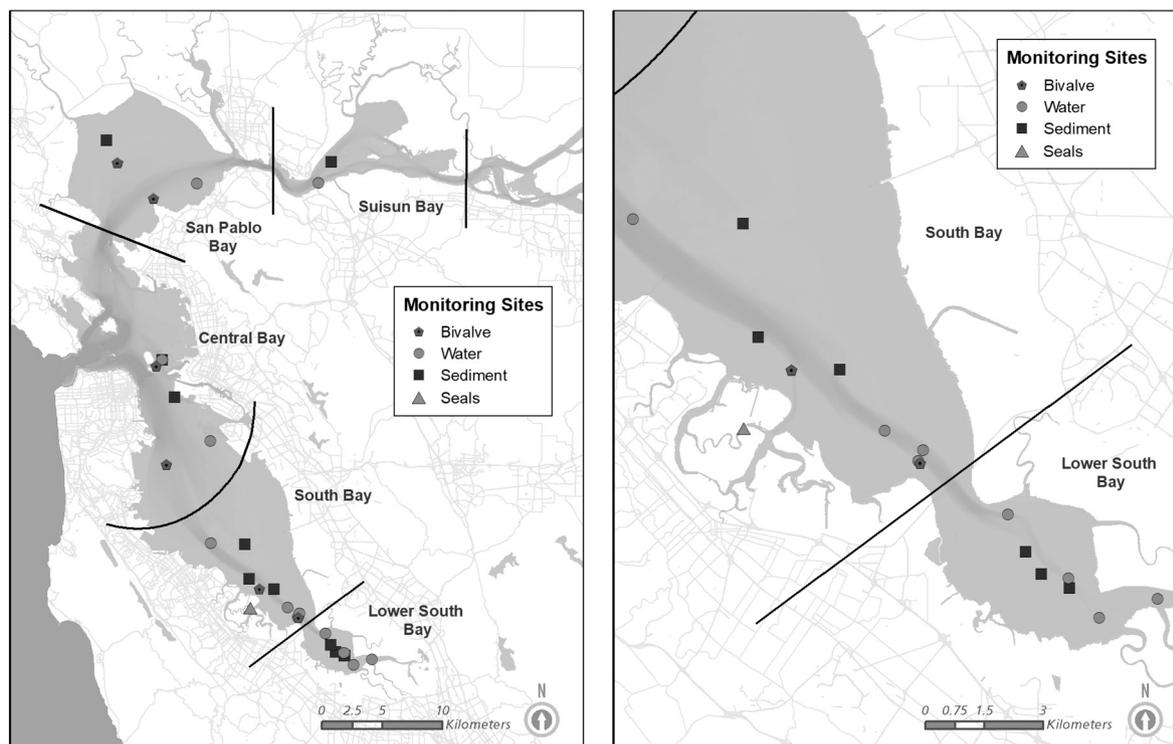


Fig. 1. San Francisco Bay sample sites (left), with a closer view of the South and Lower South Bay sites (right).

subjected to accelerated solvent extraction (Dionex ASE 350, Sunnyvale, CA, USA), employing two 5-min extraction cycles with DCM at 100 °C and 1500 psi. The sediment extract was divided into two halves with equal volumes. One half was treated with pre-activated copper powder to remove sulfur, and cleaned by a Shimadzu Prominence Semi-Prep HPLC (Shimadzu America Inc., Columbia, MD) equipped with a Phenogel size exclusion chromatography column (350 × 21.1 mm, 5 μ, 100 Å, Phenomenex, Torrance, CA). The mobile solvent was 100% DCM and the flow rate was set at 4 mL/min. Target analytes were collected in the fraction eluted from 16 to 45 min. The resulting extract was further cleaned on a 2-g Isolute® silica SPE cartridge which was pre-conditioned with 10 mL HEX. After the sample was loaded, the first fraction was eluted with 3 mL HEX and discarded. The second fraction was eluted with 11 mL of a mixture of HEX:DCM mixture (6:4, v/v). The final extract was concentrated and spiked with internal standard prior to the instrumental analysis of hydrophobic flame retardants. The other half of the sediment extract was cleaned through an ammonium silica cartridge, following the same SPE method used for the analysis of phosphate flame retardants in aqueous water.

The extract of biological tissues following ASE was subjected to moisture removal and gravimetric determination of lipid content by using 10% of the extract. The remaining extract was divided into two halves, one for the determination of halogenated flame retardants and the other for the determination of phosphate flame retardants, using the same cleanup methods employed for sediment analysis. The extract of solid phases of water was also divided into two halves for the determination of halogenated or phosphate flame retardants, respectively, following the same cleanup methods mentioned above.

2.3. Instrumental analysis

The instrumental determination of hydrophobic, brominated and DP-related flame retardants, excluding HBCDs, was conducted on an Agilent 7890B GC coupled to an Agilent 5977A MS (Agilent Tech., Palo Alto, CA). The GC was equipped with a 15 m DB-5HT column (0.25 mm i.d., 0.1 μm film thickness, J&W Scientific, Folsom, CA).

Identification and quantification of individual substances was achieved via selected ion monitoring (SIM) of characteristic ions in electron capture negative ionization (ECNI) mode (Table S3). After GC-MS analysis, the same extract was solvent exchanged to methanol and determined for HBCDs on an Agilent 1260 HPLC coupled to a 3200 Q Trap triple quadrupole/linear ion trap MS (AB Sciex; Toronto, Canada). The HPLC system was equipped with a Waters Xterra® phenyl column (2.1 mm × 100 mm, 3.5 μm particle size). The MS was equipped with a TurboIonSpray® electrospray ionization (ESI) probe operated in the multiple reaction monitoring (MRM) mode for quantitative measurement of HBCD diastereomers (Table S3). Phosphate flame retardants were determined on the same LC-MS/MS system equipped with a Kinetex EVO C18 column (2.1 mm × 100 mm, 5 μm particle size; Phenomenex, Torrance, CA). The SIM ions or MRM ion pairs of target analytes, as well as the detailed GC or LC programs, are summarized in Table S3.

2.4. Quality control

Five spiking tests per matrix and extraction revealed average absolute recoveries of target analytes ranging from 66% to 105% for phosphate flame retardants and 63% to 96% for hydrophobic, halogenated flame retardants prior to adjustment with the recoveries of respective surrogate standards (Table S1), which ranged from 81% to 92% for phosphate flame retardant analysis and from 69% to 93% for halogenated flame retardant analysis. PBDE measurements for the National Institute of Standards and Technology (NIST) reference sediment (SRM 1944) and reference fish tissue (SRM 1947) showed average agreement ranging from 83% to 97% relative to reference levels for up to eight congeners (Table S4). The instrumental detection limit (IDL) was defined as three times the standard deviation of the noise from the instrumental determination. The method limit of quantification (MLOQ) of an analyte was assessed by multiplying a Student's t-value designated for a 99% confidence level with standard deviations in replicate analyses ($n = 8$) of each matrix. The MLOQ for each analyte in each matrix is summarized in Table S3.

Field and lab replicate analysis on dissolved phase water samples typically revealed standard deviations < 15% of measured concentrations. Exceptions with analytical values well above MLOQs include TCPP, TDCPP, TPhP, TnBP, TBEP, EHDPP, and TCrP in the dissolved phase of water; these values are considered semi-quantitative. Limited homogenization of filtered water prior to extraction may explain the higher variability in replicate measures of these analytes in dissolved phase. Replicates in other matrices did not display this level of variability.

2.5. Statistical analysis

Individual flame retardant concentrations in each matrix were analyzed for correlations using Spearman's rank correlation tests, chosen due to the non-normal distribution of results, small sample size, and the test's limited sensitivity to outliers. The correlation analyses were conducted using R 2.10.1 (R Development Core Team, 2009) on compounds that were detected in at least 50% of the samples. In addition, cluster analysis (OriginPro 2017, OriginLab Corporation) was performed to assess correlations among total concentrations of flame retardant classes (PBDEs, HBCDs, additional brominated flame retardants, DP-related substances, and phosphate flame retardants) present in water and sediment. Sample sizes for bivalves and harbor seals were deemed too low for robust cluster analysis. Statistical significance was determined using a p -value < 0.05.

3. Results and discussion

3.1. Brominated flame retardants

3.1.1. Polybrominated diphenyl ethers

As hydrophobic compounds, PBDEs generally partition to sediment. Summed PBDE concentrations in Bay sediment were <5 ng/g dry weight (dw), and were dominated by BDE-209, the primary component of the commercial mixture DecaBDE (Table 1). BDE-209 is the dominant congener in sediment collected from a variety of locations worldwide, including Asia, Europe, and the Great Lakes (Moon et al., 2007). Sediment levels of BDE-47 (median 0.31 ng/g dw; Table 1), a major component of commercial mixture PentaBDE, were consistent with a recently documented decline in contamination in San Francisco Bay over the last decade (Sutton et al., 2015), likely due to a California ban and U.S. industry phase-out of PentaBDE.

Deployed bivalves provide an integrated measure of contaminant exposure from food, water, and sediment. Summed PBDE concentrations in Bay bivalves were <30 ng/g lipid weight (lw) and were dominated by BDE-47 (Table 1); no BDE-209 was detected. Bivalves from the reference site also contained a low level of BDE-47 (0.26 ng/g lw; Table S8). BDE-47 has declined significantly in deployed Bay bivalves over the last decade (Sutton et al., 2015), and levels reported here are consistent with those reported recently (e.g., in 2012; Sutton et al., 2015).

Harbor seal blubber is an ideal matrix for study of hydrophobic contaminants that accumulate in higher trophic organisms from food sources, which for Bay harbor seals includes, at minimum, 22 species of fish and one species of crustacean (Gibble and Harvey, 2015). Harbor seals residing in San Francisco Bay generally exhibit relatively high site fidelity (Nickel, 2003), such that contaminant exposure is likely to be derived from sources within the Bay. Summed PBDE concentrations in Bay harbor seal blubber collected for this study ranged between 270 and 1100 ng/g lw (median 390 ng/g lw; Table 1); BDE-47 was the dominant congener. Concentrations of PBDEs in blubber were an order of magnitude or more higher than any other flame retardant class analyzed. With the exception of BDE-209, PBDEs have been shown to bioaccumulate and biomagnify within marine and estuarine food webs (Shaw et al., 2009; Brandsma et al., 2015); higher levels of PBDEs in higher trophic organisms like Bay harbor seal blubber, relative

to lower trophic organisms such as bivalves, are consistent with this behavior.

Summed PBDE levels in these 2014 blubber samples were generally lower than observed in three previous studies of Bay harbor seal blubber, including samples of five deceased adult harbor seals collected in 2007 and 2008 (530–5075, median 770 ng/g lw; Klosterhaus et al., 2012), 35 recently weaned harbor seal pups captured in 2007 and 2008 (200–10,000, geometric mean 1100 ng/g lw; Greig et al., 2011), and three deceased adult harbor seals collected in 1997 and 1998 (1944, 2985, 8325 ng/g lw; She et al., 2002). Measurements are suggestive of declining levels of PBDEs in Bay harbor seals. Temporal trend studies indicate recent declines in PBDEs in other marine mammal populations (Law et al., 2012; Zhu et al., 2014).

BDE-47 was detected at low levels in ambient Bay water, and BDE-49, -99, and -100 were detected intermittently (Tables S5–S6). The amount of water sampled at each site, 4 L, was not sufficient for frequent detection of hydrophobic contaminants (Sections 3.1–3.2), and was better suited for detection of highly soluble contaminants (Section 3.3).

3.1.2. Hexabromocyclododecanes

Commercial mixtures of HBCD, consisting primarily of diastereoisomer γ -HBCD with smaller amounts of α -HBCD and β -HBCD, have been widely used as flame retardants in polystyrene foam building insulation, upholstery textiles, and to a smaller degree in electronic housings (Covaci et al., 2006). Two of three diastereoisomers, α - and γ -HBCD, were commonly detected in Bay sediment (Table 1). Summed concentrations (non-detect [nd] to 0.33 ng/g dw; median 0.12 ng/g dw) were significantly lower than PBDEs. The isomer profile was dominated by γ -HBCD (67–80%), followed by α -HBCD (17–23%), similar to that found in commercial mixtures, as well as in sediment from other locations (Covaci et al., 2006). Levels were generally lower than those in ten Bay sediment samples (0.1–1.7 ng/g dw; median 0.3 ng/g dw) collected in 2007, as well as in sediment from the Great Lakes (0.04–3.1 ng/g dw; Yang et al., 2012), and from estuaries in Australia (1.8–5.3 ng/g dw; Drage et al., 2015) and China (0.03–634 ng/g dw; Feng et al., 2012; Zhang et al., 2013). In contrast, Bay levels were comparable to or higher than found in coastal sediments near the Yangtze River Delta (nd to 0.16 ng/g dw; Zhu et al., 2014).

α -HBCD and γ -HBCD were frequently detected in deployed bivalve and harbor seal blubber samples at levels significantly lower than PBDEs (Table 1). The tissue isomer profiles showed enrichment of α -HBCD (bivalve α -HBCD 60–100%; harbor seal blubber α -HBCD 67–86%), a widely reported observation (Covaci et al., 2006; Isobe et al., 2012; Klosterhaus et al., 2012; Munsch et al., 2015; Ruan et al., 2018) that may be caused by factors including bioisomerization of γ - and β -HBCD to α -HBCD, faster metabolism of γ - and β -HBCD, and the higher water solubility of α -HBCD (Covaci et al., 2006).

Bay bivalve HBCD levels were similar to or lower than those observed in recent studies of estuarine or coastal bivalves. Analysis of 19 resident mussel samples collected along the California coast in 2009–2010, including three from San Francisco Bay, revealed intermittent detection of HBCD (α -HBCD < 0.1–1.5 ng/g dw; β -HBCD < 0.1–0.4 ng/g dw; γ -HBCD < 0.1–2.5 ng/g dw; Dodder et al., 2014) at levels comparable to or higher than observed in this study (α -HBCD < 0.14–2.2 ng/g dw; β -HBCD < 0.14–0.25 ng/g dw; γ -HBCD < 0.14–0.71 ng/g dw; Table S8). Resident bivalves may have higher levels of contamination relative to deployed bivalves given their longer exposure to contaminants. Bay mussels also showed sums of HBCDs (nd to 3.1 ng/g lw; Table S8) on the lower end of the range reported for resident mussels collected along the coasts of developing countries in Asia (<0.01–140 ng/g lw; Isobe et al., 2012); higher concentrations were reported in samples from Japan (10–1400 ng/g lw; Isobe et al., 2012) and Korea (6.0–500 ng/g lw; Ramu et al., 2007). Levels of α -HBCD in shellfish from the coast of France (0.02–0.3 ng/g wet weight [ww]; Munsch et al., 2015) were comparable to those in deployed Bay bivalves (nd to 0.23 ng/g ww; see Table S8 for moisture content).

Table 1
Brominated flame retardants in San Francisco Bay samples. Medians < MLOQ are labeled nd (non-detect).

Brominated flame retardants	Sediment (n = 10) ng/g dw			Bivalves (n = 6) ng/g lw			Harbor Seal Blubber (n = 7) ng/g lw		
	% Detect	Range	Median	% Detect	Range	Median	% Detect	Range	Median
BDE-28	70	<0.02–0.18	0.02	83	<0.14–0.69	0.18	100	0.82–2.3	1.5
BDE-47	100	0.06–0.62	0.31	100	3.5–15	4.5	100	120–850	260
BDE-49	60	<0.02–0.07	0.03	100	0.33–1.6	0.51	100	11–18	15
BDE-66	0	<0.02	–	0	<0.14	–	0	<0.60	–
BDE-85	0	<0.02	–	0	<0.14	–	0	<0.60	–
BDE-99	90	<0.02–0.27	0.12	100	0.97–4.4	1.3	100	36–69	50
BDE-100	90	<0.02–0.29	0.08	100	2.0–5.9	2.3	100	7.2–54	23
BDE-138	0	<0.02	–	0	<0.14	–	0	<0.60	–
BDE-153	100	0.02–0.13	0.08	100	0.59–1.1	0.79	100	28–64	53
BDE-154	70	<0.02–0.05	0.02	100	0.23–0.69	0.34	100	8.4–130	32
BDE-183	90	<0.02–0.07	0.02	0	<0.28	–	0	<0.60	–
BDE-196	10	<0.03–0.03	nd	0	<0.28	–	0	<1.0	–
BDE-197	20	<0.03–0.07	nd	0	<0.28	–	0	<1.0	–
BDE-201	30	<0.03–0.09	nd	0	<0.28	–	0	<1.0	–
BDE-202	0	<0.03	–	0	<0.28	–	43	<0.60–6.7	nd
BDE-203	70	<0.03–0.07	0.04	17	<0.28–0.72	nd	14	<1.0–1.5	nd
BDE-206	60	<0.03–0.15	nd	0	<0.28	–	0	<1.0	–
BDE-207	70	<0.03–0.20	0.05	0	<0.28	–	0	<1.0	–
BDE-208	50	<0.03–0.08	nd	0	<0.28	–	0	<1.0	–
BDE-209	100	0.11–2.8	0.77	0	<0.70	–	0	<1.5	–
Sum of PBDEs	–	0.27–4.5	1.7	–	7.9–29	10	–	270–1100	390
α-HBCD	70	<0.01–0.07	0.03	83	<0.14–2.2	0.35	100	3.1–18	4.60
β-HBCD	30	<0.01–0.02	nd	17	<0.14–0.25	nd	43	<0.60–2.8	nd
γ-HBCD	70	<0.01–0.24	0.09	50	<0.14–0.71	nd	86	<0.60–6.1	1.3
TBP-AE	100	0.03–0.10	0.05	33	<0.14–0.27	nd	0	<0.60	–
BTBPE	30	<0.03–0.07	nd	50	<0.14–0.66	nd	0	<1.0	–
DBDPE	0	<0.05	–	0	<0.42	–	0	<1.6	–
EH-TBB	10	<0.02–0.04	nd	0	<0.28	–	100	4.0–27	9.2
BEHTBP	80	<0.02–0.48	0.11	17	<0.28–0.26	nd	43	<0.60–3.0	nd
HBBZ	90	<0.02–0.79	0.31	33	<0.14–1.4	nd	100	2.3–7.4	5.3
HCCPD	0	<0.02	–	0	<0.28	–	0	<0.60	–
HCDBCO	0	<0.03	–	0	<0.56	–	0	<1.0	–
PBBA	20	<0.02–0.07	nd	0	<0.42	–	14	<0.60–18	nd
PBBB/PBT	0	<0.02	–	0	<0.28	–	0	<0.60	–
BB-101	10	<0.02–0.03	nd	100	0.62–1.4	0.79	100	0.68–4.9	2.9
PBBZ	0	<0.03	–	0	<0.14	–	0	<1.0	–
PBEB	0	<0.02	–	0	<0.28	–	0	<0.60	–
α-DBE-DBCH	50	<0.03–0.21	0.03	0	<0.28	–	0	<1.0	–
β-DBE-DBCH	20	<0.03–1.6	nd	17	<0.28–0.93	nd	0	<1.0	–
γ-DBE-DBCH	30	<0.03–1.1	nd	0	<0.28	–	0	<1.2	–
TBCT	0	<0.03	–	0	<0.42	–	100	2.1–20	5.1
TBPX	0	<0.03	–	0	<0.28	–	0	<1.0	–

Blubber from deceased adult harbor seals in San Francisco Bay had levels of HBCDs (4.4–19.3 ng/g lw) similar to those detected in this study (4.4–27 ng/g lw), and were likewise dominated by α-HBCD (Klosterhaus et al., 2012). Levels of α-HBCD in blubber from adult harbor seals stranded along the northwest Atlantic coast from 2001 to 2006 (2–29 ng/g lw; Shaw et al., 2012) were also comparable. HBCDs were not detected in Bay water (Tables S5–S6); as noted above, a larger volume of water would be needed to detect these contaminants.

3.1.3. Other brominated flame retardants

Among the 19 other brominated flame retardants analyzed (Table 1), HBBZ was most abundant in sediment, with concentrations comparable to BDE-47 and ranging from nd to 0.79 ng/g dw. Several others were detected at lower levels, including TBP-AE, BTBPE, EH-TBB, BEHTBP, PBBA, BB-101, and DBE-DBCH (or TBECH).

Five of these may be compared with results from the previous analysis of flame retardants in 2007 Bay sediment (Klosterhaus et al., 2012). BEHTBP, an ingredient in flame retardants including Firemaster 550, Firemaster 600, and DP-45, was detected for the first time in the present study of 2014 Bay sediment, perhaps due in part to the lower MLOQ achieved. The other brominated Firemaster 550 and 600 component, EH-TBB, was also detected in this study for the first time, in a single sediment sample at a level near the MLOQ. While the present analysis detected HBBZ widely in sediment, the previous study did not detect it

at all. In contrast, BTBPE was detected at similar levels in both studies (present < 0.03–0.07 ng/g dw; Klosterhaus et al. (2012) < 0.03–0.1 ng/g dw) and PBEB was only detected in the earlier study.

Levels of several brominated flame retardants in Bay sediment were generally comparable to or lower than found in estuarine or marine sediment from China (Chen et al., 2013; Zhu et al., 2013; Liu et al., 2014; Wang et al., 2015a; Zhen et al., 2016) and Europe (López et al., 2011; Sühring et al., 2015, 2016). Levels of BTBPE, DBDPE, DBE-DBCH, HCDBCO, TBCT, and TBPX were also generally lower in the Bay relative to the Laurentian Great Lakes (Yang et al., 2012). In contrast, HBBZ in Bay sediment (<0.02–0.79 ng/g dw) was often higher than reported for the Great Lakes (<0.005–0.43 ng/g dw; Yang et al., 2012).

Among these brominated flame retardants, BB-101 was detected at the highest levels in bivalves (0.62–1.4 ng/g lw, median 0.79 ng/g lw; Table 1). Other analytes were detected sporadically. Resident bivalves from coastal Asia often have detectable levels of DBDPE (Isobe et al., 2012; Sun et al., 2015), unlike deployed Bay bivalves; occasional detections of BTBPE (Isobe et al., 2012) and TBPX (Sun et al., 2015) are also reported. BTBPE was found in just three of ten Bay bivalve samples, and TBPX was not detected. Shellfish from the coast of France contained levels of DBDPE, BTBPE, and HBBZ that were generally below the MLOQs of the method used in the present study (Munsch et al., 2015). EH-TBB was detected in wild mussels and BTBPE in clams from the northern coast of Spain (Villaverde-de-Sáa et al., 2013).

Harbor seal blubber contained notable levels of EH-TBB (4.0–27 ng/g lw, median 9.2 ng/g lw), HBBZ (2.3–7.4 ng/g lw, median 5.3 ng/g lw), TBCT (2.1–20 ng/g lw, median 5.1 ng/g lw), and BB-101 (0.68–4.9 ng/g lw, median 2.9 ng/g lw). BEHTBP and PBBA were detected sporadically and at levels significantly lower than PBDEs. The brominated components of Firemaster 550 and other flame retardants, EH-TBB and BEHTBP, were not detected in a previous study of Bay harbor seal blubber (Klosterhaus et al., 2012). In contrast, PBEB was detected in this earlier study, but at levels (0.07–0.50 ng/g lw) lower than the MLOQ in this study (0.60 ng/g ww). HBBZ was not detected (<0.30 ng/g ww) in this earlier study of Bay harbor seals as well (Klosterhaus et al., 2012). Differences between the previous study and the present one may reflect an increase in Firemaster 550 components in the Bay, differences in the behavior of the seals sampled, or could be partially due to variation in sample pretreatment and instrumental analysis.

There is a dearth of data for alternative brominated flame retardants in harbor seals. Blubber from harbor porpoises stranded along coastal U.K. in 2008 contained quantifiable levels of PBEB and EH-TBB, the latter at lower levels than seen in Bay blubber (<0.6–3.4 ng/g ww; Law et al., 2013; relative to Bay values of 3.6–24 ng/g ww; Table S9); other compounds in Bay harbor seal blubber, including HBBZ, TBCT, PBBA, and BEHTBP, were either not detected, or detected at levels below the MLOQ. Blubber from Indo-Pacific humpback dolphins and finless porpoises in coastal waters of Hong Kong had detectable levels of EH-TBB and BEHTBP (Zhu et al., 2014; Lam et al., 2009), similar to that found in Bay harbor seal blubber; in contrast, these species also contained detectable levels of DBDPE, BTBPE, and DBE-DBCH (Zhu et al., 2014; Ruan et al., 2018), analytes not observed here. BTBPE, DBDPE, and EH-TBB were detected in blubber from ringed seals in Greenland at levels comparable to or below the MLOQs for these analytes in the present study; BEHTBP was not detected (Vorkamp et al., 2015), but was detected in three of seven Bay harbor seals. A summary of studies of blubber from various Arctic species suggests limited to no detection of DBDPE and BTBPE (de Wit et al., 2010).

Apart from PBDEs, hydrophobic, brominated flame retardants were not detected in dissolved phase water samples, and rarely detected in the particulate phase (Tables S5–S6).

3.2. Dechlorane Plus-based flame retardants

The only DP-related contaminants with consistent detections in sediment were *anti*-DP and *syn*-DP, components of Dechlorane Plus, and Dec-602 (Table 2). Current measurements of *anti*-DP and *syn*-DP (0.02–1.3 and <0.02–0.45 ng/g dw, respectively) are consistent with relative fractions found in commercial mixtures (Sverko et al., 2008), and are comparable to earlier analyses in Bay sediment (0.06–0.6 and 0.03–0.3 ng/g dw, respectively; Klosterhaus et al., 2012). Levels of DP were generally lower than observed in the top 0.5 cm of Great Lakes sediment (0.002–14 ng/g dw; Yang et al., 2011). Bay levels were also lower than generally observed in the Pearl River Delta (nd to 45 ng/g dw; He et al., 2014; Chen et al., 2013) and the coasts of northern China (*anti*-DP 0.02–4.9 ng/g dw, *syn*-DP nd to 5.4 ng/g dw; Jia et al., 2011). In contrast, comparable detections were reported in the Pearl River Estuary (nd to 2.1 ng/g dw; Sun et al., 2016; Chen et al., 2013), industrial bays in Korea (0.01–0.9 ng/g dw; Fang et al., 2014), and coastal North Sea sites (*anti*-DP nd to 0.61 ng/g dw, *syn*-DP nd to 0.92 ng/g dw; Sühling et al., 2015). Bay levels were often higher than observed in sediment samples from coastal areas of the East China Sea (0.01–0.2 ng/g dw; Wang et al., 2016b).

A limited number of analyses of other DP-related contaminants in sediment are available for comparison. North Sea sediments had levels of Dec-602 (nd to 0.47 ng/g dw) comparable to the Bay (<0.02–0.25 ng/g dw); DBALD and HCPN were also detected in North Sea sediment, but not in Bay sediment (Sühling et al., 2015). Great Lakes sediment contained detectable levels of Dec-602, -603, and -604

(Yang et al., 2011), and coastal sediment from northern China contained sporadic detections of Dec-602 and -603 (Jia et al., 2011); only Dec-602 was detected in the Bay. Cl₁₁-DP was detected in half the sediment samples from both San Francisco Bay and the Pearl River Estuary (Sun et al., 2016).

Dechlorane Plus was only occasionally detected in bivalves and harbor seal blubber; in blubber, higher frequency and/or levels of detection were observed for Dec-602 and Dec-603 (Table 2). The majority of the DP-related analytes were not detected in any Bay tissues.

Bay bivalves were less frequently contaminated by DP-related compounds relative to other regions for which data are available. Widespread detection of DP was reported in resident oysters from northern China (76% and 78% for *anti*- and *syn*-DP, respectively; Jia et al., 2011). Sporadic detection of Dec-602 and Dec-603 was also reported (Jia et al., 2011). Dechlorane Plus was likewise detected in two species of clams collected from the Pearl River Estuary (Sun et al., 2015), and in clams but not mussels or cockles from Spain (Villaverde-de-Sáa et al., 2013).

Lower DP detection frequency in harbor seal blubber in the present study, relative to 100% detection in the earlier study of San Francisco Bay seals (Klosterhaus et al., 2012), is likely due to a higher MLOQ. Higher and more ubiquitous DP contamination was reported for blubber from Indo-Pacific humpback dolphins and finless porpoises in coastal waters of Hong Kong (1.7–64 ng/g lw and 0.45–5.1 ng/g lw, respectively; Zhu et al., 2014). Levels comparable to Bay harbor seal blubber were reported for blubber from ringed seals in Greenland (*anti*-DP 0.04–1.8 ng/g ww, *syn*-DP 0.01–0.42 ng/g ww; Vorkamp et al., 2015) and porpoises in the U.K. (*anti*-DP nd to 0.36 ng/g ww, *syn*-DP nd to 0.17 ng/g ww; Law et al., 2013). DP-based flame retardants were not detected in ambient Bay water samples (Tables S5–S6).

3.3. Phosphate flame retardants

Unlike the hydrophobic flame retardants described previously, phosphate flame retardants are generally more water soluble (van der Veen and de Boer, 2012). TCPP was typically the most abundant phosphate flame retardant in Bay water samples, with concentrations (sums of dissolved phase and particle-associated contributions) ranging from 46 to 2900 ng/L (median 140 ng/L; Table 3). Levels were generally higher than measured in other estuarine or marine settings, including the southern California Bight (nd to 56 ng/L; Vidal-Dorsch et al., 2012), the River Elbe estuary and German Bight (3–250 ng/L; Bollmann et al., 2012), and the North Atlantic and Arctic Oceans (nd – 5.8 ng/L; Li et al., 2017; McDonough et al., 2018). TPHP and TBEP were typically the next most abundant, with concentrations ranging from 41 to 360 ng/L (median 90 ng/L), and from 24 to 1000 ng/L (median 69 ng/L), respectively; levels were generally higher than those found in the River Elbe estuary (0.3–4 and nd to 80 ng/L, respectively; Bollmann et al., 2012) and Maizuru Bay, Japan (6–14 and 26–62 ng/L, respectively; Harino et al., 2014). Other notable detections included TDCPP (14–450 ng/L; median 33 ng/L) and TCEP (7.4–300 ng/L; median 24 ng/L); levels were often greater than in the Southern California Bight (TCEP nd; Vidal-Dorsch et al., 2012), the River Elbe estuary (TDCPP 6–30 ng/L, TCEP 5–20 ng/L; Bollmann et al., 2012), Maizuru Bay, Japan (TDCPP 12–25 ng/L, TCEP 11–12 ng/L; Harino et al., 2014), and the North Atlantic and Arctic Oceans (TDCPP nd to 0.96 ng/L, TCEP nd to 3.8 ng/L; Li et al., 2017; McDonough et al., 2018).

In contrast, sediment samples were most contaminated by TEHP, TCrP, TPHP, TDCPP, and TBEP, with median concentrations of 8.2, 3.4, 1.9, 0.96, and 0.81 ng/g dw, respectively (Table 3), greater than the median for BDE-209. Sediments from the Great Lakes contained similar concentrations of many phosphate flame retardants (sum of phosphates 0.44–48 ng/g dw, relative to Bay sums of 9.5–33 ng/g dw; Cao et al., 2017) and those from the southern California Bight contained comparable or higher levels of TCEP, TCPP, and TDCPP (nd to 6.98, nd to 57.3, and nd to 13.6 ng/g dw, respectively; Maruya et al., 2016). Sediment

Table 2
DP-based flame retardants in San Francisco Bay samples. Medians < MLOQ are labeled nd (non-detect).

DP-based flame retardants	Sediment (n = 10) ng/g dw			Bivalves (n = 6) ng/g lw			Harbor Seal Blubber (n = 7) ng/g lw		
	% Detect	Range	Median	% Detect	Range	Median	% Detect	Range	Median
Cl ₁₀ -DP	0	<0.02	–	0	<0.14	–	0	<0.30	–
Cl ₁₁ -DP	50	<0.02–0.05	nd	0	<0.14	–	0	<0.30	–
Cplus	0	<0.02	–	0	<0.14	–	0	<0.30	–
DBALD	0	<0.02	–	0	<0.14	–	0	<0.30	–
DPMA	0	<0.03	–	0	<0.14	–	0	<0.50	–
DEC-601	0	<0.02	–	0	<0.14	–	0	<0.30	–
DEC-602	80	<0.02–0.25	0.08	0	<0.14	–	100	0.91–11	2.2
DEC-603	0	<0.02	–	0	<0.14	–	57	<0.30–3.1	0.51
DEC-604	0	<0.03	–	0	<0.14	–	0	<1.0	–
DEC-604CB	60	<0.02–0.03	0.02	0	<0.14	–	0	<0.30	–
Br-DEC604	0	<0.03	–	0	<0.28	–	0	<0.50	–
Br ₂ -DEC604	0	<0.02	–	0	<0.28	–	0	<0.30	–
Cl ₄ -DEC604	0	<0.02	–	0	<0.42	–	0	<0.30	–
Br ₂ Cl ₂ -DEC604	0	<0.02	–	0	<0.28	–	0	<0.30	–
HCPN	0	<0.02	–	0	<0.42	–	0	<0.30	–
syn-DP	90	<0.02–0.45	0.12	17	<0.14–0.20	nd	29	<0.30–1.2	nd
anti-DP	100	0.02–1.3	0.26	33	<0.14–0.28	nd	43	<0.30–1.2	nd

from the Scheldt Estuary, Holland, also showed similar levels of contamination, with lower levels of TEHP and TCrP (0.4–3.3 and nd to 0.9 ng/g dw, respectively), and comparable or higher levels of TBEP (nd to 19.6 ng/g dw; Brandsma et al., 2015), while those from Maizuru Bay, Japan had higher levels of TCEP, TDCPP, and TBEP (2–3 ng/g dw, 3–56 ng/g dw, and nd to 15 ng/g dw, respectively; Harino et al., 2014). Of note, much of San Francisco Bay is considered to be an erosional rather than depositional sediment environment (Barnard et al., 2013), such that contaminants within surface sediment samples may not fully reflect current uses within the surrounding urban setting. Marine sediment from the North Pacific and Arctic Oceans, sites farther from urban inputs, contained lower levels of phosphate flame retardants than found in the Bay, with the exception of TCEP (sum of phosphates 0.159–4.658 ng/g dw; TCEP 0.081–3.903 ng/g dw; Ma et al., 2017).

Bivalve samples were dominated by TDCPP, with 100% detection frequency and levels ranging from 2.9 to 13 ng/g lw (median 6.7 ng/g lw; Table 3), comparable to BDE-47. Lower levels of TPhP, EHDPP, TnBP, TBEP, and TCPP were also detected in over 50% of samples. In contrast, bivalves from the reference site outside of San Francisco Bay contained low but detectable levels of TDCPP (0.38 ng/g lw; see Table S8 for moisture and lipid content).

TDCPP, TCPP, and TCEP were not detected in a previous study of resident Bay and California coastal bivalves collected in 2009–2010 (Dodder et al., 2014). An earlier European study examining TDCPP, TCPP, TCEP, TPhP, and TCrP was also unable to detect these

contaminants in blue mussels (Leonards et al., 2011). In contrast, a later study of bivalves from coastal European locations measured higher levels of TBEP (up to 39.4 ng/g dw; Álvarez-Muñoz et al., 2015) than seen in Bay bivalves (up to 2.0 ng/g dw; Table S8). TBEP was frequently detected in other European biota as well (Álvarez-Muñoz et al., 2015). Meanwhile, TCEP was only detected below MLOQ in European bivalves (Álvarez-Muñoz et al., 2015); TCEP was detected at quantifiable levels in two of six Bay bivalve samples (at 0.29 and 0.13 ng/g dw; Table S8). Tri-n-butyl phosphate was the dominant phosphate flame retardant in mussels from Maizuru Bay, Japan, followed by TDCPP; levels of each (23–34 and 6–15 ng/g ww, respectively; Harino et al., 2014) were generally at least an order of magnitude higher than seen in the Bay (nd – 0.13 and 0.18–0.75 ng/g ww; see Table S8 for moisture content). TBEP, TCrP, TPhP, and TCEP were also detected in Maizuru Bay bivalves (Harino et al., 2014).

Just four phosphate flame retardants were detected in harbor seal blubber (Table 3): TCPP (nd – 30 ng/g lw, median 13 ng/g lw), TDCPP (nd – 56 ng/g lw, median 4.3 ng/g lw), TCEP (nd – 8.3 ng/g lw, median 3.4 ng/g lw), and TPhP (nd – 27 ng/g lw weight, median < 1.0 ng/g lw). Levels of these flame retardants were significantly lower than levels of BDE-47. Blubber may not be an ideal matrix for examination of these less hydrophobic contaminants. Broadly speaking, low levels of phosphate flame retardants observed in wildlife are frequently attributed to rapid degradation and metabolism, suggesting that tissue levels may be a poor indicator of exposure (Strobel et al., 2018).

Table 3
Phosphate flame retardants in San Francisco Bay samples. Medians < MLOQ are labeled nd (non-detect).

Phosphate-based flame retardants	Water (n = 12) ng/L ^a			Sediment (n = 10) ng/g dw			Bivalves (n = 6) ng/g lw			Harbor Seal Blubber (n = 7) ng/g lw		
	% Detect	Range	Median	% Detect	Range	Median	% Detect	Range	Median	% Detect	Range	Median
TEP	33	<0.2–3.2	nd	20	<0.03–0.06	nd	0	<0.14	–	0	<1.0	–
TCEP	100	7.4–300	24	40	<0.03–0.13	nd	33	<0.14–0.45	nd	71	<1.0–8.3	3.4
TCPP	100	46–2900	140	100	0.26–1.6	0.54	67	<0.14–5.3	0.50	86	<2.5–30	13
TDCPP	100	14–450	33	100	0.73–2.0	0.96	100	2.9–13	6.7	71	<1.0–56	4.3
TPhP	100	41–360	90	100	0.44–7.5	1.9	67	<0.56–2.7	1.1	43	<1.0–27	nd
TnBP	100	7.8–43	13	100	0.35–1.2	0.57	83	<0.14–2.3	1.0	0	<1.5	–
TCrP	50	<0.4–33	nd	100	1.6–6.7	3.4	0	<0.35	–	0	<2.0	–
TPrP	0	<0.4	–	0	<0.05	–	0	<0.35	–	0	<2.0	–
TBEP	100	24–1000	69	100	0.51–4.8	0.81	67	<0.42–2.6	0.79	0	<2.5	–
TEHP	25	<0.4–11	nd	100	2.3–20	8.2	33	<0.42–1.9	nd	0	<5.3	–
EHDPP	8	<0.4–2.3	nd	70	<0.10–1.5	0.28	67	<0.56–6.7	1.1	0	<2.0	–
TDBPP	0	<0.8	–	80	<0.10–1.0	0.23	17	<1.1–2.7	nd	0	<2.0	–
T2iPPP	8	<0.4–0.5	nd	40	<0.10–1.4	nd	0	<0.42	–	0	<1.0	–
Sum of phosphates	–	170–5100	460	–	9.5–33	23	–	8.7–25	12	–	17–67	30

^a Values represent total water levels, including dissolved and particulate contributions; values for TCPP, TDCPP, TPhP, TnBP, TCrP, TBEP, EHDPP are considered semi-quantitative in water, quantitative in other matrices.

The four phosphate flame retardants found in Bay harbor seals were not detected in the blubber of ringed seals from Svalbard, Norway and analyzed using a method with higher detection limits; instead, occasional detection of TEHP and EHDPP was reported (Hallanger et al., 2015). In contrast, East Greenland ringed seal blubber found TEHP, TDCPP, TPhP, TnBP, and TEHP, but not TBEP (Strobel et al., 2018). These ringed seal blubber samples contained lower levels of TDCPP relative to Bay harbor seal samples (<0.17–1.2 ng/g ww vs. <1.0–37 ng/g ww [Table S9], respectively) and comparable levels of TPhP (<0.40–7.2 ng/g ww vs. <1.0–24 ng/g ww [Table S9], respectively); other detections were generally below the MLOQs of the present study. Blubber from stranded or bycaught harbor porpoises in the UK contained TEHP, TPhP, TBEP, and EHDPP (Papachlimitzou et al., 2015); the maximum TPhP level reported was 6.7 ng/g ww, relative to the maximum Bay TPhP level of 24 ng/g ww (Table S9). The three other phosphate flame retardants observed in Bay blubber, TCPP, TDCPP, and TCEP, were not detected in UK blubber, though the detection limits were relatively high (26, 8.9, and 38 ng/g ww, respectively; Papachlimitzou et al., 2015).

3.4. Statistical examination of flame retardants

Several statistically significant correlations were present in the analysis of flame retardants with $\geq 50\%$ frequency in a given matrix (Tables S13–S17). In water (both total and dissolved-phase), positive correlations were observed among chlorinated phosphate flame retardants (TCEP, TCPP, TDCPP); TnBP was also positively correlated with each of these three (Tables S13–S14). Such correlations suggest similar urban sources and/or fate processes in the San Francisco Bay region, as reflected in spatial patterns of distribution (Fig. 2; Tables S5–S6), including elevated concentrations in the South and Lower South Bays.

Southern portions of the Bay are more strongly influenced by discharges of treated wastewater and associated contaminants because these waters experience the least amount of mixing with non-effluent flow and have the highest hydraulic residence time compared to other portions of the Bay. Wastewater-derived contaminants such as pharmaceuticals (Klosterhaus et al., 2013) and triclosan (Kerrigan et al., 2015) are often observed at higher concentrations in this part of the Bay. Stormwater is also a significant influence during the wet season. Characterization of a limited number of treated wastewater effluent and stormwater samples indicated that both of these urban pathways discharge flame retardants to the Bay (Tables S10–S12). Of note, wastewater effluent was found to contain significant levels of a number of phosphate flame retardants, particularly TCPP, TDCPP, and TCEP (Table S10). Effluent concentrations were comparable to higher Bay concentrations obtained from sites in southern portions of the Bay. Local stormwater samples contained similar ranges of TCPP, TCEP, and TDCPP concentrations as found in the Bay (Tables S11–S12).

Correlations were not observed among the PBDE congeners frequently detected in water (BDE-47, -49, -99), but TDCPP was positively correlated with BDE-47 (Tables S13–S14). Both TDCPP and BDE-47 (as part of PBDE commercial mixture Penta) have been used as flame retardants in foam furniture and infant products (Stapleton et al., 2009, 2011, 2012; van Bergen and Stone, 2014; Cooper et al., 2016). Wastewater effluent samples were found to contain trace levels of PBDEs (Table S10); stormwater samples generally contained PBDEs at higher levels than found in the Bay (Tables S11–S12). Correlation analysis of water samples revealed significant positive correlation between the PBDEs and phosphate flame retardants. This analysis similarly suggests that both types of flame retardants are likely to be derived from the urban landscape.

Sediment samples contained a broader range of flame retardants, and a greater number of statistically significant correlations (Tables S15A–S15C). Several positive correlations were observed among phosphate flame retardants, and among the brominated and DP-based flame retardants. Such correlations may be explained by similar sources and/or partitioning behaviors for the respective classes of compounds. Some positive correlations were observed between both

TDCPP and TEHP and a number of brominated and DP-based flame retardants, again suggesting similar sources and/or fate processes. Higher concentrations of many of these contaminants in sediment were often found at southern sites in the Bay (Fig. 2; Table S7).

In contrast, some negative correlations were observed between other phosphate flame retardants (TPhP, TnBP, TBEP, and TDBPP) and various brominated and DP-based flame retardants, possibly reflecting differences in sources and/or partitioning and transport of these contaminants (Tables S15A–S15C). Some of the flame retardants with few statistically significant positive correlations, or more negative correlations, show higher contaminant levels in central or northern portions of the Bay (Fig. 2; Table S7). The regional distributions of these contaminants suggest the role of additional factors, which may include discrete sources or sites of higher pollutant discharge, and which are likely to be contaminant-specific.

Cluster analysis of sediment samples indicated that PBDEs and DP-related substances were closely associated with each other; these classes formed another cluster with HBCDs with modest distance (i.e., significant correlation; Fig. S2). This clustering pattern suggests that these contaminant classes may have some sources in common (Liu et al., 2016; Wu et al., 2017). In contrast, the significant distance between this cluster and the other two classes examined, the remaining hydrophobic, brominated flame retardants and the phosphate flame retardants, may be attributed to differences in their sources and/or environmental fate in the Bay.

For bivalve samples, several statistically significant, positive correlations were observed among PBDE congeners, as well as between α - and γ -HBCD (dw and lw basis; Tables S16A–S16B). The dominant PBDE congener, BDE-47, was not correlated with either α -HBCD or γ -HBCD. The previous study of San Francisco Bay identified a significant correlation between BDE-47 and summed HBCDs (lw basis) in shiner surfperch, a sport fish species, though not in sediment (Klosterhaus et al., 2012). Among the broader brominated flame retardant analytes, a positive correlation was observed between BTBPE and BDE-99. A positive correlation was also observed between EHDPP and BDE-153 (dw and lw basis).

For harbor seal blubber samples, observed correlations (ww and lw basis) appear scattered across the different classes of flame retardants, with few patterns evident (Tables S17A–S17B). There were no observed correlations among phosphate flame retardants. There were only a few positive correlations among PBDE congeners, while BDE-47 was only positively correlated with α -HBCD, γ -HBCD (lw only), and TBCT. Meanwhile, α - and γ -HBCD were positively correlated with each other, but the two DP-based flame retardants (Dechlorane 602 and 603) were not. BB-101 was negatively correlated with TCEP and positively correlated with BDE-153 (ww only) and BDE-154. The lack of defined patterns of correlation observed in harbor seal blubber likely reflects the diverse contaminant exposures possible among individuals living in the same general location due to variations in age, sex, and diet, as well as the metabolism and relative lipophilicity specific to each compound.

3.5. Environmental implications: Comparison to toxicity thresholds

Limited toxicity data for marine and estuarine settings suggest some concern may be warranted for current levels of TDCPP and TPhP in the Bay. Concentrations of TDCPP (median 33 ng/L total water, 29 ng/L dissolved phase; Tables 3, S5) frequently exceeded a marine predicted no effect concentration (PNEC) of 20 ng/L (ECHA, 2018a). TDCPP levels at some Bay sites also exceeded a level shown to reduce body length in the model organism *Daphnia magna* (65 ± 7.1 ng/L; Li et al., 2015). Meanwhile, levels of TPhP in some southern Bay samples (e.g., 360 ng/L total water, 300 ng/L dissolved phase; Tables S5–S6) approached a marine PNEC of 370 ng/L (ECHA, 2018b). Additional monitoring is underway to ascertain whether these concentrations are typical for the Bay. In contrast, the relatively high levels of TCPP and TBEP detected in the Bay were significantly below available marine PNECs (TCPP 64–420 $\mu\text{g/L}$ [ECHA, 2018c]; TBEP 2.4 $\mu\text{g/L}$ [ECHA, 2018d]).

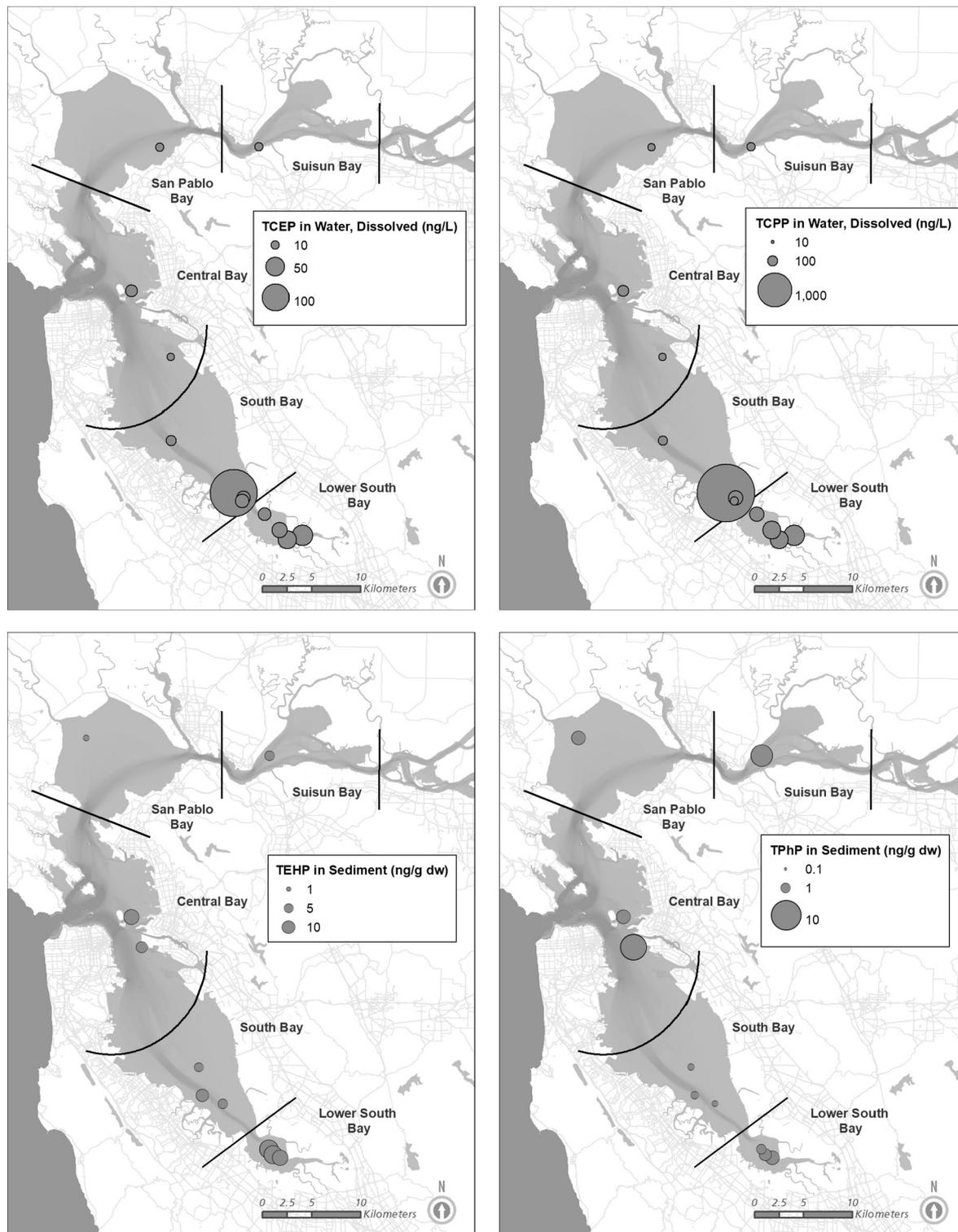


Fig. 2. Concentrations of select phosphate flame retardants in San Francisco Bay. Dissolved phase water concentrations of TCEP (upper left) and TCPP (upper right) show similar spatial distributions, with higher levels in the South and Lower South Bays. Sediment concentrations of TEHP (lower left) show a similar spatial distribution, in contrast to sediment concentrations of TPhP (lower right).

Studies indicate that many members of the phosphate flame retardant family can produce the same types of toxic impacts in exposed organisms; this suggests that evaluation of the risks posed by individual contaminants may not fully capture the potential impacts of exposure to environmentally relevant mixtures. For example, *in vitro* and *in vivo* analyses indicate multiple members of this group can cause endocrine disruption, with observations of estrogenic (TDCPP, TPhP, TnBP,

TCrP; [Kojima et al., 2013; Liu et al., 2013; Suzuki et al., 2013; Zhang et al., 2014; Wang et al., 2015b]), antiestrogenic (TCEP, TEHP, T2iPPP; [Suzuki et al., 2013; Zhang et al., 2014]) and antiandrogenic responses (TCPP, TDCPP, TPhP, TnBP, TCrP, T2iPPP; [Kojima et al., 2013; Suzuki et al., 2013]). Studies in fish show measurable sex hormone disruption or reproductive impacts at exposure levels for individual phosphate flame retardants that are significantly higher than found in San

Francisco Bay (Liu et al., 2012, 2013; Wang et al., 2015b; Zhu et al., 2015). Rather than considering each contaminant individually, sums of specific contaminants with the same mode of action could provide a more useful indicator of potential for risk, though varying potency and antagonistic interactions must also be considered.

While PBDE contamination was once of moderate concern for the Bay, observed declines now suggest low concern (Sutton et al., 2015, 2017). For example, a study of polychaete larval settlement and growth found BDE-47 exposure triggered effects in three species at a sediment concentration of 3.0 ng/g dw, with a no observable effect concentration (NOEC) of 0.5 ng/g dw (Lam et al., 2010); just one of ten Bay sediment samples exceeded the NOEC (0.62 ng/g dw; Table S7). A previous study of California harbor seals found correlation between higher PBDE levels in blood samples and higher white blood cell counts, suggesting that high levels of contaminants could potentially be linked to increased rates of infection (Neale et al., 2005); toxicity thresholds for harbor seals have not been developed. A study of grey seals found a significant relationship between total blubber PBDE levels above 1500 ng/g lw and circulating thyroid hormone concentrations (Hall et al., 2003); the highest level of PBDE contamination observed in the seven Bay seals was 1100 ng/g lw. A study of killer whales in the North-east Pacific suggested via a food web bioaccumulation model that a sediment summed PBDE concentration of 1.0 ng/g dw could be considered a protective benchmark (Alava et al., 2016). Seven of ten Bay sediment samples exceeded this conservative threshold.

4. Conclusions

Periodic monitoring to track a broad range of flame retardant analytes is recommended as a means of observing trends impacted by changes in flammability standards and manufacturing practices. Levels of flame retardants in Bay matrices reported in this study relative to those measured in a previous Bay study (Klosterhaus et al., 2012), or in monitoring conducted elsewhere in the world, are consistent with temporal trends or spatial patterns in production and use of individual chemical flame retardants. In particular, detection of a broad array of flame retardants in Bay matrices is consistent with recent product testing that indicates a number of alternative compounds are now in current use, in some cases as replacements for PBDEs (Stapleton et al., 2009, 2011, 2012; van Bergen and Stone, 2014; Cooper et al., 2016).

The uniquely broad flame retardant dataset presented here can be used to establish a baseline against which future measurements in the region may be compared; continued monitoring can help determine whether these compounds are increasing in use, or if there may be a general shift away from flame retardant additives due to changes in flammability standards. Special attention should be granted to TDCPP and TPhP, as Bay concentrations were observed at levels comparable to toxicity thresholds (ECHA 2018a,b).

Acknowledgments

Funding for this study (SFEI Contribution No. 859) was provided by the Regional Monitoring Program for Water Quality in San Francisco Bay. Handling and sampling of seals was conducted under National Marine Fisheries Service permit #16991 and San Jose State University IACUC protocol #1010 issued to Moss Landing Marine Laboratories. The authors are grateful to J. Harvey, E. McHuron, and staff and volunteers from Moss Landing Marine Laboratories, The Marine Mammal Center, and Don Edwards Wildlife Reserve for support and assistance sampling harbor seals. The authors thank J. Ross and the data management team as well as R. Askevold and P. Kauhanen at the San Francisco Estuary Institute. W. Arnold, M. Connor, J. Davis, M. Diamond, D. Muir, D. Schlenk, M. Sedlak, H. Stapleton, P. Trowbridge, D. Yee, and anonymous reviewers provided constructive comments on the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.10.096>.

References

- Alava, J.J., Ross, P.S., Gobas, F.A., 2016. Food web bioaccumulation model for resident killer whales from the northeastern Pacific Ocean as a tool for the derivation of PBDE-sediment quality guidelines. *Arch. Environ. Contam. Toxicol.* 70, 155–168.
- Álvarez-Muñoz, D., Rodríguez-Mozaz, S., Maulvault, A.L., Tediosi, A., Fernández-Tejedor, M., Van den Heuvel, F., et al., 2015. Occurrence of pharmaceuticals and endocrine disrupting compounds in macroalgae, bivalves, and fish from coastal areas in Europe. *Environ. Res.* 143, 56–64.
- Babrauskas, V., Lucas, D., Eisenberg, D., Singla, V., Dedeo, M., Blum, A., 2012. Flame retardants in building insulation: a case for re-evaluating building codes. *Build. Res. Inf.* 40, 738–755.
- Barnard, P.L., Schoellhamer, D.H., Jaffe, B.E., McKee, L.J., 2013. Sediment transport in the San Francisco Bay coastal system: an overview. *Mar. Geol.* 345, 3–17.
- BEARHFTI (Bureau of Electronic Appliance Repair, Home Furnishings and Thermal Insulation), 2013. Technical Bulletin 117–2013: Requirements, Test Procedure and Apparatus for Testing the Smolder Resistance of Materials Used in Upholstered Furniture. Department of Consumer Affairs, Bureau of Electronic Appliance Repair, Home Furnishings and Thermal Insulation http://www.bearhfti.ca.gov/about_us/tb117_2013.pdf. Accessed date: 31 January 2018.
- van Bergen, S., Stone, A., 2014. Flame Retardants in General Consumer and Children's Products. Hazardous Waste and Toxics Reduction Program, Washington State Department of Ecology, Olympia, Washington.
- BHFTI (Bureau of Home Furnishings and Thermal Insulation, now known as BEARHFTI), 2000. Technical Bulletin 117: Requirements, Test Procedure and Apparatus for Testing the Flame Retardance of Resilient Filling Materials Used in Upholstered Furniture. Department of Consumer Affairs, Bureau of Home Furnishings and Thermal Insulation <http://www.bearhfti.ca.gov/industry/117.pdf>. Accessed date: 31 January 2018.
- Bollmann, U.E., Moller, A., Xie, Z., Ebinghaus, R., Einax, J.W., 2012. Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. *Water Res.* 46, 531–538.
- Brandsma, S.H., Leonards, P.E., Leslie, H.A., de Boer, J., 2015. Tracing organophosphorus and brominated flame retardants and plasticizers in an estuarine food web. *Sci. Total Environ.* 505, 22–31.
- Cao, D., Guo, J., Wang, Y., Li, Z., Liang, K., Corcoran, M.B., et al., 2017. Organophosphate esters in sediment of the Great Lakes. *Environ. Sci. Technol.* 51, 1441–1449.
- Chen, S.J., Ma, Y.J., Wang, J., Chen, D., Luo, X.J., Mai, B.X., 2009. Brominated flame retardants in children's toys: concentration, composition, and children's exposure and risk assessment. *Environ. Sci. Technol.* 43, 4200–4206.
- Chen, S.J., Feng, A.H., He, M.J., Chen, M.Y., Luo, X.J., Mai, B.X., 2013. Current levels and composition profiles of PBDEs and alternative flame retardants in surface sediments from the Pearl River Delta, southern China: comparison with historical data. *Sci. Total Environ.* 444, 205–211.
- Cooper, E.M., Kroeger, G., Davis, K., Clark, C.R., Ferguson, P.L., Stapleton, H.M., 2016. Results from screening polyurethane foam based consumer products for flame retardant chemicals: assessing impacts on the change in the furniture flammability standards. *Environ. Sci. Technol.* 50, 10653–10660.
- Covaci, A., Gerecke, A.C., Law, R.J., Voorspoels, S., Kohler, M., Heeb, N.V., et al., 2006. Hexabromocyclododecanes (HBCDs) in the environment and humans: a review. *Environ. Sci. Technol.* 40, 3679–3688.
- Covaci, A., Harrad, S., Abdallah, M.A., Ali, N., Law, R.J., Herzke, D., et al., 2011. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. *Environ. Int.* 37, 532–556.
- van der Veen, I., de Boer, J., 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. *Chemosphere* 88, 1119–1153.
- Dodder, N.G., Maruya, K.A., Lee Ferguson, P., Grace, R., Klosterhaus, S., La Guardia, M.J., et al., 2014. Occurrence of contaminants of emerging concern in mussels (*Mytilus* spp.) along the California coast and the influence of land use, storm water discharge, and treated wastewater effluent. *Mar. Pollut. Bull.* 81, 340–346.
- Drage, D., Mueller, J.F., Birch, G., Eaglesham, G., Hearn, L.K., Harrad, S., 2015. Historical trends of PBDEs and HBCDs in sediment cores from Sydney Estuary, Australia. *Sci. Total Environ.* 512–513, 177–184.
- ECHA (European Chemicals Agency), 2018a. Tris[2-chloro-1-(chloromethyl)ethyl] Phosphate: Brief Profile. <https://echa.europa.eu/brief-profile/-/briefprofile/100.033.767>. Accessed date: 31 January 2018.
- ECHA (European Chemicals Agency), 2018b. Triphenyl Phosphate: Brief Profile. <https://echa.europa.eu/brief-profile/-/briefprofile/100.003.739>. Accessed date: 31 January 2018.
- ECHA (European Chemicals Agency), 2018c. Tris(2-chloro-1-methylethyl) Phosphate: Brief Profile. <https://echa.europa.eu/brief-profile/-/briefprofile/100.033.766>. Accessed date: 31 January 2018.
- ECHA (European Chemicals Agency), 2018d. Tris(2-butoxyethyl) phosphate: Brief Profile. <https://echa.europa.eu/brief-profile/-/briefprofile/100.001.021>. Accessed date: 31 January 2018.
- Fang, M., Kim, J.C., Chang, Y.S., 2014. Investigating Dechlorane Plus (DP) distribution and isomer specific adsorption behavior in size fractionated marine sediments. *Sci. Total Environ.* 481, 114–120.

- Feng, A.H., Chen, S.J., Chen, M.Y., He, M.J., Luo, X.J., Mai, B.X., 2012. Hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) in riverine and estuarine sediments of the Pearl River Delta in southern China, with emphasis on spatial variability in diastereoisomer- and enantiomer-specific distribution of HBCD. *Mar. Pollut. Bull.* 64, 919–925.
- Gibble, C.M., Harvey, J.T., 2015. Food habits of harbor seals (*Phoca vitulina richardii*) as an indicator of invasive species in San Francisco Bay, California. *Mar. Mamm. Sci.* 31, 1014–1034.
- Greig, D.J., Ylitalo, G.M., Wheeler, E.A., Boyd, D., Gulland, F.M.D., Yanagida, G.K., Harvey, J.T., Hall, A.J., 2011. Geography and stage of development affect persistent organic pollutants in stranded and wild-caught harbor seal pups from central California. *Sci. Total Environ.* 409, 3537–3547.
- Hall, A.J., Kalantzi, O.L., Thomas, G.O., 2003. Polybrominated diphenyl ethers (PBDEs) in grey seals during their first year of life – are they thyroid hormone endocrine disruptors? *Environ. Pollut.* 126, 29–37.
- Hallanger, I.G., Sagerup, K., Evensen, A., Kovacs, K.M., Leonards, P., Fuglei, E., et al., 2015. Organophosphorous flame retardants in biota from Svalbard, Norway. *Mar. Pollut. Bull.* 101, 442–447.
- Harino, H., Yatsuzuka, E., Yamao, C., Ueno, M., Ohji, M., 2014. Current status of organophosphorus compounds contamination in Maizuru Bay, Japan. *J. Mar. Biol. Assoc. UK* 94, 43–49.
- He, M.J., Luo, X.J., Wu, J.P., Chen, S.J., Wei, S.Q., Mai, B.X., 2014. Isomers of Decchlorane Plus in an aquatic environment in a highly industrialized area in southern China: spatial and vertical distribution, phase partition, and bioaccumulation. *Sci. Total Environ.* 481, 1–6.
- Isobe, T., Ogawa, S.P., Ramu, K., Sudaryanto, A., Tanabe, S., 2012. Geographical distribution of non-PBDE-brominated flame retardants in mussels from Asian coastal waters. *Environ. Sci. Pollut. Res. Int.* 19, 3107–3117.
- Jia, H., Sun, Y., Liu, X., Yang, M., Wang, D., Qi, H., et al., 2011. Concentration and bioaccumulation of Decchlorane compounds in coastal environment of northern China. *Environ. Sci. Technol.* 45, 2613–2618.
- Kerrigan, J.F., Engstrom, D.R., Yee, D., Super, C., Erickson, P.R., Grandbois, M., et al., 2015. Quantification of hydroxylated polybrominated diphenyl ethers (OH-BDEs), trichloro-, and related compounds in freshwater and coastal systems. *PLoS One* 10, e0138805.
- Klosterhaus, S.L., Stapleton, H.M., La Guardia, M.J., Greig, D.J., 2012. Brominated and chlorinated flame retardants in San Francisco Bay sediments and wildlife. *Environ. Int.* 47, 56–65.
- Klosterhaus, S.L., Grace, R., Hamilton, M.C., Yee, D., 2013. Method validation and reconnaissance of pharmaceuticals, personal care products, and alkylphenols in surface waters, sediments, and mussels in an urban estuary. *Environ. Int.* 54, 92–99.
- Kojima, H., Takeuchi, S., Itoh, T., Iida, M., Kobayashi, S., Yoshida, T., 2013. In vitro endocrine disruption potential of organophosphate flame retardants via human nuclear receptors. *Toxicology* 314, 76–83.
- Lam, J.C., Lau, R.K., Murphy, M.B., Lam, P.K., 2009. Temporal trends of hexabromocyclododecanes (HBCDs) and polybrominated diphenyl ethers (PBDEs) and detection of two novel flame retardants in marine mammals from Hong Kong, South China. *Environ. Sci. Technol.* 43, 6944–6949.
- Lam, C., Neumann, R., Shin, P.K., Au, D.W., Qian, P.Y., Wu, R.S., 2010. Polybrominated diphenylethers (PBDEs) alter larval settlement of marine benthic polychaetes. *Environ. Sci. Technol.* 44, 7130–7137.
- Law, R.J., Barry, J., Barber, J.L., Bersuder, P., Deaville, R., Reid, R.J., et al., 2012. Contaminants in cetaceans from UK waters: status as assessed within the cetacean strandings investigation programme from 1990 to 2008. *Mar. Pollut. Bull.* 64, 1485–1494.
- Law, R.J., Losada, S., Barber, J.L., Bersuder, P., Deaville, R., Brownlow, A., et al., 2013. Alternative flame retardants, Decchlorane Plus and BDEs in the blubber of harbour porpoises (*Phocoena phocoena*) stranded or bycaught in the UK during 2008. *Environ. Int.* 60, 81–88.
- Leonards, P., Steindal, E.H., Veen, Ivd, Berg, V., Bustnes, J.O., Leeuwen, S., 2011. Screening of Organophosphor Flame Retardants 2010. SPFO-Report 1091/2011. TA-2786/2011.
- Li, H., Su, G., Zou, M., Yu, L., Letcher, R.J., Yu, H., et al., 2015. Effects of tris(1,3-dichloro-2-propyl) phosphate on growth, reproduction, and gene transcription of *Daphnia magna* at environmentally relevant concentrations. *Environ. Sci. Technol.* 49, 12975–12983.
- Li, J., Xie, Z., Mi, W., Lai, S., Tian, C., Emeis, K.C., et al., 2017. Organophosphate esters in air, snow, and seawater in the North Atlantic and the Arctic. *Environ. Sci. Technol.* 51, 6887–6896.
- Liu, X., Ji, K., Choi, K., 2012. Endocrine disruption potentials of organophosphate flame retardants and related mechanisms in H295R and MVLN cell lines and in zebrafish. *Aquat. Toxicol.* 114–115, 173–181.
- Liu, X., Ji, K., Jo, A., Moon, H.B., Choi, K., 2013. Effects of TDCPP or TPP on gene transcriptions and hormones of HPG axis, and their consequences on reproduction in adult zebrafish (*Danio rerio*). *Aquat. Toxicol.* 134–135, 104–111.
- Liu, H.H., Hu, Y.J., Luo, P., Bao, L.J., Qiu, J.W., Leung, K.M., et al., 2014. Occurrence of halogenated flame retardants in sediment off an urbanized coastal zone: association with urbanization and industrialization. *Environ. Sci. Technol.* 48, 8465–8473.
- Liu, L., Venier, M., Salamova, A., Hites, R.A., 2016. A novel flame retardant in the Great Lakes atmosphere: 3,3',5,5'-Tetrabromobisphenol A bis(2,3-dibromopropyl) ether. *Environ. Sci. Technol. Lett.* 3, 194–199.
- López, P., Brandsma, S.A., Leonards, P.E., de Boer, J., 2011. Optimization and development of analytical methods for the determination of new brominated flame retardants and polybrominated diphenyl ethers in sediments and suspended particulate matter. *Anal. Bioanal. Chem.* 400, 871–883.
- Ma, Y., Xie, Z., Lohmann, R., Mi, W., Gao, G., 2017. Organophosphate ester flame retardants and plasticizers in ocean sediments from the North Pacific to the Arctic Ocean. *Environ. Sci. Technol.* 51, 3809–3815.
- Maruya, K.A., Dodder, N.G., Sengupta, A., Smith, D.J., Lyons, J.M., Heil, A.T., et al., 2016. Multimedia screening of contaminants of emerging concern (CECs) in coastal urban watersheds in southern California (USA). *Environ. Toxicol. Chem.* 35, 1986–1994.
- McDonough, C.A., De Silva, A.O., Sun, C., Cabrerizo, A., Adelman, D., Soltwedel, T., et al., 2018. Dissolved organophosphate esters and polybrominated diphenyl ethers in remote marine environments: Arctic surface water distributions and net transport through Fram Strait. *Environ. Sci. Technol.* 52, 6208–6216.
- Moon, H.B., Kannan, K., Lee, S.J., Choi, M., 2007. Polybrominated diphenyl ethers (PBDEs) in sediment and bivalves from Korean coastal waters. *Chemosphere* 66, 243–251.
- Munsch, C., Olivier, N., Veyrand, B., Marchand, P., 2015. Occurrence of legacy and emerging halogenated organic contaminants in marine shellfish along French coasts. *Chemosphere* 118, 329–335.
- Neale, J.C.C., Gulland, F.M.D., Schmelzer, K.R., Harvey, J.T., Berg, E.A., Allen, S.G., Greig, D.J., Grigg, E.K., Tjeerdema, R.S., 2005. Contaminant loads and hematological correlates in the harbor seal (*Phoca vitulina*) of San Francisco Bay, California. *J. Toxicol. Environ. Health Part A* 68, 617–633.
- Nickel, B.A., 2003. Movement and Habitat Use Patterns of Harbor Seals in the San Francisco Estuary, CA. San Francisco State University, San Francisco, CA.
- Papachlimitzou, A., Barber, J.L., Losada, S., Bersuder, P., Deaville, R., Brownlow, A., et al., 2015. Organophosphorus flame retardants (PFRs) and plasticizers in harbour porpoises (*Phocoena phocoena*) stranded or bycaught in the UK during 2012. *Mar. Pollut. Bull.* 98, 328–334.
- Petreas, M., Gill, R., Takaku-Pugh, S., Lytle, E., Parry, E., Wang, M., et al., 2016. Rapid methodology to screen flame retardants in upholstered furniture for compliance with new California labeling law (SB 1019). *Chemosphere* 152, 353–359.
- R Development Core Team, 2009. www.r-project.org.
- Ramu, K., Kajiwar, N., Isobe, T., Takahashi, S., Kim, E.Y., Min, B.Y., et al., 2007. Spatial distribution and accumulation of brominated flame retardants, polychlorinated biphenyls and organochlorine pesticides in blue mussels (*Mytilus edulis*) from coastal waters of Korea. *Environ. Pollut.* 148, 562–569.
- Ruan, Y., Lam, J.C.W., Zhang, X., Lam, P.K.S., 2018. Temporal changes and stereoisomeric compositions of 1,2,5,6,9,10-hexabromocyclododecane and 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane in marine mammals from the South China Sea. *Environ. Sci. Technol.* 52, 2517–2526.
- Shaw, S.D., Berger, M.L., Brenner, D., Kannan, K., Lohmann, N., Papke, O., 2009. Bioaccumulation of polybrominated diphenyl ethers and hexabromocyclododecane in the northwest Atlantic marine food web. *Sci. Total Environ.* 407, 3323–3329.
- Shaw, S.D., Berger, M.L., Weijs, L., Covaci, A., 2012. Tissue-specific accumulation of polybrominated diphenyl ethers (PBDEs) including Deca-BDE and hexabromocyclododecanes (HBCDs) in harbor seals from the northwest Atlantic. *Environ. Int.* 44, 1–6.
- She, J., Petreas, M., Winkler, J., Visita, P., McKinney, M., Kopec, D., 2002. PBDEs in the San Francisco Bay Area: measurements in harbor seal blubber and human breast adipose tissue. *Chemosphere* 46, 697–707.
- She, J., Holden, A., Adelsbach, T.L., Tanner, M., Schwarzbach, S.E., Yee, J.L., et al., 2008. Concentrations and time trends of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in aquatic bird eggs from San Francisco Bay, CA 2000–2003. *Chemosphere* 73, S201–S209.
- Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A., et al., 2009. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. *Environ. Sci. Technol.* 43, 7490–7495.
- Stapleton, H.M., Klosterhaus, S., Keller, A., Ferguson, P.L., van Bergen, S., Cooper, E., et al., 2011. Identification of flame retardants in polyurethane foam collected from baby products. *Environ. Sci. Technol.* 45, 5323–5331.
- Stapleton, H.M., Sharma, S., Getzinger, G., Ferguson, P.L., Gabriel, M., Webster, T.F., et al., 2012. Novel and high volume use flame retardants in US couches reflective of the 2005 PentaBDE phase out. *Environ. Sci. Technol.* 46, 13432–13439.
- Stockholm Convention on Persistent Organic Pollutants, 2017. The 17 New POPs. United Nations Environment, Geneva, Switzerland <http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx>, Accessed date: 31 January 2018.
- Strobel, A., Willmore, W.G., Sonne, C., Dietz, R., Letcher, R.J., 2018. Organophosphate esters in East Greenland polar bears and ringed seals: adipose tissue concentrations and in vitro depletion and metabolite formation. *Chemosphere* 196, 240–250.
- Sührling, R., Barber, J.L., Wolschke, H., Kotke, D., Ebinghaus, R., 2015. Fingerprint analysis of brominated flame retardants and dechloranes in North Sea sediments. *Environ. Res.* 140, 569–578.
- Sührling, R., Busch, F., Fricke, N., Kotke, D., Wolschke, H., Ebinghaus, R., 2016. Distribution of brominated flame retardants and dechloranes between sediments and benthic fish – a comparison of a freshwater and marine habitat. *Sci. Total Environ.* 542, 578–585.
- Sun, R.X., Luo, X.J., Tan, X.X., Tang, B., Li, Z.R., Mai, B.X., 2015. Legacy and emerging halogenated organic pollutants in marine organisms from the Pearl River Estuary, South China. *Chemosphere* 139, 565–571.
- Sun, Y.X., Zhang, Z.W., Xu, X.R., Hao, Q.W., Hu, Y.X., Zheng, X.B., et al., 2016. Spatial and vertical distribution of Decchlorane Plus in mangrove sediments of the Pearl River Estuary, South China. *Arch. Environ. Contam. Toxicol.* 71, 359–364.
- Sutton, R., Sedlak, M.D., Yee, D., Davis, J.A., Crane, D., Grace, R., et al., 2015. Declines in polybrominated diphenyl ether contamination of San Francisco Bay following production phase-outs and bans. *Environ. Sci. Technol.* 49, 777–784.

- Sutton, R., Sedlak, M., Sun, J., Lin, D., 2017. Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations; 2017 Revision. San Francisco Estuary Institute, Richmond, CA <http://www.sfei.org/documents/contaminants-emerging-concern-san-francisco-bay-strategy-future-investigations-2017> (accessed January 31, 2018).
- Suzuki, G., Tue, N.M., Malarvannan, G., Sudaryanto, A., Takahashi, S., Tanabe, S., et al., 2013. Similarities in the endocrine-disrupting potencies of indoor dust and flame retardants by using human osteosarcoma (U2OS) cell-based reporter gene assays. *Environ. Sci. Technol.* 47, 2898–2908.
- Sverko, E., Tomy, G.T., Marvin, C.H., Zaruk, D., Reiner, E., Helm, P.A., et al., 2008. Dechlorane Plus levels in sediment of the lower Great Lakes. *Environ. Sci. Technol.* 42, 361–366.
- USEPA (United States Environmental Protection Agency), 2014. An Alternatives Assessment for the Flame Retardant Decabromodiphenyl Ether (DecaBDE). Design for the Environment. U.S. Environmental Protection Agency, Washington, DC.
- Vidal-Dorsch, D.E., Bay, S.M., Maruya, K., Snyder, S.A., Trenholm, R.A., Vanderford, B.J., 2012. Contaminants of emerging concern in municipal wastewater effluents and marine receiving water. *Environ. Toxicol. Chem.* 31, 2674–2682.
- Villaverde-de-Sáa, E., Valls-Cantenys, C., Quintana, J.B., Rodil, R., Cela, R., 2013. Matrix solid-phase dispersion combined with gas chromatography-mass spectrometry for the determination of fifteen halogenated flame retardants in mollusks. *J. Chromatogr. A* 1300, 85–94.
- Vorkamp, K., Bossi, R., Riget, F.F., Skov, H., Sonne, C., Dietz, R., 2015. Novel brominated flame retardants and Dechlorane Plus in Greenland air and biota. *Environ. Pollut.* 196, 284–291.
- Wang, L., Zhao, Q., Zhao, Y., Zheng, M., Lou, Y., Yang, B., 2015a. New non-PBDE brominated flame retardants in sediment and plant samples from Jiaozhou Bay wetland. *Mar. Pollut. Bull.* 97, 512–517.
- Wang, Q., Lam, J.C., Han, J., Wang, X., Guo, Y., Lam, P.K., et al., 2015b. Developmental exposure to the organophosphorus flame retardant tris(1,3-dichloro-2-propyl) phosphate: estrogenic activity, endocrine disruption and reproductive effects on zebrafish. *Aquat. Toxicol.* 160, 163–171.
- Wang, P., Zhang, Q., Zhang, H., Wang, T., Sun, H., Zheng, S., et al., 2016a. Sources and environmental behaviors of Dechlorane Plus and related compounds – a review. *Environ. Int.* 88, 206–220.
- Wang, G., Peng, J., Hao, T., Liu, Y., Zhang, D., Li, X., 2016b. Distribution and region-specific sources of Dechlorane Plus in marine sediments from the coastal East China Sea. *Sci. Total Environ.* 573, 389–396.
- de Wit, C.A., 2002. An overview of brominated flame retardants in the environment. *Chemosphere* 46, 583–624.
- de Wit, C.A., Herzke, D., Vorkamp, K., 2010. Brominated flame retardants in the Arctic environment – trends and new candidates. *Sci. Total Environ.* 408, 2885–2918.
- Wu, Y., Zhou, Y.H., Qiu, Y.L., Chen, D., Zhu, Z.L., Zhao, J.F., et al., 2017. Occurrence and risk assessment of trace metals and metalloids in sediments and benthic invertebrates from Dianshan Lake, China. *Environ. Sci. Pollut. Res. Int.* 24, 14847–14856.
- Yang, R., Wei, H., Guo, J., McLeod, C., Li, A., Sturchio, N.C., 2011. Historically and currently used Dechloranes in the sediments of the Great Lakes. *Environ. Sci. Technol.* 45, 5156–5163.
- Yang, R., Wei, H., Guo, J., Li, A., 2012. Emerging brominated flame retardants in the sediment of the Great Lakes. *Environ. Sci. Technol.* 46, 3119–3126.
- Zhang, Y., Ruan, Y., Sun, H., Zhao, L., Gan, Z., 2013. Hexabromocyclododecanes in surface sediments and a sediment core from rivers and harbor in the northern Chinese city of Tianjin. *Chemosphere* 90, 1610–1616.
- Zhang, Q., Lu, M., Dong, X., Wang, C., Zhang, C., Liu, W., et al., 2014. Potential estrogenic effects of phosphorus-containing flame retardants. *Environ. Sci. Technol.* 48, 6995–7001.
- Zhen, X., Tang, J., Xie, Z., Wang, R., Huang, G., Zheng, Q., et al., 2016. Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants (aBFRs) in sediments from four bays of the Yellow Sea, North China. *Environ. Pollut.* 213, 386–394.
- Zhu, B., Lam, J.C., Yang, S., Lam, P.K., 2013. Conventional and emerging halogenated flame retardants (HFRs) in sediment of Yangtze River Delta (YRD) region, East China. *Chemosphere* 93, 555–560.
- Zhu, B., Lai, N.L., Wai, T.C., Chan, L.L., Lam, J.C., Lam, P.K., 2014. Changes of accumulation profiles from PBDEs to brominated and chlorinated alternatives in marine mammals from the South China Sea. *Environ. Int.* 66, 65–70.
- Zhu, Y., Ma, X., Su, G., Yu, L., Letcher, R.J., Hou, J., et al., 2015. Environmentally relevant concentrations of the flame retardant tris(1,3-dichloro-2-propyl) phosphate inhibit growth of female zebrafish and decrease fecundity. *Environ. Sci. Technol.* 49, 14579–14587.