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REGIONAL MONITORING
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IN SAN FRANCISCO BAY

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Flame retardants and plastic additives in San Francisco Bay: Targeted monitoring of organophosphate esters and bisphenols

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Executive Summary

Organophosphate esters (OPEs) and bisphenols are two classes of mobile, endocrine-disrupting chemicals (EDCs) that are ubiquitously detected in environmental matrices due to high global production and use, particularly as plastic and polymer additives. In a 2017 San Francisco Bay-wide study of 22 OPEs and 16 bisphenols in open-Bay water samples, concentrations were quantified and compared to protective ecotoxicity thresholds, where available, to assess potential risks to wildlife. Analysis was conducted using liquid chromatography-electrospray ionization-triple quadrupole mass spectrometry. Fifteen of 22 OPEs were detected, with median total concentrations (sum of dissolved- and particulate-phase contributions) in the order: tris(1-chloro-2-propyl) phosphate (TCPP) > triphenyl phosphate (TPhP) > tris(2-butoxyethyl) phosphate (TBEP) > tri-n-butyl phosphate (TnBP) > triethyl phosphate (TEP) > tris(1,3-dichloro-2-propyl) phosphate (TDCPP). Concentrations of TDCPP surpassed its marine predicted no-effect concentration (PNEC) of 20 ng/L at some sites (2.8–23 ng/L; median 6.2 ng/L). Only two of 16 bisphenols, bisphenol A (BPA) and bisphenol S (BPS), were detected, with total concentrations ranging from <0.7–35 ng/L and <1–120 ng/L, respectively. These levels were in the range of a PNEC for BPA of 60 ng/L. Concentrations of OPEs and bisphenols observed in this study were consistent with concentrations in other estuarine and marine settings globally; several OPEs were found at lower levels than in a screening study of Bay water conducted in 2013.

Both OPEs and bisphenols merit classification as emerging contaminants of Moderate Concern for the Bay within the tiered, risk-based framework developed by the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP). Factors considered in this classification include: 1) the presence of individual contaminants in the Bay at levels comparable to or exceeding protective thresholds; 2) the potential for cumulative impacts with respect to endocrine disruption and other toxic effects; and 3) the expected increase in manufacturing and use for many members of the two classes. Periodic monitoring of OPEs and bisphenols in surface water is recommended to track trends in the Bay in response to shifts in production and manufacturing. In addition, a screening study of bisphenols in contaminant pathways (i.e., wastewater and stormwater) and Bay sediment is recommended to investigate the relative discharge and occurrence of bisphenols, particularly in light of the range of partitioning behaviors expected from different members of this class of contaminants.

Highlights

- Fifteen of 22 organophosphate esters and two of 16 bisphenols were detected in 22 open-Bay water samples collected in 2017.
- In a few samples, concentrations of TDCPP exceeded its marine PNEC.
- Concentrations in the present study were comparable to those observed in other similar environs.
- Organophosphate esters and bisphenols were classified as Moderate Concern for the Bay due to proximity of concentrations to available ecotoxicity thresholds, potential for cumulative adverse toxic effects, and projected increases in manufacturing.

1. Introduction

According to the United Nations' Global Chemicals Outlook II, annual production of plastic is projected to increase from nearly 350 million tons in 2017 to over 2 billion tons by 2050 (United Nations [UN], 2019). The rapid growth of the plastics economy drives increasing demand for chemical additives used in the production of polymers and the manufacture of consumer goods. Similarly, the production and use of some flame retardants are expected to increase in the coming years. Organophosphate esters, used both as flame retardants and plastic additives, and bisphenols, used principally as plastic additives, are two classes of synthetic EDCs that are manufactured at high volumes, are polar and water-soluble, and are difficult to remove via traditional wastewater-treatment processes. These compounds are considered emerging contaminants, a broad term that describes chemicals that are rarely regulated and have the potential to enter the environment and harm humans or wildlife.

In the 2000s, organophosphate esters, which can contain alkyl-, aryl-, or halogenated functional groups, became even more popular for their use as flame retardants in consumer and industrial products included in voluntary and regulatory flammability standards, especially with the phase-out of polybrominated diphenyl ethers (Stapleton et al., 2012; Cooper et al., 2016; Rodgers et al., 2018). In addition to use as flame retardants, OPEs are used as plastic and hydraulic-fluid additives, antifoaming agents, and lacquer and floor polish ingredients (Li et al., 2017; Rodgers et al., 2018). Globally, they are produced at high volumes, with US aggregate production and import volumes for TPhP and TCPP (all OPE acronyms defined in Table S1) in the millions and tens of millions of pounds, respectively, in 2015 (U.S. Environmental Protection Agency [USEPA], 2016). Use of OPEs has drastically increased in recent decades and is projected to continue expanding (Greaves and Letcher, 2017).

Organophosphate esters can enter the environment via multiple routes, including volatilization, particle abrasion, or leaching from consumer products (Wei et al., 2015; Li et al., 2017). They are highly mobile contaminants and have been detected in remote locations, indicating their capacity for long-range transport (Li et al., 2017; McDonough et al., 2018).

Though OPE toxicity is not well understood, endocrine-disrupting effects have been demonstrated at environmentally relevant levels (Bollmann et al., 2012; Harino et al., 2014; Venier et al., 2014). Organophosphate esters have also been linked to cancer, neurotoxicity, and adverse effects on fertility (Wei et al., 2015). Three OPEs—tris(2-chloroethyl) phosphate (TCEP), TDCPP, and tris(2,3-dibromopropyl) phosphate (TDBPP)—are listed as carcinogens on California's Proposition 65 List (Office of Environmental Health Hazard Assessment [OEHHA], 2019).

Similar to OPEs, some bisphenols are produced at high volumes worldwide, with US production and import volumes of BPA and BPS in the billions and millions of pounds, respectively (USEPA, 2016). Bisphenols also have varying chemical structures and properties, which allow for an array of desirable characteristics (e.g., durability, non-corrosivity, stability) and a plethora of applications in industrial and consumer products. Bisphenols are best known as stabilizing agents, and for their use as building blocks in polycarbonate plastics involved in diverse products such as medical devices, water pipes, baby products, and vehicles. They are also used in the production of flame retardants and as thermal reactants in paper products; antioxidants in tire production; epoxy linings in food-packaging; and additives in textiles and clothing, lacquers and

varnishes, and more (Heemken et al., 2001; Chen et al., 2016; Björnsdotter et al., 2017; Xue et al., 2017).

Bisphenols have been observed in both the wastewater and stormwater pathways (Boyd et al., 2004; Jackson and Sutton, 2008; Vidal-Dorsch et al., 2012; Björnsdotter et al., 2017; Fairbairn et al., 2018), indicating migration from products and into waterways. The persistence of bisphenol compounds vary but many are considered to have low to moderate persistence in surface water (Björnsdotter et al., 2017).

Studies have shown that BPA causes adverse estrogenic effects and, in some cases, with potencies comparable to naturally occurring hormones (Héliès-Toussaint et al., 2014; Rosenmai et al., 2014; Chen et al., 2016; Björnsdotter et al., 2017). In addition to endocrine-disrupting effects, BPA has also been linked to cytotoxicity, genotoxicity, mutagenicity, neurotoxicity, cancer, obesity, reproductive and developmental effects, miscarriages, and immunological effects (Carlisle et al., 2009; Björnsdotter et al., 2017). It is listed on California's Proposition 65 List for developmental toxicity and female reproductive toxicity (OEHHA, 2019).

When the US Food and Drug Administration banned the use of BPA in baby bottles in 2012, industry began substituting other bisphenol compounds or “alternatives” for BPA. Increases in these alternatives have already been observed in global environmental matrices (Wu et al., 2018), as well as in human urine (Ye et al., 2015). Production of all bisphenols has increased substantially and is forecast to continue growing (Rochester and Bolden, 2015). Popular “BPA free” disclaimers on products imply that other BPA alternatives are, presumably, “safer” alternatives. Though little is known about the toxicity of BPA alternatives, they are structurally similar to BPA, and some have demonstrated links to the same array of toxic effects at similar, and sometimes greater, potencies (Naderi et al., 2014; Rosenmai et al., 2014; Rochester and Bolden, 2015; Chen et al., 2016; Mu et al., 2018).

San Francisco Bay serves as an important place to understand environmental occurrence of these two classes of EDCs. In 2013, a screening study of flame retardants was conducted to gain a snapshot of environmental exposure to brominated, chlorinated, and organophosphate ester flame retardants (Sutton et al., 2019). Eleven of 13 OPEs analyzed were detected in 10 water samples (average detection rate 63%, sum of OPEs ranged from 170–5100 ng/L) (Table 1). In some cases, total TDCPP concentrations in water far exceeded its marine PNEC (20 ng/L) (European Chemicals Agency [ECHA], 2019h), suggesting the need for further monitoring in the Bay.

In contrast, little previous monitoring has been conducted for bisphenols in the Bay. Bisphenol A was not detected in a 2009-2010 study, likely due to the method limit of quantification (2500 ng/L), which was well above possible thresholds of concern (Klosterhaus et al., 2013). Bisphenol A was, however, detected in three Oakland wastewater treatment plant (WWTP) effluent samples with concentrations of 310 ng/L and 380 ng/L, and one non-detect (< 250 ng/L) (Jackson and Sutton, 2008).

To advance our understanding of the risks posed by these EDCs, there is a need to fill environmental monitoring data gaps. In recognition of the shifting and generally increasing use of OPEs and bisphenols, targeted monitoring of 22 OPEs and 16 bisphenols was conducted in samples of surface water collected from the Bay in 2017. Observed concentrations of OPEs were compared to concentrations found in 2013, and levels of both OPEs and bisphenols were

compared to levels seen in other estuarine and marine environments, as well as to available ecotoxicity thresholds.

2. Materials and methods

2.1 Sample collection

Water samples were collected at 22 sites during the dry season, from August 29 to September 7, 2017, as part of a biennial water cruise conducted by the Regional Monitoring Program for Water Quality in San Francisco Bay (<http://www.sfei.org/rmp>). Additionally, two field duplicates and one field blank were collected (Figures 1 and S1). Surface-water grab samples were collected in 4 L amber glass bottles approximately one meter below the surface, kept under 4°C, and extracted within 72 hours of collection.

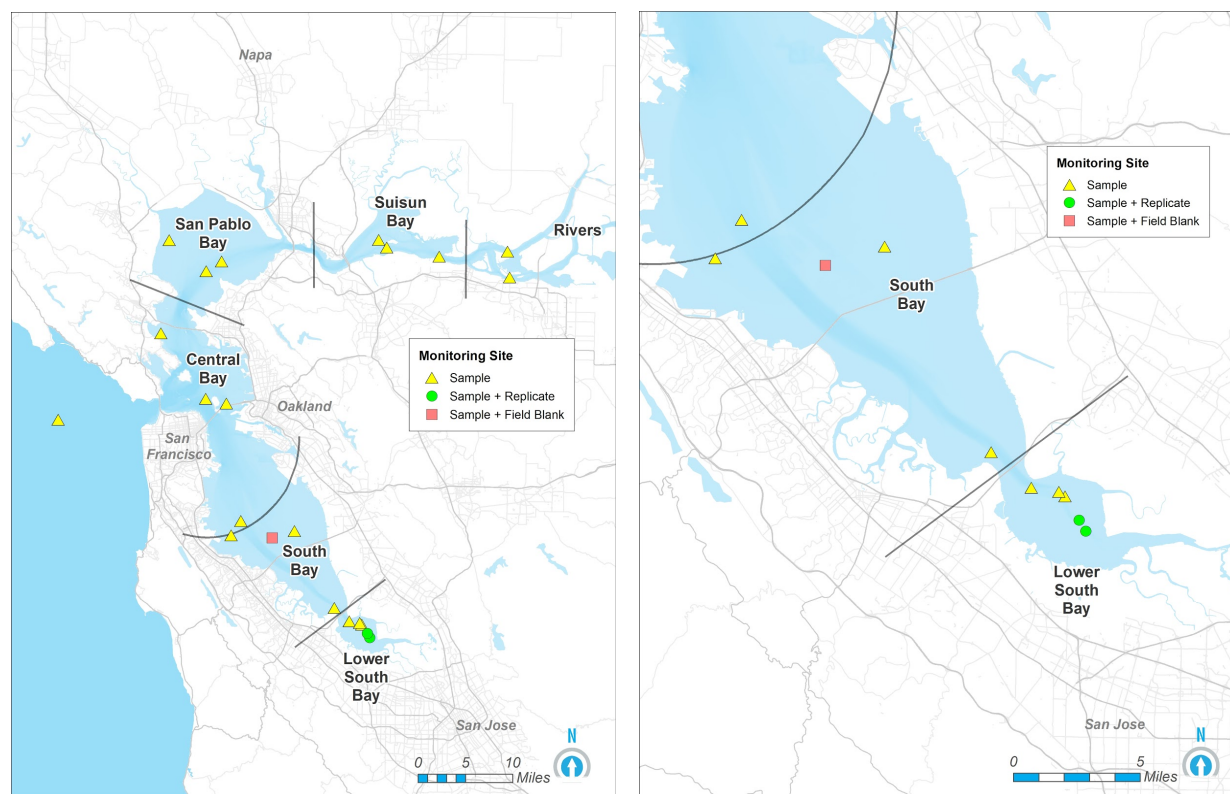


Figure 1. San Francisco Bay sample sites (left), with a closer view of South and Lower South Bay sites on the right.

2.2 Sample extraction and treatment

Upon receipt at the analytical laboratory, samples were filtered through a 0.45- μ m Whatman filter to allow measurement of total suspended solids (TSS) and to separate dissolved and particulate phases. Detailed information on standards and reagents is provided in Supplementary Information.

Filtered water samples (roughly 1 L) were adjusted to approximately pH 3, spiked with surrogate standards (including d_{27} -TnBP, d_{12} -TCEP, d_{15} -TDCPP, d_{15} -TEP, d_{15} -TPhP, $^{13}\text{C}_2$ -TBEP, d_{16} -BPA,

d₈-BPS), and 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 minutes during each extraction. The extracts were combined, concentrated, and divided into two halves. One half was concentrated to near dryness under gentle nitrogen flow, re-constituted with 200 µL methanol, and spiked with internal standard d₆-BPA prior to instrumental analysis for bisphenols. 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 with 15 mL each of methanol, DCM, and hexane (HEX) in sequence. After sample loading, the SPE cartridge was cleaned with a 2 mL mixture of HEX:DCM (20:80, v/v), and target analytes 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 an internal standard (¹³C₁₈-TPhP) for the determination of OPEs.

Dried particulates extracted from the water samples (on the filter) were spiked with surrogate standards and extracted with 5 mL of a 1:1 (v/v) mixture of hexane and dichloromethane under ultrasonication for 5 min. After centrifugation, the supernatant was transferred to a new glass tube. The extraction was repeated twice and the extracts were combined, concentrated, and divided into two halves. The bisphenol half was treated the same as the dissolved phase; the OPE half was cleaned through an ammonium silica cartridge, following the same SPE method used for the analysis of OPEs in the dissolved phase.

2.3 Instrumental analysis

A total of 38 flame retardants and plastic additives were determined on a Shimadzu high-performance liquid chromatograph (HPLC) coupled to an AB Sciex Q Trap 5500 mass spectrometer (MS) equipped with a TurboIonSpray® electrospray ionization (ESI) probe. The polarity of electrospray ionization was positive (ESI⁺) for the OPE analysis, while it was negative (ESI⁻) for the bisphenol analysis. The multiple reaction monitoring ion pairs of target analytes, as well as the detailed liquid chromatography programs, are summarized in Table S2.

2.4 Quality control

Average recoveries across three blank spikes and five matrix spikes deviated less than 35% for all analytes (see Supplementary Information). Relative standard deviations (RSDs) for blank-spike and matrix-spike replicates averaged within 10% or better.

The instrument detection limit (IDL) was defined as three times the standard deviation of the noise from the instrumental determination. The method detection limit (MDL) 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 MDL for each analyte in each matrix is summarized in Table S2.

One field blank and four laboratory blanks were analyzed alongside field samples. Results for field samples were blank corrected. Three of the four laboratory blanks showed dissolved TPhP contamination (average value = 1.5 ng/L). Field sample results were censored where dissolved TPhP levels fell below 3x the standard deviation observed in laboratory blanks (eight of the 22 sites). Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) was also observed in laboratory blanks at levels low enough such that no TDCPP data were censored. In addition, field blank contamination for dissolved bisphenol F (BPF) was high enough that all results were censored

(see Tables S4, S5, & S6 for pre-censored dissolved-phase, particulate, and total BPF concentrations, respectively). Ninety-nine percent of the data were reportable, with only 1% of the dissolved phase results censored for blank contamination and none of the particulate analytes censored.

Analysis of two field replicate samples revealed precision or RSDs for dissolved TCEP, TCPP, TDCPP, TPhP, TBEP, triisobutyl phosphate (TiBP), and BPS, and particulate TBEP greater than 100% for field replicates, which rendered these results semi-quantitative (Table S3). The variability observed for these analytes in the dissolved phase could have occurred as a result of the extraction or cleaning processes and could be the cause of the disparities between field samples and replicates.

3. Results and discussion

3.1 Organophosphate esters

Thirteen of 22 OPEs were detected in the dissolved phase, and 12 of 22 were detected in the particulate phase (see Table S4, S5, and S6 for site-by-site dissolved, particulate, and total concentrations, respectively). Dissolved phase TCEP, TCPP, TDCPP, TiBP, TnBP, and TEP were detected in all samples, with another three OPEs detected in at least half of the 22 sites (Table 1). Particulate tris(2-ethylhexyl) phosphate (TEHP) was detected in all samples with another six OPEs detected in at least half of the 22 sites (Table 1).

Tris(1-chloro-2-propyl) phosphate (TCPP) was generally observed at the highest levels across the Bay, with total concentrations ranging from 15 to 150 ng/L (median 42 ng/L; Table 1). The percentage contribution of TCPP concentrations to $\Sigma_{22}\text{OPEs}$ across all 22 sites ranged from 16–66% (median 47%). Triphenyl phosphate and TBEP were the next most abundant, with total concentrations ranging from <0.4 to 63 ng/L (median 9.5 ng/L), and from 0.4 to 63 ng/L (median 7.6 ng/L), respectively. Other notable detections included TnBP (2.7–15 ng/L; median 7.0 ng/L), TEP (4.2–21 ng/L; median 6.7 ng/L), TDCPP (2.8–23 ng/L; median 6.2 ng/L), and TCEP (3.5–19 ng/L; median 5.3 ng/L). Bay water samples were dominated by chlorinated OPEs (Cl-OPEs), which made up 63% of $\Sigma_{22}\text{OPEs}$, followed by alkyl-OPEs (27% of $\Sigma_{22}\text{OPEs}$), and aryl-OPEs (9% of $\Sigma_{22}\text{OPEs}$; Table 1). Chlorinated OPEs are generally more persistent in the environment than alkyl/aryl-OPEs (van der Veen and de Boer, 2012; McDonough et al., 2018).

Table 1

Organophosphate esters (OPEs) in San Francisco Bay water samples collected in 2013 (Sutton et al., 2019) and in 2017 (present study). Values represent total water concentrations, the summation of dissolved- and particulate-phase contributions. Median values < MDL are labeled “nd” (non-detect).

OPE	Class	Log K _{ow} ^d	PNEC (ng/L) ^f	2013 (n = 12) ng/L ^a				2017 (n = 22) ng/L ^b				
				% Detect	Range	Median	Mean	% Detect	Range	Median	Mean	% Dissolved
V6	Chlorinated	3.4 ^e	7400					27	<1.2–2.4	nd	0.50	100
TCEP	Chlorinated	1.4	-	100	7.4–300	24	48	100	3.5–19	5.3	8.3	97
TCPP	Chlorinated	2.6	6400–420000	100	46–2900	140	390	100	15–150	42	65	93
TDCPP	Chlorinated	3.7	20	100	14–450	33	73	100	2.8–23	6.2	9.0	98
TDBPP	Brominated	4.3	-	0	-	-	-	0	-	-	-	-
BPA-BDPP	Aryl	7.5 ^e	-					27	<0.5–0.67	nd	0.09	0
RBDPP	Aryl	5.7 ^e	42					0	-	-	-	-
T2iPPP	Aryl	7.0 ^e	-	8	<0.4–0.5	nd	0.08	0	-	-	-	-
T35DMPP	Aryl	6.1 ^e	-					0	-	-	-	-
BPDPP	Aryl	5.1 ^e	-					5	<0.6–0.74	nd	0.03	100
2iPPDPP	Aryl	5.3	-					9	<0.4–0.28	nd	0.02	0
CrDPP	Aryl		-					0	-	-	-	-
TCrP	Aryl		100	50	<0.4–33	nd	8.1	0	-	-	-	-
IDDPP	Aryl	5.4	38					50	<0.5–4.8	0.38	0.79	100
EHDPP	Aryl	5.7	-	8	<0.4–2.3	nd	0.19	41	<0.4–8.1	nd	1.2	45
TPhP ^c	Aryl	4.6	370	100	41–360	90	130	68	<0.4–63	9.5	15	71
TBEP	Alkyl	3.8	2400	100	24–1000	69	190	100	0.4–63	7.6	15	62
TEHP	Alkyl	8.8 ^e	-	25	<0.4–11	nd	1.7	100	0.1–8.4	2.1	2.9	10
TiBP	Alkyl	3.3 ^e	1400					100	0.67–2.6	1.0	1.3	92
TPrP	Alkyl	1.9	-	0	-	-	-	0	-	-	-	-
TnBP	Alkyl	4.0	35000	100	7.8–43	13	17	100	2.7–15	7.0	7.5	89
TEP	Alkyl	0.8	63000	33	<0.2–3.2	nd	0.36	100	4.2–21	6.7	9.7	91
ΣOPEs		-	-	-	170–5100	460	850	-	35–290	100	130	

^a Values for TCPP, TDCPP, TCrP, EHDPP, TPhP, TBEP, TnBP in 2013 are considered semi-quantitative

^b Values for TCEP, TCPP, TDCPP, TPhP, TBEP, and TiBP in 2017 are considered semi-quantitative

^c TPhP field results were censored from eight of 22 sites due to blank contamination. Triphenyl phosphate was considered not detected at these eight sites in “% Detect” and were completely omitted from the calculation of the median and mean

^d Log K_{ow} obtained from USEPA 2019

^e Log K_{ow} is predicted rather than demonstrated

^f PNECs obtained from ECHA 2019a–ECHA 2019k

All OPEs showed similar spatial distributions, with higher levels in Lower South Bay, except for TPhP (Figure 2) and TEHP (Supplementary Information). A similar geographic distribution was observed for many OPEs in monitoring conducted in 2013 (Sutton et al., 2019). Lower South Bay is disproportionately influenced by pollutants discharged in wastewater compared to the rest of the Bay because it has a small water volume relative to WWTP discharges, and has a longer residence time than the rest of the Bay due to infrequent mixing with marine or freshwater.

Due to their ubiquitous presence in a variety of consumer products, OPEs are frequently found in indoor dust and air (Stapleton et al., 2012; Wei et al., 2015; Rodgers et al., 2018), and can transfer from clothing and other textiles that, when washed, result in down-the-drain discharges of OPEs to sewers (Saini et al., 2016). Hydrophilic compounds like OPEs are often more difficult to remove during wastewater treatment processes and are commonly discharged. Of the 13 OPEs analyzed in 2013, 12 were detected in final effluent from at least one of the three participating WWTPs discharging to the Bay (Sutton et al., 2019). The $\Sigma_{13}\text{OPEs}$ from these three WWTPs were 3100 ng/L, 3400 ng/L, and 7900 ng/L, respectively. It is possible that higher levels of OPEs in Lower South Bay are related to the greater influence of WWTP effluent on the subembayment's water quality.

Organophosphate esters can also be transported to the Bay through stormwater. These contaminants can enter stormwater through a variety of pathways, including volatilization of OPEs from consumer products, insulation, building, and decorative materials and subsequent deposition in rainwater; leaching of OPEs from various products and materials; and transport of trash containing OPEs in stormwater. Lower South Bay is also influenced by stormwater inflows. All thirteen OPEs analyzed in 2013 were detected in at least one of eight stormwater samples collected (Sutton et al., 2019). The range and median of $\Sigma_{13}\text{OPEs}$ from these eight samples were 290–4600 ng/L and 2800 ng/L, respectively. The contaminant contributions of these two pathways, along with the hydrodynamics of Lower South Bay, may explain the higher concentrations in surface waters compared to the rest of the Bay.

Triphenyl phosphate and TBEP were also present at notable concentrations at a site outside the Golden Gate Bridge (Figure 2). Prior observations of these contaminants in water and sediment samples also revealed differing geographic distributions relative to many other OPEs, suggesting the role of discrete sources or sites of higher pollutant discharge, which may be contaminant-specific (Sutton et al., 2019).

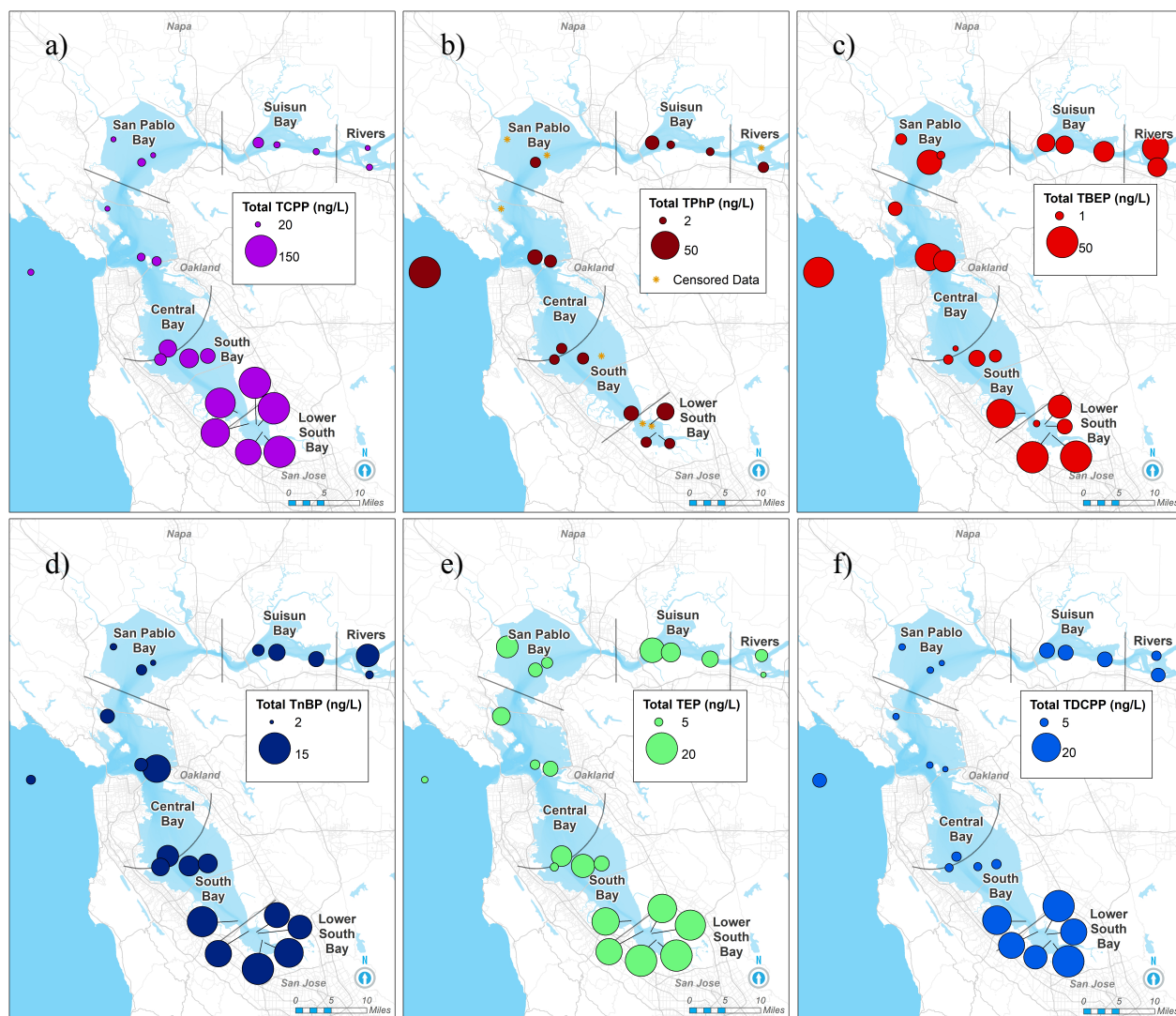


Figure 2. Concentrations of the six most abundant organophosphate esters in San Francisco open-Bay water samples: TCP (a), TPhP (b), TBEP (c), TnBP (d), TEP (e), and TDCPP (f). The maximum concentration of each compound, and therefore the maximum size of the circle represented in each map, varies between figures. See Figure S2 for concentration maps for additional OPEs detected in at least 50% of Bay samples.

Levels of OPEs in 2017 were lower than those observed in 2013 (Table 1). The range and median for the Σ_{13} OPEs across all sites in 2013 were 170–5100 ng/L and 460 ng/L, respectively. In contrast, in 2017, the Σ_{22} OPEs these values were 35–290 ng/L and 100 ng/L. Of the thirteen OPEs analyzed in 2013, only TEHP, 2-ethylhexyl-diphenyl phosphate (EHDPP), and TEP had concentrations in 2017 that were either similar or higher. Concentrations of the remaining ten OPEs decreased in range, median, and mean. The difference in OPE levels could be due to a number of factors, including site selection and timing of sample collection. Another possible factor is a significant drought that occurred in California from December 2011 to March 2017, which could have led to increased concentrations of urban-derived contaminants discharged from WWTPs due to water conservation measures, as well as decreased dilution from river inputs.

Concentrations of individual OPEs detected in the Bay in 2017 were on the higher end of available monitoring data in estuarine or marine environments. Results from 12 water bodies (eight marine, one river estuary, and three freshwater estuaries) are summarized in Table 2. Bay TCPP concentrations in 2017 (15–150 ng/L; mean 65 ng/L) were only exceeded by the Elbe River Estuary (31–310 ng/L; mean 93 ng/L; Bollmann et al., 2012). Bay levels of TPhP (<0.4–63 ng/L; mean 15 ng/L), TBEP (0.4–63 ng/L; mean 15 ng/L), and TnBP (2.7–15 ng/L; mean 7.5 ng/L) were comparable to levels found in Maizuru Bay (TPhP 6–14 ng/L; mean 9 ng/L; TBEP 26–62 ng/L; mean 37 ng/L; and TnBP 7–10 ng/L; mean 8 ng/L; Harino et al., 2014). Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) concentrations in the Bay (2.8–23 ng/L; mean 9.0) were similar to those seen in Long Island, New York (8.9–25 ng/L; mean 16 ng/L; Kim et al., 2018), and in Maizuru Bay (12–25 ng/L; mean 18 ng/L; Harino et al., 2014). Observations reported in other locations were generally lower than those observed in the Bay in 2017, as well as in 2013. No marine or estuarine monitoring data were found for V6, BPA-BDPP, CrDPP, IDDPP, 2iPPDPP, BPDPP, T2iPPP, or T35DMPP (see Table S1 for OPE acronyms) in our literature review that was limited to estuarine waters, open oceans, and large lakes.

Table 2

Comparison of OPE concentrations from San Francisco Bay to levels in other estuaries and marine areas (ng/L). Values represent total water levels. Medians < MDL are labeled “nd” (non-detect).

Compound	n	Range	Median	Mean	Location ^b	Year	Reference
TCEP	22	3.5–19	5.3	8.3	SF Bay	2017	Present study
	12	7.4–300	24	48	SF Bay	2013	Sutton et al., 2019
	25	nd–2.4	0.61	0.70	Greenland & Norwegian Seas	2014	Li et al., 2017
	9	nd–0.39	nd	0.81	Fram Straight (deep water)	2014-2015	McDonough et al., 2018 ^a
	6	0.82–2	1.3	1.4	Canadian Arctic	2015-2016	McDonough et al., 2018 ^a
	7	11–12		11	Maizuru Bay	2009	Harino et al., 2014
	5			1.5	Lake Erie	2012	Venier et al., 2014 ^c
	5			0.28	Lake Huron	2012	Venier et al., 2014 ^c
	5			0.38	Lake Michigan	2012	Venier et al., 2014 ^c
	3	nd	nd	nd	Long Island, NY	2017	Kim and Kannan, 2018
TCPP	22	15–150	42	65	SF Bay	2017	Present study
	12	46–2900	140	390	SF Bay	2013	Sutton et al., 2019
	25	2.8–5.8	1.6	1.8	Greenland & Norwegian Seas	2014	Li et al., 2017
	9	nd–5.4x10 ⁻²	4.0x10 ⁻²	3.6x10 ⁻²	Fram Straight (deep water)	2014-2015	McDonough et al., 2018 ^a
	6	0.93–5.7	2.9	3.10	Canadian Arctic	2015-2016	McDonough et al., 2018 ^a
	5			12	Lake Erie	2012	Venier et al., 2014 ^c
	5			2.6	Lake Huron	2012	Venier et al., 2014 ^c
	5			3.0	Lake Michigan	2012	Venier et al., 2014 ^c
	18	3–28			German Bight	2010	Bollmann et al., 2012
	56	40–250	65	93	Elbe River Estuary	2010	Bollmann et al., 2012
TDCPP	3	26–36		32	Long Island, NY	2017	Kim and Kannan, 2018
	20	nd–42		nd	Southern California	2006-2007	Vidal-Dorsch et al., 2012
	22	2.8–23	6.2	9.0	SF Bay	2017	Present study
	12	14–450	33	73	SF Bay	2013	Sutton et al., 2019
	25	nd–4.3x10 ⁻²	4x10 ⁻³	7x10 ⁻³	Greenland & Norwegian Seas	2014	Li et al., 2017
	9	1.6x10 ⁻³ –7.1x10 ⁻³	2.8x10 ⁻³	3.5x10 ⁻³	Fram Straight (deep water)	2014-2015	McDonough et al., 2018 ^a
	6	nd–0.96	0.76	0.62	Canadian Arctic	2015-2016	McDonough et al., 2018 ^a
	7	12–25		18	Maizuru Bay	2009	Harino et al., 2014
	5			4.0	Lake Erie	2012	Venier et al., 2014 ^c
	5			0.87	Lake Huron	2012	Venier et al., 2014 ^c
	5			1.1	Lake Michigan	2012	Venier et al., 2014 ^c
	3	8.9–25		16	Long Island, NY	2017	Kim and Kannan, 2018

Compound	n	Range	Median	Mean	Location ^b	Year	Reference
TDBPP	22	nd	nd	nd	SF Bay	2017	Present study
	12	nd	nd	nd	SF Bay	2013	Sutton et al., 2019
	9	nd	nd	nd	Fram Straight (deep water)	2014-2015	McDonough et al., 2018 ^a
	6	nd–6.7x10 ⁻³	nd	1.7x10 ⁻³	Canadian Arctic	2015-2016	McDonough et al., 2018 ^a
	3	nd	nd	nd	Long Island, NY	2017	Kim and Kannan, 2018
RBDPP	22	nd	nd	nd	SF Bay	2017	Present study
	3	nd	nd	nd	Long Island, NY	2017	Kim and Kannan, 2018
T2iPPP	22	nd	nd	nd	SF Bay	2017	Present study
	12	0.4–0.5	nd	0.08	SF Bay	2013	Sutton et al., 2019
TCrP	22	nd	nd	nd	SF Bay	2017	Present study
	12	<0.4–33	nd	8.1	SF Bay	2013	Sutton et al., 2019
	9	nd–3x10 ⁻⁵	nd	3x10 ⁻⁶	Fram Straight (deep water)	2014-2015	McDonough et al., 2018 ^a
	7	6–49		13	Maizuru Bay	2009	Harino et al., 2014
	3	nd–0.13		0.04	Long Island, NY	2017	Kim and Kannan, 2018
EHDPP	22	<0.4–8.1	nd	1.2	SF Bay	2017	Present study
	12	<0.4–2.3	nd	0.19	SF Bay	2013	Sutton et al., 2019
	9	6.0x10 ⁻⁵ –3.3x10 ⁻⁴	2.4x10 ⁻⁴	2.1x10 ⁻⁴	Fram Straight (deep water)	2014-2015	McDonough et al., 2018 ^a
	6	nd–0.63	0.28	0.29	Canadian Arctic	2015-2016	McDonough et al., 2018 ^a
	3	nd	nd	nd	Long Island, NY	2017	Kim and Kannan, 2018
TPhP	22	<0.4–63	9.5	15	SF Bay	2017	Present study
	12	41–360	90	130	SF Bay	2013	Sutton et al., 2019
	25	nd	nd	nd	Greenland & Norwegian Seas	2014	Li et al., 2017
	9	nd–1.2x10 ⁻³	7.0x10 ⁻⁴	6.0x10 ⁻⁴	Fram Straight (deep water)	2014-2015	McDonough et al., 2018 ^a
	6	0.41–0.79	0.54	0.57	Canadian Arctic	2015-2016	McDonough et al., 2018 ^a
	7	6–14		9	Maizuru Bay	2009	Harino et al., 2014
	5			1.2	Lake Erie	2012	Venier et al., 2014 ^c
	5			0.13	Lake Huron	2012	Venier et al., 2014 ^c
	5			0.13	Lake Michigan	2012	Venier et al., 2014 ^c
	3	nd–1.6		0.53	Long Island, NY	2017	Kim and Kannan, 2018
TBEP	22	0.4–63	7.6	15	SF Bay	2017	Present study
	12	24–1000	69	190	SF Bay	2013	Sutton et al., 2019
	7	26–62		37	Maizuru Bay	2009	Harino et al., 2014
	5			75	Lake Erie	2012	Venier et al., 2014 ^c
	5			5.2	Lake Huron	2012	Venier et al., 2014 ^c
	5			2.6	Lake Michigan	2012	Venier et al., 2014 ^c
	18	nd–6			German Bight	2010	Bollmann et al., 2012
	56	nd–80	38	46	Elbe River Estuary	2010	Bollmann et al., 2012

Compound	n	Range	Median	Mean	Location ^b	Year	Reference
TEHP	3	nd–7.7		3.3	Long Island, NY	2017	Kim and Kannan, 2018
	22	0.1–8.4	2.1	2.9	SF Bay	2017	Present study
	12	<0.4–11	nd	1.7	SF Bay	2013	Sutton et al., 2019
	25	nd–6.9x10 ⁻²	nd	6x10 ⁻³	Greenland & Norwegian Seas	2014	Li et al., 2017
	9	nd–1.5x10 ⁻³	5.9x10 ⁻⁴	6.1x10 ⁻⁴	Fram Straight (deep water)	2014-2015	McDonough et al., 2018 ^a
	6	nd–4.7x10 ⁻²	2.2x10 ⁻²	2.3x10 ⁻²	Canadian Arctic	2015-2016	McDonough et al., 2018 ^a
TiBP	3	nd	nd	nd	Long Island, NY	2017	Kim and Kannan, 2018
	22	0.67–2.6	1.0	1.3	SF Bay	2017	Present study
	25	3.9x10 ⁻³ –0.64	0.23	0.26	Greenland & Norwegian Seas	2014	Li et al., 2017
	18	0.5–5			German Bight	2010	Bollmann et al., 2012
	56	10–50	26	25	Elbe River Estuary	2010	Bollmann et al., 2012
TPrP	22	nd	nd	nd	SF Bay	2017	Present study
	12	nd	nd	nd	SF Bay	2013	Sutton et al., 2019
TnBP	3	nd	nd	nd	Long Island, NY	2017	Kim and Kannan, 2018
	22	2.7–15	7.0	7.5	SF Bay	2017	Present study
	12	7.8–43	13	17	SF Bay	2013	Sutton et al., 2019
	25	nd–0.41	0.11	0.12	Greenland & Norwegian Seas	2014	Li et al., 2017
	9	nd–6.3x10 ⁻²	nd	1.0x10 ⁻²	Fram Straight (deep water)	2014-2015	McDonough et al., 2018 ^a
	6	0.17–0.63	0.45	0.43	Canadian Arctic	2015-2016	McDonough et al., 2018 ^a
	7	7–10		8	Maizuru Bay	2009	Harino et al., 2014
	5			2.2	Lake Erie	2012	Venier et al., 2014 ^c
	5			0.27	Lake Huron	2012	Venier et al., 2014 ^c
TEP	5			0.61	Lake Michigan	2012	Venier et al., 2014 ^c
	22	4.2–21	6.7	9.7	SF Bay	2017	Present study
	12	<0.2–3.2	nd	0.36	SF Bay	2013	Sutton et al., 2019
	7	3–5		4	Maizuru Bay	2009	Harino et al., 2014
	18	0.7–7			German Bight	2010	Bollmann et al., 2012
	56	10–180	20	26	Elbe River Estuary	2010	Bollmann et al., 2012
	3	0.76–1.8		1.4	Long Island, NY	2017	Kim and Kannan, 2018
ΣOPEs	22	35–290	100	130	SF Bay	2017	Present study
	12	170–5100	460	860	SF Bay	2013	Sutton et al., 2019
	25	0.35–8.4	2.6	8.3	Greenland & Norwegian Seas	2014	Li et al., 2017
	5			96	Lake Erie	2012	Venier et al., 2014 ^c
	5			7.3	Lake Huron	2012	Venier et al., 2014 ^c
	5			9.3	Lake Michigan	2012	Venier et al., 2014 ^c

Compound	n	Range	Median	Mean	Location ^b	Year	Reference
	18	5–50			German Bight	2010	Bollmann et al., 2012
	56	85-510	210	226	Elbe River Estuary	2010	Bollmann et al., 2012
	3	40–61		54	Long Island, NY	2017	Kim and Kannan, 2018

^a Concentrations were derived using passive polyethylene samplers

^b All samples were collected near the surface unless otherwise noticed

^c Data are from a mix of deep (> 50 m) and shallow (< 20 m) stations

3.2 Bisphenols

Two of the 16 bisphenols, BPA and BPS, were detected in both the dissolved and particulate phase (see Table S4, S5, and S6 for site-by-site dissolved, particulate, and total concentrations, respectively). Bisphenol A was detected at 91% (77% dissolved, 63% particulate) of the 22 sites. Bisphenol S was detected at 41% (36% dissolved, 9% particulate) of the 22 sites. Summed total concentrations of BPA and BPS across all sites ranged from <MDL–130 ng/L with a median of 17 ng/L.

Total concentrations of BPA (<0.7–35 ng/L; median 10 ng/L; mean 12 ng/L) were relatively consistent across the Bay (RSD 86%) and typically higher than BPS concentrations (<1–120 ng/L; median nd; mean 8.8 ng/L; RSD 124%) (Table 3, Figure 2). However, BPS at one site in San Pablo Bay (120 ng/L) exceeded the maximum level of BPA detected in the Bay. High spatial variability commonly associated with open-Bay water sampling and/or discrete pollution sources such as trash or leachate from paint on marine vessels, are possible explanations for the high concentration of BPS at this site.

It is worth noting that BPA is imported into and manufactured in the United States at levels approximately 1000 times greater than BPS (USEPA, 2016), but BPS was found at somewhat comparable levels, where detected. This is likely due to the longer persistence of BPS in aquatic environments relative to BPA (Danzl et al., 2009).

Table 3

Bisphenols in San Francisco Bay water samples. Values represent total water levels. The median value < MDL is labeled “nd” (non-detect). Data censored due to field blank contamination are labeled “dc.”

Bisphenol	Log K _{ow} ^b	PNEC (µg/L)	2017 (n = 22) ng/L ^a				
			% Detect	Range	Median	Mean	% Dissolved
Bisphenol A	3.4	60ng/L ^c , 150ng/L ^d	91	<0.7–35	10	12	17
Bisphenol AF	4.5		0	<0.8	-	-	
Bisphenol AP	4.9		0	<0.7	-	-	
Bisphenol B	4.1		0	<0.8	-	-	
Bisphenol BP	6.1		0	<0.8	-	-	
Bisphenol C	4.7		0	<0.7	-	-	
Bisphenol C-dichloride	3.8		0	<0.9	-	-	
Bisphenol E	3.2		0	<0.8	-	-	
Bisphenol F	3.1		dc	dc	dc	dc	
Bisphenol G	6.6		0	<1	-	-	
Bisphenol M	6.3		0	<0.9	-	-	
Bisphenol P	6.3		0	<1	-	-	
Bisphenol PH	7.2		0	<0.7	-	-	
Bisphenol S ^a	1.2		41	<1–120	nd	8.8	99
Bisphenol TMC	6.3		0	<1.1	-	-	
Bisphenol Z	5		0	<1.4	-	-	
ΣBisphenols	-		-	0.0–130	17	22	

^a Values are considered semi-quantitative

^b Based on EPIWEB 4.1

^c Weight-of-evidence derived PNEC (Wright-Walters et al., 2011)

^d European Chemicals Agency PNEC (Bakker et al., 2016)

Bisphenol A was primarily detected in the particulate phase. Despite the Sacramento and San Joaquin River sites exhibiting the lowest observed TSS concentrations, at 9 mg/L and 12 mg/L (TSS range in study 9-132 mg/L), the two highest particulate concentrations of BPA, 2300 ng/g dw and 2100 ng/g dw, respectively, were measured at these locations. Concentrations of BPA on river site particles (on a gram dry weight [dw] basis) exceeded the particulate BPA median concentration (295 ng/g dw) by an order of magnitude. The only two detected values for particulate BPS occurred in Suisun Bay, at 38 ng/g dw and 13 ng/g dw, with associated TSS levels at 30 mg/L and 25 mg/L, respectively. High particulate concentrations of BPA and BPS observed in North Bay and river sites, despite low TSS levels, may suggest the Sacramento–San Joaquin Delta is a potential pathway by which particulate bisphenols enter the Bay.

Relatively high levels of BPA were detected in Lower South Bay. Bisphenol S was also commonly detected in this subembayment. As with OPEs, widespread use of these compounds in consumer products has likely led to higher occurrences in both WWTP effluent and stormwater, which, combined with increased residence time and reduced mixing with marine or freshwater flow in Lower South Bay, translates to higher concentrations in this region.

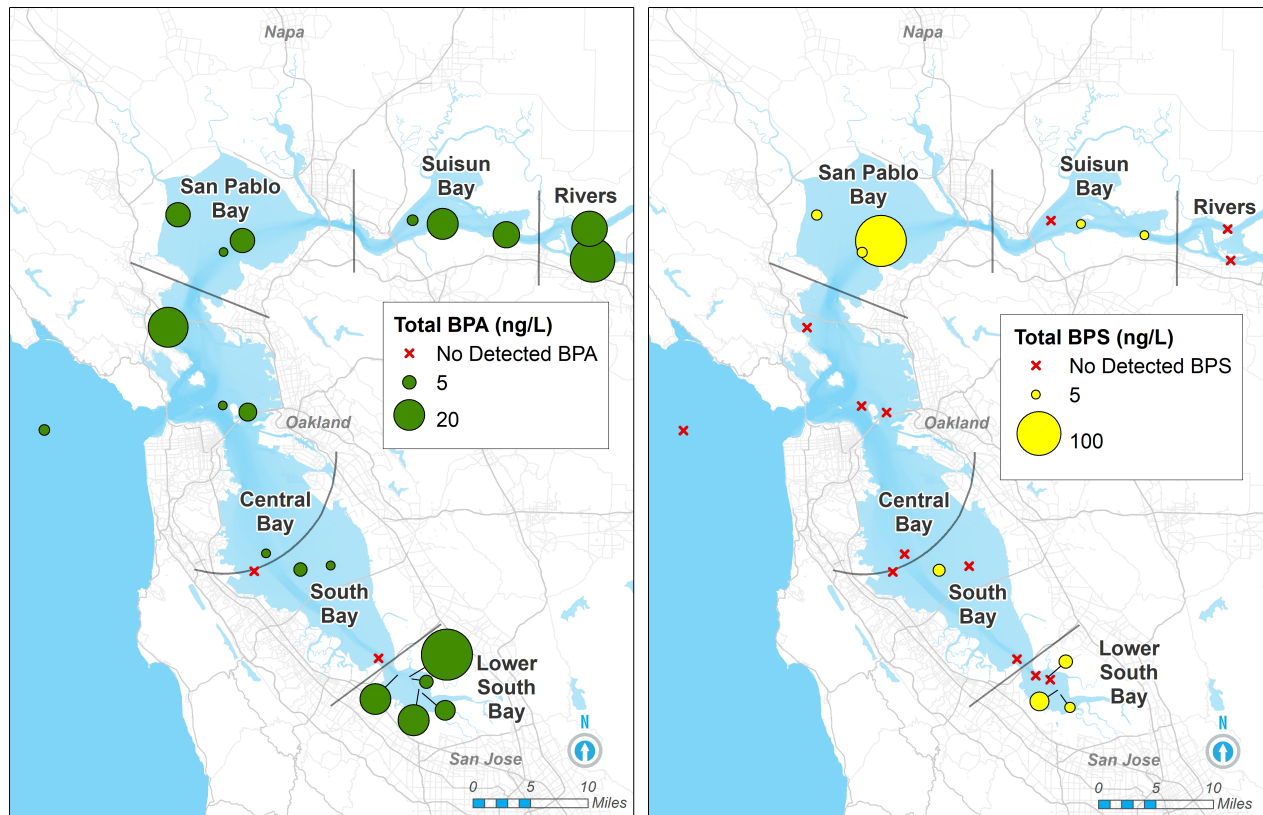


Figure 3. Concentrations of total BPA (left) and total BPS (right).

The literature review herein determined environmental monitoring data for other bisphenols were scarce (Table 4) and only BPA was monitored in other estuaries. Levels of BPA in San Francisco Bay were within the broad range of concentrations observed in several estuarine and marine environments, a range that varies by four to five orders of magnitude (Table 4). A review of 32 North American studies from 1996-2004 found the 95th percentile for BPA to be 24 ng/L in marine waters (Staples et al., 2018). Several wastewater treatment plant studies (Sosiak et al.,

2005; Jackson and Sutton, 2008; Jonkers et al., 2010; Vidal-Dorsch et al., 2012; Sánchez-Avila et al., 2013; Xu et al., 2014; Meador et al., 2016) revealed WWTP effluent to be a considerable source of BPA to the environment. Based on data from other regions and limited data from the Bay Area, stormwater could also be a significant pathway (Boyd et al., 2004; Fairbairn et al., 2018).

One review of BPS in the environment found BPS to be globally ubiquitous in the environment and at concentrations rivaling those of BPA in water samples (Wu et al., 2018). While BPA is still the most commonly monitored bisphenol, BPS, BPF, and bisphenol AF (BPAF) have also been measured and, in some cases, have surpassed levels of BPA (Chen et al., 2016).

Table 4

Comparison of BPA concentrations from San Francisco Bay to levels in other freshwater estuaries and marine areas (ng/L). Values represent total water levels. Medians < MDL are labeled “nd” (non-detect).

n	Range	Median	Mean	Location	Type	Year	Reference
22	<0.7–35	10	12	SF Bay	Estuary	2017	Present study
5	<4200	-	-	SF Bay	Estuary	2009-2010	Klosterhaus et al., 2013
1	190			Abbotts Lagoon, CA	Marine	1999	Kratzer et al., 2006
20	<4.1	<4.1		Napa and Sacramento Rivers, CA	River Delta	2007	Lavado et al., 2009
20	<50			Southern California	Marine	2006-2007	Vidal-Dorsch et al., 2012
6	<9.4			Puget Sound, WA	Estuary	2003-2004	Jack and Lester, 2007
66	nd–23	4		Puget Sound, WA	Estuary	2010	Staples et al., 2018
3	2.8–4.3			Puget Sound, WA	Estuary	2013-2014	Meador et al., 2016
7	1.5–57	19	21	Lake Pontchartrain, LA	Estuary	2003	Boyd et al., 2004
5	1.4–57	22	26	Lake Pontchartrain, LA	Estuary	2008	Wang et al., 2012
32		1.1		North America	Marine	1996-2014	Staples et al., 2018
22	nd–8	2		Barkley Sound, Canada	Estuary	2010	Staples et al., 2018
17	nd–2.6	0.31		Halifax Harbour, Canada	Marine	2002-2005	Robinson et al., 2009
96	nd–880	nd	39	Mondego River, Portugal	Estuary	2005-2006	Ribeiro et al., 2009a
52	nd–250	nd		Sado River, Portugal	Estuary	2005-2006	Ribeiro et al., 2009b
72	<80–11000	1100	2500	Douro River, Portugal	Estuary	2005-2006	Ribeiro et al., 2009c
32	8.5–190	51	68	Mondego River, Portugal	Estuary	2010	Rocha et al., 2014b
10	10–68	41	39	Gulf of Gdańsk, Poland	Marine	2011	Staniszewska et al., 2014
30	1.9–36	12	14	Lima River, Portugal	Marine	2011	Rocha et al., 2014a
28	<1.1–17	<1.1	0.7	Portugal	Estuary	2006	Jonkers et al., 2010
20	<1.1–13	0.7	2.1	Portugal	Marine	2006	Jonkers et al., 2010
9	5–770			Spain	Estuary	2009	Sánchez-Avila et al., 2013
12	1.4–33			Spain	Marine	2009	Sánchez-Avila et al., 2013
19	nd–250	nd	21	North Sea, Germany	Marine	1998-1999	Heemken et al., 2001
22	nd–150	5.9		Venice Lagoon, Italy	Marine	2001-2002	Pojana et al., 2004 and 2007
22	11–52		25	Thermaikos Gulf, Greece	Marine	2005-2006	Arditsoglou and Voutsas, 2012
10	<3–16	7	7.3	Adriatic Sea, Slovenia	Marine	2015	Cerkvenik-Flajs et al., 2018
96	<32–320	<32		Netherlands	Marine	1999	Belfroid et al., 2002
456		7		Europe	Marine	1996-2014	Staples et al., 2018
5	7.6–75	11	26	Hangzhou Bay, China	Marine	2012	Yang et al., 2014
36	2–93			Jiaozhou Bay, China	Marine	2005	Fu et al., 2007
72	14–210	53	92	Cape D'Aguilar Marine Reserve	Marine	2012	Xu et al., 2015

n	Range	Median	Mean	Location	Type	Year	Reference
3	11–410		65	Cape D'Aguilar Marine Reserve	Marine (wet season)	2012	Xu et al., 2014
3	25–240		70	Cape D'Aguilar Marine Reserve	Marine (dry season)	2012	Xu et al., 2014
13	<5–58	<5	11	Japan	Estuary	2001–2002	Kawahata et al., 2004
28	<6.3–2500	40	360	Singapore	Marine	2000	Basheer et al., 2004

3.3 Environmental implications

3.3.1 Ecological impacts: Comparison to toxicity thresholds

When evaluating the concerns associated with emerging contaminants in the Bay, the RMP uses a risk-based approach that begins with a comparison of the levels measured in Bay matrices to available toxicity thresholds. In 2017, total concentrations of TDCPP at three sites in Lower South Bay met or exceeded the 20 ng/L PNEC with concentrations of 20 ng/L, 22 ng/L and 23 ng/L (Table S6). Peak concentrations for isodecyl diphenyl phosphate (IDDPP) and TPhP reached 13% and 17% of their associated PNECs, respectively. There are no available PNECs for TCEP (3.5–19 ng/L), TEHP (0.1–8.4 ng/L), EHDPP (<0.4–8.1 ng/L), and other OPEs (BPA-BDPP, 2iPPDPP, and BPDPP) with maximum concentrations <1 ng/L. All remaining OPEs were either detected at levels significantly below their PNECs or were not detected in any samples. Previous monitoring of water samples collected in 2013 found both TDCPP and TPhP reaching levels greater than available PNECs (Table 1).

Though numerous toxicity studies have been conducted for BPA, conflicting data and non-monotonic dose-response curves have led to the generation of multiple PNECs in the literature. A prime example, the European Chemicals Agency (Bakker et al., 2016) was criticized for questionable study selection in determination of a BPA marine PNEC of 150 ng/L because it excluded a toxicity evaluation of *Marisa cornuarietis*, the most sensitive species (Oehlmann et al., 2008). In contrast, Wright-Walters et al. (2011) used a weight of evidence approach to evaluate 61 BPA toxicity studies involving 24 marine and freshwater organisms to derive a marine PNEC of 60 ng/L. Total concentrations of BPA in the Bay (<0.7–35 ng/L) were in the range of the more protective Wright-Walters et al. BPA PNEC of 60 ng/L (Table 3). There is no available PNEC for BPS or any of the other 14 bisphenols analyzed in this study. Bisphenol S was detected with total concentrations as high as 120 ng/L.

While only a few OPE and bisphenol compounds were detected at levels that may warrant concern with respect to their individual toxicity thresholds, a total of 15 OPEs and 2 bisphenols were detected in Bay water. Multiple members of each of these classes of compounds are linked to estrogenic effects, as well as a wide variety of additional toxicity endpoints. These effects have been demonstrated in cell assays (for bisphenols: Héliers-Toussaint et al., 2014; Rosenmai et al., 2014; for OPEs: Kojima et al., 2013; Liu et al., 2013; Suzuki et al., 2013), whole organisms (for bisphenols: Aluru et al., 2010; Naderi et al., 2014; for OPEs: Liu et al., 2013; Wang et al., 2015; Zhu et al., 2015), and humans (for bisphenols: Chen et al., 2016; Björnsdotter et al., 2017; for OPEs: van der Veen and de Boer, 2012).

In addition to toxicity studies that evaluate individual compounds, importance should be placed on developing an understanding of the cumulative impacts caused by exposure to mixtures of multiple chemicals. Given our incomplete current understanding of toxic effects caused by contaminants in isolation, as well as by the cocktail of OPEs, bisphenols, and other EDCs present in Bay water, evaluating their impacts in isolation is clearly inadequate.

Until significant toxicological advances are made to elucidate the impacts of exposure to chemical mixtures, an extra degree of precaution is warranted when evaluating the risks posed by classes such as OPEs and bisphenols due to uncertainty. Key sources of uncertainty include varying potencies of members of a chemical class, and synergistic and antagonistic interactions among compounds. Additionally, the OPEs and bisphenols monitored herein are only a small

fraction of contaminants present in the environment, and unknown interactions with environmental stressors cannot be ignored. A simple sum of risks presented by individual compounds is unlikely to be an accurate depiction of the potential impacts of environmental exposure to mixtures but at least represents a step toward understanding their potential cumulative impacts.

3.3.2 Risk evaluation for San Francisco Bay

The RMP assigns emerging contaminants monitored in Bay water, sediment, and aquatic life to tiers in the Program's Tiered, Risk-based Framework (Lin et al., 2018). The degree of concern associated with a particular chemical class guides RMP monitoring activities and water-quality management actions. The criteria listed below are used for placement in each tier:

- High Concern – Bay occurrence data suggest a high probability of a moderate- or high-level effect on Bay wildlife;
- Moderate Concern – Bay occurrence data suggest a high probability of a low-level effect on Bay wildlife;
- Low Concern – Bay occurrence data suggest a high probability of minimal effect on Bay wildlife;
- Possible Concern – Uncertainty in toxicity thresholds suggests uncertainty in the level of effect on Bay wildlife. If Bay occurrence data exist, they may be constrained by analytical methods with insufficient sensitivity.

Secondary factors that may impact tier assignments include trends in use of the chemical or trends in Bay concentrations, as well as the potential for cumulative impacts.

3.3.2.1 OPEs

Previously, OPEs had been classified as a Possible Concern for the San Francisco Bay within the RMP Tiered, Risk-based Framework (Lin et al., 2018). Previous water, sediment, tissue, and pathways monitoring for OPEs revealed the presence of OPEs in the Bay at levels that suggested particular concern was warranted for TDCPP and TPhP (Sutton et al., 2019), due to presence at levels greater than European Chemicals Agency PNECs (ECHA, 2019a–2019k).

In the present study, TDCPP was detected at or above the marine PNEC of 20 ng/L in Bay water samples collected in 2017. Additionally, 14 other OPEs were detected. Widespread and increasing production and use of OPEs, presence in the Bay at concentrations above a PNEC, and concerns around cumulative toxic effects indicate OPEs merit classification as a Moderate Concern for the Bay.

3.3.2.2 Bisphenols

Previously, bisphenols had been classified as a Possible Concern for the San Francisco Bay within the RMP Tiered, Risk-based Framework, largely because prior analysis of BPA used an insufficiently sensitive screening method. Analysis of Bay water samples collected in 2017 revealed the presence of both BPA and BPS at levels similar to the Wright-Walter et al. (2011) PNEC of 60 ng/L. Widespread and increasing production and use of bisphenols, presence in the Bay at concentrations in range of a PNEC, observed increases in bisphenols in environmental matrices outside of the Bay (Xu et al., 2015), and concerns around cumulative toxic effects indicate bisphenols merit classification as a Moderate Concern for the Bay.

4. Conclusions and next steps

Data presented in the current study, along with past monitoring of OPEs (Sutton et al., 2019), are confirmation that aquatic life are exposed to an ever-evolving array of potentially harmful chemicals. In addition to specific concerns about TDCPP and BPA due to concentrations near or exceeding protective ecotoxicity thresholds, environmental risk from OPEs and bisphenols is best evaluated by considering these as classes of compounds, factoring in their co-occurrence in environmental matrices, and their potential to produce cumulative impacts in exposed organisms. As OPE and bisphenol production continues to increase and evolve in response to market demands and shifting regulations, so will the importance of understanding the associated environmental presence and impacts of these classes of emerging contaminants of Moderate Concern for the Bay.

Based on the available science, an appropriate monitoring strategy for both contaminant classes includes regular monitoring in Bay water to track temporal trends of individual compounds due to shifts in manufacturing and use. Regular monitoring can also provide an increased understanding of the spatial distribution of these contaminants within the Bay.

In addition, bisphenols should be monitored in Bay Area wastewater and stormwater to improve our understanding of sources and pathways. Data on pathways is particularly limited for the broad array of bisphenols used as replacements for BPA. Organophosphate esters are already target analytes in an ongoing, multi-year RMP study of emerging contaminants stormwater in order to fill data gaps previously identified in the RMP's synthesis and strategy on alternative flame retardants (Lin and Sutton, 2018).

Screening of bisphenols in sediment and, possibly, biota, will allow us to better assess the presence and fate of a broader array of bisphenols in the Bay ecosystem. Though the tendency of bisphenols to partition to sediment is not well characterized (Choi and Lee, 2017), BPA, BPF, and BPS have been detected in sediment samples around the U.S. (Liao et al., 2012). Determination of bisphenols in Bay sediment could help provide a baseline against which future monitoring may be compared.

Bisphenol A has been globally detected in marine (Xu et al., 2015; Cerkvenik-Flajs et al., 2018) and estuarine (Meador et al., 2016) wildlife tissues. In a comparison of water and tissue concentrations of nine bisphenol compounds in Lake Taihu, Wang et al. (2017) found the potential for bisphenol compounds to bioaccumulate was significantly correlated with their octanol-water partitioning coefficient (LogK_{ow}). Monitoring of both sediment and biota could provide information related to use and persistence of specific compounds. This can be particularly important should manufacturers continue to make potentially regrettable substitutions that drive use of data-poor contaminants within each of these chemical classes.

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