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Executive Summary

Bisphenols are a class of synthetic, mobile, endocrine-disrupting chemicals. Bisphenol A (BPA), the most well-studied bisphenol, is produced and used in vast quantities worldwide—especially in polycarbonate plastics and as a polymer additive. Recently, some manufacturers have begun using alternative bisphenol compounds, such as bisphenol F (BPF) and bisphenol S (BPS). These uses of bisphenols have led to widespread bisphenol detections in the environment and wildlife. The present study examined wastewater effluent in the San Francisco Bay Area and San Francisco Bay sediment samples for 17 bisphenols. The effluent samples were compared to available stormwater runoff data to better understand bisphenol transport, fate, and potential risks to wildlife.

Five of 17 bisphenols were detected in effluent from six wastewater treatment plants (WWTPs) that comprise about 70% of the effluent discharged into the Bay. BPA, BPF, and BPS were predominantly detected (≥83% of samples), with median and maximum concentrations of 41 and 62 ng/L, 30 and 128 ng/L, and 24 and 55 ng/L, respectively. The sum of bisphenols for all WWTP effluent samples showed median and maximum concentrations of 96 and 246 ng/L, and estimated per capita loads with median and maximum concentration of 0.024 and 0.054 mg per capita per day. All data were normally distributed within two standard deviations of the mean, indicating no unusual or outlier detections. A previous study conducted on effluent in the Bay in 2006 at a single WWTP found BPA at levels above 300 ng/L, suggesting a notable decrease in BPA concentrations over this time span.

For comparison with wastewater, an analysis of samples from 18 stormwater sites found four bisphenols, with BPA and BPF comprising the majority of detections, exhibiting median and maximum concentrations of 30 and 741 ng/L, and 8.6 and 96 ng/L, respectively. This indicates both wastewater effluent and stormwater runoff are important pathways of bisphenols to the Bay. These results also highlighted the presence of BPF and BPS, consistent with higher recent use as replacements for BPA. Concentrations of bisphenols were generally consistent with similar studies globally for wastewater effluent and stormwater runoff.

Due to the significant influence of wastewater and stormwater in the South and Lower South Bay, margin sediment samples from these areas were examined. BPA and BPF were detected at all 12 sites, with median and maximum concentrations of 7.6 and 19 ng/g dw and 3.3 and 14 ng/g dw. Though no individual concentrations of BPA and BPF were above the best available sediment toxicity threshold of 25 ng/g dw, summed concentrations for each site in an area with significant influence of wastewater and stormwater surpassed it (31 and 33 ng/g). Concentrations of bisphenols in Bay sediment were generally similar to other estuarine and marine environments.

Across all matrices, concentrations of BPA and BPF were strongly correlated, suggesting similar sources, pathways, and/or fate. Further, BPA and BPF displayed comparable median concentrations in multiple matrices. This is interesting to note as prior information indicates BPA was imported and manufactured in significantly greater

quantities than BPF in the US, suggesting recent growth in use of BPF as a BPA alternative.

Results from this study support the continued classification of bisphenols as Moderate Concern for the Bay under the tiered risk-based framework developed by the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP). Concentrations of bisphenols in sediment remain within range of ecological toxicity thresholds, indicating potential risks to Bay biota. Continued monitoring of Bay water and sediment is recommended to monitor potential BPA alternatives and track temporal trends due to shifts in production and use. In addition, periodic screening studies in wastewater and stormwater are suggested to detect emerging bisphenols of concern early, as these pathways are generally the most concentrated. Expansion of screening studies to include Bay biota would further the understanding of fate and potential impacts of bisphenols in the Bay.

1. Introduction

Bisphenols are environmentally mobile, synthetic organic chemicals with broad applications in commerce. Their chemical structures consist of two phenols connected by a range of functional groups; associated properties including thermal stability, non-reactivity, and recalcitrance. The vast applications of bisphenol A (BPA), the most well-known and widely used member of this class, have resulted in its classification as a high production volume chemical worldwide, with aggregate import and production in the US in the hundreds of thousands of metric tons in 2019 (US EPA, 2020). Bisphenols, especially BPA, are primary components in polycarbonate plastics, which are used in a diverse array of products including water pipes, water bottles, toys, medical devices, food and drink packaging, and electronics (Chen et al., 2016; Hahladakis et al., 2022). Bisphenols are also used in the epoxy resin linings that are found in metal-based food and beverage cans, as well as in the production of flame retardants (Chen et al., 2016; Liu et al., 2021; Rosenfeld & Feng, 2011). Further notable uses include as reactants in thermal paper products, and additives in tires, textiles, and paints (Björnsdotter et al., 2017; Capolupo et al., 2018; Xue et al., 2017).

Bisphenols are known endocrine disrupting compounds, mimicking estrogen and causing a wide array of negative health effects in humans and wildlife (Catenza et al., 2021; Liu et al., 2021; Wang et al., 2018). Human health concerns led to bans of BPA in key products, with several states, including California, and the federal government implementing restrictions since 2009. These bans have predominantly targeted plastic products with food contact including baby bottles, sippy cups, and sports bottles (NCSL, 2017). As the first bans on BPA were coming into place in the US, industry overall began to substitute BPA with structurally similar bisphenols. Production of alternatives such as bisphenol F (BPF) and bisphenol S (BPS) has grown significantly and is expected to continue to increase (Catenza et al., 2021; Rochester & Bolden, 2015). BPF and BPS are the most common alternatives used in consumer products, including personal care and food contact products (Chen et al., 2016; Rochester and Bolden, 2015).

Less is known about the toxicity of BPA alternatives, though the similarities in structure and functionality have indicated similar toxic effects with the same, or even greater, potencies than BPA (Chen et al., 2016; Mu et al., 2018; Rochester and Bolden, 2015). A review conducted by Biomonitoring California in 2012 identified several of the replacements as likely to be toxic or very toxic to aquatic organisms, according to US EPA criteria (OEHHA, 2012).

Due to their high production and use and chemical properties, BPA and several alternatives are consistently entering the environment and already have been internationally observed in air, sediment, soil, stormwater, surface water, and wildlife (Catenza et al., 2021; Chen et al., 2016; Corrales et al., 2015; Gewurtz et al., 2021; Hahladakis et al., 2022; Liu et al., 2021; Q. Wang et al., 2017; Wu et al., 2018). As a class, bisphenols are expected to mimic many of the properties of well-studied BPA including its relatively high mobility and moderate water-solubility. Some bisphenols are more hydrophobic and have greater likelihood to partition into sediment, with moderate

potential for persistence and bioaccumulation in biota—though significant amounts can be metabolized (Corrales et al., 2015; Liu et al., 2021; Q. Wang et al., 2017). More study is needed to understand persistence and fate of bisphenol analogues beyond BPA.

Within San Francisco Bay, limited data exist for bisphenols. In 2006, three effluent samples from an Oakland wastewater treatment plant (WWTP) were analyzed using a screening method with a relatively high detection limit (250 ng/L); two samples contained notable levels of BPA at 310 and 380 ng/L (Jackson & Sutton, 2008). A Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) study of Bay margin sediment in 2017 detected BPA at one out of 12 sites, likely due to the relatively high method detection limits associated with the broad screening method used (Heberger et al., 2020). Additionally, the RMP analyzed bisphenols in Bay surface water in 2017 using a more sensitive analytical method (Shimabuku et al., 2022). BPA and BPS were the only two quantified out of 16 bisphenols; BPF was also observed, though detection in a field blank limited quantification. Total water concentrations of BPA (median: 10 ng/L; max: 35 ng/L) and bisphenol S (median: <1 ng/L; max: 35 ng/L) in Bay surface water samples were near protective thresholds for aquatic biota for BPA. These findings led to the classification of bisphenols as contaminants of Moderate Concern in the Bay according to the RMP tiered risk-based framework for emerging contaminants (Sutton et al., 2017). However, ambient water monitoring alone may not provide a comprehensive screening for the presence of various bisphenols in the Bay ecosystem.

To advance understanding of the transport and fate of bisphenols in San Francisco Bay, targeted monitoring of 17 bisphenols was conducted in wastewater effluent and archived margin sediment samples. Effluent concentrations were also compared to available concentrations in urban stormwater runoff from an ongoing, multi-year RMP screening study, to assess the relative importance of these pathways. Observed concentrations in all matrices were compared to previous studies in the Bay as well as to levels reported in other estuarine and marine environments. Contaminant concentrations were compared to ecotoxicity thresholds to further inform the classification of bisphenols within the RMP tiered, risk-based framework for emerging contaminants (Sutton et al., 2017). The results provided a basis to establish a strategy for future monitoring in the Bay to inform management decisions and actions.

2. Methods

2.1. Study Design and Sample Collection

Effluent samples were collected in August and September 2020 from six wastewater facilities in San Francisco Bay: Central Contra Costa Sanitary District (CCCSD), East Bay Dischargers Authority (EBDA), East Bay Municipal Utility District (EBMUD), Palo Alto Wastewater Treatment (PA), San Francisco Public Utilities Commision Southeast Treatment Plant (SEP) and San Jose-Santa Clara Regional Wastewater Facility (SJSC). The primary objective of this study is to analyze samples from the dominant effluent flows discharged into the Bay, with the six sampled facilities producing a combined ~70% of discharged wastewater effluent flows.

In addition, the chosen wastewater facilities represent a range of characteristics of Bay facilities including service population, treatment type, and geographic location, as described in Table 1 and Figure A1. SJ-SC, the largest effluent discharger in this study, and PA, the smallest discharger, are both located in the Lower South Bay, an important area to monitor due to the greater impact of wastewater effluent relative to other subembayments. Both facilities incorporate tertiary treatment into their treatment trains, though SJ-SC utilizes the unique feature of biological nutrient removal (BNR), while PA uses the more common trickling filter and activated sludge (AS) treatment. The second largest facility, EBDA, is unique in that it discharges effluent coming from several WWTPs including the City of San Leandro Water Pollution Control Plant, Oro Loma Sanitary District/Castro Valley Sanitary District Water Pollution Control Plant, City of Hayward Water Pollution Control Facility, Union Sanitary District Alvarado Treatment Plant, Dublin-San Ramon Sanitary District Wastewater Treatment Facility, and City of Livermore Water Reclamation Plant. This facility allows us to capture a greater portion of discharges into the Bay, but provides no information on the potential effect of different treatment types.

Table 1. Characteristics of wastewater facilities sampled for bisphenols. Noted flows are in million gallons per day (mgd).

Wastewater Facility	Estimated Population	Permitted ADWF (mgd)	2020/2021 ADWF (mgd)	Secondary Treatment Type	Tertiary Treatment (Yes/No)
CCCSD	500,000	53.8	31.4	AS	No
EBDA	1,000,000	107.8	60.2	AS, TF/AS, TF/Solids Contact	No
EBMUD	740,000	120	45.3	High Purity Oxygen	No
PA	236,000	39	17.1	TF/AS	Yes
SEP (SFPUC)	580,000	85.4	42.2	High Purity Oxygen	No
SJ-SC	1,400,000	167	76.1	AS/BNR	Yes

ADWF: Average Dry Water Flow, AS: Advanced Sludge, TF:Trickling Filter, BNR:Biological Nutrient Removal

On opposite sides of the Central Bay, EBMUD and SEP (SFPUC) are similarly sized dischargers (in the middle of the sampled group) using the same treatment type, high purity oxygen in AS treatment. Further, these facilities, along with SJ-SC, represent the flows from the largest urban centers in the Bay. CCCSD, the largest WWTP in the North Bay, discharges at levels slightly below those at these Central Bay facilities and uses the common AS treatment.

Each facility was sampled twice, on separate dates, during this time period. Samples were collected mid-week to avoid variations in product use that may occur during the weekend. At the same time, two field duplicates and two field blanks were collected at EBMUD and PA. Effluent samples were 24 hour composite samples transferred from an automatic sampler bottle to 1 L amber glass bottles, kept under 4°C, and extracted within 72 hours of collection.

Concentrations in effluent samples were compared to unpublished concentrations reported for an ongoing study of emerging contaminants in stormwater (Sutton et al., in preparation). A brief description of the methods associated with this study is here provided for completeness. Stormwater samples were collected at 15 sites in the Bay Area from fall 2018 to spring 2021 (water years 2019-2021; Figure A1). Some sites were sampled multiple times over the course of the multi-year study. A field blank was also collected as well as two additional reference site samples. Samples consisted of time-weighted composites collected during significant storm events, and were stored in 1 L amber glass bottles. Samples were refrigerated, shipped overnight for analysis, and extracted upon receipt.

Margin sediment samples (areas in the band below mean higher high water and above -1.0 ft mean lower low water) were collected from 12 sites between June and July 2017, as a part of the South Bay margins sediment cruise conducted by the RMP (Figure A1). The South and Lower South Bays and southern sloughs represent regions of the Bay that are strongly influenced by both wastewater effluent and urban stormwater runoff. Sediment samples were collected using a 0.1 m modified Van Veen sediment grab of the top 5 cm. A stainless steel scoop was used to remove surface sediment and directly fill 60 mL glass jars. Samples were subsequently frozen and stored at -18°C.

2.2. Laboratory Analysis

All samples were analyzed under supervision of Dr. Da Chen at Jinan University and Dr. Jia Liu at Southern Illinois University using methods described extensively in Shimabuku et al. (2022). Briefly, samples were extracted and subsequently analyzed using a highly sensitive liquid chromatography–electrospray ionization(-)-triple quadrupole mass spectrometry (LC-ESI(-)-QQQ-MS/MS) method for aqueous samples, and adapted for sediment samples. Determination of target analyte concentrations was generally based on calibration curves developed based on 5-7 standard solutions (0–50 ng/mL). For stormwater samples, both dissolved and particulate phase samples were analyzed. In contrast, effluent samples contained insufficient particulate material for analysis, so concentrations reported represent the dissolved phase.

The analysis included the following suite of 17 bisphenol compounds across all matrices: bisphenol A, A diglycidyl ether (BADGE), AF, AP, B, BP, C, C-dichloride, E, F, G, M, P, PH, S, TMC, and Z; method detection limits (MDLs) for each matrix are noted below in Table 2.

Table 2. Method detection limits (MDLs) for all bisphenols and matrices analyzed.

Analyte	Effluent MDLs (ng/L)	Stormwater MDLs (ng/L)	Sediment MDLs (ng/g)
Bisphenol A	0.7	0.2 - 0.4	1.1
Bisphenol A diglycidyl ether	1.2	0.4 - 0.8	3.0
Bisphenol AF	0.8	0.2 - 0.4	1.5
Bisphenol AP	0.7	0.2 - 0.4	1.5
Bisphenol B	0.8	0.2 - 0.4	1.4
Bisphenol BP	0.8	0.3 - 0.6	1.5
Bisphenol C	0.7	0.2 - 0.4	1.1
Bisphenol C-dichloride	0.9	0.3 - 0.6	1.8
Bisphenol E	0.8	0.3 - 0.6	1.2
Bisphenol F	0.8	0.2 - 0.4	1.2
Bisphenol G	1.0	0.3 - 0.6	1.6
Bisphenol M	0.9	0.3 - 0.6	1.6
Bisphenol P	1.0	0.3 - 0.6	2.0
Bisphenol PH	0.7	0.2 - 0.4	1.3
Bisphenol S	1.0	0.3 - 0.6	2.0
Bisphenol TMC	1.1	0.3 - 0.6	1.8
Bisphenol Z	1.4	0.4 - 0.8	2.7

2.3. Quality Control

Laboratory results were reviewed utilizing RMP QAPP methods (Yee et al., 2021), which indicated good method performance. Average recovery in five spiked samples of surrogate standards (d_6-BPA, d_{10}-BPF, and d_8-BPS) in blank water (blank spikes) deviated less than 35% for all samples and analytes (i.e., recovery was 65-135% of 10 ng/L spikes), except BPS, which had an average recovery of 63%. Therefore, for wastewater samples, all BPS field samples were flagged for recovery deviation with replicates having relative standard deviations (RSDs) within 20% or better. Additionally, two field replicate samples were analyzed with relative percent differences (RPDs) within 15% for all analytes where the average concentrations were at least three times the MDL. The analysis of a pair of field blanks as well as four filter blanks and six laboratory blanks showed no detection of bisphenols.

For stormwater, analysis of dissolved and particulate phases, respectively, of five blank spikes and matrix spikes also deviated less than 35%. Four laboratory replicates and a blind field duplicate had average RPDs within 15% for all analytes where the average concentrations were at least 3x the MDL. Analysis of field (two dissolved, one particulate) and laboratory blanks (four dissolved, three particulate) showed minor detections of some bisphenols, with all standard deviations below the respective MDLs. Results for field samples were blank corrected using the average blank value of the detected analyte. Stormwater MDLs were lower than wastewater MDLs due to reduced matrix interference and additional optimization of instrumental parameters.

Similar to other matrices, four analyzed sediment blank spikes fell within 35% difference for all analytes. The RSDs for replicate blank spikes were all within 8%. Analysis of four lab blanks did not find any bisphenols.

For all matrices, a variety of summary statistics were calculated for concentrations of field samples, with any non-detects treated as 0, a standard practice within the RMP. Raw data were evaluated for normality using the Shapiro-Wilks test, which indicated normal distributions only for bisphenols detected in wastewater effluent.

The parametric Pearson correlation test was used to analyze correlations among bisphenols in effluent due to their normal distributions. In stormwater and sediment, the non-parametric Spearman's correlation test was used to analyze correlations due to the lack of normal distribution and the limited sensitivity of this test to outliers. These correlation tests were only run on bisphenols detected in at least 50% of samples in a specific matrix. The statistical significance level was set to $\alpha = 0.05$ and all analyses were conducted using Microsoft Excel.

3. Results and Discussion

3.1. Pathways to the Bay: Bisphenols in Wastewater and Stormwater

In wastewater effluent samples, 5 of 17 bisphenols were detected (see Table 3 for summary statistics and Table A1 for individual sample data). BPA (range: 1.6–62 ng/L; median: 41 ng/L) and BPF (range: 2.6–128 ng/L; median: 30 ng/L) were found in all samples (n = 12) while BPAF, BPE, and BPS were detected in 17%, 25%, and 83% of samples, respectively. No other analytes were detected in any samples. The summed concentrations of bisphenols ranged from 4.2–246 ng/L, with median, mean, and 90th percentile values of 96, 106, and 206 ng/L, respectively (Table 3).

Table 3. Summary statistics (where ND = 0) for bisphenols A, AF, E, F and S detected in Bay Area wastewater effluent. All concentration values are in ng/L.

	Bisphenol A	Bisphenol AF	Bisphenol E	Bisphenol F	Bisphenol S	Sum of Bisphenols
Detection Frequency (n = 12)	100%	17%	25%	100%	83%	-
Minimum	1.6	ND	ND	2.6	ND	4.2
Maximum	62	1.0	1.4	128	55	246
Median	41	ND	ND	30	24	96
Mean	34	0.15	0.28	48	23	106
90th percentile	54	0.72	1.1	104	47	206
Standard Deviation	20	0.35	0.51	43	17	77
MDL	<0.7	<0.8	<0.8	<0.8	<1	-

Bisphenol concentrations generally varied across wastewater facilities (Figure 1), with coefficients of variation for BPA, BPF, and BPS near or above 100%. All the data for individual analytes fell within two standard deviations of the means, indicating no unusual or outlier detections. BPAF and BPE were only detected at EBDA and EBMUD and at relatively low concentrations, within range of the MDLs. Further analysis estimating the per capita bisphenol loads in each WWTP (range: 0.001–0.054 in mg per capita per day; Table A2) showed similar loads across facilities, with all estimates also within two standard deviations of the mean. Across two different sampling dates at WWTPs, most analytes had an RPD less than 35%, with the exceptions being small differences in the infrequently observed BPAF and BPE. This shows a notable consistency in samples at each facility compared to the greater variability displayed between the facilities.

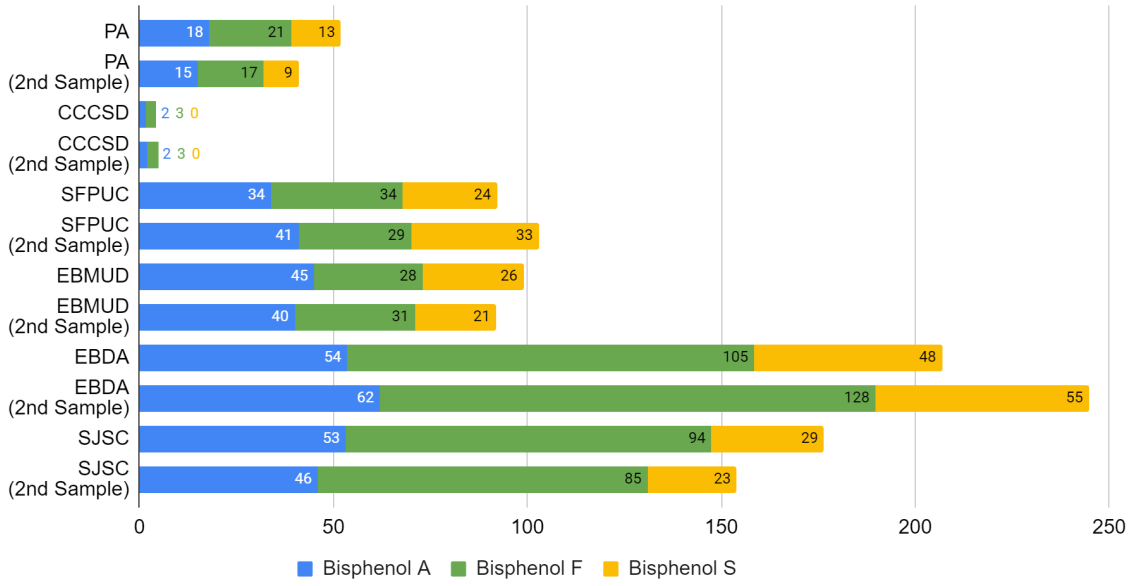

Figure 1. Detected concentrations of BPA, BPF, and BPS across six Bay Area WWTPs organized by increasing flow to the Bay (top to bottom). All concentrations in ng/L.

Pearson's correlation tests showed a strong positive correlation between paired combinations of BPA, BPF, and BPS ($p < 0.01$, all $r > 0.85$), suggesting broad similarities in their sources, transport, and/or fate. There was no clear association between treatment type and concentrations of bisphenols based on this limited set of data. One study indicated a greater capacity for more advanced tertiary treatment to remove BPA, followed by secondary treatment, then lagoon treatment, with chemically assisted primary treatment providing minimal removal (range: 1%-77% removal) (Guerra et al., 2015). The difference in BPA removal efficiency in that study could be due to increased biodegradation in certain bioreactor configurations.

Bisphenols other than BPA in wastewater effluent are not currently well studied. The few available studies examining bisphenols in effluent are shown in Table A3. One particularly comparable study of WWTP effluent collected in 2015 in Albany, NY, showed high ranges of detected BPA, BPF, and BPS compared to this study (Table A3), though the means were within range of or higher than those in this study (Xue & Kannan, 2019). Overall, concentrations of BPA, often the most abundantly observed bisphenol in wastewater across studies, were generally similar or lower in the Bay Area relative to those reported domestically and internationally. At EBMUD, BPA concentrations in this study (45 and 40 ng/L) were also much lower than those from a 2006 study at the same WWTP (380, 310, and <250 ng/L; Jackson & Sutton, 2008). This apparent decrease in BPA at EBMUD coincides with product bans in California and the US. In contrast, mean concentrations of BPF and BPS were similar to Albany, NY, values but higher than those reported in earlier studies conducted internationally (Karthikraj & Kannan, 2017; Sun et al., 2017), consistent with recent increases in use of these replacements for BPA.

To aid in interpretation of the wastewater effluent data, currently available data from an unpublished study (Sutton et al., in preparation) to monitor bisphenols in Bay Area stormwater are included for comparison. Preliminary data show the detection of four bisphenol analogues—A, F, S, and Z—in sites across the Bay (see Table 4 for summary statistics of total water concentrations and Table A4 for individual dissolved and total water concentrations). Among all water samples, BPA (range: 1.7–741 ng/g; median: 30 ng/L) was detected in all samples and BPF was detected in most (94%; range: ND–96 ng/L; median 8.6 ng/L). BPS and BPZ were found in 44% and 11% of samples, respectively, with no other analytes observed. The summed concentration of detected bisphenols at each site ranged from 1.7–853 ng/L with median, mean, and 90th percentile values of 38, 145, and 384 ng/L, respectively.

When examining bisphenol concentrations in pathways to the Bay, our focus is generally on the total concentration that is discharged. For stormwater analysis, the focus is on total (dissolved and particulate fractions) water concentrations, as this matrix contains significant quantities of suspended particles that may harbor bisphenols. In contrast, treated wastewater effluent contains relatively low levels of suspended particles, so low that concentrations of particle-bound contaminants could not be measured in our samples. Thus, while our wastewater effluent concentrations are derived from measurements of the dissolved phase only, the small amount of solids in these samples relative to stormwater suggests that these concentrations are a useful representation of the amount of bisphenols entering the Bay via this pathway.

Table 4. Summary statistics (where ND = 0) for bisphenols A, F, S, and Z detected in Bay Area stormwater from 2018-2021 (Sutton et. al., in preparation). All concentrations are total (dissolved and particulate) values and are in ng/L.

	Bisphenol A	Bisphenol F	Bisphenol S	Bisphenol Z	Sum of Bisphenols
Detection Frequency (N = 18)	100%	94%	44%	11%	-
Minimum	1.7	ND	ND	ND	1.7
Maximum	741	96	20	3.3	853
Median	30	8.6	ND	ND	38
Mean	117	22	5.1	0.23	145
90th percentile	323	80	17	0.24	384
Standard Deviation	192	31	7.6	0.79	225
MDL	0.2 - 0.4	0.2 - 0.4	0.3 - 0.6	0.4 - 0.8	-

Concentrations of bisphenols across stormwater sites varied, especially BPA, with a high coefficient of variation of 164%. This was largely due to the influence of an outlier sample at site Line 12H (Table A4), which had concentrations of BPA and BPF well above most other sites. South Bay sites also showed comparably high levels of bisphenols, matching trends in other matrices. Reference sites showed the presence of

some bisphenols, with the Berryessa Creek site (South Bay) matching closely with median levels of BPA and BPF (34 and 9.2 ng/L, respectively), suggesting it may not be a good reference location for this contaminant class. The Rodeo Creek (North Bay) site exhibited only minor concentrations of BPF (2.5 ng/L). Sites in the East and South Bays above the median for sums of bisphenols warrant further review to understand the sources of bisphenols, which will be further explored in a full report on emerging contaminants in stormwater (Sutton et al., in preparation).

Spearman's correlation tests showed a strong positive correlation between paired combinations of BPA, BPF, and BPS ($p < 0.01$, all $r > 0.80$) across stormwater sites. BPA and BPF showed similar levels of contribution of the dissolved phase to total phase with medians at 27% and 44%, respectively (Table A4). However, BPS exhibited concentrations predominantly in the dissolved phase, with most samples showing no particulate phase concentrations. The octanol-water partition coefficient ($\log K_{ow}$) for BPS of 1.2 is lower than for BPA (3.4) and BPF (3.1), which explains this different partitioning behavior (US EPA, 2012).

Examination of stormwater studies in the US and internationally show widespread detection of BPA with limited study of other bisphenols. BPA concentrations were lower in this study when compared to concentrations in other urban areas, though generally within the same order of magnitude (Table A5). One study of urban areas across the US found BPF at similar levels to those in the Bay Area, indicating its widespread and increasing use as a substitute for BPA (Masoner et al., 2019).

Comparison of the wastewater and stormwater datasets shows comparable concentrations of BPA, with medians of 41 and 30 ng/L, respectively. However, BPF and BPS concentrations were detected at consistently higher levels in wastewater effluent than stormwater. Within both matrices, additional bisphenols were detected, highlighting potential emerging replacements for BPA. Continued analysis of these matrices is important for early identification of BPA substitutes and overall understanding of the pathways of bisphenols to the Bay.

3.2. Bisphenols in Margin Sediment

Analysis of margin sediment showed the presence of BPA and BPF in all 12 samples (see Table 5 for summary statistics and Table A6 for individual sample data). All other analytes were not detected in any samples. The sum of concentrations of BPA and BPF across all sites ranged from 3.6–33 ng/g dry weight (dw) with median, mean, and 90th percentile values of 11, 18, and 30 ng/g dw, respectively (Table 5).

Concentrations of BPA were generally similar to BPF across all sites (Figures A2 and A3). The $\log K_{ow}$s are nearly the same for both BPA (3.4) and BPF (3.1), suggesting similar partitioning behavior. Spearman's correlation test showed a strong positive correlation ($p < 0.01$, $r = 0.86$) between BPA and BPF in sediment, further indicating similarities in their sources, pathways, and/or fate in the environment.

Table 5. Summary statistics for BPA and BPF detected in Bay Area margin sediment. All concentration values are in ng/g dw.

	Bisphenol A	Bisphenol F	Sum of Bisphenols
Detection Frequency (n = 12)	100%	100%	-
Minimum	2.1	1.5	3.6
Maximum	19	14	33
Median	7.6	3.3	11
Mean	11	7.0	18
90th Percentile	17	13	30
Standard Deviation	4.6	4.4	8.9
MDL	<1.1	<1.2	-

For both bisphenols, concentrations generally increased from north to south, with the average sum of bisphenols in South Bay (SB) sites (9 ng/g dw) four times lower than in southern slough (SOSL) sites (Figures A2 and A3). This geographic trend is consistent with wastewater effluent as an important pathway for bisphenols to enter the Bay, as the southern slough sites are strongly influenced by flows from the San Jose-Santa Clara Regional Wastewater Facility, the largest wastewater discharger in the Bay (Figure 1). Southern slough sites may also receive significant discharges of urban stormwater runoff, another important pathway for BPA and BPF (Table 4). A previous screening study of these Bay margin samples detected BPA at a single LSB site (of 12 total SB and LSB sites) at an estimated 71 ng/g dw, below the reporting limit for this sample (Heberger et al., 2020). Though reporting limits were high for the previous study (between 50 ng/g dw to 100 ng/g dw), this semiquantitative measurement is consistent with greater levels of contamination at sites located further south in the Bay.

Data for bisphenols in estuarine or marine sediment are scarce. Data from studies examining a variety of bisphenols in marine surface sediment are available in Table A7. Concentrations of BPA and BPF within this study were generally similar to reported concentrations both in the US and globally, with BPA concentrations highest in all studies. Across all of these studies, the individual concentrations of BPA and BPF as well as the sum of bisphenols were within an order of magnitude. Some studies have detected BPS in sediment, though levels were generally lower than BPA and BPF (Liu et al., 2021; Wu et al., 2018).

3.3. Risk Evaluation for San Francisco Bay

Studies have shown that BPA elicits a multitude of adverse estrogenic effects and, in some cases, with potencies comparable to naturally occurring hormones (Björnsdotter et al., 2017; Chen et al., 2016; Héliès-Toussaint et al., 2014; Rosenmai et al., 2014). 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 (Björnsdotter et al., 2017; Carlisle et al., 2009). It is listed on California's Proposition 65 List for developmental toxicity and female reproductive toxicity (OEHHA, 2021).

Numerous aquatic toxicity studies have been conducted for BPA, leading to a robust understanding of toxicological risk to aquatic organisms. For example, 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 an overall aquatic PNEC of 60 ng/L. In contrast to BPA, most other bisphenols are poorly understood with respect to potential toxicity (Pelch et al., 2019). However, they are structurally similar to BPA, and some have demonstrated links to the same array of toxic effects at similar, and sometimes greater, potencies (Chen et al., 2016; Mu et al., 2018; Naderi et al., 2014; Rochester & Bolden, 2015; Rosenmai et al., 2014; L. Wang et al., 2018). Considering their structural similarities, bisphenols are expected to have overlapping modes of action and likely exhibit additive toxicity (Pelch et al., 2019). As a result, a more protective risk evaluation using a read-across approach and the more robust BPA threshold for less well-studied bisphenols, both independently and together as summed concentrations assuming additive toxicity, is warranted.

For all bisphenols, including BPA, available sediment toxicity testing data are limited. Given the paucity of data, robust sediment thresholds based on sediment toxicity testing have not been developed. Instead, available thresholds are based on an equilibrium-partitioning approach, in which a value to protect organisms exposed to sediment pore water is estimated based on a water threshold (Di Toro et al., 1991). This method is more uncertain than using data from toxicity testing of benthic species. Using the organic carbon-water partition coefficient (K_{oc}) for BPA of 708 L/kg and normalizing the value to 1% organic carbon in sediment, Environment and Climate Change Canada (ECCC) developed a Federal Environmental Quality Guideline of 25 ng/g dw (Environment and Climate Change Canada, 2018). The ECCC sediment threshold was derived using a water threshold of 3.5 µg/L based on a species sensitivity curve that included 15 studies and 16 species, which is not as protective as the Wright-Walters et al. threshold of 60 ng/L. Preliminary PNECs for sediment have been derived for several other bisphenols using the same equilibrium-partitioning approach as part of REACH registrations. A sediment threshold for BPF is currently unavailable, so the read-across approach was used based on the BPA sediment threshold for this structurally related contaminant.

No samples had individual concentrations of BPA or BPF above the ECCC guideline of 25 ng/g (maxima of 19 ng/g and 14 ng/g, respectively). However, summed concentrations of BPA and BPF from sites SOSL15 and SOSL16 (33 and 31 ng/L, respectively) exceeded this threshold, indicating potential risks to Bay biota, especially in the southern sloughs. These sums may be biased low, as they do not include contributions from other bisphenols that could be present at levels below MDLs (i.e., non-detects were treated as 0). However, based on available information on bisphenol manufacture, use, and occurrence worldwide, BPA and BPF are anticipated to make up the majority of the bisphenols in Bay sediment, and trace levels of other bisphenols would not change the outcome of this risk evaluation. Overall, these findings support the

current classification of bisphenols as emerging contaminants of Moderate Concern in the Bay.

While San Francisco Bay biota are not expected to be exposed to undiluted wastewater effluent or stormwater runoff, individual BPA and summed bisphenol concentrations in several of these samples (maximum of 741 ng/L) exceeded the water threshold of 60 ng/L. Combined with measures of bisphenols in Bay water (Shimabuku et al., 2022), these data also indicate potential risks to Bay biota.

4. Recommended Monitoring Strategy

This study fills important data gaps on the contaminant pathways, occurrence, and fate of bisphenols, which were classified as Moderate Concern for San Francisco Bay based on ambient water data collected in 2017 (Table 6; Shimabuku et al., 2020, 2022). Wastewater effluent was identified as an important pathway for BPA, BPF, and BPS; other bisphenols were observed sporadically and at lower concentrations. Unpublished observations from an ongoing study of stormwater runoff indicated this is also an important pathway by which BPA, BPF, and, to a lesser extent, BPS enter the Bay. Meanwhile, concentrations of BPA and BPF in margin sediment collected from sites strongly influenced by wastewater and stormwater provide further support for the Moderate Concern classification within the RMP tiered risk-based framework.

Of particular interest, this study and prior work (Shimabuku et al., 2020, 2022) indicate levels of BPF and BPS can be similar to those of BPA in pathways and Bay matrices (Table 6), despite far lower production volumes, with limited production or import volumes reported for the US just a few years ago (USEPA, 2020). This suggests significantly increasing use of these BPA alternatives, and potential ecological concern for contaminant exposure individually and as mixtures. The class-based approach to monitoring emerging contaminants, a key component of the RMP CEC strategy (Sutton et al., 2017), is designed to address both well-studied contaminants like BPA, and related, data-poor alternatives such as BPF and BPS. Monitoring of broader classes of contaminants defined by similarities in chemical structure and/or function can provide early insights to identify problematic compounds with recent increases in use, which may turn out to be regrettable substitutes.

Table 6. Comparison of ranges and medians of bisphenols A, F, and S detected in pathways to and matrices within the San Francisco Bay including wastewater effluent, stormwater, and sediment (this study) as well as ambient Bay water from a previous RMP monitoring study (Shimabuku et al., 2022).

	Range			**Median**		
Matrix	Bisphenol A	Bisphenol F	Bisphenol S	Bisphenol A	Bisphenol F	Bisphenol S
Wastewater Effluent (ng/L)	1.6 - 62	2.6 - 128	<1 - 55	41	30	24
Stormwater (Total) (ng/L)	1.7 - 741	(<0.2 - 0.4) - 96	(<0.3 - 0.6) - 20	30	8.6	<0.3 - 0.6
Bay Water (Total) (ng/L)	<0.7 - 35	dc	<1 - 120	10	dc	<1
Sediment (ng/g dw)	2.1 - 19	1.5 - 14	<2	7.6	3.3	<2

For BPF in Bay water, data censored due to field blank contamination are labeled “dc.”

We recommend continued monitoring of bisphenols in Bay water and sediment via the RMP Status and Trends monitoring program. Regular monitoring can be used to track temporal trends of individual compounds due to shifts in manufacturing and use, and provide an increased understanding of the spatial distribution of these contaminants within the Bay. In particular, sediment monitoring could be confined to strategic sampling sites where these contaminants are likely to be detected at higher concentrations, with a specific focus on evaluating temporal trends. We recommend using an analytical method that can at minimum quantify BPA, BPF, and BPS at ng/L and ng/g (dw) concentrations.

Periodic collection of screening data on bisphenols in wastewater and stormwater is also recommended to assess temporal trends; such studies could be conducted in coordination with Bay Status and Trends water monitoring efforts. Of note, low and sporadic concentrations of other bisphenols, including BPAF, BPE, and BPZ, were observed in samples from pathways, but not in more dilute samples of ambient water and sediment in the Bay. Because pathways generally contain higher concentrations of contaminants due to their more direct connection to sources in urban settings, these matrices are ideal for early detection of compounds that have been more recently incorporated into consumer and industrial products. Therefore, it may be more appropriate to prioritize screening wastewater and stormwater for a broader set of bisphenols.

In addition, a screening study of bisphenols in Bay biota would allow better assessment of the presence, fate, and potential impacts of bisphenols in the Bay ecosystem. BPA has been detected in various wildlife tissues elsewhere including marine medaka fish (Xu et al., 2015), marine mussels (Cerkvenik-Flajs et al., 2018; Liao & Kannan, 2019), and estuarine chinook salmon and staghorn sculpin (Meador et al., 2016), but has not been investigated in the Bay. In a comparison of water and tissue concentrations of nine bisphenol compounds in Lake Taihu, Q. Wang et al. (2017) found the potential for bisphenol compounds to bioaccumulate was significantly correlated with their $\log K_{ow}$. This can be particularly important should manufacturers continue to use potentially regrettable, data-poor substitutes. Lower trophic level organisms such as bivalves and prey fish could be more appropriate for monitoring, as food web biomagnification is not anticipated. Analysis of both bisphenols and their conjugates may be needed to fully assess exposure in biota.

The recommendations described above can provide for early identification and tracking of regrettable substitutes, science that can be used to inform management actions to protect water quality and beneficial uses.

References

Björnsdotter, M. K., Boer, J. de, & Ballesteros-Gómez, A. (2017). Bisphenol A and replacements in thermal paper: A review. *Chemosphere*, *182*, 691–706. https://doi.org/10.1016/j.chemosphere.2017.05.070

Capolupo, M., Díaz-Garduño, B., & Martín-Díaz, M. L. (2018). The impact of propranolol, 17α-ethinylestradiol, and gemfibrozil on early life stages of marine organisms: Effects and risk assessment. *Environmental Science and Pollution Research*, *25*(32), 32196–32209. https://doi.org/10.1007/s11356-018-3185-6

Carlisle, J., Chan, D., Golub, M., Henkel, S., Painter, P., & Wu, K. L. (2009). *Toxicological Profile for Bisphenol A* (p. 66). Office of Environmental Health Hazard Assessment.

Catenza, C. J., Farooq, A., Shubear, N. S., & Donkor, K. K. (2021). A targeted review on fate, occurrence, risk and health implications of bisphenol analogues. *Chemosphere*, *268*, 129273. https://doi.org/10.1016/j.chemosphere.2020.129273

Cerkvenik-Flajs, V., Fonda, I., & Gombač, M. (2018). Analysis and Occurrence of Bisphenol A in Mediterranean Mussels (Mytilus galloprovincialis) Sampled from the Slovenian Coastal Waters of the North Adriatic Sea. *Bulletin of Environmental Contamination and Toxicology*, *101*(4), 439–445. https://doi.org/10.1007/s00128-018-2415-4

Chen, D., Kannan, K., Tan, H., Zheng, Z., Feng, Y.-L., Wu, Y., & Widelka, M. (2016). Bisphenol Analogues Other Than BPA: Environmental Occurrence, Human Exposure, and Toxicity—A Review. *Environmental Science & Technology*, *50*(11), 5438–5453. https://doi.org/10.1021/acs.est.5b05387

Corrales, J., Kristofco, L. A., Steele, W. B., Yates, B. S., Breed, C. S., Williams, E. S., & Brooks, B. W. (2015). Global Assessment of Bisphenol A in the Environment: Review and Analysis of Its Occurrence and Bioaccumulation. *Dose-Response*, *13*(3), 155932581559830. https://doi.org/10.1177/1559325815598308

Di Toro, D. M., Zarba, C. S., Hansen, D. J., Berry, W. J., Swartz, R. C., Cowan, C. E., Pavlou, S. P., Allen, H. E., Thomas, N. A., & Paquin, P. R. (1991). Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry*, *10*(12), 1541–1583. https://doi.org/10.1002/etc.5620101203

Environment and Climate Change Canada. (2018, June 8). *Canadian Environmental Protection Act, 1999 Federal Environmental Quality Guidelines—Bisphenol A* [Guidance]. https://www.canada.ca/en/environment-climate-change/services/evaluating-existing-substances/federal-environmental-quality-guidelines-bisphenol-a.html

Fairbairn, D. J., Elliott, S. M., Kiesling, R. L., Schoenfuss, H. L., Ferrey, M. L., & Westerhoff, B. M. (2018). Contaminants of emerging concern in urban stormwater: Spatiotemporal patterns and removal by iron-enhanced sand filters (IESFs). *Water Research*, *145*, 332–345. https://doi.org/10.1016/j.watres.2018.08.020

Gernjak, W., Lampard, J., & Tang, J. (2017). Characterisation of chemical hazards in stormwater. *Cooperative Research Centre for Water Sensitive Cities*, 14.

Gewurtz, S. B., Tardif, G., Power, M., Backus, S. M., Dove, A., Dubé-Roberge, K., Garron, C., King, M., Lalonde, B., Letcher, R. J., Martin, P. A., McDaniel, T. V., McGoldrick, D. J., Pelletier, M., Small, J., Smyth, S. A., Teslic, S., & Tessier, J. (2021). Bisphenol A in the Canadian environment: A multimedia analysis. *Science of The Total Environment*, *755*, 142472. https://doi.org/10.1016/j.scitotenv.2020.142472

Guerra, P., Kim, M., Teslic, S., Alaee, M., & Smyth, S. A. (2015). Bisphenol-A removal in various wastewater treatment processes: Operational conditions, mass balance, and optimization. *Journal of Environmental Management*, *152*, 192–200. https://doi.org/10.1016/j.jenvman.2015.01.044

Hahladakis, J. N., Iacovidou, E., & Gerassimidou, S. (2022). An overview of the occurrence, fate, and human risks of the bisphenol‐A present in plastic materials, components, and products. *Integrated Environmental Assessment and Management*, ieam.4611. https://doi.org/10.1002/ieam.4611

Heberger, M., Sutton, R., Buzby, N., Sun, J., Lin, D., Mendez, M., Hladik, M., Orlando, J., Sanders, C., & Furlong, E. (2020). *Current-Use Pesticides, Fragrance Ingredients, and Other Emerging Contaminants in San Francisco Bay Margin Sediment and Water* (SFEI Contribution No. 934). San Francisco Estuary Institute. https://www.sfei.org/documents/current-use-pesticides-fragrance-ingredients-and-other-emerging-contaminants-san-francisco

Héliès-Toussaint, C., Peyre, L., Costanzo, C., Chagnon, M.-C., & Rahmani, R. (2014). Is bisphenol S a safe substitute for bisphenol A in terms of metabolic function? An in vitro study. *Toxicology and Applied Pharmacology*, *280*(2), 224–235. https://doi.org/10.1016/j.taap.2014.07.025

Jackson, J., & Sutton, R. (2008). Sources of endocrine-disrupting chemicals in urban wastewater, Oakland, CA. *Science of The Total Environment*, *405*(1–3), 153–160. https://doi.org/10.1016/j.scitotenv.2008.06.033

Karthikraj, R., & Kannan, K. (2017). Mass loading and removal of benzotriazoles, benzothiazoles, benzophenones, and bisphenols in Indian sewage treatment plants. *Chemosphere*, *181*, 216–223. https://doi.org/10.1016/j.chemosphere.2017.04.075

Liao, C., & Kannan, K. (2019). Species-specific accumulation and temporal trends of bisphenols and benzophenones in mollusks from the Chinese Bohai Sea during 2006–2015. *Science of The Total Environment*, *653*, 168–175. https://doi.org/10.1016/j.scitotenv.2018.10.271

Liao, C., Liu, F., Moon, H.-B., Yamashita, N., Yun, S., & Kannan, K. (2012). Bisphenol Analogues in Sediments from Industrialized Areas in the United States, Japan, and Korea: Spatial and Temporal Distributions. *Environmental Science & Technology*, *46*(21), 11558–11565. https://doi.org/10.1021/es303191g

Liao, C., Shi, J., Wang, X., Zhu, Q., & Kannan, K. (2019). Occurrence and distribution of parabens and bisphenols in sediment from northern Chinese coastal areas. *Environmental Pollution*, *253*, 759–767. https://doi.org/10.1016/j.envpol.2019.07.076

Liu, J., Zhang, L., Lu, G., Jiang, R., Yan, Z., & Li, Y. (2021). Occurrence, toxicity and ecological risk of Bisphenol A analogues in aquatic environment – A review. *Ecotoxicology and Environmental Safety*, *208*, 111481. https://doi.org/10.1016/j.ecoenv.2020.111481

Masoner, J. R., Kolpin, D. W., Cozzarelli, I. M., Barber, L. B., Burden, D. S., Foreman, W. T., Forshay, K. J., Furlong, E. T., Groves, J. F., Hladik, M. L., Hopton, M. E., Jaeschke, J. B., Keefe, S. H., Krabbenhoft, D. P., Lowrance, R., Romanok, K. M., Rus, D. L., Selbig, W. R., Williams, B. H., & Bradley, P. M. (2019). Urban Stormwater: An Overlooked Pathway of Extensive Mixed Contaminants to Surface and Groundwaters in the United States. *Environmental Science & Technology*, *53*(17), 10070–10081. https://doi.org/10.1021/acs.est.9b02867

Meador, J. P., Yeh, A., Young, G., & Gallagher, E. P. (2016). Contaminants of emerging concern in a large temperate estuary. *Environmental Pollution*, *213*, 254–267. https://doi.org/10.1016/j.envpol.2016.01.088

Mu, X., Huang, Y., Li, X., Lei, Y., Teng, M., Li, X., Wang, C., & Li, Y. (2018). Developmental Effects and Estrogenicity of Bisphenol A Alternatives in a Zebrafish Embryo Model. *Environmental Science & Technology*, *52*(5), 3222–3231. https://doi.org/10.1021/acs.est.7b06255

Naderi, M., Wong, M. Y. L., & Gholami, F. (2014). Developmental exposure of zebrafish (Danio rerio) to bisphenol-S impairs subsequent reproduction potential and hormonal balance in adults. *Aquatic Toxicology*, *148*, 195–203. https://doi.org/10.1016/j.aquatox.2014.01.009

NCSL. (2017). *State Statutes on Chemical Safety*. NCSL Policy Update. https://www.ncsl.org/research/environment-and-natural-resources/ncsl-policy-update-state-statutes-on-chemical-safety.aspx#toxic

OEHHA. (2012). *Preliminary Screen for Possible Future Consideration as Potential Designated Chemicals for Biomonitoring California. Some Bisphenol A Substitutes and Structurally Related Compounds.* Materials for March 16, 2012 Meeting Scientific Guidance Panel (SGP).

OEHHA. (2021). *The Proposition 65 List*. Office of Environmental Health Hazard Assessment. https://oehha.ca.gov/proposition-65/proposition-65-list

Pelch, K., Wignall, J. A., Goldstone, A. E., Ross, P. K., Blain, R. B., Shapiro, A. J., Holmgren, S. D., Hsieh, J.-H., Svoboda, D., Auerbach, S. S., Parham, F. M., Masten, S. A., Walker, V., Rooney, A., & Thayer, K. A. (2019). A scoping review of the health and toxicological activity of bisphenol A (BPA) structural analogues and functional alternatives. *Toxicology*, *424*, 152235. https://doi.org/10.1016/j.tox.2019.06.006

Rochester, J. R., & Bolden, A. L. (2015). Bisphenol S and F: A Systematic Review and Comparison of the Hormonal Activity of Bisphenol A Substitutes. *Environmental Health Perspectives*, *123*(7), 643–650. https://doi.org/10.1289/ehp.1408989

Rosenfeld, P. E., & Feng, L. G. H. (2011). 17—Mercury, BPA, and Pesticides in Food. In P. E. Rosenfeld & L. G. H. Feng (Eds.), *Risks of Hazardous Wastes* (pp. 223–235). William Andrew Publishing. https://doi.org/10.1016/B978-1-4377-7842-7.00017-9

Rosenmai, A. K., Dybdahl, M., Pedersen, M., Alice van Vugt-Lussenburg, B. M., Wedebye, E. B., Taxvig, C., & Vinggaard, A. M. (2014). Are Structural Analogues to Bisphenol A Safe Alternatives? *Toxicological Sciences*, *139*(1), 35–47. https://doi.org/10.1093/toxsci/kfu030

Shimabuku, I., Chen, D., Wu, Y., Miller, E., Sun, J., & Sutton, R. (2022). Occurrence and risk assessment of organophosphate esters and bisphenols in San Francisco Bay, California, USA. *Science of The Total Environment*, *813*, 152287. https://doi.org/10.1016/j.scitotenv.2021.152287

Shimabuku, I., Chen, D., Wu, Y., Sun, J., & Sutton, R. (2020). *Flame retardants and plastic additives in San Francisco Bay: Targeted monitoring of organophosphate esters and bisphenols* (SFEI Contribution No. 925). San Francisco Estuary Institute. https://www.sfei.org/documents/flame-retardants-and-plastic-additives-san-francisco-bay-targeted-monitoring

Sun, Q., Wang, Y., Li, Y., Ashfaq, M., Dai, L., Xie, X., & Yu, C.-P. (2017). Fate and mass balance of bisphenol analogues in wastewater treatment plants in Xiamen City, China. *Environmental Pollution*, *225*, 542–549. https://doi.org/10.1016/j.envpol.2017.03.018

Sutton, R., Miller, E., Gilbreath, A., Moran, K., Mendez, M., & Lin, D. (in preparation). *Contaminants of Emerging Concern in Urban Stormwater Runoff*. SFEI.

Sutton, R., Sedlak, M., Sun, J., & Lin, D. (2017). *Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations 2017 Revision* (p. 78). San Francisco Estuary Institute.

US EPA. (2012). *Estimation Programs Interface Suite™ for Microsoft® Windows, v4.1*. United States Environmental Protection Agency.

US EPA. (2020). *2020 Chemical Data Reporting Results*. United States Environmental Protection Agency, Washington DC. https://www.epa.gov/chemical-data-reporting/access-cdr-data

Wang, L., Wang, Z., Liu, J., Ji, G., Shi, L., Xu, J., & Yang, J. (2018). Deriving the freshwater quality criteria of BPA, BPF and BPAF for protecting aquatic life. *Ecotoxicology and Environmental Safety*, *164*, 713–721. https://doi.org/10.1016/j.ecoenv.2018.08.073

Wang, Q., Chen, M., Shan, G., Chen, P., Cui, S., Yi, S., & Zhu, L. (2017). Bioaccumulation and biomagnification of emerging bisphenol analogues in aquatic organisms from Taihu Lake, China. *Science of The Total Environment*, *598*, 814–820. https://doi.org/10.1016/j.scitotenv.2017.04.167

Wright-Walters, M., Volz, C., Talbott, E., & Davis, D. (2011). An updated weight of evidence approach to the aquatic hazard assessment of Bisphenol A and the derivation a new predicted no effect concentration (Pnec) using a non-parametric methodology. *Science of The Total Environment*, *409*(4), 676–685. https://doi.org/10.1016/j.scitotenv.2010.07.092

Wu, L.-H., Zhang, X.-M., Wang, F., Gao, C.-J., Chen, D., Palumbo, J. R., Guo, Y., & Zeng, E. Y. (2018). Occurrence of bisphenol S in the environment and implications for human exposure: A short review. *Science of The Total Environment*, *615*, 87–98. https://doi.org/10.1016/j.scitotenv.2017.09.194

Xie, J., Zhao, N., Zhang, Y., Hu, H., Zhao, M., & Jin, H. (2022). Occurrence and partitioning of bisphenol analogues, triclocarban, and triclosan in seawater and sediment from East China Sea. *Chemosphere*, *287*, 132218. https://doi.org/10.1016/j.chemosphere.2021.132218

Xu, E. G. B., Morton, B., Lee, J. H. W., & Leung, K. M. Y. (2015). Environmental fate and ecological risks of nonylphenols and bisphenol A in the Cape D'Aguilar Marine Reserve, Hong Kong. *Marine Pollution Bulletin*, *91*(1), 128–138. https://doi.org/10.1016/j.marpolbul.2014.12.017

Xue, J., & Kannan, K. (2019). Mass flows and removal of eight bisphenol analogs, bisphenol A diglycidyl ether and its derivatives in two wastewater treatment plants in New York State, USA. *Science of The Total Environment*, *648*, 442–449. https://doi.org/10.1016/j.scitotenv.2018.08.047

Xue, J., Liu, W., & Kannan, K. (2017). Bisphenols, Benzophenones, and Bisphenol A Diglycidyl Ethers in Textiles and Infant Clothing. *Environmental Science & Technology*, *51*(9), 5279–5286. https://doi.org/10.1021/acs.est.7b00701

Yee, D., Wong, A., & Weaver, M. (2021). *2021 Quality Assurance Program Plan for the Regional Monitoring Program for Water Quality in San Francisco Bay* (SFEI Contribution No. 1048). San Francisco Estuary Institute.

Appendix

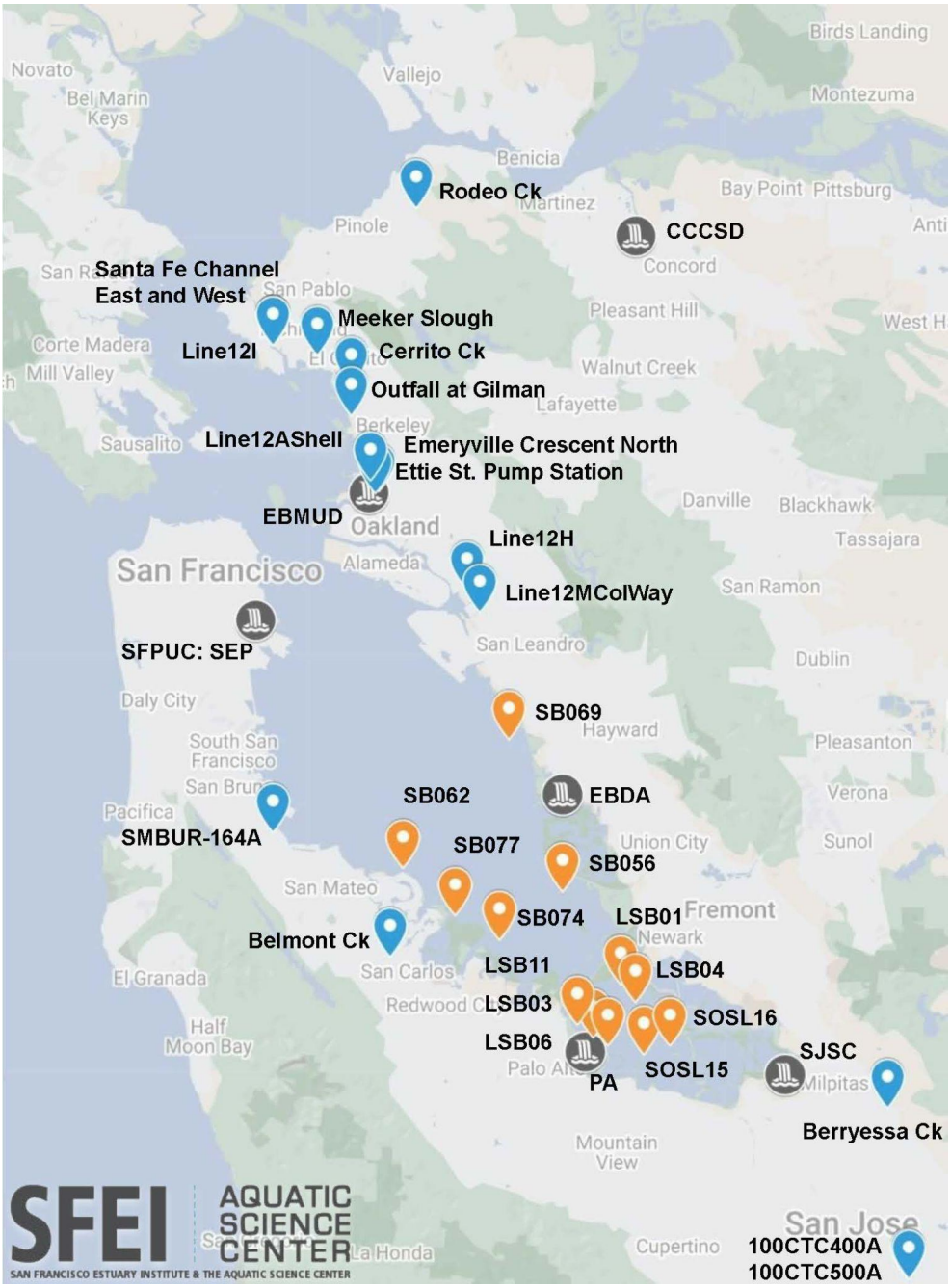

Figure A1. Map of all sites sampled for this study. Wastewater facilities are denoted by grey markers. Stormwater sites are shown as blue markers and sediment sites are shown as orange markers.

Wastewater Data

Table A1. Concentrations of detected bisphenols (A, AF, E, F, and S) in San Francisco Bay wastewater effluent. All values are in ng/L (dissolved phase).

WWTP	Bisphenol A	Bisphenol AF	Bisphenol E	Bisphenol F	Bisphenol S	Sum of Bisphenols
CCCSD (1st Sample)	1.6	ND	ND	2.6	ND	4.2
CCCSD (2nd Sample)*	2.0	ND	ND	3.0	ND	5.0
EBDA (1st Sample)	54	1.0	1.4	105	48	209
EBDA (2nd Sample)*	62	ND	0.8	128	55	246
EBMUD (1st Sample)	45	ND	ND	28	26	99
EBMUD (2nd Sample)*	40	0.8	1.1	31	21	94
PA (1st Sample)	18	ND	ND	21	13	52
PA (2nd Sample)*	15	ND	ND	17	9	41
SFPUC (1st Sample)	41	ND	ND	29	33	103
SFPUC (2nd Sample)*	41	ND	ND	29	33	103
SJSC (1st Sample)	53	ND	ND	94	29	177
SJSC (2nd Sample)*	46	ND	ND	85	23	154
EBDA (1st Sample) Duplicate	55	1.0	1.3	111	50	219
PA (2nd Sample)* Duplicate	15	ND	ND	18	10	44

**Second samples were taken a week after the first.*
Samples in yellow are field duplicates and not included in data analysis for summary statistics.

Table A2. Estimated daily per capita loads of bisphenols A, F, and S from wastewater effluent to San Francisco Bay. All mass loadings are in mg per capita per day.

	Daily Effluent Flow Rate* (mgd)	Estimated Population Service Area	Mass Load of BPA	Mass Load of BPF	Mass Load of BPS	Mass Load for Sum of Bisphenols
CCCSD	31.7	500,000	0.000	0.001	0.000	0.001
CCCSD (2nd Sample)	31.9		0.000	0.001	0.000	0.001
EBDA	59	1,000,000	0.012	0.023	0.011	0.047
EBDA (2nd Sample)	58		0.014	0.028	0.012	0.054
EBMUD	47	740,000	0.011	0.007	0.006	0.024
EBMUD (2nd Sample)	43		0.009	0.007	0.005	0.021
PA	17.2	236,000	0.005	0.006	0.004	0.014
PA (2nd Sample)	17.6		0.004	0.005	0.003	0.012
SFPUC	40	580,000	0.009	0.009	0.006	0.024
SFPUC (2nd Sample)	40		0.011	0.008	0.009	0.027
SJSC	79	1,400,000	0.011	0.020	0.006	0.038
SJSC (2nd Sample)	77		0.010	0.018	0.005	0.032
Median	-	-	0.009	0.007	0.005	0.024
Mean	-	-	0.008	0.011	0.005	0.025
Standard Deviation	-	-	0.004	0.009	0.004	0.016

**Flow rates for the day of sampling at each facility are shown*

Table A3. Comparison of San Francisco Bay bisphenol effluent concentrations to other effluent concentrations globally. All values are in ng/L.

Compound	N	Range	Median	Mean	Location	Year	Reference
Bisphenol A	12	1.6 - 62	40.5	34.3	San Francisco Bay, CA, USA	2020	This Study
	49	16 - 1100	177	231	Xiamen City, China	2016	Sun et al., 2017
	32	ND - 3380	-	39*	Albany Area, NY, USA	2015	Xue & Kannan, 2019
	198	5 - 7400	150	-	Several Areas in Canada	2009 - 2013	Guerra et al., 2015
	5	1.1 - 14.2	8.1	5.2	Several Areas in India	2012	Karthikraj & Kannan, 2017
	3	ND - 380	310	230	San Francisco Bay	2006	Jackson & Sutton, 2012
Bisphenol F	12	2.6 - 128	30	48	San Francisco Bay, CA, USA	2020	This Study
	49	ND - 35	ND	1.67	Xiamen City, China	2016	Sun et al., 2017
	32	ND - 556	-	66*	Albany Area, NY, USA	2015	Xue & Kannan, 2019
	5	ND - 2.1	ND	0.6	Several Areas in India	2012	Karthikraj & Kannan, 2017
Bisphenol S	12	ND - 55	23.7	23.5	San Francisco Bay, CA, USA	2020	This Study
	49	ND - 3.7	ND	0.6	Xiamen City, China	2016	Sun et al., 2017
	32	ND - 444	-	26*	Albany Area, NY, USA	2015	Xue & Kannan, 2019
	5	ND - 4.3	2.5	2.4	Several Areas in India	2012	Karthikraj & Kannan, 2017
Sum of Bisphenols	12	245.6	96.5	106.3	San Francisco Bay, CA, USA	2020	This Study
	32	ND - 3890	-	156*	Albany Area, NY, USA	2015	Xue & Kannan, 2019
	5	2.2 - 17.6	7.2	9.6	Several Areas in India	2012	Karthikraj & Kannan, 2017

**Geometric means were used for this study.*

Stormwater Data

Table A4. Concentrations of detected bisphenols (A, F, S, and Z) in dissolved and total (dissolved and particulate phases) fractions in stormwater entering San Francisco Bay. All values are in ng/L.

Site	Year	Bisphenol A			Bisphenol F			Bisphenol S			Bisphenol Z			Sum of Bisphenols		
		Diss.	Total	Diss. / Total	Diss.	Total	Diss. / Total	Diss.	Total	Diss. / Total	Diss.	Total	Diss. / Total	Diss.	Total	Diss. / Total
SMBUR-164A	Nov 2018	1.5	12	0.13	0.8	6.4	0.13	ND	ND	-	ND	ND	-	2.3	18	0.13
Belmont Creek	Jan 2021	1.7	10	0.17	1.4	7	0.20	ND	ND	-	ND	ND	-	3.1	17	0.18
100CTC400A	Jan 2019	51	99	0.52	12	16	0.75	19	19	1.0	ND	ND	-	82	134	0.61
100CTC500A	Jan 2019	79	415	0.19	53	76	0.70	19	20	0.95	ND	ND	-	151	511	0.30
Line12AShell (1)	Nov 2018	5.7	9.2	0.62	0.5	8.4	0.06	ND	ND	-	3.3	3.3	1.0	9.5	21	0.45
Line12MColWay	Nov 2018	48	169	0.28	71	89	0.80	12.5	12.5	1.00	0.81	0.81	1.0	132	271	0.49
Ettie Street Pump Station (1)	Feb 2019	31	34	0.91	8.5	8.7	0.98	ND	ND	-	ND	ND	-	40	43	0.92
Line12AShell (2)	Feb 2019	0.8	2.3	0.35	ND	2.3	-	ND	ND	-	ND	ND	-	0.8	4.6	0.17
Meeker Slough	Feb 2019	0.7	1.7	0.41	ND	ND	-	ND	ND	-	ND	ND	-	0.7	1.7	0.41
Line12H	Nov 2019	17	741	0.02	42	96	0.44	13	16	0.81	ND	ND	-	72	853	0.08
Line12I	Nov 2019	7.5	25	0.30	3.5	6.2	0.56	1.8	1.8	1.0	ND	ND	-	13	33	0.39

Site	Year	Bisphenol A			Bisphenol F			Bisphenol S			Bisphenol Z			Sum of Bisphenols		
		Diss.	Total	Diss. Total	Diss.	Total	Diss. Total	Diss.	Total	Diss. Total	Diss.	Total	Diss. Total	Diss.	Total	Diss. Total
Santa Fe Channel East	Nov 2019	12	163	0.07	4	26	0.15	2.6	2.6	1.0	ND	ND	-	19	192	0.10
Santa Fe Channel West	Nov 2019	6.4	76	0.08	5.5	15	0.37	3.1	3.1	1.0	ND	ND	-	15	94	0.16
Cerrito Creek	Jan 2020	2.9	17	0.17	ND	1	-	ND	ND	-	ND	ND	-	2.9	18	0.16
Ettie Street Pump Station (2)	Jan 2020	261	284	0.92	29	30	0.97	16	16	1.0	ND	ND	-	306	330	0.93
Emeryville Crescent North (1)	Jan 2020	2.1	8	0.26	0.67	1.6	0.42	ND	ND	-	ND	ND	-	2.8	10	0.28
Outfall at Gilman St	Jan 2020	1.8	38	0.05	0.75	13	0.06	ND	ND	-	ND	ND	-	2.6	51	0.05
Emeryville Crescent North (2)	Jan 2021	1.6	5.7	0.28	0.5	1.1	0.45	ND	ND	-	ND	ND	-	2.1	6.8	0.31
Berryessa Creek	Jan 2019	1.4	34	0.04	ND	9.2	-	ND	ND	-	4.4	4.4	1.0	5.8	48	0.12
Rodeo Creek	Jan 2019	ND	ND	-	ND	2.5	-	ND	ND	-	1	1	1.0	1.0	3.5	0.29

Samples in orange denote Peninsula sites, those in blue denote South Bay sites, and green denotes East Bay sites. Samples in grey show Reference sites, which were not included in the data analysis for summary statistics. Diss. denotes dissolved concentrations.

Table A5. Comparison of San Francisco Bay bisphenol stormwater concentrations to other stormwater concentrations globally. All values are in ng/L.

Compound	N	Range	Median	Mean	Location	Year	Reference
Bisphenol A	20	1.7 - 741	30	117	San Francisco Bay, CA, USA	2020	This Study
	50	ND - 2770	263	487	Several urban areas in the US	2016 - 2017	Masoner et al., 2019
	36	ND - 580	ND	-	Minneapolis - St. Paul, MN, USA	2016	Fairbairn et al., 2018
	46	2000 (Max)	155	-	Several urban areas in Australia	2011 - 2014	Gernjak et al., 2017
	21	207 (Q20) - 817 (Q80)	-	552	Urban areas in Lyon, France	2011 - 2013	Gasperi, et al. 2013
Bisphenol F	20	ND - 96	8.6	22	San Francisco Bay, CA, USA	2020	This Study
	50	ND - 141	29	17	Several urban areas in the US	2016 - 2017	Masoner et al., 2019
Bisphenol S	20	ND - 20	ND	5.1	San Francisco Bay, CA, USA	2020	This Study
Bisphenol Z	20	ND - 3.3	ND	0.23	San Francisco Bay, CA, USA	2020	This Study
Sum of Bisphenols	20	1.7 - 853	38	145	San Francisco Bay, CA, USA	2020	This Study

Sediment Data

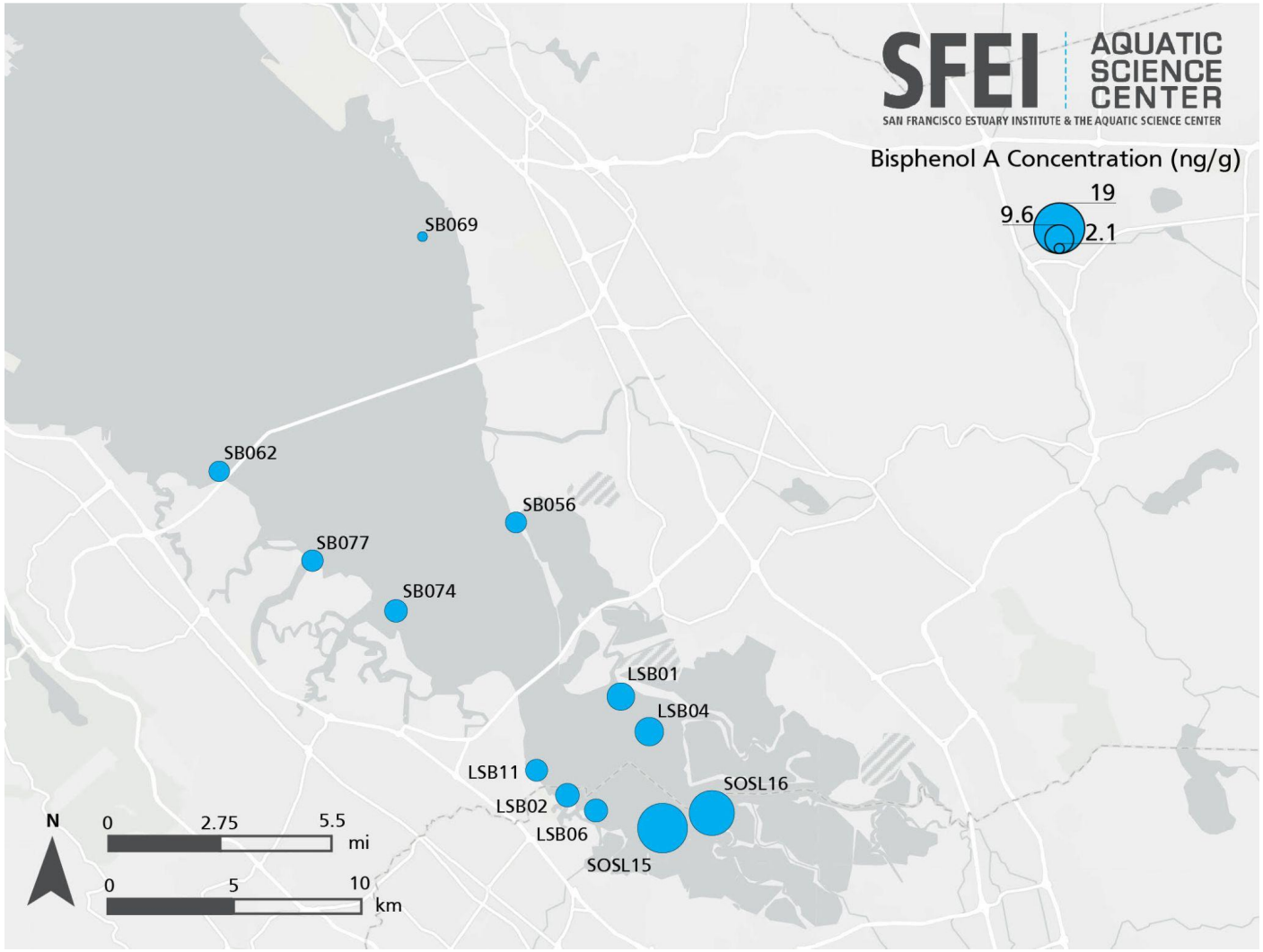

Figure A2. Concentrations of BPA in sediment across San Francisco Bay margin sites. Circles increase in size (small, medium, and large) to denote increasing concentrations in ng/g dry weight. SB - South Bay; LSB - Lower South Bay; SOSL - Southern Sloughs.

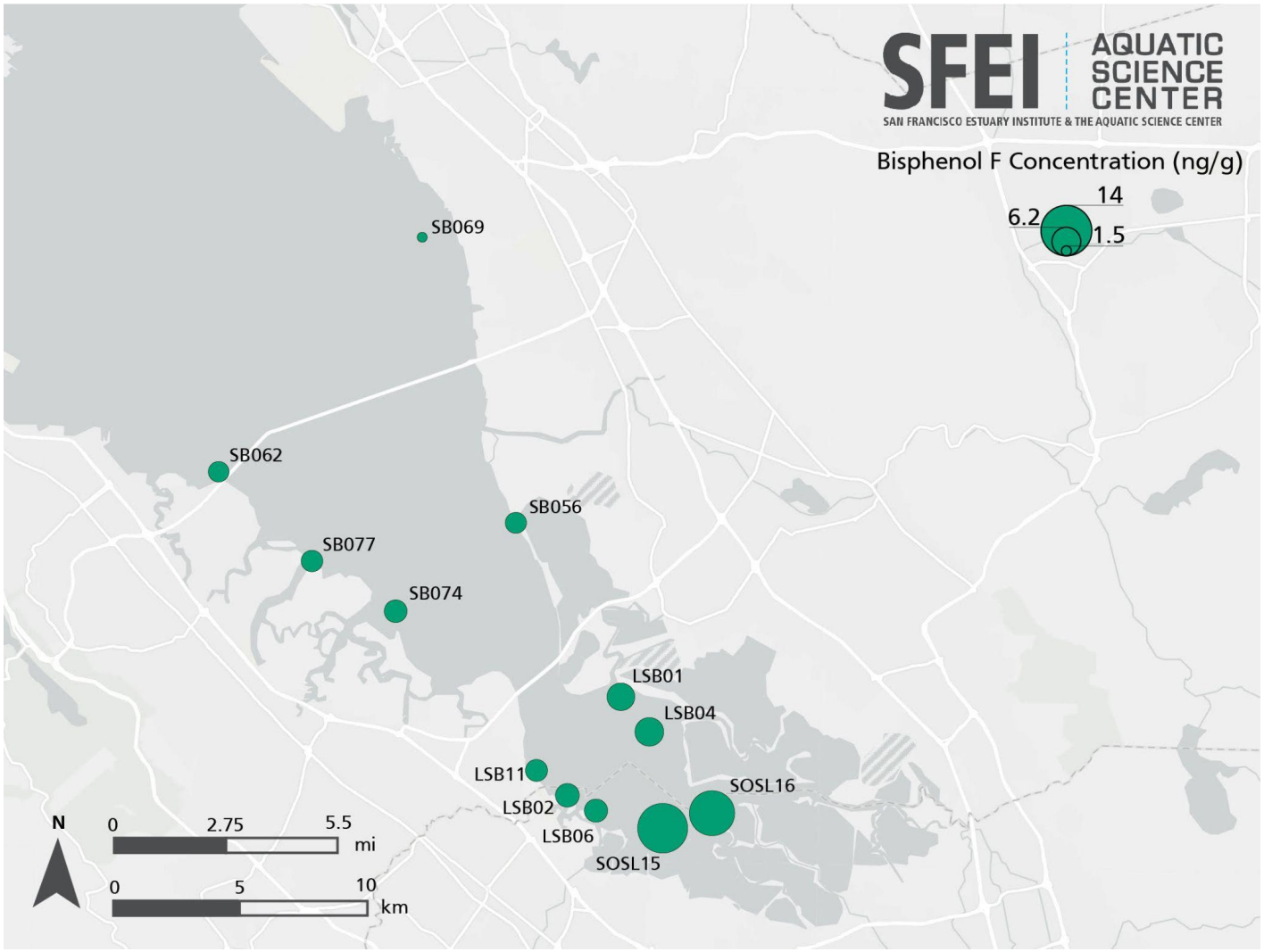

Figure A3. Concentrations of BPF in sediment across San Francisco Bay margin sites. Circles increase in size (small, medium, and large) to denote increasing concentrations in ng/g dry weight. SB - South Bay; LSB - Lower South Bay; SOSL - Southern Sloughs.

Table A6. Individual sample concentrations of detected bisphenols (A and F) in San Francisco Bay sediment. All values are in ng/g (dw).

Site Name	Bay Segment	Bisphenol A	Bisphenol F	Sum of Bisphenols
SB056	South Bay	6.8	4.6	11
SB062		6.6	2.3	8.9
SB069		2.1	1.5	3.6
SB074		7.5	3.1	11
SB077		7.0	2.0	9.0
LSB01	Lower South Bay	9.6	5.2	15
LSB02		7.9	3.0	11
LSB04		10	6.2	16
LSB06		7.7	3.5	11
LSB11		7.2	2.8	10
SOSL15	Southern Sloughs	19	14	33
SOSL16		17	14	31

Table A7. Comparison of San Francisco Bay bisphenol sediment concentrations to those in other estuaries and marine locations. All values are in ng/g (dw).

Compound	N	Range	Median	Mean	Location	Year	Reference
Bisphenol A	12	2.1 - 19	7.6	11	San Francisco Bay, USA	2017	This Study
	12	ND - 71	ND	6	San Francisco Bay, USA	2017	Heberger et al., 2020
	28	2.2 - 34	14	13	East China Sea, Zhejiang, China	2019	Xie et al., 2022
	48	ND - 116	2.0	1.9*	Bohai Sea and Yellow Sea, Northern China	2012, 2016	Liao et al., 2019
	82	ND - 106	1.5	5.1	Rivers, Lakes, and Bays in Midwestern and Eastern USA	1998 - 2012	Liao et al., 2012
Bisphenol F	12	1.5 - 14	3.3	7.0	San Francisco Bay, USA	2017	This Study
	28	ND - 5.4	1.6	1.6	East China Sea, Zhejiang, China	2019	Xie et al., 2022
	48	ND - 4.4	2.1	1.1*	Bohai Sea and Yellow Sea, Northern China	2012, 2016	Liao et al., 2019
	82	ND - 27.5	ND	0.21	Rivers, Lakes, and Bays in Midwestern and Eastern United States	1998 - 2012	Liao et al., 2012
Sum of Bisphenols	12	3.6 - 33	11	18	San Francisco Bay, USA	2017	This Study
	28	3.7 - 36	12	15	East China Sea, Zhejiang, China	2019	Xie et al., 2022
	48	ND - 119	4.6	4.6*	Bohai Sea and Yellow Sea, Northern China	2012, 2016	Liao et al., 2019
	82	ND - 138	3.2	8.6	Rivers, Lakes, and Bays in Midwestern and Eastern United States	1998 - 2012	Liao et al., 2012

**Geometric means were used for this study.*