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IN SAN FRANCISCO BAY

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PFAS in San Francisco Bay Water

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Executive Summary

Per- and polyfluoroalkyl substances (PFAS), a family of thousands of synthetic, fluorine-rich compounds commonly referred to as “forever chemicals,” are known for their thermal stability, non-reactivity, and surfactant properties. These unique compounds have widespread uses across consumer, commercial, and industrial products, resulting in widespread occurrence in the environment and wildlife across the globe. This study analyzed ambient surface water in San Francisco Bay for 40 PFAS to discern the occurrence, fate, and potential risks to ecological and human health.

Eleven of 40 PFAS were detected in ambient surface water collected in 2021 from 22 sites in the Bay. Seven PFAS (PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFHxS, and PFOS), were found in at least 50% of samples. PFHxA and PFOA were the most frequently detected analytes (detection frequencies of 86% and 77%, respectively). PFPeA and PFHxA were generally found at the highest concentrations across sites, with median and maximum concentrations of 1.6 and 4.8 ng/L and 1.5 and 5.7 ng/L, respectively. Pairwise Spearman's correlations revealed strong positive correlations ($p < 0.001$; $r > 0.77$) among the seven PFAS detected in at least 50% of sites, suggesting significant similarities between their sources, pathways, and/or fate in the environment. PFBA, PFNA, PFDA, and 6:2 FTS were found at a limited number of sites in the Bay. 6:2 FTS was found at a single site at 14 ng/L, the highest concentration of any individual PFAS in the Bay. The sums of detected PFAS for all sites had median and maximum concentrations of 10 and 29 ng/L, respectively.

A previous, limited screening of ambient surface water at five Bay sites in 2009 revealed generally similar individual and summed PFAS concentrations as those identified in this study. A temporal analysis using the 2009 study found few statistically significant differences between the datasets, with only short-chain compounds showing a statistically significant increase in the Bay from 2009 to 2021 ($p = 0.03$). Concentrations of PFAS in both studies were generally consistent with similar studies globally for surface water.

An examination of spatial variation of PFAS across the Bay found that all seven dominant PFAS, and sums of PFAS, were significantly higher in the South and Lower South Bays compared to Central and North Bays. This trend is consistent with the limited flushing and longer residence times within the Lower South Bay in particular, and the strong influence of both wastewater and stormwater as contaminant pathways for PFAS in this relatively small subembayment. Concentrations of PFAS in Bay Area stormwater and wastewater studies were compared to ambient Bay water. Stormwater collected in 2010 and 2011 had elevated levels of PFAS compared to those in surface water, with PFOS, PFOA, and PFHxA primarily detected at most sites. Ongoing monitoring efforts are underway to further assess the presence of PFAS in stormwater. The sum of PFAS (median: 58 ng/L; maximum: 100 ng/L) in recent Bay Area wastewater effluent measurements was roughly three times higher than the sum of PFAS in ambient water. A broader array of PFAS were found in effluent than surface water, though trends were similar for both matrices with short-chain compounds, especially PFPeA and PFHxA, being dominant.

Results from this study support the continued classification of PFAS 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 individual PFAS and their sums across sites in ambient surface water remain below available ecotoxicity thresholds, though these thresholds do not consider potential bioaccumulative effects. However, the 90th percentile concentrations of PFOA and PFOS in water exceed available human health screening levels for seafood ingestion, consistent with a recent RMP sport fish study indicating potential concern. To improve our understanding of PFAS occurrence and track temporal and spatial trends across the Bay, continued monitoring of ambient water is recommended, with additional use of the total oxidizable precursors (TOP) method that can quantify the potential contributions of unknown PFAS precursors. In addition, periodic screening studies in wastewater and stormwater are suggested for early detection of emerging PFAS of concern and potential trends, as these pathways are generally the most concentrated. Sustained, multi-matrix monitoring of this important class of contaminants of emerging concern is a high priority for the RMP.

1. Introduction

1.1. PFAS Definitions

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are an extensive family of thousands of synthetic fluorine-rich chemicals. The Organisation for Economic Cooperation and Development (OECD) has recently established a broadly inclusive definition of PFAS that essentially encompasses all fluorinated substances containing at least one fully fluorinated methyl or methylene carbon atom (OECD, 2018, 2021). A similar, slightly broader definition used in California legislation specifies the PFAS class includes all organic compounds with one fully fluorinated carbon atom (AB-652, 2021; AB-1200, 2021; SB-343, 2021).

Within this broad family, PFAS are further separated into classes distinguished by those with and without a polymeric structure. Nonpolymer PFAS are composed of two significant subclasses: polyfluoroalkyl and perfluoroalkyl substances. Polyfluoroalkyl substances have a carbon backbone that is not fully fluorinated and thus, contain at least one carbon-hydrogen bond or one unsaturated carbon bond. The inclusion of non-fluorinated bonds makes these compounds susceptible to breakdown and act as precursors that degrade to terminal PFAS, stable perfluoroalkyl substances that do not degrade further under environmental conditions. These precursor transformation pathways are identified in red or pink in Figure 1. Several of the groups of compounds within the polyfluoroalkyl substances class also contain compounds known as intermediate transformation products, which are transient compounds formed in the transformation process to terminal products (Figure 1).

In contrast, perfluoroalkyl substances are fully fluorinated, meaning that no carbon-hydrogen bonds are present, and only fluorine atoms are bonded to the carbon alkyl backbone of the molecule. Perfluoroalkyl acids (PFAAs) are the most well-known group and are recalcitrant to breakdown under environmental conditions. The two major subgroups of PFAAs, perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs), are terminal degradation products of many perfluorinated compounds (Figure 1). These subgroups are differentiated as long-chain and short-chain to classify those that behave similarly in the environment (OECD/UNEP Global PFC Group, 2013). Long-chain compounds are PFCAs with eight or more carbons, like perfluorooctanoic acid (PFOA), and PFSAs with six or more carbons, such as perfluorooctane sulfonic acid (PFOS). Short-chain compounds refer to PFCAs with seven or fewer carbons, such as perfluorobutanoic acid (PFBA), and PFSAs with five or fewer carbons including perfluorobutanesulfonic acid (PFBS). Other perfluoroalkyl groups, like perfluoroalkane sulfonamides (FASAs), consist of precursors that break down into terminal PFAAs.

Other PFAS include polymers, large molecules with similar units (monomers) bonded together in a repeating pattern. Two subclasses of PFAS polymers include fluoropolymers, compounds with a carbon-only backbone directly attached to fluorine, and side-chain fluorinated polymers, molecules with fluorinated side-chain branches and nonfluorinated backbones. These side-chain branch bonds may react and liberate non-polymer PFAS.

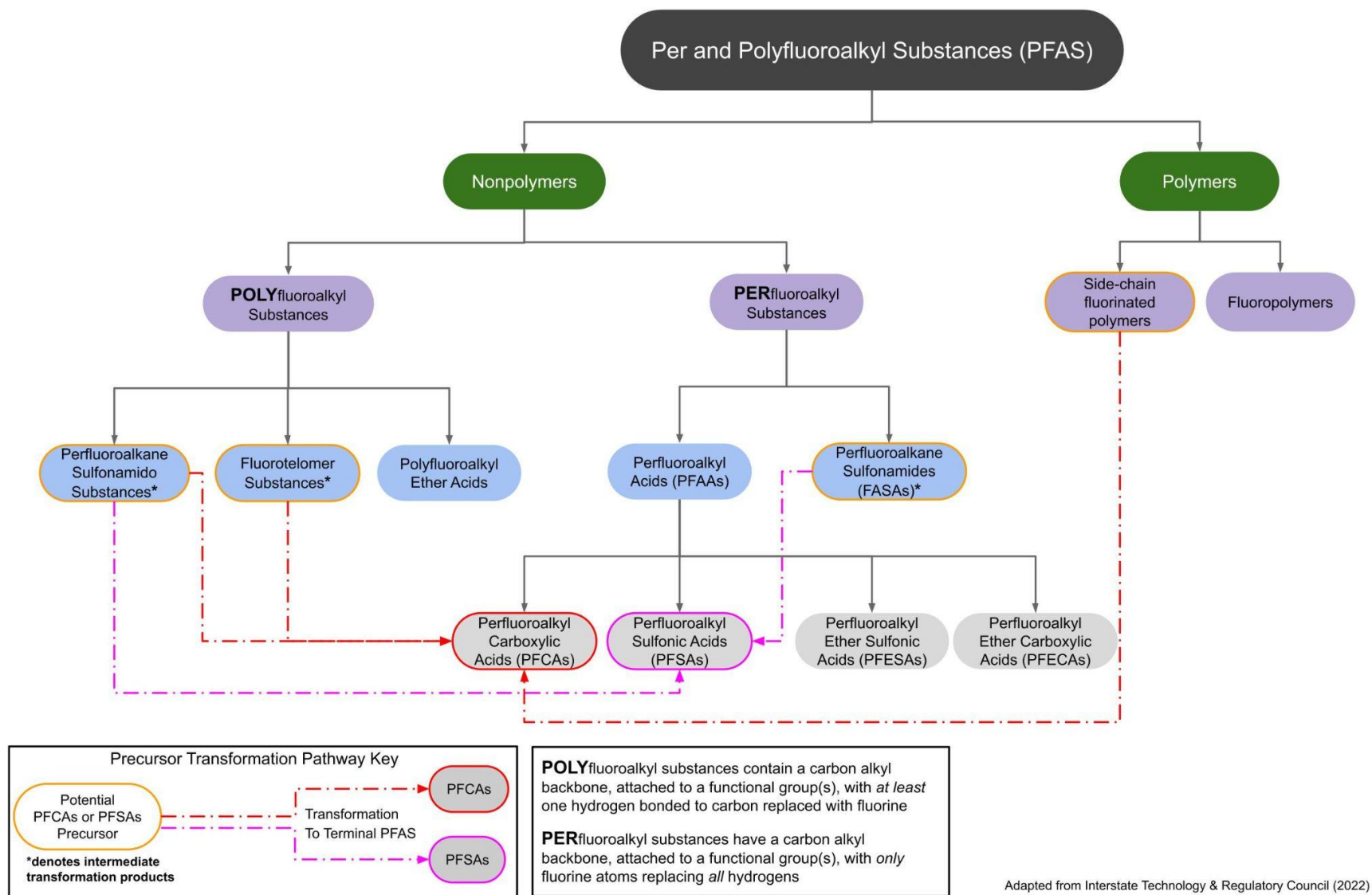


Figure 1. PFAS family tree with precursor transformation pathways identified. This figure is adapted from ITRC (2022).

1.2. Background

Compounds within the PFAS class generally share important physical and chemical properties such as recalcitrance and surfactant characteristics. These special attributes have allowed for a plethora of applications, with numerous PFAS used in consumer, commercial, and industrial applications including: food packaging materials, cosmetics and personal care products, waterproof textiles, stain-resistant carpets and furniture, fire-suppression foams, processing aids for the production of fluoropolymers like Teflon, mist suppressants in metal-plating, and hydraulic aviation fluids (3M, 1999; Buck et al., 2011; ITRC, 2022; KEMI, 2015; USEPA, 2022a).

The widespread use of PFAS, their extremely high persistence in the environment, and the bioaccumulation potential and toxicity of some PFAS have caused major concern for this class of chemicals. PFOS and PFOA, the most well-studied PFAS, have been the regulatory focus based on their extensive toxicity profiles highlighting a range of toxic effects, multi-year half-lives in human blood, and bioaccumulation in aquatic food webs (DeWitt, 2015; Sunderland et al., 2019). In the US, production of PFOS was phased out by 2002, and production of PFOA was phased out by 2015. This federal action was part of a broader international collaboration to reduce human and environmental risks associated with exposure to these compounds.

As use of PFOA and PFOS has been restricted, industries have substituted short-chain PFAS (Brendel et al., 2018; Z. Wang et al., 2013). Other alternatives including perfluorinated alkyl ethers, like GenX (also known as HFPO-DA), and polyfluorinated substances have emerged as alternatives in the manufacture of fluoropolymers (Y. Wang et al., 2019). Given the similarity in structure and preliminary testing conducted to date, researchers believe these compounds will exhibit similar toxicological responses, physical and chemical characteristics, and environmental persistence as better-studied long-chain compounds (Brendel et al., 2018; Kjølholt et al., 2015; Y. Wang et al., 2019). Notably, replacement products typically exhibit much shorter bioaccumulation half-lives and greater environmental mobility than their longer-chain predecessors.

Some governmental and non-governmental entities have moved toward restricting the entire class of PFAS in particular use categories. California's Department of Toxic Substances Control's Safer Consumer Products Program established a clear rationale for management actions directed at the entire PFAS class (Bălan et al., 2021). DTSC has begun to apply this approach to carpets and rugs made or sold in California as well as treatments containing PFAS for converted textiles or leathers. Similarly, California has used a class-wide approach in banning PFAS in certain firefighting foams, as well as in paper-based food packaging and products intended for infants and children, both of which take effect in 2023. Recently, California also passed legislative bans on cosmetics and textile products that will take effect in 2025.

Over the past two decades, ubiquitous environmental detections of PFAS have been documented by studies worldwide. Since 2004, the RMP has detected PFAS across matrices in San Francisco Bay with a series of monitoring projects on harbor seals, cormorants, fish, bivalves, sediment, ambient water, wastewater, and stormwater. In 2004 and 2006, concentrations of PFOS in Bay harbor seals and bird eggs were some

of the highest detected globally (Sedlak & Greig, 2012). Ongoing, triennial bird egg monitoring has indicated decreasing levels of PFOS in South Bay cormorants, though the most recent concentrations still may pose a risk to hatching success (Sedlak et al., 2017). In addition, sport fish monitoring, especially in South Bay fish, has shown PFAS persisting over time at concentrations exceeding thresholds for human consumption advisories that have been established by other states (Buzby et al., 2021).

Studies of pathways to the Bay have found a variety of PFAS across sites. A variety of PFAS have been found in wastewater effluent in the Bay, with similar levels of short-chain PFAS and decreasing levels of long-chain PFAS across all temporal studies (Houtz et al., 2016; Sedlak et al., 2017). The State Water Resources Control Board (SWRCB) has issued investigative orders to test drinking water, wastewater, and other matrices at numerous sites across the state, focusing on locations near airports, military bases, landfills, and other potential sources of PFAS to the environment, and to share the information collected through a public database called Geotracker (SWRCB, 2022a). Within this scope, a recent regional study of influent, effluent, and biosolids on behalf of the Bay Area Clean Water Agencies (BACWA) detected various PFAS across each matrix (Mendez et al., 2021). Stormwater has been monitored less frequently, with the most recent study (2010-2011) finding detectable levels of PFAS, especially in more urbanized areas (Houtz & Sedlak, 2012). An ongoing study of stormwater aims to further evaluate the occurrence of PFAS in this pathway (Sutton et al., in preparation).

Surface water and sediment have received more limited study within the Bay. Water samples were collected during the 2009 dry season from five open Bay (ambient) sites, one from each embayment, and during the 2009/2010 wet season (Water Year 2010) at five nearshore (margin) sites (Sedlak et al., 2018). In open Bay water, the highest concentrations of PFAS observed included PFOA (median: 1.4 ng/L; maximum: 8.6 ng/L) and PFOS (median: <0.97 ng/L; maximum: 6.3 ng/L). The highest concentrations of PFAS were observed in the margins, with levels at one site an order of magnitude higher than all other sites (median: 15 ng/L; maximum: 670 ng/L). In general, PFOS and many of the short-chain PFCAs such as PFBA, perfluoropentaonic acid (PFPeA), perfluorohexanoic acid (PFHxA), and perfluoroheptanoic acid (PFHpA) were detected in ambient and margin water samples collected in South Bay. Method detection limits (MDLs) ranged from 0.68-15.9 ng/L, with MDLs for PFCAs and PFSA specifically ranging from 0.97-2.0 ng/L. For most PFAS analytes, these MDLs are higher than those in the present study.

PFAS as a class are contaminants of Moderate Concern for the Bay, suggesting a high probability of a low level effect on Bay wildlife, under the RMP tiered risk-based framework for emerging contaminants (Sutton et al., 2017). In order to better understand occurrence and risks of PFAS in San Francisco Bay, targeted monitoring of 40 PFAS was conducted at 22 ambient Bay water sites in 2021. Observed concentrations in this study were compared to the previous water monitoring results as an initial temporal comparison. Bay water concentrations were also compared to available PFAS data in Bay Area wastewater and stormwater. PFAS levels were compared to available thresholds for protection of aquatic and human health. We also provide a strategy for future PFAS monitoring in the Bay to inform management actions.

2. Methods

2.1. Sample Collection

Dry season Bay water samples were collected between September 28 and October 5, 2021, as part of the biannual RMP Status and Trends water monitoring cruise. Bay water samples from 22 sites were collected by dipping a stainless steel bailer over the side of the vessel via a cotton rope, and filling pre-cleaned sample containers (500 mL, HDPE) with Bay water. The bailer was cleaned between sites using a horse hair brush and Alconox detergent, multiple DI rinses, two methanol rinses, and two UPLC grade water rinses. Two field replicates and two field blanks were also collected. Field blanks were collected by opening a sample bottle (pre-filled with PFAS-free water) while the field sample was being collected. Samples were stored on wet ice in coolers (1 to 5°C) on the boat, and placed in the freezer at the end of each sampling day. Clean gloves were worn to avoid contaminating samples, and care was taken to minimize contact with materials that may contain PFAS (e.g., waterproof clothing, food packaging, paper towels, aluminum foil). After sample collection was complete, samples were shipped overnight on ice to the analytical laboratory SGS AXYS (Sidney, British Columbia, Canada), where the samples were kept frozen until analysis. All samples were analyzed within the recommended hold time of 90 days.

2.2. Laboratory Analysis

Water samples were analyzed for target PFAS compounds using SGS AXYS method MLA-110 (USEPA method 1633). The target analyte list includes 40 compounds listed in Table A1. Unfiltered (total water) samples were spiked with isotope-labeled surrogate standards and then extracted and cleaned through Solid Phase Extraction (SPE). Sample extracts were analyzed by ultra performance liquid chromatography/mass spectrometry (UPLC-MS/MS) with reported sample concentrations determined by isotope dilution/internal standard quantification.

SGS AXYS provided measurements that included values above standard reporting limits (RLs), as well as values above lower MDLs (Table A1). For this study, MDLs were based on the lowest calibration standard (referred to as “A-Cal” in MLA-110), a more sensitive method that allows for quantification of lower concentrations. Values between the RL and the MDL have greater uncertainty, and may be considered semi quantitative. For this report, we have generally used all reported values in our analyses, with appropriate caveats.

2.3. Quality Control

Field sample results were reported as surrogate corrected, with average recoveries calculated on surrogate spikes in five lab control samples (LCS). All recoveries were within 65-135% targets, meeting data quality objectives for quantitative results. Additionally, two field replicates samples and the LCS exhibited relative percent differences (RPDs) within 35% for all analytes, also meeting noted objectives. For this analysis, the original field sample and field replicate were averaged as a single data

point (Table A2). The analysis of a pair of field blanks as well as two laboratory blanks showed no detection of any PFAS.

A variety of summary statistics were calculated to summarize the distribution of measured PFAS concentrations in field samples, with any non-detects (NDs) treated as zero, a standard practice within the RMP. Raw data were evaluated for normality using the Shapiro-Wilks test, which indicated normal distributions for sums of PFAS in each subembayment except Central Bay. Two datasets, one combining SB and LSB data ("all of South Bay"), and another for the other subembayments of the Bay ("all of NB and CB"), showed normal distributions for sums of PFAS. The dataset for all subembayments except LSB ("remaining subembayments") was not normally distributed. For analytes detected in at least 50% of samples, nearly all (except PFOA) were not normally distributed.

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 PFAS detected in at least 50% of samples. In addition, the two sample t-test was used to examine the temporal and spatial correlations between individual and sums of PFAS across Bay sites. The variance of each dataset was calculated to determine the appropriate t-test for each comparison. When distributions were not normal, the Mann-Whitney-Wilcoxon test was used to investigate spatial and temporal correlations. When distributions were normal, variance was determined and a student t-test was used with or without equal variance. All tests were conducted using Microsoft Excel with the statistical significance level set to $\alpha = 0.05$.

3. Results and Discussion

3.1. Occurrence and Contaminant Correlations

In Bay water samples, 11 of 40 PFAS were detected, with seven observed at concentrations higher than the RL in samples from at least half of the 22 sites examined (summary statistics in Table 2; full data in Table A2). PFHxA was observed at the highest number of sites across the Bay (86%), with a maximum concentration of 5.7 ng/L and median of 1.5 ng/L. Other PFAS with detection frequencies at or above 50% (n = 22) include PFOA, detected at 17 sites (maximum: 3.2 ng/L; median 0.84 ng/L); PFPeA, detected at 15 sites (maximum: 4.8 ng/L; median 1.6 ng/L); PFOS, detected at 14 sites (maximum: 4.7 ng/L; median 0.86 ng/L); PFBS, detected at 13 sites (maximum: 2.7 ng/L; median: 0.53 ng/L); PFHpA, detected at 12 sites (maximum: 1.7 ng/L; median: 0.56 ng/L); and perfluorohexane sulfonic acid (PFHxS), detected at 11 sites (maximum: 2.3 ng/L; median: 0.27 ng/L). All seven are also terminal degradation products of many precursor compounds. Concentrations of the seven most abundant PFAS are shown in Figure 2.

Table 2. Summary statistics (where ND = 0) for PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFHxS, and PFOS detected in ambient water samples from San Francisco Bay. All concentrations are in nanograms per liter (ng/L).

	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFHxS	PFOS	Sum of PFAS
Detection Frequency (n = 22)	68%	86%	55%	77%	59%	50%	64%	-
Minimum	ND	ND	ND	ND	ND	ND	ND	ND
Maximum	4.8	5.7	1.7	3.2	2.7	2.3	4.7	29
Median	1.6	1.5	0.56	0.84	0.53	0.27	0.86	5.9
Mean	1.7	2.1	0.55	1.1	0.68	0.76	1.5	10
90th Percentile	3.8	4.5	1.4	2.4	1.7	2.2	4.0	25
Standard Deviation	1.5	1.7	0.59	0.93	0.82	0.90	1.6	10
MDL	> 0.89	> 0.44	> 0.44	> 0.44	> 0.44	> 0.44	> 0.44	-

Other detections included PFBA (range: ND-3.9 ng/L, detected at 6 sites), PFNA (range: ND-0.60 ng/L, detected at 3 sites), and PFDA (range: ND-0.48 ng/L, detected at 2 sites). Among PFAS more recently added to standardized analytical methods, including precursors, only 6:2 fluorotelomer sulfonate (FTS) was detected, at a single site in the Bay at the highest level relative to any other PFAS detection (14 ng/L).

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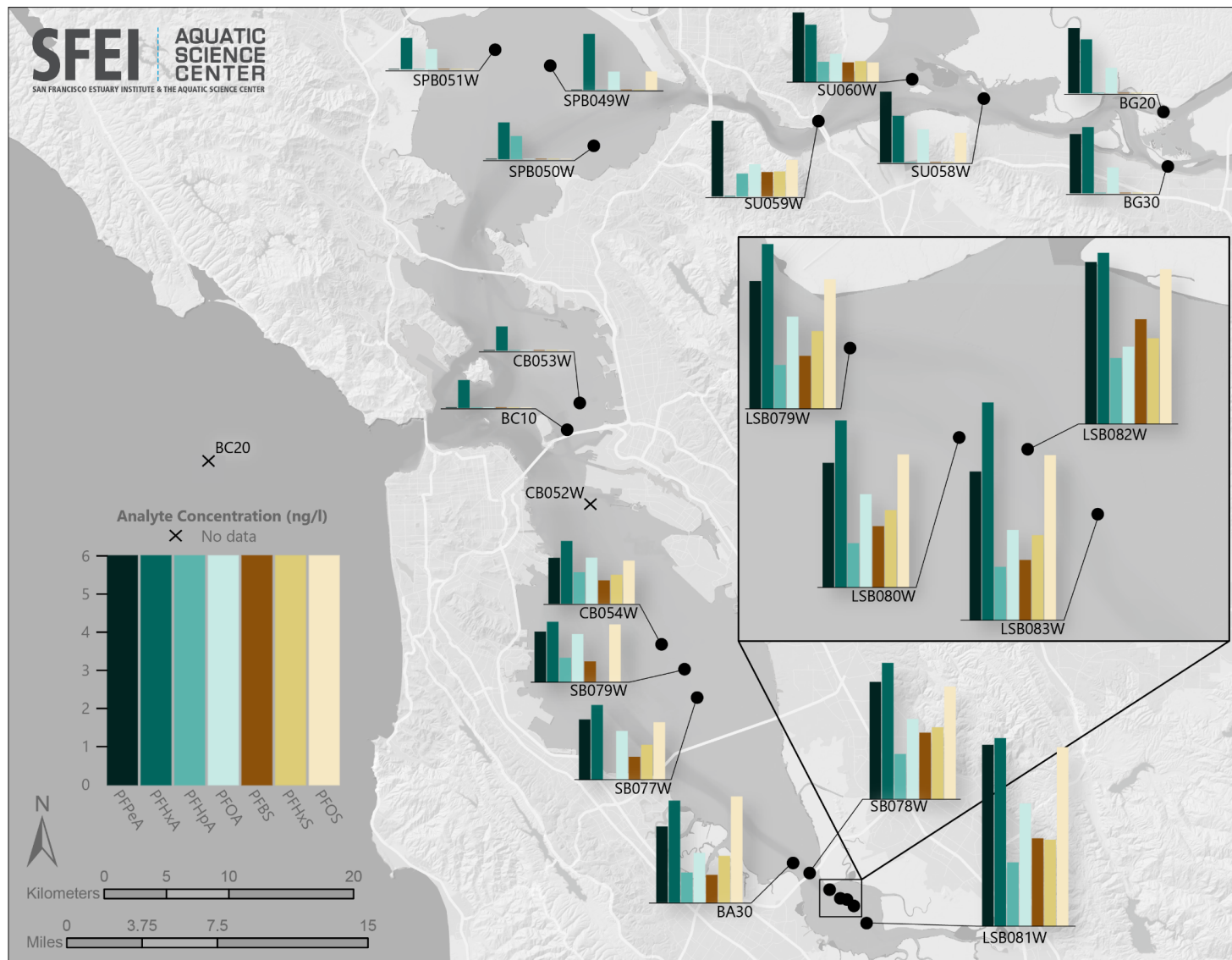


Figure 2. Concentrations of the seven most abundant PFAS detected in ambient water samples from San Francisco Bay: PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFHxS, and PFOS. All concentrations are in ng/L.

Another way to examine the data is to consider the NDs to be half the MDL, which can reduce a bias towards lower values inherent in the RMP's standard substitution of zero for NDs. Analysis of the data using half the MDL for NDs showed most values for the sums of PFAS at individual sites increased by around 30 ng/L, resulting in an increased median and mean of 38 and 42 ng/L, respectively (Figure 3). The means of the sum of PFAS using ND as zero (10 ng/L) and half the MDL (42 ng/L), suggests a wider range of potential estimated concentrations across the Bay. This analysis indicates that, in some cases, alternate means of handling NDs may significantly impact interpretation of risks and trends, and this should be taken into consideration. More sensitive methods are needed for PFAS analytes of particular interest to provide a robust basis for assessment.

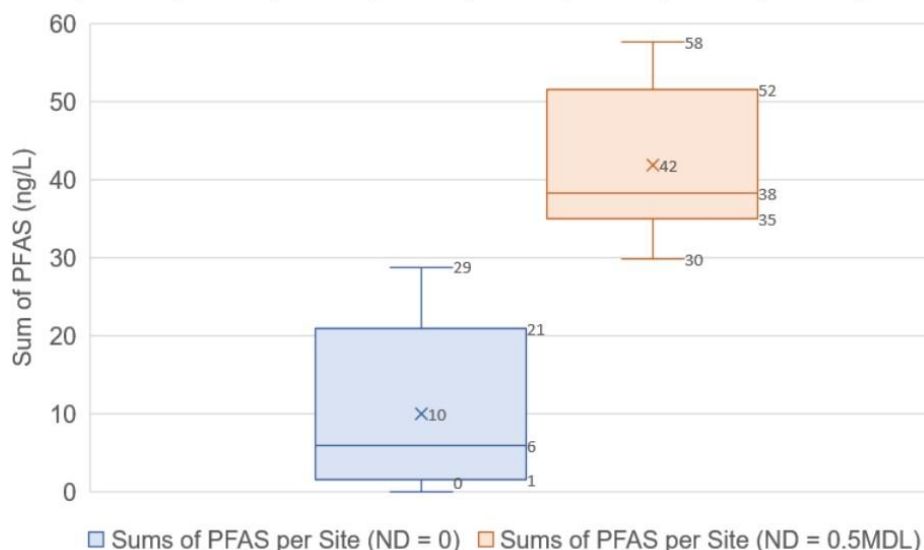


Figure 3. Box plot of the sum of PFAS data per site when non-detects (NDs) are considered zero (in blue) and half the MDL (in orange). Within each box, the horizontal line marks median values, x denotes mean values, boxes extend from the 25th to the 75th percentile of each dataset's distribution of values, and whiskers denote the range.

Spearman's correlation tests revealed widespread statistically significant ($p < 0.001$; $r > 0.77$) positive correlations between analytes detected in $\geq 50\%$ of samples (PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFHxS, and PFOS; Table A3). Analysis of PFAS concentrations demonstrated especially strong positive correlations between PFOS and PFBS ($r = 0.96$), and PFOS and PFOA ($r = 0.95$) as well as between PFBS and PFHxS ($r = 0.94$). The significant positive correlations among PFAS implies similar patterns in their sources, presence in contaminant pathways, and/or fate in the Bay.

Relative to a limited 2009 screening of PFAS in five ambient Bay water samples, one from each subembayment, 2021 concentrations are generally similar for most PFAS detected (Sedlak et al., 2018). Comparisons using a Mann-Whitney-Wilcoxon test indicated that for all seven analytes measured in both studies, as well as the sum of PFAS with NDs treated as zero, there were no statistically significant temporal

differences (Table A4). The three most abundant analytes remained the same across those analyzed in both studies, with PFHxA, PFOS, and PFOA constituting the majority of the summed PFAS burden throughout the Bay. However, the abundance of these three analytes was reversed between these studies, with PFHxA dominating the concentrations measured in 2021, followed by PFOS and PFOA, while the 2009 study found PFOA to be the primary PFAS in the Bay, followed by PFOS and PFHxA. This apparent decline in the dominance of PFOS and PFOA corresponds with production phaseouts in the US.

While a statistically significant trend is not yet evident, a comparison of PFAS concentrations suggests the possibility that PFOA may be showing signs of decline in Bay waters (Table A4). In 2009, PFOA concentrations ranged from ND to 8.6 ng/L (median 1.4 ng/L) in the Bay, while in 2021, concentrations ranged from ND to 3.2 ng/L (median 0.84 ng/L). However, since the 2009 study only included five samples, any apparent decreases in concentration must be viewed with caution.

Using the Mann-Whitney-Wilcoxon test, short-chain compounds showed a statistically significant increase in the Bay from 2009 to 2021 ($p = 0.03$; Table A5). The increase of short-chain compounds from 2009 to 2021 coincides with their rise in use as replacements of long-chain PFAS. Inspection of individual short-chain PFAS levels provides additional, limited evidence to suggest increasing concentrations for a few compounds. For example, concentrations of the short-chain perfluorocarboxylic acid (PFPeA) ranged from ND to 2.5 ng/L (median: <1 ng/L, MDL) in 2009, while in 2021 they ranged from ND to 4.8 ng/L (median 1.6 ng/L). Apparent increases in abundance of short-chain perfluorosulfonate PFBS, which had no to low detections in 2009 relative to frequent detections in 2021, may be influenced by methodological improvements resulting in a more sensitive method with lower MDLs.

Since 2009, the suite of PFAS analyzed has expanded to include more precursors; none were measured except for 6:2 FTS, a precursor to terminal C4-C6 PFCAs. It was only found at one site in Central Bay, albeit at the highest single PFAS concentration measured in the study, at 14 ng/L. Newly developed PFAS such as GenX and ADONA were not observed in Bay waters analyzed with MDLs comparably higher than other PFAS (1.69-2.10 ng/L).

A review of the literature indicates that concentrations of individual PFAS detected in the Bay in 2021 were within the range of concentrations found in selected estuarine or marine environments domestically and globally (Table A8). San Francisco Bay concentrations in total water were generally higher than dissolved phase concentrations detected in the Gironde Bay of France, with mean San Francisco Bay concentrations for PFPeA, PFHxA, PFHpA, PFOA, PFOS, and 6:2 FTS higher than the maximum concentrations of these contaminants reported in France (0.52 ng/L to 1.1 ng/L; Munoz et al., 2017). Dissolved concentrations were used as a comparison since the Gironde Bay is a macrotidal Bay, with several samples showing significant levels of suspended sediments, suggesting the dissolved phase is likely to be more similar to the total water concentrations in this study (where suspended solids were minor).

However, recent studies in Pensacola Bay, Florida, and Melbourne, Australia reported levels similar to or higher than those observed in San Francisco Bay (Allinson et al., 2019; da Silva et al., 2022). Maximum concentrations in the Pensacola study were consistently an order of magnitude higher than those found in San Francisco Bay, ranging from 17 ng/L to 59 ng/L for PFPeA, PFHxA, PFHpA, PFOA, and PFHxS, compared to maxima of 1.7 ng/L to 5.7 ng/L for those analytes in San Francisco Bay (da Silva et al., 2022). Reported mean concentrations for these analytes were more similar in magnitude. PFOS was observed at much higher concentrations in Pensacola, with a reported maximum of 269 ng/L and median concentration of 3.29 ng/L, compared to 4.7 ng/L and 0.86 ng/L, respectively, in San Francisco Bay. This finding is consistent with Pensacola as the site of major Naval sites with known PFAS contamination, as well as hydrodynamic patterns that extend the residence times in some regions. Similar trends were found in comparing the San Francisco Bay to estuarine concentrations in Melbourne, Australia. Mean concentrations of PFPeA, PFHxA, PFHpA, PFOA, PFBS, and PFBA were higher in Melbourne (4.1 ng/L to 7.8 ng/L; Allinson et al., 2019) compared to those found in San Francisco (0.55 ng/L to 2.1 ng/L). PFHxS and PFOS mean concentrations in Melbourne dwarfed those measured in San Francisco Bay, at 17 ng/L and 34 ng/L, relative to 0.76 ng/L and 1.48 ng/L, respectively. Similar to Pensacola, Melbourne has more limited tidal flushing in some regions, meaning longer residence times for contaminants.

3.2. Spatial Distribution and the Contributions of Pathways

San Francisco Bay PFAS monitoring indicates temporally consistent geospatial trends in relative contaminant distribution. The 2009 study showed no detections of PFAS in Central Bay and San Pablo Bay, limited PFAS levels in Suisun Bay, and higher concentrations of PFAS in South and Lower South Bays. This spatial trend was similar in this latest round of sampling, with South and Lower South Bays again yielding the majority of the PFAS observed, and lower levels in Central Bay, Suisun Bay and San Pablo Bay. In addition to these five subembayments, samples were also collected from Sacramento and San Joaquin river sites in 2021. Only PFCAs (PFPeA, PFHxA, and PFOA) were detected at these sites. No PFAS were detected at the single ocean site beyond the Golden Gate.

Concentrations of the seven PFAS detected $\geq 50\%$ were tested for spatial variation in the Bay using the Mann-Whitney-Wilcoxon test to compare two non-normal sample population distributions. The two different sets of sample populations compared were: Lower South Bay versus the remaining subembayments (Table A6); and a grouping of Lower South Bay and South Bay (“all of South Bay”) versus the remaining subembayments (“all of North Bay and Central Bay”; Table A7). When population distributions were normal, variance was determined and a student t-test was used with or without equal variance.

All seven of the PFAS analyzed and frequently detected (PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFHxS, and PFOS) as well as the sum of PFAS showed statistically higher levels in both Lower South Bay and “all of South Bay” than the rest of the Bay. A similar analysis with additional groupings of short-chain (PFPeA, PFHxA, PFHpA, and

PFBS) and long-chain (PFOA, PFHxS, and PFOS) PFAS found the same trend of statistically higher levels in both Lower South Bay and “all of South Bay” when compared to the remaining subembayments. Concentrations of short-chain and long-chain PFAS were not statistically different in the Bay as a whole (considering all subembayments together; Table A5) and in individual subembayments (considering each subembayment separately; Table A5).

The higher levels of PFAS in South and Lower South Bays reflects the more limited tidal flushing in southern stretches of the Bay, and is consistent with wastewater effluent and stormwater runoff as important pathways for PFAS, especially given this region’s relatively long residence times. Prior wet season monitoring (2009/2010) of five margin Bay sites likely to be influenced by stormwater runoff revealed higher concentrations of PFAS relative to open Bay sites in the same subembayments (Sedlak et al., 2018), providing additional evidence to support the importance of this pathway for contaminants to reach the Bay.

Recent studies in the Bay Area have begun to characterize PFAS concentrations in these pathways. A 2010/2011 stormwater project detected 11 PFAS at 10 sites, including the seven dominant compounds identified in this study (Houtz & Sedlak, 2012). The primary PFAS detected were PFOS, PFOA, and PFHxA, with median and maximum concentrations of 15 and 26 ng/L, 7.3 and 16 ng/L, and 4.5 and 9.7 ng/L, respectively (NDs were treated as zeros). These concentrations in stormwater are elevated compared to Bay water, consistent with the more concentrated nature of pathways. More urban sites showed greater concentrations of PFAS overall, with low concentrations of the short-chain PFAS observed across sites. The results of a total oxidizable precursor (TOP) analysis, which quantifies the presence of precursors likely to transform over time to terminal PFAS like PFOA, indicated a significant presence of precursors in stormwater. To better understand the presence of PFAS and other emerging contaminants in stormwater, a four-year study (water years 2019-2022) of PFAS and other emerging contaminants in stormwater is underway, with PFAS levels to be further explored in a full report (Sutton et al., in preparation).

Characterization of PFAS in wastewater is also a major focus in the Bay Area. Most recently, a 2020 study of wastewater influent, effluent, and biosolids conducted on behalf of BACWA at 12 municipal wastewater treatment facilities found 31 of 40 analytes (Mendez et al., 2021). The median and maximum concentrations of summed PFAS in effluent, where NDs are 0, were 58 ng/L and 100 ng/L. These values are about three times greater than those measured in surface water, which is expected of wastewater effluent as wastewater collects many potential domestic and industrial PFAS users. Across all facilities, the predominant PFAS detected were short-chain PFAS, especially PFBA, PFPeA, and PFHxA. These results, along with noted trends in Bay water, are consistent with expected increases in manufacture and use of short-chain PFAS worldwide. A second phase of BACWA’s study aims to understand major sources to municipal wastewater to answer important management questions.

Earlier wastewater studies provide further insights regarding the presence of precursors in this pathway, as well as temporal trends. As part of a 2014 study, effluent from eight

facilities was analyzed for PFAS using both target and TOP methods. The TOP analysis found mass concentrations of terminal PFCAs increased an average of 124% (Houtz et al. 2016), indicating a strong influence of PFAS precursors discharged to Bay receiving waters. The precursors transformed mainly to C6 or shorter compounds, suggesting that few of the precursors are long-chain molecules. Previous wastewater effluent measurements as part of both 2009 and 2014 studies generally showed similar concentrations of short-chain PFAS relative to 2020 data, while levels of certain long-chain PFAS have exhibited declines (Houtz et al., 2016; Mendez et al., 2021).

As additional information on PFAS concentrations in wastewater and stormwater pathways is revealed through ongoing and future studies in the Bay Area, understanding of the relative influences of these pathways on PFAS contamination of the San Francisco Bay will improve.

3.3. Risk Evaluation for San Francisco Bay

Exposure to some PFAS has been associated with a wide range of toxic effects, with most studies focused on PFOA and PFOS. Studies based on laboratory animals and human populations exposed to higher concentrations provide evidence that well-studied PFAS such as PFOS and PFOA can be classified as multi-system and developmental toxicants (DeWitt, 2015), and tend to cause liver damage, adverse developmental effects, and suppression of the immune system in humans and wildlife. These effects may occur at exposure to environmentally relevant concentrations (Lau et al., 2007; Tahziz et al., 2021; Z. Wang et al., 2017).

To date, much of the regulatory focus has been on the long-chain perfluoroalkyl compounds, such as PFOS and PFOA, in part based on their extensive toxicity profiles, multi-year half-lives in human blood, past production volumes, bioaccumulation in aquatic food webs, and extremely high persistence in the environment.

Although they have not been as well studied, the available information suggests that based on the similar structure of PFAS alternatives to PFOS and PFOA, the alternatives will likely have similar toxicological profiles (Z. Wang et al., 2014, 2017). PFAS, particularly the long-chain compounds, bioaccumulate in the food web (Burkhard, 2020; Z. Wang et al., 2015), with apex predators such as polar bears, sea otters, and seals having some of the highest tissue concentrations (Houde et al., 2006, 2011; Sturm & Ahrens, 2010). Short-chain compounds are known to enrich in plants, though they are typically assumed to have a lower bioaccumulation potential in animals compared to long-chain compounds (Brendel et al., 2018). In general, PFASs are more bioaccumulative than PFCAs (Conder et al., 2008).

Because of a concern around the toxicological effects of all PFAS, there is movement by some governmental and non-governmental entities toward assessing and regulating PFAS as a class or as subgroups, rather than by individual compounds (Kwiatkowski et al., 2020). However, there are currently insufficient data to reliably predict how different PFAS might interact with one another, preventing reliable PFAS mixture risk assessment (Ankley et al., 2020).

Much of the regulatory focus in developing thresholds has been on drinking water and direct exposure to human health risk levels. California's State Water Resources Control Board established drinking water response levels (RLs) of 10 ng/L for PFOA and 40 ng/L for PFOS (SWRCB, 2022b). They also set drinking water notification levels (NLs), health-based concentrations that indicate the need for notification and further monitoring and assessment, of 5.1 ng/L for PFOA and 6.5 ng/L for PFOS (SWRCB, 2022b). In 2021, the SWRCB issued a NL and RL of 0.5 ng/L and 5 ng/L, respectively, for PFBS; in 2022, the agency issued a NL and RL of 3 ng/L and 20 ng/L, respectively, for PFHxS (SWRCB, 2022b). California's Office of Environmental Health Hazard Assessment (OEHHA) has recently proposed public health goals (PHGs) of 0.007 ng/L for PFOA and 1 ng/L for PFOS, based on increased risk of kidney, liver, and pancreatic cancer (OEHHA, 2021). The Agency for Toxic Substances and Disease Registry (ATSDR, a federal public health agency of the U.S. Department of Health and Human Services) has developed minimum risk level (MRL) screening values for PFOA, PFOS, PFHxS, and PFNA that can be converted into drinking water concentrations. When ATSDR uses an average child's weight and water intake to convert these MRLs into drinking water concentrations, the individual PFOA, PFOS, PFHxS, and PFNA concentrations are 21 ng/L, 14 ng/L, 140 ng/L, and 21 ng/L, respectively (ATSDR, 2018). The USEPA set its first drinking water lifetime health advisory levels in 2016 at 70 ng/L for combined PFOA and PFOS, with emerging toxicity concerns leading to steep reductions to 0.004 ng/L for PFOA and 0.02 ng/L PFOS in June 2022 (USEPA, 2022c). At the same time, the USEPA released health advisories of 0.01 ng/L for GenX and 2 ng/L for PFBS. The 90th percentile concentrations of PFOA and PFOS in Bay water exceeded only the most protective thresholds (the OEHHA PHGs and USEPA drinking water advisory levels); this has limited relevance for the RMP because San Francisco Bay is not a drinking water source.

In contrast to drinking water, fewer thresholds exist for PFAS in surface water. The USEPA has drafted freshwater aquatic life water quality criteria for PFOA and PFOS. The chronic draft criteria are 94 µg/L (94,000 ng/L) for PFOA and 8.4 µg/L (8,400 ng/L) for PFOS (USEPA, 2022b). Water quality criteria are recommended non-enforceable values that can be used to establish state standards to protect aquatic life. Insufficient data were available to develop estuarine/marine criteria. The San Francisco Bay Regional Water Quality Control Board (Regional Water Board) staff also developed interim final Groundwater Environmental Screening Levels (ESLs) for PFOS and PFOA in aquatic habitats for ecotoxicity (PFOS: 75 ng/L, PFOA: 4,400 ng/L) and human health via seafood ingestion (PFOS: 0.0047 ng/L, PFOA: 0.022 ng/L) (SFBRWQCB, 2020). ESLs have not yet been derived for other PFAS. As with all the ESLs, the PFOS and PFOA ESLs are guidance intended to assist Regional Water Board staff currently overseeing the investigation and cleanup of PFAS spills and releases, so their use is not mandatory. However, they represent additional thresholds that can be used for comparison with environmental concentrations. Divine et al. (2020) developed recommended water quality risk-based screening levels for 23 individual PFAS using USEPA's Great Lakes Initiative methods developed to provide criterion values protective of aquatic life in mixing zones. These thresholds are designed to be protective of

freshwater aquatic plants, aquatic invertebrates, fish, and amphibians. Because they were calculated only for freshwater species, they are less representative for estuarine and marine species. The recommended water quality chronic risk-based screening levels range between 200 ng/L for 10:2 fluorotelomer sulfonic acid (10:2 FTCA) and 3.9×10^6 ng/L for PFOA; the recommended PFOS chronic risk-based screening level is 51,000 ng/L.

None of the individual PFAS analyte concentrations exceeded the USEPA draft water quality criteria, the Regional Water Board groundwater ESLs for ecotoxicity, or the recommended water quality risk-based screening levels developed by Divine et al. (2020). The sums of PFAS also are far below all of these individual compound ecotoxicity thresholds, indicating that if these contaminants exhibit additive toxicity, current concentrations may pose low potential risk to Bay biota. However, currently available ecotoxicity thresholds are based on algae, invertebrate, and fish toxicity testing data and do not account for bioaccumulation in higher trophic level aquatic organisms like piscivorous birds and marine mammals, and thus may underestimate risks to these important Bay organisms. Considering the NDs to be half the MDL did not affect threshold exceedances.

In contrast, the 90th percentile concentrations of PFOA and PFOS exceed the Regional Water Board groundwater ESLs for human health via seafood ingestion. Considering the NDs to be half the MDL did not affect threshold exceedances. The seafood ingestion ESLs have some uncertainty due to potential differences between fish species in bioaccumulation from water to fish tissues. These thresholds are based on lifetime one in one million cancer risk to the 95th percentile upper bound estimate of fish ingestion rate, and are thus also highly conservative.

The exceedance of PFOA and PFOS seafood ingestion thresholds is qualitatively consistent with recent sport fish monitoring in the Bay also indicating a potential human health concern. Concentrations of PFAS in Bay fish, particularly in South Bay, are persisting over time at levels that exceed thresholds that have been established by other states for development of consumption advisories (Buzby et al., 2021).

Overall, PFAS in San Francisco Bay waters appear to be a potential human health concern in terms of seafood ingestion, rather than a concern for aquatic biota. These findings support the current classification of PFAS as emerging contaminants of Moderate Concern in the Bay.

4. Recommended Monitoring Strategy

This study fills important data gaps on the occurrence and fate of PFAS, which were previously classified as Moderate Concern for the San Francisco Bay based on their frequent detection, known environmental persistence, and potential toxicity, especially in Bay biota (Miller et al., 2020; Sedlak et al., 2017). Monitoring of ambient water is important to understand exposure levels of PFAS to aquatic biota, especially those species consumed by humans. Limited available data collected over approximately 12 years suggest concentrations of PFAS in ambient water do not show significant signs of decline over time throughout the Bay. South and Lower South Bay sites, strongly influenced by wastewater and stormwater due in large part to long residence times, exhibited statistically significant greater sums of PFAS when compared to the rest of the Bay.

Notably, the growing body of work within the Bay indicates that concentrations of short-chain PFAS are similar to or greater than those of long-chain PFAS. Both in this study and the recent BACWA study examining wastewater influent and effluent, short-chain PFAS were some of the most widely detected analytes. This is consistent with increasing use of PFAS alternatives, especially of the short-chain variety, as well as potential concern for contaminant exposure individually and in 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 PFOS and PFOA, and related, data-poor alternatives such as short-chain PFAS. Monitoring of broader classes of contaminants defined by similarities in chemical structure and/or function, especially ones as extensive as PFAS, can provide early insights to identify problematic compounds with recent increases in use, which may be considered regrettable substitutes.

Contaminants of Moderate Concern for the Bay may be added to RMP Status and Trends monitoring activities in appropriate matrices (Sutton et al., 2017). We recommend PFAS be included in Status and Trends monitoring of Bay water, based on detections with potential human health impacts. Regular monitoring can be used to track temporal trends of individual compounds due to shifts in manufacturing and use, including responses to recent regulations, and provide an increased understanding of the spatial distribution of these contaminants within the Bay. We also recommend using a broad analytical method with more sensitive MDLs to understand the scope of PFAS contamination in the Bay.

In addition, based on its utility in wastewater monitoring, a special study to assess ambient Bay water samples using the TOP method is recommended as an additional analysis to provide information on the presence of unidentified precursors that are likely to transform over time to terminal PFCAs (e.g., PFOA). While it does not identify specific precursors, the TOP method permits an assessment of the overall levels of persistent PFCAs and PFASs that will form in a matrix following transformation to terminal products; such information is essential for evaluating the risks to Bay wildlife.

Periodic screening of PFAS in wastewater and stormwater also recommended to assess temporal trends; such studies could be conducted in coordination with Bay

Status and Trends water monitoring efforts. Because pathways generally contain higher concentrations of contaminants due to their 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. It may also be possible to more quickly detect temporal trends in response to management actions in these more concentrated matrices.

Another important pathway for RMP consideration is the potential importance of transport of PFAS through air from local and long-range emissions sources, resulting atmospheric deposition to the Bay watershed, and subsequent transport to the Bay through stormwater runoff. Several studies have found atmospheric transport and deposition of a variety of PFAS in remote areas including snow in Antarctica and Mount Everest (Casal et al., 2017; Miner et al., 2021), which highlights the importance of long-range transport. Limited available studies domestically and internationally on both wet and dry deposition have shown widespread detections and impacts of these depositions in both local and long-range locations from PFAS sources (Cousins et al., 2022; Gewurtz et al., 2019; Pike et al., 2021; Schroeder et al., 2021; Shimizu et al., 2021). A study of atmospheric deposition in the watershed drainage area could assess the importance of this pathway to urban stormwater and the Bay. The California Air Resources Board has recently included over 200 PFAS on the list of pollutants required to be monitored under the Air Toxic Hot Spots program, which may help to fill present data gaps in atmospheric transportation of PFAS (Ruiz, 2021).

Within the larger context of Status and Trends activities in other matrices, monitoring of PFAS in Bay sediment and biota will allow us to better assess the presence and fate of PFAS in the Bay ecosystem. PFAS was previously added to Status and Trends monitoring of sport fish and bird eggs, but not sediment. This matrix will be examined as part of a special study to assess archived sediment samples for PFAS; results can inform the selection of appropriate sites for potential future Status and Trends sediment monitoring with respect to subembayment and site type (i.e., ambient, margin, near-field). Also, PFAS will be examined as part of a pilot study to assess prey fish for contaminants, as some of the highest PFAS concentrations were previously observed in Bay staghorn sculpin (Sedlak et al., 2017). A screening study of marine mammal tissues using target and nontarget methods will also be underway soon. Temporal trends in harbor seal serum concentrations have indicated high levels of PFAS, and suggest declines in PFOS; however, PFOA and other long-chain PFCAs have not shown similar declines (Sedlak et al., 2018). Results may indicate the presence of other PFAS contaminants accumulating in Bay wildlife that are not typically analyzed in targeted monitoring studies. This can be particularly important should manufacturers continue to use potentially regrettable, data-poor substitutes.

The recommended monitoring studies described above can provide needed information to identify regrettable substitutes and track temporal trends. This is important science to inform management actions to protect water quality and aquatic life.

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Appendix - Supplementary Information

Table A1. Target PFAS analyte list (MLA-110, SGS AXYS) with method detection limits (MDLs) and reporting limits (RLs) for each analyte in this study. All values are in ng/L.

PFAS Classification	PFAS Abbreviation	PFAS Name (Conjugate Base of Acids in parentheses)	Range of MDLs (ng/L)	Range of RLs (ng/L)
Perfluoroalkyl Carboxylic Acids/ Carboxylates	PFBA	Perfluorobutanoic acid (Perfluorobutanoate)	1.78-2.21	7.11-8.85
	PFPeA	Perfluoropentanoic acid (Perfluoropentanoate)	0.89-1.11	3.55-4.42
	PFHxA	Perfluorohexanoic acid (Perfluorohexanoate)	0.44-0.55	1.58-2.21
	PFHpA	Perfluoroheptanoic acid (Perfluoroheptanoate)	0.44-0.55	0.74-2.21
	PFOA	Perfluorooctanoic acid (Perfluorooctanoate)	0.44-0.55	1.78-2.21
	PFNA	Perfluorononanoic acid (Perfluorononanoate)	0.44-0.55	0.57-2.17
	PFDA	Perfluorodecanoic acid (Perfluorodecanoate)	0.44-0.55	1.78-2.21
	PFUnA	Perfluoroundecanoic acid (Perfluoroundecanoate)	0.44-0.55	1.78-2.21
	PFDoA	Perfluorododecanoic acid (Perfluorododecanoate)	0.44-0.55	1.78-2.21
	PFTTrDA	Perfluorotridecanoic acid (Perfluorotridecanoate)	0.44-0.55	1.78-2.21
	PFTeDA	Perfluorotetradecanoic acid (Perfluorotetradecanoate)	0.44-0.55	1.78-2.21
Perfluoroalkyl Sulfonic Acids/ Sulfonates	PFBS	Perfluorobutanesulfonic acid (Perfluorobutanesulfonate)	0.44-0.55	1.78-2.21
	PFPeS	Perfluoropentanesulfonic acid (Perfluoropentanesulfonate)	0.44-0.55	1.78-2.21
	PFHxS	Perfluorohexanesulfonic acid (Perfluorohexanesulfonate)	0.45-0.56	1.57-2.21
	PFHpS	Perfluoroheptanesulfonic acid (Perfluoroheptanesulfonate)	0.44-0.55	1.78-2.21
	PFOS	Perfluorooctanesulfonic acid (Perfluorooctanesulfonate)	0.44-0.55	1.78-2.21
	PFNS	Perfluorononanesulfonic acid (Perfluorononanesulfonate)	0.44-0.55	1.78-2.21
	PFDS	Perfluorodecanesulfonic acid (Perfluorodecanesulfonate)	0.44-0.55	1.78-2.21
	PFDoS	Perfluorododecanesulfonic acid (Perfluorododecanesulfonate)	0.44-0.55	1.78-2.21

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PFAS Classification	PFAS Abbreviation	PFAS Name (Conjugate Base of Acids in parentheses)	Range of MDLs (ng/L)	Range of RLs (ng/L)
Fluorotelomer Sulfonic Acids/ Sulfonates	4:2 FTS	1H, 1H, 2H, 2H-perfluorohexane sulfonic acid (1H, 1H, 2H, 2H-perfluorohexane sulfonate)	1.78-2.21	7.11-8.85
	6:2 FTS	1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (1H, 1H, 2H, 2H-perfluorooctane sulfonate)	1.60-1.99	6.40-7.96
	8:2 FTS	1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (1H, 1H, 2H, 2H-perfluorodecane sulfonate)	1.78-2.21	7.11-8.85
	3:3 FTCA	2H, 2H, 3H, 3H-perfluorohexanoic acid (2H, 2H, 3H, 3H-perfluorohexanoate)	1.78-2.21	7.11-8.85
	5:3 FTCA	2H, 2H, 3H, 3H-perfluorooctanoic acid (2H, 2H, 3H, 3H-perfluorooctanoate)	11.1-13.8	44.4-55.3
	7:3 FTCA	2H, 2H, 3H, 3H-perfluorodecanoic acid (7:3 FTCA, 2H, 2H, 3H, 3H-perfluorodecanoate)	11.1-13.8	44.4-55.3
Perfluorooctane Sulfonamides	PFOSA	Perfluorooctanesulfonamide	0.44-0.55	1.78-2.21
	N-MeFOSA	N-Methylperfluorooctanesulfonamide	0.51-0.64	2.04-2.54
	N-EtFOSA	N-Ethylperfluorooctanesulfonamide	1.11-1.38	4.44-5.53
Perfluorooctane Sulfonamido Acetic Acids/ Acetates	N-MeFOSAA	N-Methylperfluoro-1-octanesulfonamidoacetic acid (N-Methylperfluoro-1-octanesulfonamidoacetate)	0.44-0.55	1.78-2.21
	N-EtFOSAA	N-Ethylperfluoro-1-octanesulfonamidoacetic acid (N-Ethylperfluoro-1-octanesulfonamidoacetate)	0.44-0.55	1.78-2.21
Perfluorooctane Sulfonamido Ethanols	N-MeFOSE	N-Methylperfluoro-1-octanesulfonamidoethanol	4.44-5.53	17.8-22.1
	N-EtFOSE	N-Ethylperfluoro-1-octanesulfonamidoethanol	3.32-4.14	13.3-16.6

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PFAS Classification	PFAS Abbreviation	PFAS Name (Conjugate Base of Acids in parentheses)	Range of MDLs (ng/L)	Range of RLs (ng/L)
Per- and Polyfluoroether Carboxylic Acids/ Carboxylates	HFPO-DA (GenX)	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propionic acid	1.69-2.10	6.75-8.41
	ADONA	Decafluoro-3H-4,8-dioxanonoic acid (Decafluoro-3H-4,8-dioxanonoate)	1.78-2.21	7.11-8.85
	NFDHA	Perfluoro-3,6-dioxaheptanoic acid (Perfluoro-3,6-dioxaheptanoate)	0.89-1.11	3.55-4.42
	PFMBA	Perfluoro-4-methoxybutanoic acid (Perfluoro-4-methoxybutanoate)	0.44-0.55	1.78-2.21
	PFMPA	Perfluoro-3-methoxypropanoic acid (Perfluoro-3-methoxypropanoate)	0.89-1.11	3.55-4.42
Perfluoroalkylether Sulfonic Acids/Sulfonates	9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (9-chlorohexadecafluoro-3-oxanonane-1-sulfonate)	1.78-2.22	7.11-8.85
	11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11-chloroeicosafluoro-3-oxaundecane-1-sulfonate)	1.78-2.22	7.11-8.85
	PFEESA	Perfluoro(2-ethoxyethane)sulfonic acid (Perfluoro(2-ethoxyethane)sulfonate)	0.44-0.55	1.78-2.21

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Table A2. Concentrations of detected analytes in Bay Area ambient water samples. All concentration values are in ng/L.

Site	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFHxS	PFOS	PFBA	PFNA	PFDA	6:2 FTS	Sum of PFAS
BG20	1.7*	1.4*	ND	0.65*	ND	ND	ND	ND	ND	ND	ND	3.8
BG30	1.5*	1.7*	ND	0.66*	ND	ND	ND	ND	ND	ND	ND	3.9
SU058W	1.8*	1.2*	ND	0.85*	ND	ND	0.76*	ND	ND	ND	ND	4.7
SU059W	2.0*	ND	0.59*	0.83*	0.63*	0.64*	0.95*	ND	ND	ND	ND	5.6
SU060W	1.8*	1.5*	0.53*	0.74*	0.51*	0.55*	0.51*	ND	ND	ND	ND	6.2
SPB049W	ND	1.5*	ND	0.47*	ND	ND	0.47*	ND	ND	ND	ND	2.4
SPB050W	ND	0.95*	0.59*	ND	ND	ND	ND	ND	ND	ND	ND	1.5
SPB051W	ND	0.81*	ND	0.52*	ND	ND	ND	ND	ND	ND	ND	1.3
BC10	ND	0.72*	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.72
BC20	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-
CB052W	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-
CB053W	ND	0.62*	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.62
CB054W^	1.2*	1.6*	0.81*	1.2*	0.60*	0.75*	1.1*	ND	ND	ND	ND	7.3
BA30	2.0*	2.7	0.78*	1.29	0.71*	1.21*	2.8	ND	ND	ND	ND	11
SB077W	1.6*	2.0*	ND	1.3*	0.59*	0.91*	1.5*	ND	ND	ND	14	22
SB078W	3.1*	3.6	1.2*	2.1	1.7*	1.9*	3.0	2.7*	ND	ND	ND	19
SB079W	1.3*	1.6*	0.64*	1.3*	0.54*	ND	1.5*	ND	ND	ND	ND	6.9
LSB079W	3.3*	4.3	1.1*	2.4	1.4*	2.0	3.4	2.7*	ND	ND	ND	21
LSB080W	3.3*	4.4	1.2*	2.4	1.6*	2.0*	3.5	3.2*	ND	ND	ND	22
LSB081W^	4.8	4.9	1.7*	3.2	2.3	2.3	4.7	3.9*	0.60*	0.48*	ND	29
LSB082W	4.2	4.5	1.7*	2.0*	2.7	2.2	4.1	3.6*	0.53*	ND	ND	26
LSB083W	3.9	5.7	1.4*	2.4	1.6*	2.2	4.3	3.9*	0.48*	0.48*	ND	26

Samples in red denote Delta (river) sites, those in orange denote Suisun Bay sites, those in yellow denote San Pablo Bay sites, those in green denote Central Bay sites, those in blue denote South Bay sites and those in purple indicate Lower South Bay sites.

* denotes levels measured above the MDL but below the RL and may be considered semi quantitative

^Noted concentrations at these sites are the average of two samples

Table A3. Spearman's rank correlation coefficients for compounds detected in $\geq 50\%$ of sites ($n = 22$; all $p < 0.001$).

	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFHxS
PFHxA	0.80					
PFHpA	0.78	0.77				
PFOA	0.91	0.89	0.80			
PFBS	0.87	0.80	0.92	0.90		
PFHxS	0.87	0.82	0.86	0.88	0.96	
PFOS	0.87	0.85	0.87	0.95	0.94	0.91

Table A4. Comparison of sample populations from 2009 RMP study of PFAS in ambient Bay water (Sedlak et al., 2018) and this study for PFAS detected in both studies and in $\geq 50\%$ of sites across the Bay in 2021 ($n = 22$). P-values were determined using the Mann-Whitney-Wilcoxon test with a 0.05 significance level unless otherwise noted.

Analyte	P-value	Non-identical Populations	2009		2021	
			Median	Mean	Median	Mean
PFPeA	0.22		0	0.78	1.64	1.7
PFHxA*	0.18		0	1.07	1.54	2.07
PFHpA	0.90		0	0.68	0.56	0.55
PFOA	0.57		1.38	2.59	0.84	1.1
PFBS	0.06		0	0	0.53	0.68
PFHxS	0.49		0	0.53	0.27	0.76
PFOS	0.75		0	1.84	0.86	1.48
Short-Chain	0.03	X	0	0.63	0.81	1.25
Long-Chain	0.69		0	1.65	0.74	1.11
Sum of PFAS*	0.49		2.4	8.78	5.88	10.02

*P-values were determined using the t-test of unequal variances since the sample populations were both normal distributions with different variances.

Table A5. Comparison of sample populations of short-chain (PFPeA, PFHxA, PFHpA, and PFBS) and long-chain (PFOA, PFHxS, and PFOS) PFAS from various Bay and subembayment sites for PFAS detected in $\geq 50\%$ of sites ($n = 22$). Sample populations from Lower South Bay (LSB) and South Bay (SB), Central Bay (CB), San Pablo Bay (SPB), Suisun Bay (SU), and two river sites—San Joaquin River and Sacramento River—(“all NB & CB sites”), and all sites excluding the LSB (“Remaining Subembayments”). P-values were determined using the Mann-Whitney-Wilcoxon test with a 0.05 significance level unless otherwise noted.

Sites Included	P-value	Non-identical Populations	Short-Chain PFAS		Long-Chain PFAS	
			Median	Mean	Median	Mean
All Sites (2021)	0.68		0.81	1.25	0.74	1.11
LSB Sites (2021)	1.72		3	3	2.41	2.88
All LSB & SB Sites (2021)	0.65		1.73	2.33	2.22	2.29
All NB & CB Sites (2021; CB, SPB, SU, & river sites)	0.35		0	0.51	0	0.3
Remaining Subembayments (2021; All sites excluding LSB)	0.45		0.59	0.74	0.47	0.59
All Sites (2009)	1.31		0	0.63	0	1.65

Table A6. Comparison of sample populations from the LSB and the remaining subembayments of the Bay (including SB, CB, SPB, SU, and river sites) for PFAS detected in $\geq 50\%$ of sites ($n = 22$). P-values were calculated using the Mann-Whitney-Wilcoxon test with a 0.05 significance level unless otherwise noted.

Analyte	P-value	Non-identical Populations	Lower South Bay		Remaining Subembayments	
			Median	Mean	Median	Mean
PFPeA	0.0009	X	3.89	3.90	1.32	1.06
PFHxA*	2.0E-07	X	4.48	4.76	1.40	1.28
PFHpA	0.0015	X	1.39	1.41	0	0.30
PFOA	0.0012	X	2.41	2.49	0.66	0.70
PFBS	0.002	X	1.60	1.92	0	0.31
PFHxS	0.0009	X	2.22	2.15	0	0.35
PFOS	0.0009	X	4.05	3.99	0.47	0.74
Short-Chain	5.0E-08	X	3	3	0.59	0.74
Long-Chain	3.0E-08	X	2.41	2.88	0.47	0.59
Sum of PFAS	0.002	X	25.60	24.60	3.92	5.73

*P-values were determined using the t-test of equal variances since the sample populations were both normal distributions with similar variances.

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Table A7. Comparison of sample populations from LSB and SB (“all of South Bay”) and the remaining subembayments of the Bay (including CB, SPB, SU, and river sites; “All of NB & CB”) for PFAS detected in $\geq 50\%$ of sites ($n = 22$). P-values were determined using the Mann-Whitney-Wilcoxon test with a 0.05 significance level unless otherwise noted.

Analyte	P-value	Non-identical Populations	LSB & SB sites		All of NB & CB	
			Median	Mean	Median	Mean
PFPeA	0.0009	X	3.26	3.05	0	0.77
PFHxA*	0.0002	X	4.31	3.72	0.95	0.92
PFHpA	0.001	X	1.07	1.15	0	0.19
PFOA	9.0E-05	X	2.10	2.04	0.52	0.46
PFBS	0.0003	X	1.57	1.46	0	0.13
PFHxS	0.0007	X	2.02	1.64	0	0.15
PFOS	9.0E-05	X	3.39	3.18	0	0.29
Short-Chain	2.0E-09	X	1.73	2.33	0	0.51
Long-Chain	1.0E-10	X	2.22	2.29	0	0.3
Sum of PFAS*	6.0E-05	X	21.51	20.26	2.41	2.92

*P-values were determined using the t-test of unequal variances since the sample populations were both normal distributions with different variances.

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Table A8. Comparison of San Francisco Bay PFAS ambient water concentrations to those in other estuaries and marine locations. All values are in ng/L.

Compound	N	Detection Frequency	Range	Median	Mean	Location	Year	Reference
PFPeA	22	68%	ND - 4.8	ND	1.70	San Francisco Bay, USA	2021	This Study
	5	40%	ND - 2.5	ND	0.80	San Francisco Bay, USA	2009	Sedlak et al., 2018
	45	42%	0.53 - 52	0.53	-	Pensacola, USA	2020	da Silva et al., 2022
	42	88%	ND - 0.96	-	-	Gironde, France	2016	Munoz et al., 2017*
	5	100%	1.2 - 9.7	3.1	4.5	Melbourne, Australia	2012	Allinson et al., 2019
PFHxA	22	86%	ND - 5.7	1.5	2.1	San Francisco Bay, USA	2021	This Study
	5	40%	ND - 3.7	ND	1.1	San Francisco Bay, USA	2009	Sedlak et al., 2018
	45	100%	0.22 - 43	0.66	-	Pensacola, USA	2020	da Silva et al., 2022
	42	93%	ND - 0.94	-	-	Gironde, France	2016	Munoz et al., 2017*
	5	100%	1.5 - 23	2.1	7.8	Melbourne, Australia	2012	Allinson et al., 2019
PFHpA	22	55%	ND - 1.7	0.56	0.55	San Francisco Bay, USA	2021	This Study
	5	40%	ND - 2.4	ND	0.68	San Francisco Bay, USA	2009	Sedlak et al., 2018
	45	98%	0.23 - 17	0.51	-	Pensacola, USA	2020	da Silva et al., 2022
	42	100%	0.02 - 0.52	-	-	Gironde, France	2016	Munoz et al., 2017*
	5	100%	1.2 - 8.9	1.8	4.1	Melbourne, Australia	2012	Allinson et al., 2019
PFOA	22	77%	ND - 3.21	0.84	1.1	San Francisco Bay, USA	2021	This Study
	5	60%	ND - 8.6	1.4	2.6	San Francisco Bay, USA	2009	Sedlak et al., 2018
	45	100%	0.30 - 19	0.97	-	Pensacola, USA	2020	da Silva et al., 2022
	42	90%	ND - 0.69	-	-	Gironde, France	2016	Munoz et al., 2017*
	5	100%	1.7 - 9.2	2.2	4.8	Melbourne, Australia	2012	Allinson et al., 2019
PFBS	22	59%	ND - 2.7	0.53	0.68	San Francisco Bay, USA	2021	This Study
	5	0%	ND	ND	ND	San Francisco Bay, USA	2009	Sedlak et al., 2018
	45	98%	0.34 - 6.0	0.74	-	Pensacola, USA	2020	da Silva et al., 2022
	42	93%	ND - 0.85	-	-	Gironde, France	2016	Munoz et al., 2017*
	5	100%	0.4 - 7.0	0.8	3.1	Melbourne, Australia	2012	Allinson et al., 2019
PFHxS	22	50%	ND - 2.3	0.27	0.76	San Francisco Bay, USA	2021	This Study
	5	20%	ND - 2.7	ND	0.53	San Francisco Bay, USA	2009	Sedlak et al., 2018
	45	100%	0.27 - 59	1.2	-	Pensacola, USA	2020	da Silva et al., 2022
	42	98%	ND - 1.1	-	-	Gironde, France	2016	Munoz et al., 2017*
	5	100%	3 - 42	7	17	Melbourne, Australia	2012	Allinson et al., 2019

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Compound	N	Detection Frequency	Range	Median	Mean	Location	Year	Reference
PFOS	22	63%	ND - 4.7	0.86	1.5	San Francisco Bay, USA	2021	This Study
	5	40%	ND - 6.3	ND	1.8	San Francisco Bay, USA	2009	Sedlak et al., 2018
	45	100%	0.68 - 269	3.3	-	Pensacola, USA	2020	da Silva et al., 2022
	42	95%	ND - 1.1	-	-	Gironde, France	2016	Munoz et al., 2017*
	5	100%	3.9 - 75	14	34	Melbourne, Australia	2012	Allinson et al., 2019
PFBA	22	27%	ND - 3.9	ND	0.91	San Francisco Bay, USA	2021	This Study
	5	20%	ND - 3.0	ND	0.60	San Francisco Bay, USA	2009	Sedlak et al., 2018
	45	56%	0.83 - 11	1.2	-	Pensacola, USA	2020	da Silva et al., 2022
	42	60%	ND - 1.3	-	-	Gironde, France	2016	Munoz et al., 2017*
	5	100%	1.7 - 11	2.9	5.7	Melbourne, Australia	2012	Allinson et al., 2019
PFNA	22	13%	ND - 0.60	ND	0.07	San Francisco Bay, USA	2021	This Study
	5	40%	ND - 2.4	ND	0.69	San Francisco Bay, USA	2009	Sedlak et al., 2018
	45	96%	0.13 - 4.3	0.21	-	Pensacola, USA	2020	da Silva et al., 2022
	42	67%	ND - 0.67	-	-	Gironde, France	2016	Munoz et al., 2017*
	5	100%	0.2 - 6.4	1.2	2.3	Melbourne, Australia	2012	Allinson et al., 2019
PFDA	22	09%	ND - 0.48	ND	0.04	San Francisco Bay, USA	2021	This Study
	5	0%	ND	ND	ND	San Francisco Bay, USA	2009	Sedlak et al., 2018
	45	84%	0.04 - 2.2	0.09	-	Pensacola, USA	2020	da Silva et al., 2022
	42	17%	ND - 0.09	-	-	Gironde, France	2016	Munoz et al., 2017*
	5	100%	0.2 - 1.7	0.50	0.80	Melbourne, Australia	2012	Allinson et al., 2019
6:2 FTS	22	04%	ND - 14	ND	0.65	San Francisco Bay, USA	2021	This Study
	5	-	-	-	-	San Francisco Bay, USA	2009	Sedlak et al., 2018
	45	100%	0.20 - 164	0.72	-	Pensacola, USA	2020	da Silva et al., 2022
	42	0%	ND - 0.18	-	-	Gironde, France	2016	Munoz et al., 2017*
	5	-	-	-	-	Melbourne, Australia	2012	Allinson et al., 2019

**For this study, only dissolved concentrations were compared due to the strong influence of suspended sediment in samples compared to San Francisco Bay.*