



Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts



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ABSTRACT

In late 2014, wastewater effluent samples were collected from eight treatment plants that discharge to San Francisco (SF) Bay in order to assess poly- and perfluoroalkyl substances (PFASs) currently released from municipal and industrial sources. In addition to direct measurement of twenty specific PFAS analytes, the total concentration of perfluoroalkyl acid (PFAA) precursors was also indirectly measured by adapting a previously developed oxidation assay. Effluent from six municipal treatment plants contained similar amounts of total PFASs, with highest median concentrations of PFHxA (24 ng/L), followed by PFOA (23 ng/L), PFBA (19 ng/L), and PFOS (15 ng/L). Compared to SF Bay municipal wastewater samples collected in 2009, the short chain perfluorinated carboxylates PFBA and PFHxA rose significantly in concentration. Effluent samples from two treatment plants contained much higher levels of PFASs: over two samplings, wastewater from one municipal plant contained an average of 420 ng/L PFOS and wastewater from an airport industrial treatment plant contained 560 ng/L PFOS, 390 ng/L 6:2 FtS, 570 ng/L PFPeA, and 500 ng/L PFHxA. The elevated levels observed in effluent samples from these two plants are likely related to aqueous film forming foam (AFFF) sources impacting their influent; PFASs attributable to both current use and discontinued AFFF formulations were observed. Indirectly measured PFAA precursor compounds accounted for 33%–63% of the total molar concentration of PFASs across all effluent samples and the PFAA precursors indicated by the oxidation assay were predominately short-chained. PFAS levels in SF Bay effluent samples reflect the manufacturing shifts towards shorter chained PFASs while also demonstrating significant impacts from localized usage of AFFF.

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1. Introduction

Poly- and perfluoroalkyl substances (PFASs) are a class of chemicals whose notable uses include imparting oil and water repellency in consumer products and reducing surface tension in firefighting foams. Two 8-carbon (C8) PFASs, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), were historically manufactured in the largest quantities (Wang et al., 2014; Paul et al., 2009) and have been detected in surface waters (Huset et al., 2008; Ahrens et al., 2009; Zushi and Masunaga, 2009; Meyer et al., 2011), humans (Wang et al., 2011a; Kato et al., 2011; Yeung et al., 2013a, 2013b; Wu et al., 2015), and biota (Giesy and

Kannan, 2001; Houde et al., 2011) in areas far from known point sources.

Over the last fifteen years, the production of C8-based PFASs has been phased out by some of their largest manufacturers and the U.S. and Europe have taken steps to regulate or limit the production and import of PFOS and PFOA (U.S. EPA, 2006, U.S. EPA, 2013, Commission Regulation No 552/2009). As a result of these changes, PFOS and PFOA have largely declined in concentration in the blood of Americans and Europeans (Wang et al., 2011a; Kato et al., 2011; Yeung et al., 2013a, 2013b). As C8 compounds have been phased out, the production of PFASs containing C4 and C6 perfluorinated moieties has increased, and PFASs containing C2 and C3 perfluorinated groups connected by ether linkages are also being manufactured (Wang et al., 2015).

Municipal and industrial wastewaters are an important type of real-time tracker of PFASs that humans and wildlife may be exposed to. The perfluoroalkyl acids (PFAAs) are very non-reactive

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to typical wastewater and drinking water treatment processes, and only long-chain PFAAs are effectively removed by sorption (Schultz et al., 2006; Appleman et al., 2014; Guo et al., 2010). Polyfluorinated compounds can undergo transformation during treatment processes, but their products are often other measurable PFASs that contain a similarly sized (*i.e.*, equivalent or one to two carbons shorter) perfluorinated group (Rhoads et al., 2008; Schultz et al., 2006). Because of their potential to form PFAAs, these polyfluorinated compounds are often referred to as PFAA precursors. Thus, PFASs measured in effluent are likely to reflect PFASs in current use products, along with PFASs in historical products still in use or slowly released into wastewater. PFOS and PFOA were still the main forms of PFAAs in municipal wastewater treatment plant (WWTP) effluent five to ten years after the major phase-outs of C₈-based PFASs commenced (Schultz et al., 2006; Ahrens et al., 2009; Guo et al., 2010; Klosterhaus et al., 2013), suggesting a lingering C8 source associated with consumer products.

In a large, urbanized metropolitan area like the San Francisco Bay (SF Bay) Area, the discharge of WWTP effluent may represent a large contribution to the total PFASs in the receiving water body. From 2004 to 2009, PFOS was observed in SF Bay seals and cormorant eggs at concentrations an order of magnitude greater than those collected nearby from a less-urbanized setting (Sedlak and Greig 2012), and wastewater was speculated to be one potential source of exposure. Six SF Bay wastewater samples collected in 2009 contained an average of 24 ng/L PFOS (Klosterhaus et al., 2013), similar to concentrations observed in municipal effluent in other regions (Schultz et al., 2006; Boulanger et al., 2005; Ahrens et al., 2009; Guo et al., 2010). More than 300 million gallons per day (MGD) (1.1 million m³) of WWTP effluent is discharged to SF Bay with design loading rates varying from <1 MGD to more than 100 MGD (Pacific Institute, 2009). Both individual high volume plants with high concentrations and the aggregate loading from all the treatment plants combined could present a major source of PFASs to the region. The current profile and concentrations of PFASs in SF Bay WWTP effluent may be an important predictor of wildlife PFAS exposure going forward.

In this study, final effluent was collected from eight WWTPs that discharge to SF Bay and analyzed for a suite of twenty PFASs. The samples were also oxidized with hydroxyl radical to quantify the total oxidizable PFAA precursor concentration by adapting a previously developed method (Houtz and Sedlak, 2012; Houtz et al., 2013). One of our objectives was to understand how PFAS profiles have changed in WWTP effluent as a result of manufacturing changes. These data were used to provide temporal and spatial significance to the high levels of PFASs previously observed in SF Bay wildlife. Additionally, the total oxidizable precursor assay was used to evaluate the extent to which effluent may serve as a source of future PFAAs such as PFOS and PFOA through the transformation of PFAA precursors. Differences in PFAS concentrations among effluent samples were explained in part by PFAS sources within the sewersheds, namely aqueous film forming foam (AFFF). While AFFF is typically associated with elevated PFAS concentrations in groundwater (Schultz et al., 2004; Houtz et al., 2013; Backe et al., 2013; McGuire et al., 2014), this study demonstrates that AFFF may be a significant contributor to elevated levels of PFASs in industrial and municipal wastewater.

2. Material and methods

2.1. Materials

All analytical standards of PFASs and their stable-isotope surrogates were purchased from Wellington Laboratories (Guelph, Ontario). PFAS abbreviations are defined in Table S1. Milli-Q water

was used from an in-house system. JT Baker brand UPLC-grade methanol, ammonia strong, and ammonium acetate were purchased from VWR. >99.5% purity potassium persulfate, sodium hydroxide, and concentrated hydrochloric acid were purchased from Fisher Scientific.

2.2. Collection and storage of wastewater effluent

Single grab samples of treated final effluent were collected during peak diurnal flow in September and October 2014 from eight WWTPs that discharge to SF Bay. 1-L polypropylene containers were filled with 500 mL to 1 L of final effluent from discharge outlets considered free of Teflon-coated materials. Collection occurred during the dry season to minimize storm water inflow and infiltration. A field replicate and a field blank (Milli-Q water) were included for quality control (Table S2). WWTP operators measured total suspended solids (TSS) at the time of sample collection (Table 1). Details of treatment plant loads, hydraulic retention times, and relevant treatment train steps are reported in Table 1. To verify higher levels of PFASs observed at Fairfield Suisun and San Francisco Airport Industrial WWTPs in 2014, an additional effluent sample was collected from each plant in June 2015.

Samples were received blind at the laboratory and were subsequently stored at 4 °C. Samples were oxidized, extracted, and analyzed within three weeks of sample receipt.

2.3. Oxidation of wastewater samples for indirect measurement of PFAA precursors

Each effluent sample was aliquoted into duplicate 50-mL subsamples to be oxidized for indirect measurement of PFAA precursors according to a previously developed method (Houtz and Sedlak, 2012; Houtz et al., 2013). Samples were diluted two-fold in a basic persulfate solution prepared in Milli-Q water for a final concentration of 60 mM persulfate and 125 mM NaOH. The samples were thermalized in 125 mL HDPE-plastic bottles overnight at 85 °C in a temperature-controlled water bath, resulting in the decomposition of persulfate to sulfate radical and subsequent scavenging by hydroxide to form hydroxyl radical. Following thermolysis, samples were neutralized to a pH between 5 and 9 using concentrated HCl.

This method efficiently converts PFAA precursor compounds in the sample to PFAAs (Houtz and Sedlak, 2012). In previous control experiments, only PFCA products were generated from the oxidation of runoff and groundwater samples amended with fluorotelomer compounds and perfluorinated sulfonamido compounds (Houtz and Sedlak, 2012; Houtz et al., 2013). In this study, an expanded set of PFAA precursors that included polyfluorinated phosphinates (PFPIs) were amended to wastewater samples in control experiments; a mixture of PFCAs and perfluorinated phosphonic acids (PFPA) resulted from the oxidation of 6:6, 6:8, and 8:8 PFPI in wastewater samples (Fig. S1a–b). Other PFAA precursors containing a bond between phosphorous and a perfluorinated group may also be expected to generate PFPA products upon oxidation. The molar concentration of additional PFCAs and PFPA generated in the sample is a conservative estimate of the concentration of PFAA precursors present in the sample (Houtz and Sedlak, 2012).

Additional details of the validation of this method in wastewater and the anticipated products and yields from various PFAA precursors are included in the SI.

2.4. Sample extraction and analysis

Oxidized and unoxidized wastewater samples were prepared

Table 1
Characteristics of WWTPs included in this study.

Wastewater treatment plant	Effluent TSS, mg/L	Flow, MGD	Hydraulic residence time, hours	Relevant treatment steps
San Jose Santa Clara (SJ Santa Clara)	1.0	83	8–10	Filtration
East Bay Dischargers Association (EBDA) ^a	9.0	50	10–23	
East Bay Municipal Utilities District (EBMUD)	13	46	12–18	
Central Contra Costa	5.3	30	6–7	UV disinfection
Palo Alto	0.50	20	22	Filtration
Fairfield Suisun (Oct 2014)	1.4	12	24	Filtration, UV disinfection
Fairfield Suisun (June 2015)	<1.0	12	24	Filtration, UV disinfection
San Mateo	5.5	8.5	15	Filtration
San Francisco Airport Industrial (SFO) (Oct 2014)	5.1	0.63	6	
San Francisco Airport Industrial (SFO) (June 2015)	5.1	0.63	6	

^a Combined effluent of multiple plants with a single discharge point.

for analysis of twenty individual PFAS analytes by concentrating them with solid phase extraction (SPE) (Oasis WAX SPE cartridges, 3 cm³, 60 mg, 30 µm; Waters, Milford, MA). Fifty-mL duplicate aliquots of each sample were spiked with 20 ng/L internal standard mixture prior to extraction. An extraction blank and oxidized blank were included with each set of 8–12 extracted samples. SPE cartridges were pre-conditioned on an SPE manifold (Supelco) with 3 mL each of 0.5% NH₄OH in methanol, acetonitrile, and Milli-Q water before pulling the sample through under vacuum. After extraction, cartridges were rinsed with 2 mL HPLC-grade water, dried under vacuum for twenty minutes, and eluted with 4 mL acetonitrile and 4 mL 0.5% NH₄OH in methanol. Samples were evaporated to near dryness and reconstituted in 250 µL methanol. Reconstituted extracts were heated for 30 min at 40 °C and vortexed before transferring to HPLC vials containing 250 µL of Milli-Q water. PFAS measurements in procedural blanks are reported in Table S2. Limits of detection and quantification are reported in Table S3 and accuracy, precision, and recoveries are reported in Table S4.

Samples were analyzed by UPLC-MS/MS using a Shimadzu Nexera UPLC and a SciEx 5500 QTrap operating in multiple reaction monitoring mode. The UPLC was modified to minimize background contamination by replacing accessible PTFE lines with PEEK tubing. The solvent degasser was bypassed and solvents were degassed offline. A Waters Cortecs UPLC C18 column (1.6 µm, 3.0 × 30 mm) was placed after the mixing point of solvents and before the injector to delay and separate background PFAS signals from sample PFAS signals. PFASs were separated on a Waters Acquity UPLC BEH C18 column (1.7 µm, 2.1 × 50 mm). Details of the UPLC and analytical methods can be found in Tables S5–S7.

3. Results and discussion

3.1. PFAS levels in WWTP effluent

Fifteen analytes were present above method detection limits in all wastewater samples (Fig. 1a–b). In the eight samples from treatment plants collected in 2014, PFHxA was detected at highest median concentrations (24 ng/L), followed by PFOA (23 ng/L), PFBA (19 ng/L), PFOS (15 ng/L), PFPeA (9.7 ng/L), PFNA (9.0 ng/L), PFHxS (4.9 ng/L), and PFBS (2.8 ng/L). Low levels of the C6 and C8 PFPAs, PFHxPA (1.3 ng/L, median) and PFOPA (0.9 ng/L, median) were also detected in all 2014 wastewater effluent samples. Four PFAA precursors were present above detection limits in all samples; 6:2 FtS was measured at a median concentration of 3.4 ng/L, and MeFOSAA (2.1 ng/L), EtFOSAA (1.4 ng/L), and 8:2 FtS (0.9 ng/L) were also detectable in all samples.

Of the eight WWTPs sampled in 2014, six had total individual PFAS concentrations between 80 and 160 ng/L (Fig. 1a), while Fairfield Suisun and SFO Industrial had significantly higher total

concentrations (390 ng/L and 2900 ng/L, respectively) (Fig. 1b). Fairfield Suisun contained elevated levels of PFOS (220 ng/L), PFHxS (19 ng/L), and 6:2 FtS (15 ng/L) but otherwise contained similar concentrations of PFASs to the other six low concentration effluent samples. SFO Industrial effluent contained higher concentrations of PFASs across the range of analytes (Fig. 1b). Due to the elevated levels of PFASs observed in effluent from these two sites, a second set of effluent samples from these plants was collected in June 2015 to verify whether elevated concentrations might be routinely observed. Effluent from Fairfield Suisun contained approximately three times as much PFOS (620 ng/L) and twice as much PFOA (68 ng/L) as it had in 2014, while most analytes in SFO Industrial effluent were within ±35% of the concentrations measured in 2014.

3.2. Temporal changes in PFASs in SF Bay WWTP effluent

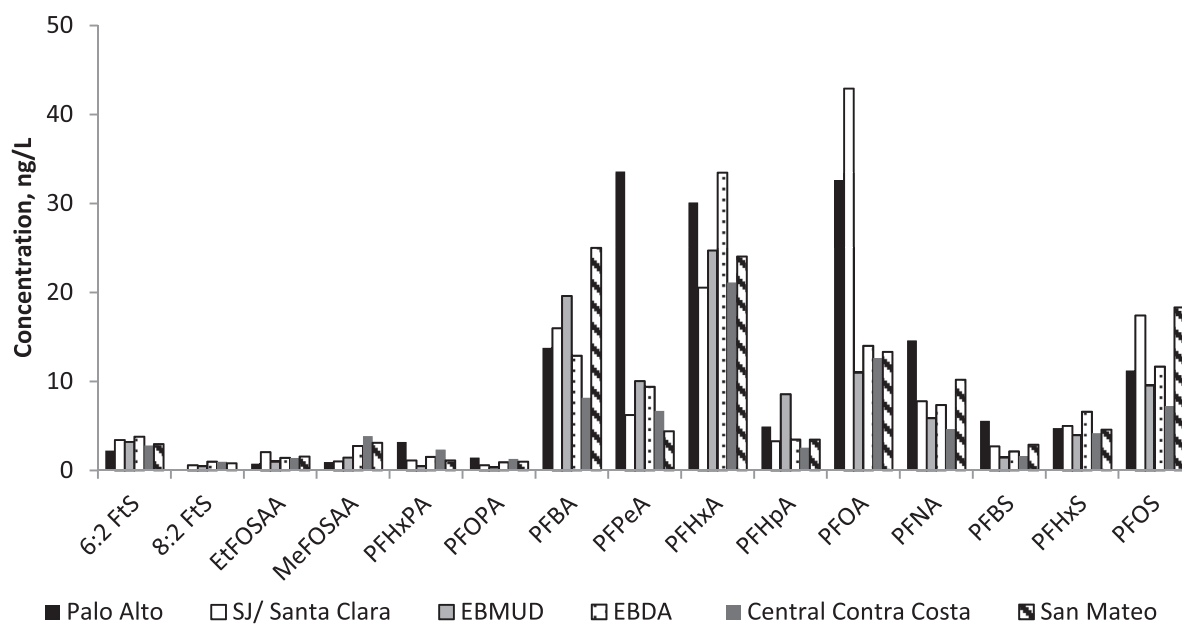
PFASs in wastewater effluent discharged to SF Bay were previously measured in 2009 (Table 2) (Klosterhaus et al., 2013); average values and standard deviations for seven PFCAs and three PFASs were reported for final effluent collected from six unspecified municipal WWTPs. When considering the six municipal treatment plants in this study that contained similar amounts of PFASs (Fig. 2a), PFBA, PFPeA, and PFHxA rose in average concentration 150%–220% since 2009. An unpaired *t*-test showed that the increases seen in PFBA and PFHxA were statistically significant at *p* < 0.019 and at *p* < 0.008, respectively; PFPeA increases were not statistically significant. Average concentrations of PFOA and PFOS in municipal WWTP effluent declined by 34% and 47%, respectively, from 2009 to 2014. These changes were not statistically significant, largely because much more variation was observed in PFOA and PFOS WWTP effluent concentrations in 2009 than in 2014 (Table 2). The concentration of PFOS in Fairfield Suisun WWTP effluent is ten to thirty times higher than the 2009 average PFOS concentration, significantly outside of the range of PFOS measured in municipal effluent that year.

Changes in PFAS production are reflected in these PFAS temporal changes in SF Bay municipal WWTP effluent. The rise in short chain C4 and C6 PFCAs reflects the increase in production of C6 fluorotelomer compounds, which are capable of transforming to C4 to C6 PFCAs in the presence of aerobic WWTP bacteria (Lee et al., 2010; Wang et al., 2011b). High variance in WWTP effluent concentrations of PFOA and PFOS in 2009 make it more challenging to point to concrete trends with those analytes.

3.3. PFAA precursors measured by oxidation

Oxidation of each effluent sample revealed the presence of polyfluorinated PFAA precursor compounds that were not directly detected as specific analytes (Figs. 2–3). The total molar concentration of PFASs was approximated by the summation of measured

a



b

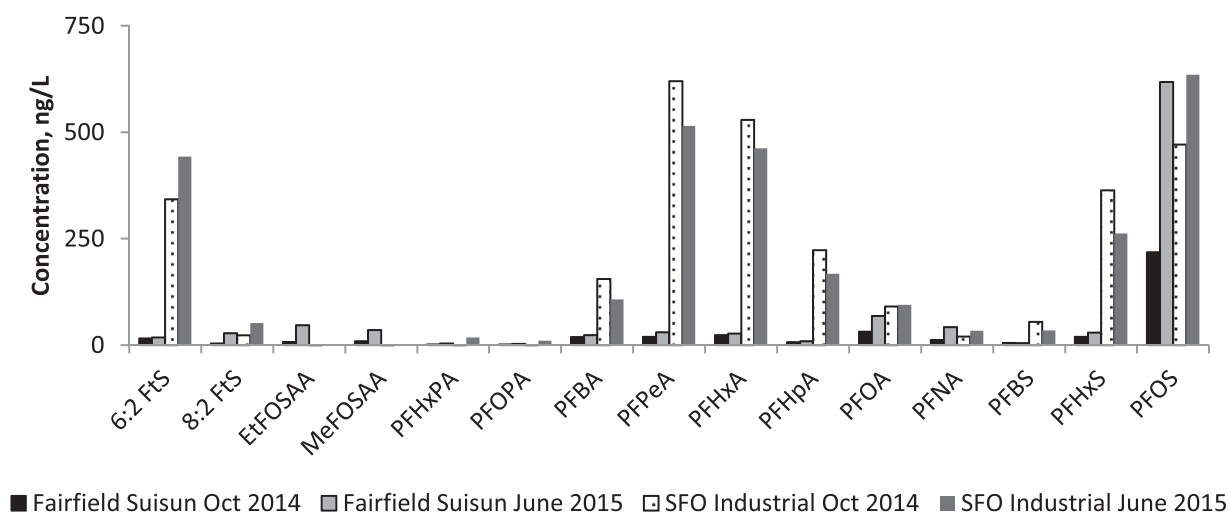


Fig. 1. Concentrations of PFASs in (a) effluent samples from six WWTPs collected in Fall 2014 and (b) effluent samples from two additional WWTPs collected in Fall 2014 and Summer 2015.

Table 2

Average concentrations (\pm standard deviation) of PFASs in domestic WWTP effluent discharged to SF Bay in 2009 (Klosterhaus et al., 2013) and 2014 (this study).

Average concentration, ng/L	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS
Effluent, 2009 (n = 6) ^a	7.4 \pm 4.7	6.7 \pm 7.5	17 \pm 4.0	5.3 \pm 1.2	32 \pm 30	12 \pm 5.6	3.8 \pm 1.8	6.0 \pm 6.5	5.5 \pm 5.5	24 \pm 32
Effluent, 2014 (n = 6) ^b	16 \pm 5.8	12 \pm 11	26 \pm 5.1	4.4 \pm 2.2	21 \pm 13	8.4 \pm 3.6	3.5 \pm 1.7	2.7 \pm 1.5	4.8 \pm 0.9	13 \pm 4.4

^a The PFAS concentrations reported from 2009 are from undisclosed WWTPs (Klosterhaus et al., 2013). Some or all of the WWTPs may be the same as those reported in the 2014 average.

^b Average 2014 PFAS values and their standard deviations are calculated from the six WWTPs reported in Fig. 1a.

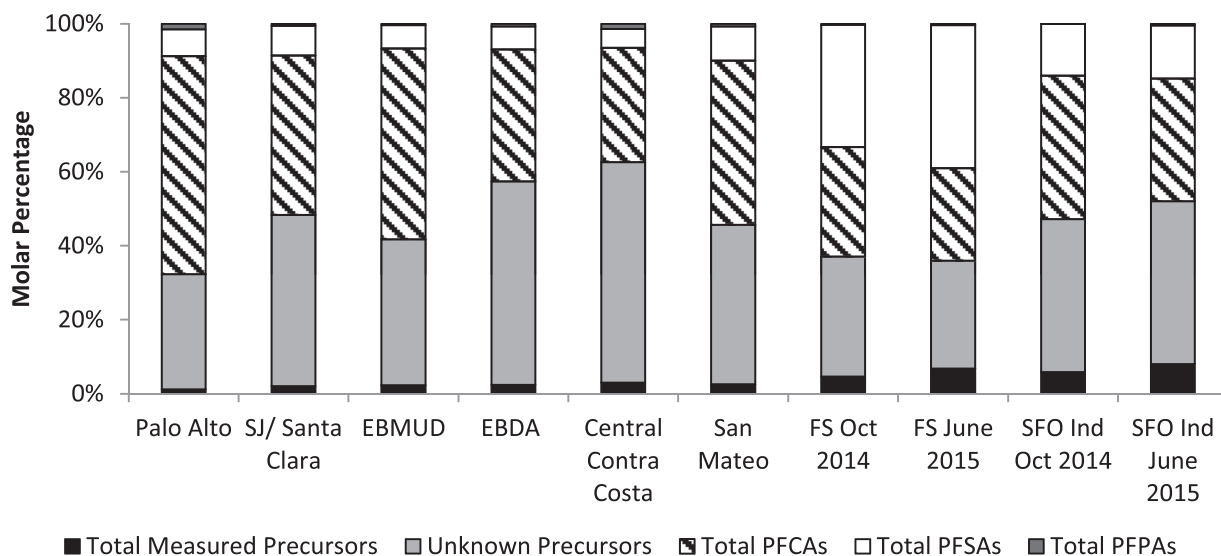


Fig. 2. Molar percentage of measured precursors, unknown precursors, and total measured PFCAs, PFSAs, and PFPAs in WWTP effluent samples. The concentration of unknown precursors is the total concentration of PFAAs generated upon oxidation, less the oxidation products expected from the precursors directly measured.

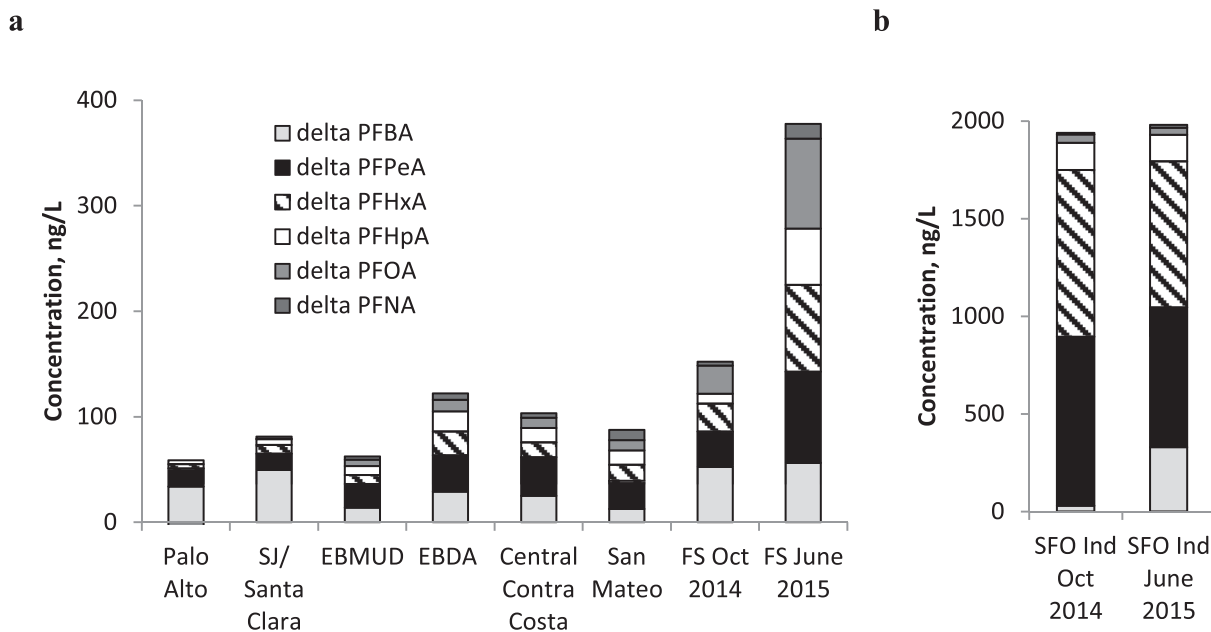


Fig. 3. a–b: Concentrations (ng/L) of individual PFAAs generated in oxidized wastewater samples. Production of PFPAs was negligible. “Delta” refers to the ng/L increase observed in that analyte’s concentration after the sample was oxidized.

PFCAs, PFSAs, PFPAs, measured precursors, and unknown precursors (*i.e.*, the summation of delta [PFCAs] not attributable to PFCAs generated by measured precursors). The molar fraction of PFAA precursors ranged from 33% (Palo Alto) to 63% (Central Contra Costa) of the total concentration of PFASs. Notably, the most PFAS-contaminated effluent samples, Fairfield Suisun and SFO Industrial, contained between 36% and 52% PFAA precursors, which is within the range observed among the less PFAS-contaminated effluent from other WWTPs. The oxidation products generated from measured precursors accounted for 3.0%–18% of the increase in PFCAs observed. 6:2 FtS accounted for the greatest fraction of oxidation products attributable to measured PFAA precursors in all samples, and in particular in SFO Industrial and Fairfield Suisun effluent samples.

The concentrations of PFAA precursor compounds in aqueous samples have been quantified in a handful of previous studies via the total oxidizable precursor assay (Ye et al., 2014; Houtz and Sedlak, 2012; Houtz et al., 2013); compared to those samples, these effluent samples have a somewhat higher percentage of PFAA precursors. In this study, PFCA mass concentrations increased by 124%, on average, after oxidation and the molar fraction of PFAA precursor concentrations was, on average, 46% of total PFASs. In 2013 samples collected from the Tama River region in Japan, effluent concentrations of PFCAs increased by an average of 21% after oxidation (Ye et al., 2014). PFCAs in river water increased by 28% in the Tama River and 69% in the Tama River’s tributaries. In urban runoff collected around SF Bay in 2010, PFCA concentrations increased by a median of 64% after oxidation (Houtz and Sedlak,

2012). In groundwater collected from AFFF-impacted sites in 2011, about 25% of total PFASs were precursors, and 55% were identified by direct measurement. While these effluent samples contain a higher fraction of PFAA precursors than observed in other environmental samples, they will not increase overall PFAA loading by more than a factor of two or three upon eventual transformation to PFAAs.

Most PFCAs generated in samples were C6 and shorter (Fig. 3a–b), suggesting minor presence of long-chain PFAA precursors (Fig. 3a–b). The production of PFOA and PFHpA indicate the presence of C8-based precursors such as 8:2 fluorotelomer compounds and perfluorooctane sulfonamido compounds; PFNA is also generated in small amounts by 8:2 fluorotelomer compounds, as well as PFAA precursor compounds with longer perfluorinated chain lengths (Houtz and Sedlak, 2012). With the exception of Fairfield Suisun (FS), more than 62% by mass (>72% by mole) of PFCAs generated by oxidizing each effluent sample was composed of PFBA, PFPeA, and PFHxA.

In Palo Alto and San Jose/Santa Clara effluent, no increase in PFOA and minimal production of PFHpA were observed, suggesting a lack of C8-precursors (Fig. 3a). (Note: the generation of PFOA from the 2–3 ng/L of directly measured C8 precursors was within the range of precision of PFOA measurement (12%, Table S4) for those oxidized samples.) These two effluent samples also have the greatest concentrations of PFOA, which may indicate that C8-precursors are transformed to PFOA at greater rates in these treatment plants. Alternatively, these two plants have the lowest total suspended solids (TSS) concentrations (Table 1), so C8-precursors, which are more likely to be particle associated, may be removed in these plants through filtering.

Oxidation products in Fairfield Suisun effluent are 26%–40% C7 and longer, by mass, suggesting a higher percentage of long-chain PFAA precursors than other samples. The high percentage of long chain precursors may be related to the same C8-based PFAS source in Fairfield Suisun's sewershed that led to the effluent's disproportionately high percentage of PFOS (Fig. 1b). However, like Palo Alto and San Jose/Santa Clara, Fairfield Suisun also has very low TSS and enhanced removal of C8-based precursors would be expected.

3.4. Sources of elevated PFASs in wastewater effluent

The higher levels of PFASs observed in effluent from the Fairfield Suisun and SFO Industrial WWTPs are likely related to AFFF usage and subsequent transport of AFFF-related constituents to those two treatment plants. PFOS is a principal ingredient of historical formulations of AFFF manufactured by 3 M (Place and Field, 2012; Houtz et al., 2013), and 6:2 FtS is a putative breakdown product of PFASs found in fluorotelomer-based AFFF manufactured by Ansul, National Foam, and possibly others (Houtz et al., 2013). 6:2 FtS was recently observed as a biotransformation product of Ansul AFFF incubated in aerobic soil microcosms (Harding-Marjanovic et al., 2015) and of an Ansul ingredient, 6:2 fluorotelomercaptoalkylamido sulfonate, incubated in activated sludge (Weiner et al., 2013). Both 6:2 FtS and PFOS are commonly observed at AFFF firefighter training areas at the highest levels of all PFASs (Moody et al., 2003; Schultz et al., 2004; Backe et al., 2013; Houtz et al., 2013). Second, both WWTPs have customers that use AFFF. The SFO Airport uses AFFF in emergencies and for periodic proficiency testing. Fairfield Suisun receives approximately 10% of its flow (personal communication with treatment plant operator) from a nearby U.S. Air Force Base that uses AFFF in emergencies and, historically, for firefighter training (AFCEC, 2015).

AFFF management practices at the SFO Airport suggest that much of the PFAS contamination in the final effluent of its industrial plant measured in this study is a residual from historical AFFF usage

and annual testing of AFFF products. The industrial plant only intentionally receives AFFF-impacted waste once a year, when AFFF is tested to ensure it meets the Federal Aviation Administration's foam performance standards. Testing of AFFF occurred over a several day period approximately one month after the 2014 sample was collected and seven months before the 2015 sample was collected. Based on discussions with the plant operators, AFFF was discharged to the plant within hours to days. Thus, neither effluent sample reported here is likely to be heavily impacted by a recent AFFF introduction event. When AFFF is employed for emergencies, runoff from the area of usage is typically diverted and collected for off-site treatment and disposal and not delivered to the industrial plant.

The type of AFFF currently used by SFO Airport suggests that the high levels of PFOS observed in the treatment plant effluent are from a historical residual. Since 2008, SFO Airport has purchased approximately 9000 gallons of Ansulite 3% AFFF (personal communication with treatment plant). This type of AFFF is likely to form the observed 6:2 FtS and shorter chain PFCAs such as PFHxA, PFPeA, and PFBA from its 6:2 fluorotelomer-based PFAS ingredients (Place and Field, 2012; Harding-Marjanovic et al., 2015; Weiner et al., 2013). However, PFOS should not be introduced from this type of AFFF and is more likely the result of washoff from historical usage of AFFF manufactured by 3 M. Safety data sheets maintained at SFO indicate that at one time, AFFF manufactured by 3 M was used by the airport.

Fairfield Suisun WWTP receives approximately 10% of its flow from Travis Air Force Base (AFB), but it does not receive any regular or planned AFFF inputs from the AFB. According to a recent Air Force Civil Engineering Center (AFCEC) Report on PFASs at Travis, the AFB has two firefighter training areas on-site where AFFF has impacted underlying groundwater (AFCEC, 2015). The groundwater is treated in an on-site system using activated carbon and is not discharged into the sanitary sewer. However, floor drains in at least one airplane hangar and one fire station at the AFB flow into the sanitary sewer (AFCEC, 2015); accidental AFFF releases occurred in 2011 and 2014 in the hangar connected to the sanitary sewer (AFCEC, 2015).

The AFCEC (2015) report notes that Ansulite 3% AFFF was stored at Travis AFB in 2014; no mention is made of the use of AFFF manufactured by 3 M, but the presence of $\mu\text{g/L}$ concentrations of PFOS in groundwater on site is a likely indicator of its historical use at Travis. Final effluent at Fairfield Suisun has concentrations of PFOS that are elevated ten to thirty times compared to the WWTPs without known AFFF inputs. If the high levels of PFOS are the result of AFFF usage at Travis AFB, it is likely from washoff of historical contamination of the hangars, AFFF distribution systems, or sewage lines. 6:2 FtS, the primary compound measured here that would be related to Travis's known Ansulite usage, was elevated three to six times in Fairfield Suisun effluent compared to effluent from the WWTPs without known AFFF inputs.

Unlike SFO Airport, Fairfield Suisun WWTP receives wastewater from many industrial, commercial, and municipal users. Travis AFB is a possible source of Fairfield Suisun's high PFOS levels due to its significant contribution to Fairfield's overall flow and its history of AFFF usage, but it may not be the primary source of Fairfield Suisun's PFOS contamination.

4. Conclusions

The impact of each individual plant is determined both by its overall flow and its level of PFAS contamination. The WWTP with the highest effluent flow rate, San Jose/Santa Clara WWTP, discharges the greatest mass of PFASs for all analytes except PFOS. Its effluent discharge point is within ten miles of Mowry Slough,

where some of the highest global levels of PFOS have been recorded in cormorant eggs and harbor seals (Sedlak and Greig, 2012). Due to its comparatively highly contaminated effluent, SFO Industrial may be a source of significant PFAS exposure immediately adjacent to its outfall or right after AFFF testing events, but its typical contribution to overall PFAS loading is among the smallest of all the plants. Fairfield Suisun effluent may have a significant localized and Bay-wide impact with its PFOS loading, as it is responsible for at least 40% of the mass of PFOS discharged from all the plants in this study combined.

The determination of total PFAA precursor concentrations in effluent samples indicated that 33%–63% of PFASs in effluent are a mixture of PFAA precursor compounds, which are not-routinely-quantified. While this contribution will increase the overall PFAS loading of WWTP effluent to the Bay, it will change it by less than an order of magnitude. Additionally, most effluent samples pose an insignificant source of additional PFOS and PFOA via the eventual transformation of PFAA precursors, as most PFAA precursors in effluent are C6 and shorter. Biosolids from these wastewater treatment plants may contain significantly higher amounts of PFOS and PFOA and their precursors (Sepulvado et al., 2011; Lindstrom et al., 2011).

PFAS contamination from AFFF is typically associated with groundwater (Moody et al., 2003; Schultz et al., 2004; Houtz et al., 2013; Backe et al., 2013) and accidental releases to surface water (Moody et al., 2002; Awad et al., 2011; Kärrman et al., 2013). This study is among the first to demonstrate that AFFF may be a primary source of PFAS contamination to effluent, and that PFASs in AFFF-impacted wastewater may occur at much higher levels than in typical municipal wastewater. While effluent discharges to SF Bay do not impact local drinking water, AFFF-impacted wastewater may be especially problematic in cases where wastewater is intentionally or inadvertently reused as a drinking water source.

Disclaimer

The views expressed herein are those of the authors and do not necessarily reflect those of the California Department of Toxic Substances Control.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.02.055>.

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