Study of Per- and Polyfluoroalkyl Substances in Bay Area POTWs

Phase 1 Memo

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Abstract

Wastewater influent, effluent, and biosolids were collected from sixteen treatment facilities within the San Francisco Bay Region to assess the presence of per- and polyfluoroalkyl substances (PFAS). Samples were analyzed by LC-MS/MS and 40 PFAS analytes were quantified by isotope dilution/internal standard quantification methods (target method). Additionally, the presence of PFAS precursors for influent and biosolids were assessed by converting oxidizable PFAS to terminal PFAS in samples prior to analysis by LC-MS/MS (Total Oxidizable Precursors or TOP method). Through target analysis, sampled municipal POTWS exhibited comparable concentrations for the sum of quantified PFAS, with median concentrations of 27 ng/L in influent, 58ng/L in effluent, and 178 ng/L in biosolids. The sum of quantified PFAS TOP concentrations were significantly higher across matrices studied, with median concentrations of 231 ng/L in influent and 594 ng/L in biosolids. These results emphasize the importance of evaluating PFAS precursors to understand the scope of PFAS presence in wastewater samples. While we did not observe a correlation between PFAS concentrations in samples from facilities receiving higher proportions of industrial flows, we recommend further investigation of the relative importance of specific industrial and commercial flows compared to residential flows in Phase 2 evaluations to inform major sources of PFAS to wastewater.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS), such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are an extensive class of fluorine-rich specialty compounds known for their thermal stability, non-reactivity, and surfactant properties. These unique characteristics make them useful for a variety of applications. More than 4,700 PFAS are used in consumer, commercial, and industrial applications, including food packaging materials, waterproof textiles, stain-resistant carpets and furniture, fire-suppression foams, and processing aids to produce fluoropolymers like Teflon, mist suppressants in metal-plating, and hydraulic aviation fluids. These same properties also make them persistent in the environment and potentially toxic to human and ecological health.

To understand the scope of PFAS contamination in California, the State Water Board (SWB) developed a statewide assessment requiring testing of drinking water systems and site investigations of locations likely to contain PFAS, including publicly-owned treatment works (POTWs) as a part of the July 2020 State Water Board Investigative Order (SWRCB, 2020). Agencies that are a part of the San Francisco Bay Regional Water Quality Control Board (Region 2) agencies were exempt from the investigative order to conduct a two-phase regional study in conjunction with the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP), led by the San Francisco Estuary Institute (SFEI), to address the monitoring needs of the SWB efficiently as well as inform the monitoring strategy, management actions, and program decisions of the RMP.

This draft report details the findings and analysis of the data collected from Phase 1 of the Study of PFAS in Bay Area POTWs. The purpose of Phase 1 was to analyze samples from a representative subset of Bay Area POTWs to measure concentrations of PFAS in various matrices, including wastewater influent, effluent, and biosolids. The POTWs included in Phase 1 were carefully selected to provide a representative sample set of Region 2 facilities to examine the range of PFAS concentrations in wastewater matrices and the diverse characteristics that may influence PFAS concentrations to be investigated in Phase 2. The study objectives for Phase 2 will be developed based on the results from Phase 1.

2. Methods

Sampling and analysis were completed following the Phase 1 Sampling and Analysis Plan (SAP), which contains the details of the sampling strategy, including study design, coordination of sample collection, data quality assurance, and reporting associated with the Study of PFAS in Bay Area POTWs (Mendez et al., 2020). In addition, the Phase 1 Monitoring Report (Mendez et al., 2021) details the realized collection and reporting of the data. This section will provide a summary of the information presented in these two documents.

2.1 Selection of Study Participants

To inform the selection of representative POTWs, a questionnaire was developed similar to the one required by the SWB Order to obtain relevant facility information, including potential industrial sources of PFAS and biosolids reuse and disposal practices. Questionnaire responses and specific characteristics of each facility can be found in Appendix A. The questionnaires were thoroughly reviewed, with POTW selection based on consideration of the following factors:

- **Discharge volume:** Sampling at the largest facilities was prioritized to capture dominant flows to the Bay. A few small and medium sized facilities are also represented.
- **Service population and industries:** Chosen facilities range from minimal industrial sources to those with a more significant percentage of flows coming from industrial sources, particularly sources related to fabricated metals, electronics manufacturing, airports, and military bases.
- **Participation in previous Bay RMP PFAS study in 2014:** All facilities that participated in the previous RMP PFAS study (Houtz et al., 2016) are included to evaluate changes in specific PFAS concentrations.
- **Treatment type:** Different secondary treatment technologies, including advanced secondary treatment processes, are included to allow the evaluation of treatment processes on PFAS concentrations.

- **Geographic location:** Selected facilities are geographically diverse and represent all sub embayments.

Table 1 and Figure 1 show the selected Region 2 facilities chosen to participate in this study, as well as important IDs used to report target analysis results and relevant lab QA to Geotracker.

Table 1. Participating Region 2 facilities with related acronyms, Geotracker ID, and CIWQS ID.

Region 2 Facilities	Acronyms	Geotracker Global ID	CIWQS ID
Central Contra Costa Sanitary District	CCCSD	NPD100051616	213875
City of San Mateo Wastewater Treatment Plant	CSM	NPD100051601	255420
Dublin San Ramon Sanitary District Wastewater Treatment Plant	DSRSD	NPD100051638	220792
East Bay Dischargers Association	EBDA	NPD100053240	222123
East Bay Municipal Utility District Main Wastewater Treatment Plant	EBMUD	NPD100051573	222132
Fairfield-Suisun Sewer District	FSSD	NPD100051485	225526
Novato Sanitary District	NSD	NPD100051924	244705
Oceanside Water Pollution Control Plant (SFPUC)	OSP	NPD100051512	256498
Palo Alto Regional Water Quality Control Plant	PA	NPD100051503	247457
San Francisco International Airport Mel Leong Treatment Plant	SFOS	NPD100051556	256507
San Francisco International Airport Mel Leong Treatment Industrial Plant	SFOI	NPD100051556	256507
San Jose-Santa Clara Regional Wastewater Facility	SJSC	NPD100051475	255333
Southeast Water Pollution Control Plant (SFPUC)	SEP	NPD100051513	256499
Union City Sanitary District	USD	NPD100051936	269042
Vallejo Flood & Wastewater District	VFWD	NPD100051544	270006
Valley Water[1]	VW	-	-

[1] Reverse osmosis concentrate (ROC) was collected at Valley Water (VW) at its Advanced Water Purification Facility (AWPF) for target analysis, though this data was not uploaded to Geotracker.

Figure 1. Map of Region 2 facilities selected to participate in this study.

2.2 Field Sample Collection

A. Target Analysis

All POTWs collected grab samples of each matrix (i.e., influent, effluent, and biosolids) for target analysis (see section 2.4 A) except EBDA and VW. EBDA receives treated wastewater effluent from several POTWs and discharges these combined flows at one sampling location; thus, only effluent samples can be collected. VW only collected ROC samples. A subgroup of facilities (CCCSD, FSSD, and SFOI) collected 24-hour composite influent and effluent samples concurrently to compare to grab samples to understand if detected concentrations of PFAS in grab samples are representative and inform differences in sampling methods. This subset of POTWs also collected same-day replicates to assess differences due to sampling methods, as well as field samples on a second date to assess daily or weekly variations in sampled concentrations. The complete list of influent, effluent, and biosolids samples collected for target analysis and their sampling locations is shown in the Phase 1 Monitoring Report (Mendez et al., 2021).

B. TOP Analysis

All POTWs, except EBDA and VW, collected grab samples of influent and biosolids for total oxidizable precursors (TOP) analysis (see section 2.4 B). Some facilities collected replicates to assess variations due to the sampling method. The complete list of influent and biosolids samples collected for TOP analysis and their specific sampling locations is shown in the Phase 1 Monitoring Report (Mendez et al., 2021). The results of TOP analysis were not uploaded to Geotracker.

2.3 QA/QC Sample Collection

Field QA/QC samples, specifically field and equipment rinse blanks, were collected at a few facilities for each matrix (i.e., influent, effluent, and biosolids). These samples were collected for both sampling methods (grab and composite). The chosen subset of POTWs represents a diverse group within Region 2 with the intention that QA/QC samples collected are representative of all samples collected as a part of this study. The complete list of samples collected for QA/QC is shown in the Phase 1 Monitoring Report (Mendez et al., 2021).

2.4 SGS AXYS Analytical Methods

All samples were analyzed by SGS AXYS for PFAS using either Target Analysis (MLA-110) or Total Oxidizable Precursor Analysis (MLA-111). Detailed sample procedures are described in Standard Operating Procedures stored at SFEI, and briefly summarized below. Biosolid samples were also analyzed for Percent Solids. Aqueous samples are reported in units of ng/L; biosolid samples are reported in units of ng/g dry weight (dw), and percent solids content (%).

A. Target Analysis (MLA-110)

Samples from all matrices (i.e., influent, effluent, and biosolids) were analyzed for target PFAS using SGS AXYS Method MLA-110 (summarized in MSU-110 Rev in the Appendix of Mendez et al., 2021) with a complete list of analytes and typical reporting limits (RLs) shown in Table 2. The samples were spiked with isotope-labeled surrogate standards and then extracted and cleaned through Solid Phase Extraction (SPE). Sample extracts were analyzed by liquid chromatography/mass spectrometry (LC-MS/MS) with reported sample concentrations determined by isotope dilution/internal standard quantification.

B. TOP Analysis (MLA-111)

Samples from influent and biosolids were analyzed through TOP analysis using SGS AXYS Method MLA-111, with a complete list of analytes and typical RLs shown in Table 3. The TOP method indirectly quantifies oxidizable PFAS precursors by conversion to terminal perfluorinated carboxylates (PFCAs). Samples are oxidized using persulfate and then, after cooling and pH adjustment, spiked with isotope-labeled quantification standards. Further, the samples are extracted and cleaned using weak anion-exchange SPE. Extracts are analyzed via LC-MS/MS, with the reported concentrations determined by isotope/dilution internal standard quantification. The reported concentrations represent the sum of quantified PFCAs after sample oxidation. Oxidation is monitored using a reaction monitoring standard that is spiked into the sample and control matrix. Overall, this method is used to understand the presence of oxidizable precursors that may not be included in target analysis.

3. Results and Discussion

3.1 General QA/QC findings

The results of PFAS target analysis on all QA/QC samples (i.e., field and equipment rinse blanks) collected at POTWs are displayed in Table 4. Out of twenty QA/QC samples, and 40 analytes (800 analyses), there were only 6 detections with 99% (794/800) of analyses showing no detection. A small set of compounds were detected in both equipment and field blanks, with most detections being only slightly above detection limits. One compound, 6:2 FTS, was detected in a field blank at 80 ng/L, which is significantly higher than any other field blank as well as field samples. While this high blank detection indicates a possible source of field contamination, field samples collected with the field blank were below detection limits.

Overall, about half the analytes were not detected in any field samples, and two-thirds were found in fewer than half of the field samples. Recoveries in LCS and MS/MSD samples for most analytes were within targets listed in the DoD QSM, or 65%-135% for those analytes not explicitly listed (relevant DoD QSM pages found in Mendez et al., 2020. A few individual analytes with results outside of the target range had their results flagged in the database. There were no lab replicates of unspiked samples, but MS/MSD pairs were reported, meeting the DoD QSM target for RPDs of 30% for all the MSD pairs in a quantitative range (>RL).

Overall, the data are largely quantitative, and no significant contamination or other QA/QC issues were observed. The full set of data for this study including QA/QC samples is available in Appendix B.

Table 2. Target PFAS analyte list (MLA-110, SGS AXYS) including expected reporting limits (RLs) for aqueous and biosolids samples.

Abbreviation	Geotracker PARLABEL	PFAS Chemical Name (Acid/Conjugate Base)	Aqueous RLs (ng/L)	Biosolids RLs (ng/g dw)
PFBA	PFTBA	Perfluorobutanoic acid (Perfluorobutanoate)	1.6	0.32
PFPeA	PFPA	Perfluoropentanoic acid (Perfluoropentanoate)	0.8	0.16
PFHxA	PFHA	Perfluorohexanoic acid (Perfluorohexanoate)	0.4	0.08
PFHpA	PFHPA	Perfluoroheptanoic acid (Perfluoroheptanoate)	0.4	0.08
PFOA	PFOA	Perfluorooctanoic acid (Perfluorooctanoate)	0.4	0.08
PFNA	PFNA	Perfluorononanoic acid (Perfluorononanoate)	0.4	0.08
PFDA	PFNDCA	Perfluorodecanoic acid (Perfluorodecanoate)	0.4	0.08
PFUnA	PFUNDCA	Perfluoroundecanoic acid (Perfluoroundecanoate)	0.4	0.08
PFDoA	PFDOA	Perfluorododecanoic acid (Perfluorododecanoate)	0.4	0.08
PFTrDA	PFTRIDA	Perfluorotridecanoic acid (Perfluorotridecanoate)	0.4	0.08
PFTeDA	PFTEDA	Perfluorotetradecanoic acid (Perfluorotetradecanoate)	0.4	0.08
PFBS	PFBSA	Perfluorobutanesulfonic acid (Perfluorobutanesulfonate)	0.4	0.08
PFPeS	PFPES	Perfluoropentanesulfonic acid (Perfluoropentanesulfonate)	0.4	0.08
PFHxS	PFHXSA	Perfluorohexanesulfonic acid (Perfluorohexanesulfonate)	0.4	0.08
PFHpS	PFHPSA	Perfluoroheptanesulfonic acid (Perfluoroheptanesulfonate)	0.4	0.08
PFOS	PFOS	Perfluorooctanesulfonic acid (Perfluorooctanesulfonate)	0.4	0.08
PFNS	PFNS	Perfluorononanesulfonic acid (Perfluorononanesulfonate)	0.4	0.08
PFDS	PFDSA	Perfluorodecanesulfonic acid (Perfluorodecanesulfonate)	0.4	0.08
PFDoS	-	Perfluorododecanesulfonic acid (Perfluorododecanesulfonate)	0.4	0.08
4:2 FTS	4:2FTS	1H, 1H, 2H, 2H-perfluorohexane sulfonic acid (1H, 1H, 2H, 2H-perfluorohexane sulfonate)	1.6	0.32
6:2 FTS	6:2FTS	1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (1H, 1H, 2H, 2H-perfluorooctane sulfonate)	1.6	0.32
8:2 FTS	8:2FTS	1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (1H, 1H, 2H, 2H-perfluorodecane sulfonate)	1.6	0.32
3:3 FTCA	3:3FTCA	2H, 2H, 3H, 3H-perfluorohexanoic acid (2H, 2H, 3H, 3H-perfluorohexanoate)	1.6	0.32
5:3 FTCA	5:3FTCA	2H, 2H, 3H, 3H-perfluorooctanoic acid (2H, 2H, 3H, 3H-perfluorooctanoate)	10	2
7:3 FTCA	7:3FTCA	2H, 2H, 3H, 3H-perfluorodecanoic acid (7:3 FTCA, 2H, 2H, 3H, 3H-perfluorodecanoate	10	2
PFOSA	PFOSA	Perfluorooctanesulfonamide	0.4	0.08
N-MeFOSA	MEFOSA	N-Methylperfluorooctanesulfonamide	0.4	0.08
N-EtFOSA	ETFOSA	N-Ethylperfluorooctanesulfonamide	0.4	0.08
N-MeFOSAA	NMEFOSAA	N-Methylperfluoro-1-octanesulfonamidoacetic acid (N-Methylperfluoro-1-octanesulfonamidoacetate)	0.4	0.08
N-EtFOSAA	NETFOSAA	N-Ethylperfluoro-1-octanesulfonamidoacetic acid (N-Ethylperfluoro-1-octanesulfonamidoacetate)	0.4	0.08
N-MeFOSE	MEFOSE	N-Methylperfluoro-1-octanesulfonamidoethanol	4	0.8
N-EtFOSE	ETFOSE	N-Ethylperfluoro-1-octanesulfonamidoethanol	4	0.8
HFPO-DA (GenX)	HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propionic acid (2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propionoate)	1.6	0.32
ADONA	ADONA	Decafluoro-3H-4,8-dioxanonoic acid (Decafluoro-3H-4,8-dioxanonoate)	1.6	0.32
NFDHA	NFDHA	Perfluoro-3,6-dioxaheptanoic acid (Perfluoro-3,6-dioxaheptanoate)	0.8	0.16
PFMBA	PFMBA	Perfluoro-3-methoxypropanoic acid (Perfluoro-3-methoxypropanoate)	0.8	0.08
PFMPA	PFMPA	Perfluoro-4-methoxybutanoic acid (Perfluoro-4-methoxybutanoate)	1.6	0.16
9Cl-PF3ONS	9-Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (9-chlorohexadecafluoro-3-oxano	1.6	0.32
11Cl-PF3OUdS	11-Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11-chloroeicosafluoro-3-oxaund	1.6	0.32
PFEESA	PFEESA	Perfluoro(2-ethoxyethane)sulfonic acid (Perfluoro(2-ethoxyethane)sulfonate)	0.4	0.08

Table 3: Total Oxidizable Precursors (TOP) PFAS analyte list (MLA-111, SGS-AXYS) including expected reporting limits (RLs) for aqueous samples.

Abbreviation	PFAS Chemical Name (Acid/Conjugate Base)	Aqueous RLs (ng/L)	Solids RLs (ng/g)
PFBA	Perfluorobutanoic acid (Perfluorobutanoate)	6-32 For Perfluorinated Carboxylates C4-C14	0.6-3.2 For Perfluorinated Carboxylates C4-C14
PFPeA	Perfluoropentanoic acid (Perfluoropentanoate)		
PFHxA	Perfluorohexanoic acid (Perfluorohexanoate)		
PFHpA	Perfluoroheptanoic acid (Perfluoroheptanoate)		
PFOA	Perfluorooctanoic acid (Perfluorooctanoate)		
PFNA	Perfluorononanoic acid (Perfluorononanoate)		
PFDA	Perfluorodecanoic acid (Perfluorodecanoate)		
PFUnA	Perfluoroundecanoic acid (Perfluoroundecanoate)		
PFDoA	Perfluorododecanoic acid (Perfluorododecanoate)		
PFTrDA	Perfluorotridecanoic acid (Perfluorotridecanoate)		
PFTeDA	Perfluorotetradecanoic acid (Perfluorotetradecanoate)		
PFBS	Perfluorobutanesulfonic acid (Perfluorobutanesulfonate)	8 For perfluorinated sulfonates C4-C10, C12	0.8 For perfluorinated sulfonates C4-C10, C12
PFPeS	Perfluoropentanesulfonic acid (Perfluoropentanesulfonate)		
PFHxS	Perfluorohexanesulfonic acid (Perfluorohexanesulfonate)		
PFHpS	Perfluoroheptanesulfonic acid (Perfluoroheptanesulfonate)		
PFOS	Perfluorooctanesulfonic acid (Perfluorooctanesulfonate)		
PFNS	Perfluorononanesulfonic acid (Perfluorononanesulfonate)		
PFDS	Perfluorodecanesulfonic acid (Perfluorodecanesulfonate)		
PFDoS	Perfluorododecanesulfonic acid (Perfluorododecanesulfonate)		

3.2 Comparison of Grabs and Composites

Grab and composite samples were collected from three POTWs (CCCSD, FSSD, and SFOI) to compare sampling methods and understand the representativeness of grab samples taken at all facilities in this study. As examples, Figures 2 and 3 detail the results of composite and grab influent samples from CCCSD and FSSD, respectively.

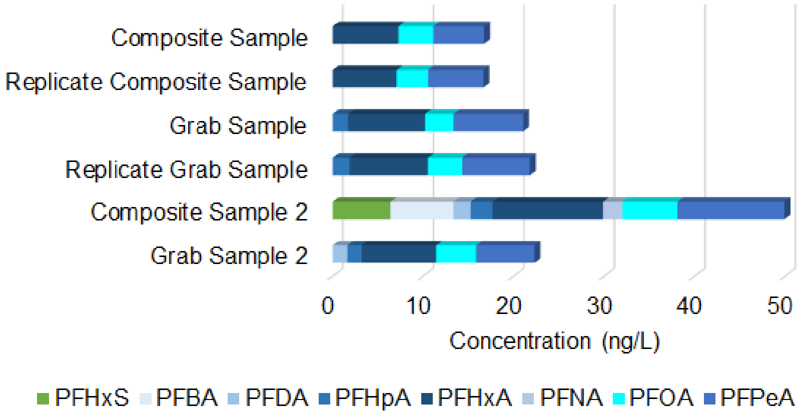

Figure 2. Comparison of composite and grab influent samples from CCCSD.

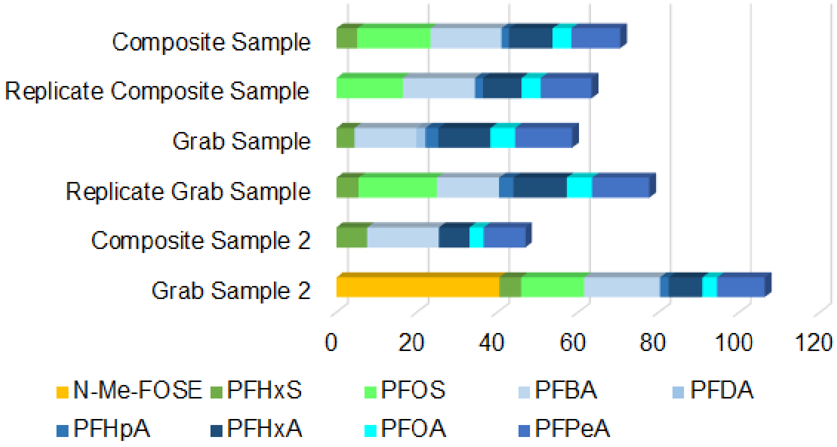

Figure 3. Comparison of composite and grab influent samples from FSSD.

In Figure 2, CCCSD composite and grab influent samples and replicates collected on the same date were nearly identical within the same method with a replicate percent difference (RPD) of 0% (composite replicate) and 3% (grab replicate) for sum of PFAS. FSSD showed a similar pattern, though RPDs for composite and grab replicates were slightly larger than those for CCCSD (RPDs of 11% and 28%, respectively). For both facilities, there is a more significant variation in some composite and grab samples collected on a different day or week (labeled “Sample 2”), with three of the four samples exceeding an RPD of 40%. Generally, sample replicates for individual analytes had an average RPD of 9% with a standard deviation of 11%. In comparison, the average RPD between the composite and grab sample was 19%, with a standard deviation of 15%.

Overall, the concentrations noted for composites and grabs were well within a factor of two, with no clear trend as to which method exhibits higher concentrations and greater variability. For all subsequent analyses, the first grab sample collected from each facility was used to compare concentrations across POTWs.

3.3 Influent

There were several PFAS measured at all POTWs and within all matrices. The complete set of data including all POTWs and analytes is available in Appendix B. Influent data are reviewed below.

The two facilities servicing an airport (SFOI and SFOS) showed a different distribution and greater PFAS concentrations when compared to municipal facilities. This trend is shown for influent samples in Figure 4, though it is present across all matrices (i.e., influent, effluent, biosolids) and analyses (target and TOP). The significant difference in concentrations and distributions of PFAS at SFOI and SFOS warranted exclusion from subsequent analyses, which focuses on municipal POTWs to understand the prevalence of PFAS at these facilities.

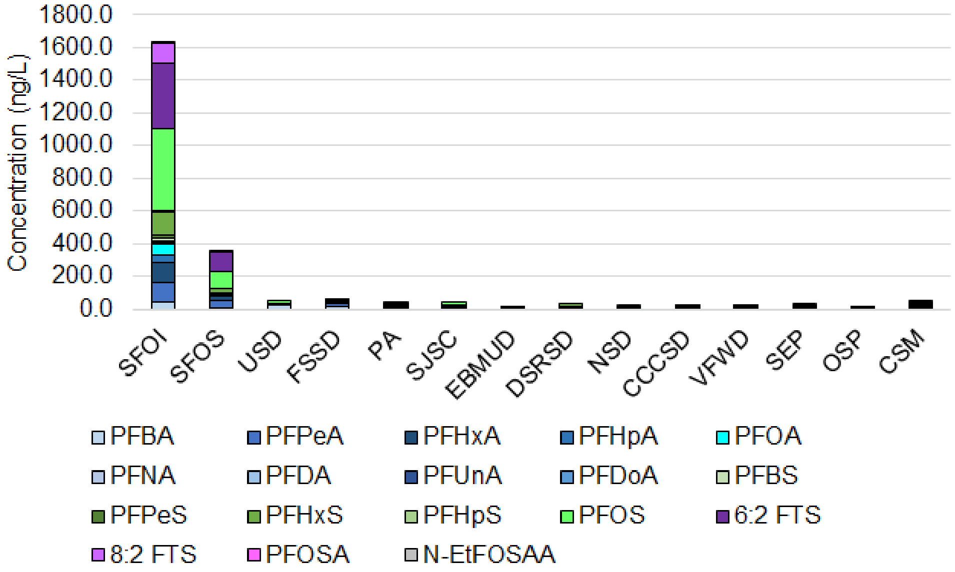

Figure 4. Concentrations of detected PFAS analytes via target method in POTW influent grab samples (first single grab), organized from largest to smallest relative contribution of industrial flows going to the facility.

Influent samples showed detection of a variety of PFAS analytes using target analysis, with results summarized in Table 4. Three analytes — PFPeA, PFHxA, and PFOA — were detected above MDLs in all samples, and had the highest median values among all quantified analytes. PFBA was detected in 42% of the samples, though at higher levels than other analytes, as noted by its higher maximum.

Table 4. Summary statistics for concentrations of detected PFAS via target method in municipal POTW influent grab samples (first single grab). All values are in ng/L.

Detected Analytes	MDLs (Range)		% Detected in Samples (Total: 12)	Minimum	Max	Median	Mean[1]
PFBA	5.81	8.25	42%	ND	23	ND	5
PFPeA	2.91	4.12	100%	4	14	6	7
PFHxA	1.45	2.06	100%	4	13	8	7
PFHpA	1.45	2.06	58%	ND	3	1.9	1
PFOA	1.45	2.06	100%	2	6	3	4
PFNA	1.45	2.91[2]	8%	ND	2	ND	ND
PFDA	1.45	2.06	8%	ND	2	ND	ND
PFBS	1.6	13.9[2]	17%	ND	6	ND	1
PFHxS	1.65	42.9[2]	33%	ND	12	ND	2
PFOS	1.81	24.9[2]	17%	ND	13	ND	2
N-EtFOSAA	1.45	2.95	8%	ND	3	ND	ND
Sum of PFAS	-	-	-	10	59	27	30

[1] Calculated with all detected values and setting non-detects (NDs) as zero.

[2] Values were flagged and considered non quantitative due to peak interference, resulting in higher MDLs.

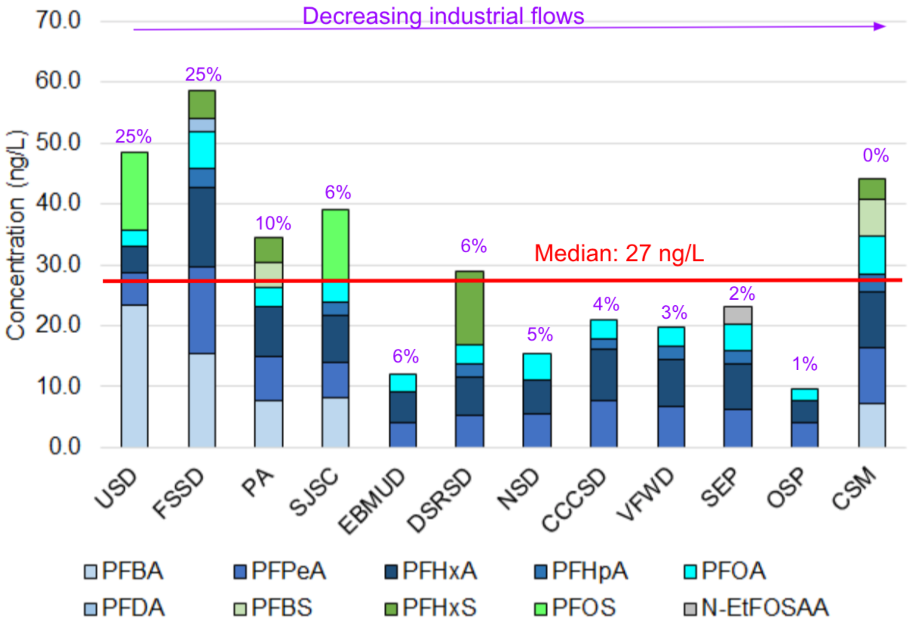

Figure 5. Concentrations of detected PFAS analytes via target method in municipal POTW influent grab samples (first single grab), organized from largest to smallest relative contribution of industrial flows going to the facility.

Total municipal POTW influent PFAS concentrations ranged from 10 to 59 ng/L with a median of 27 ng/L (Figure 5). Short-chain PFCAs (e.g., PFBA, PFPeA, PFHxA, PFHpA) were the most commonly detected analytes.. While we had hypothesized that facilities receiving a higher proportion of industrial flows would contain higher concentrations of PFAS, we did not observe a clear correlation between the proportion of industrial flows and the sum of quantified target PFAS from this dataset.

TOP analysis of influent samples exhibited notably higher concentrations of PFAS compared to target analysis, with a range of 150 - 299 ng/L and a median of 231 ng/L for sum of PFAS (Table 5). The median for sum of PFAS via TOP is over eight times greater than the sum of target analytes, indicating a considerable presence of PFAS precursors that are not quantified using the target method. When organized by industrial flows, as shown in Figure 6, there is no observed correlation between the proportion of industrial flows and the sum of analytes detected through TOP.

Table 5. Summary statistics for concentrations of detected PFAS via TOP method in municipal POTW influent grab samples. All values are in ng/L.

Detected Analytes	MDLs (Range)		% Detected in Samples (Total: 12)	Minimum	Max	Median	Mean[1]
PFBA	12.2	26.6	100%	39	85	66	64
PFPeA	6.11	13.3	100%	43	95	70	67
PFHxA	3.05	71.6[2]	92%	ND	60	45	41
PFHpA	3.05	6.64	100%	16	31	21	22
PFOA	3.05	6.64	100%	13	33	21	22
PFNA	3.09	12.2[2]	75%	ND	11	8	6
PFDA	3.12	9.69[2]	50%	ND	8	2	3
PFUnA	3.05	6.64	8%	ND	3	ND	ND
PFBS	3.05	6.64	25%	ND	8	ND	1
PFHxS	3.05	6.64	8%	ND	10	ND	1
PFOS	3.05	10.3[2]	25%	ND	12	ND	2
6:2 FTS	11	23.9	25%	ND	24	ND	5
Sum of PFAS	-	-	-	150	299	231	235

[1] Calculated with all detected values and setting non-detects (NDs) as zero.

[2] Values were flagged and considered non quantitative due to peak interference, resulting in higher MDLs.

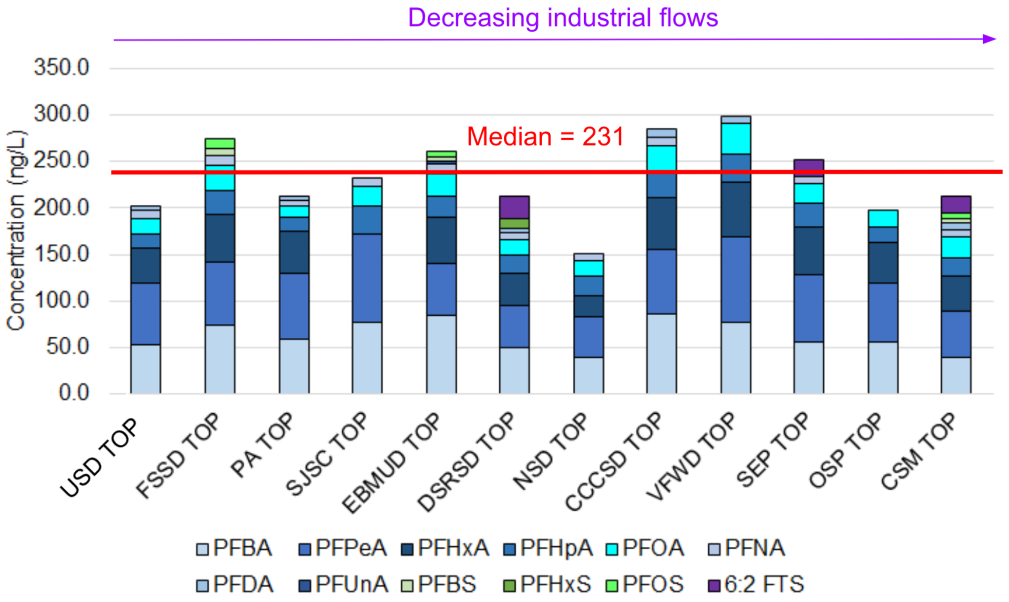

Figure 6. Concentrations of detected PFAS analytes via the TOP method in municipal POTW influent grab samples (first single grab), organized from largest to smallest input of industrial flows.

3.4 Effluent

A broad range of PFAS analytes was found in effluent samples when analyzed via target analysis, as shown in Table 6. A total of 17 analytes were detected at municipal facilities with eight, mostly short-chain PFCAs, identified above MDLs in all samples.. Highlighted in Figure 7, total municipal POTW effluent PFAS concentrations ranged from 33 - 106 ng/L with a median of 58 ng/L. We also did not find a clear correlation between the proportion of industrial flows and the sum of quantified target PFAS for effluent data.

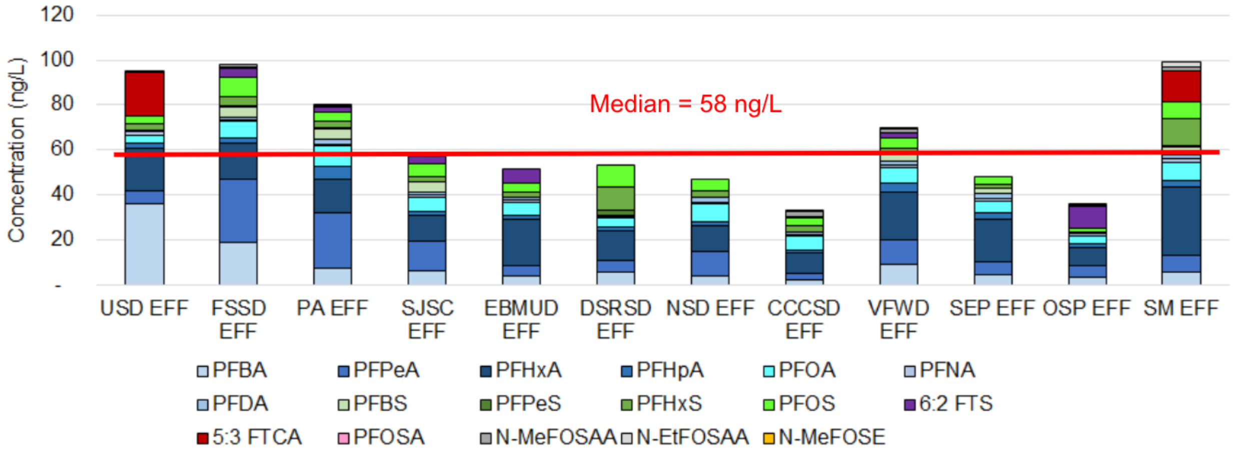

Figure 7. Concentrations of detected PFAS analytes via target method in municipal POTW effluent samples, organized from largest to smallest input of industrial flows.

Table 6. Summary statistics for concentrations of detected PFAS via target method in municipal POTW effluent grab samples (first single grab). All values are in ng/L.

Detected Analytes	MDLs (Range)		% Detected in Samples (Total: 13)	Minimum	Max	Median	Mean[1]
PFBA	1.52	2	100%	2	36	5	9
PFPeA	0.76	1	100%	3	28	8	10
PFHxA	0.38	0.5	100%	8	30	16	17
PFHpA	0.38	0.5	100%	1	6	2	2
PFOA	0.38	0.5	100%	3	9	6	6
PFNA	0.38	1.04	92%	ND	1	1	1
PFDA	0.38	0.5	100%	1	2	1	1
PFBS	0.391	19.9[2]	46%	ND	5	ND	2
PFPeS	0.382	0.622	38%	ND	2	ND	ND
PFHxS	0.38	0.5	100%	1	12	3	4
PFOS	0.38	0.5	100%	2	10	5	5
6:2 FTS	1.37	1.8	54%	ND	10	2	2
5:3 FTCA	9.5	12.5	23%	ND	20	ND	4
PFOSA	0.38	0.5	31%	ND	1	ND	ND
N-MeFOSAA	0.38	1.88	54%	ND	3	ND	1
N-EtFOSAA	0.38	0.543	31%	ND	2	ND	ND
PFMBA	0.76	1	8%	ND	1	ND	ND
Sum of PFAS	-	-	-	33	106	58	67

[1] Calculated with all detected values and setting non-detects (NDs) as zero.

[2] Values were flagged and considered non quantitative due to peak interference, resulting in higher MDLs.

Compared to the influent data, the effluent data showed a greater variety of PFAS analytes detected at greater concentrations. There were roughly 50% more analytes detected in the effluent, with the target PFAS median more than double the influent target median. This trend has been reported in other wastewater studies and can be explained by the significant presence of precursors in the influent that are converted to terminal products or other precursors that are quantified via target analysis (Guerra et al., 2014; Lenka et al., 2021). There was no clear difference between facilities that performed secondary treatment and those with advanced secondary treatment.

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has previously conducted two studies analyzing PFAS in wastewater effluents to assess concentrations of PFAS in effluents discharged to the Bay. In 2009, a blind study of six municipal POTWs reported a total of 10 analytes in sampled effluents with average values and standard deviations noted in Table 7 (Klosterhaus et al., 2013). Additionally, six municipal POTWs — CCCSD, CSM, EBDA, EBMUD, PA, and SJSC — had effluents sampled in 2014 with averages and standard deviations shown for the same ten analytes reported in the 2009 study (Table 7; Houtz et al., 2016).

Table 7. Average concentrations of detected PFAS for POTW effluent studies in 2009, 2014, and 2020 (present study). Only the target PFAS analyzed in the 2009 study are summarized here to allow for comparison across studies. All values are in ng/L.

Detected Analytes	2009 Average[1]	Standard Deviation	2014 Average[2]	Standard Deviation	2020 Average[2]	Standard Deviation
PFBA	7.4	4.7	16	5.8	7.2	5.6
PFPeA	6.3	7.5	12	11	10.4	8.0
PFHxA	17	4	26	5.1	19.5	9.3
PFHpA	5.3	1.2	4.4	2.2	2.7	1.5
PFOA	32	30	21	13	7	1.4
PFNA	12	5.6	8.4	3.6	1.1	0.2
PFDA	3.6	1.8	3.5	1.7	1.5	0.3
PFBS	5.3	6.5	2.7	1.5	2	2.3
PFHxS	5.1	5.5	4.8	0.9	4.9	4.0
PFOS	24	32	13	4.4	5.3	1.7

[1] The 2009 project included six unspecified Region 2 facilities with the average concentration shown (Klosterhaus et al., 2013). Non-detects (NDs) were set to 0.

[2] Each concentration is averaged across six participating facilities (CCCSD, CSM, EBDA, EBMUD, PA, and SJSC) for 2014 (Houtz et al., 2016) and 2020 studies. FSSD and SFOI were also sampled in 2014, but were excluded in the analysis of municipal facilities due to signs of AFFF influence. Non-detects (NDs) were set to 0.

Comparing the average concentrations of these two projects to the current study, there are noticeable declines in long-chain PFAS. Average concentrations of PFOA, PFNA, and PFOS from 2009 to 2020 decreased by 80%, 91%, and 78%, respectively. A Kruskal-Wallis test found that the change in concentrations of PFOS over time were not statistically significant ($p = 0.08$). However, differences in PFOA and PFNA over time were statistically significant, $p = 0.003$ for both analytes. A post-hoc Nemenyi Test was used to compare all pairs of groups for PFOA and PFNA. The change in concentrations of PFOA in 2020 compared to both 2009 and 2014 were significant, $p = 0.008$ and 0.012, respectively. The same pairs (2009 and 2014 compared to 2020) were also significant for PFNA ($p = 0.003$ and 0.03, respectively). None of the other comparisons were significant ($p < 0.05$).

Finally, the results of the ROC samples collected at VW are shown in Appendix B. These samples are best compared to those from SJSC, as ROC is the reject water from the purification of secondary effluent from SJSC. The average concentration of the sum of PFAS analytes in ROC was 6 times greater than at SJSC, which is consistent with general expectation of the treatment process at VW (UC, Berkeley et al., 2020).

3.5 Biosolids

The largest variety of PFAS in all matrices was detected within biosolids, with a total of 25 analytes found out of 40 analyzed (Table 8). All PFCAs within the target method were detected in the full set of samples, with long-chain PFCAs among the most extensively found (83 - 92%). 5:3 FTCA was widely detected (83%) at significantly higher concentrations than any other analyte, with a median concentration of 78 ng/g. This is more than five times greater than the next largest median of 14 ng/g for 7:3 FTCA. Generally, 5:3 FTCA is considered an intermediary transformation product, particularly for 6:2 fluorotelomer structures, and is commonly observed in landfill leachates and food contact substances (Lang et al., 2017; Schaider et al., 2017), which may explain its widespread presence at high concentrations in biosolids.

Total municipal biosolids concentrations ranged from ND to 320 ng/g, with a median of 178 ng/g. The samples at both ends of the range are likely influenced by the particular biosolids processing at the POTW. CCCSD biosolid samples are incinerated and analyzed as wet ash samples. Prior to entering the furnace, two biosolids samples were collected and analyzed (detailed in Appendix B), showing the presence of several PFAS in biosolid "cake" prior to incineration.

SJSC exhibited the highest sum of PFAS concentrations in biosolids, though this is probably because of its four-year storage and processing of biosolids in sludge beds. This process gives PFAS precursors present in biosolids the time to transform to detectable analytes, illustrated by the notable difference in the PFAS fingerprint at SJSC compared to the rest of the municipal facilities in Figure 8. Overall, biosolids exhibited a different variety of PFAS, with a focus on 5:3 and 7:3 FTCA compared to the predominance of PFCAs in target analysis of influents and effluents.

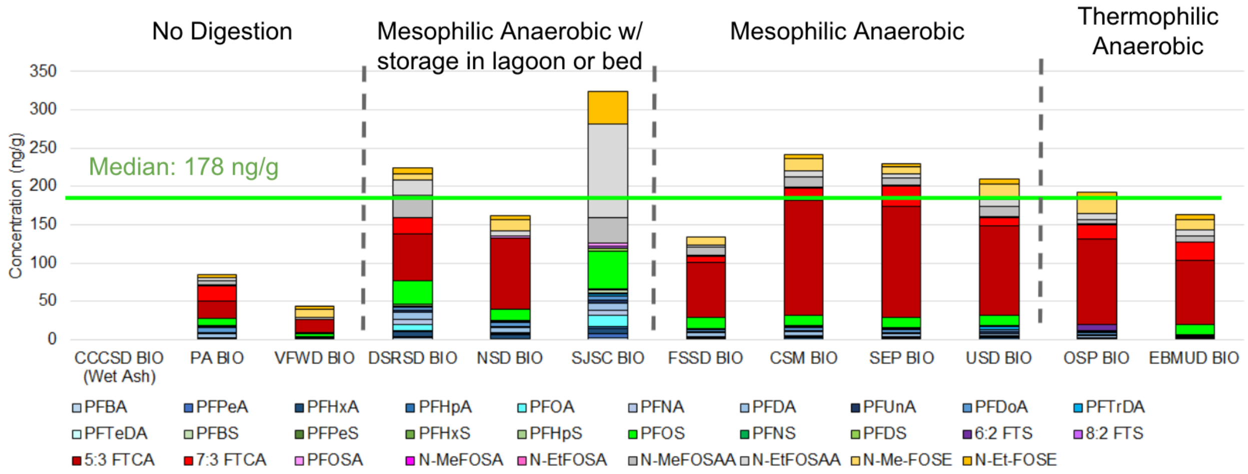

Figure 8. Concentrations of detected PFAS analytes via target method in municipal POTW biosolids samples, organized by digestion type.

Table 8. Summary statistics for concentrations of detected PFAS via target method in municipal POTW final biosolids samples. All values are in ng/g.

Detected Analytes	MDLs (Range)		% Detected in Samples (Total: 12)	Minimum	Max	Median	Mean[1]
PFBA	1.15	2.64	17%	ND	3	ND	ND
PFPeA	0.577	1.32	33%	ND	5	ND	1
PFHxA	0.288	0.674	83%	ND	7	1	2
PFHpA	0.288	0.66	17%	ND	2	ND	ND
PFOA	0.288	0.66	92%	ND	15	1	3
PFNA	0.288	0.752	92%	ND	7	1	2
PFDA	0.288	0.66	92%	ND	10	4	5
PFUnA	0.328	0.66	92%	ND	4	2	2
PFDoA	0.288	0.66	92%	ND	6	3	3
PFTrDA	0.288	0.894[2]	83%	ND	3	1	1
PFTeDA	0.288	0.66	83%	ND	2	1.5	1
PFBS	0.331	66.8	8%	ND	5	ND	ND
PFHxS	0.328	2.23	17%	ND	2	ND	ND
PFOS	0.288	7.59	83%	ND	49	13	14
PFDS	0.367	4.8[2]	17%	ND	4	ND	2
6:2 FTS	1.04	2.38	8%	ND	7	ND	7
8:2 FTS	1.15	2.64	8%	ND	2	ND	2
5:3 FTCA	7.21	16.5	83%	ND	151	78	73
7:3 FTCA	7.21	16.5	67%	ND	27	14	12
PFOSA	0.288	0.66	83%	ND	4	1	1
N-MeFOSA	0.377	0.843	8%	ND	0.5	ND	ND
N-EtFOSA	0.721	1.65	8%	ND	1	ND	ND
N-MeFOSAA	0.328	18.6[2]	75%	ND	33	8	10
N-EtFOSAA	0.288	0.957[2]	92%	ND	122	7	16
N-MeFOSE	2.88	6.6	75%	ND	21	11	10
N-EtFOSE[3]	2.16	4.94	67%	ND	42	6	8
Sum of PFAS	-	-	-	ND	320	178	166

[1] Calculated with all detected values and setting non-detects (NDs) as zero.

[2] Values were flagged and considered non quantitative due to peak interference, resulting in higher MDLs.

[3] Summary statistics are calculated out of 10 total samples since two samples were flagged as rejected.

When separated by digestion type, POTWs with no digestion showed lower concentrations of PFAS compared to the other processes (Figure 8). One potential explanation for this is the greater concentration of organic matter in undigested samples, which dilutes the concentrations of PFAS (reported per biosolid mass) compared to biosolids that have lost organic matter through digestion processes. The concentrations of PFAS across facilities performing digestion processes are relatively comparable.

TOP analysis of biosolids samples noted significantly higher concentrations compared to target analysis, with a range of 2 - 1565 ng/g and a median of 594 ng/L for the sum of TOP PFAS (Table 9). The median for sum of PFAS in biosolids via TOP is roughly three times greater than the sum of target analytes, which suggests a large presence of PFAS precursors that are not quantified using the target method. At SJSC, the difference between the sum of PFAS in TOP and target was the lowest (TOP:target ratio = 1.8), which is consistent with their longer treatment process providing for greater conversion of precursors to target products. Similar to the target method, only a small amount of PFAS were detected in the CCCSD wet ash sample. When organized by the digestion method used, there appear to be elevated levels of PFAS in facilities using sludge lagoons (Figure 9), though overall there is no observed correlation between digestion activity and the sum of analytes detected through TOP. Further study is needed to understand the transformation of PFAS through varying digestion methods.

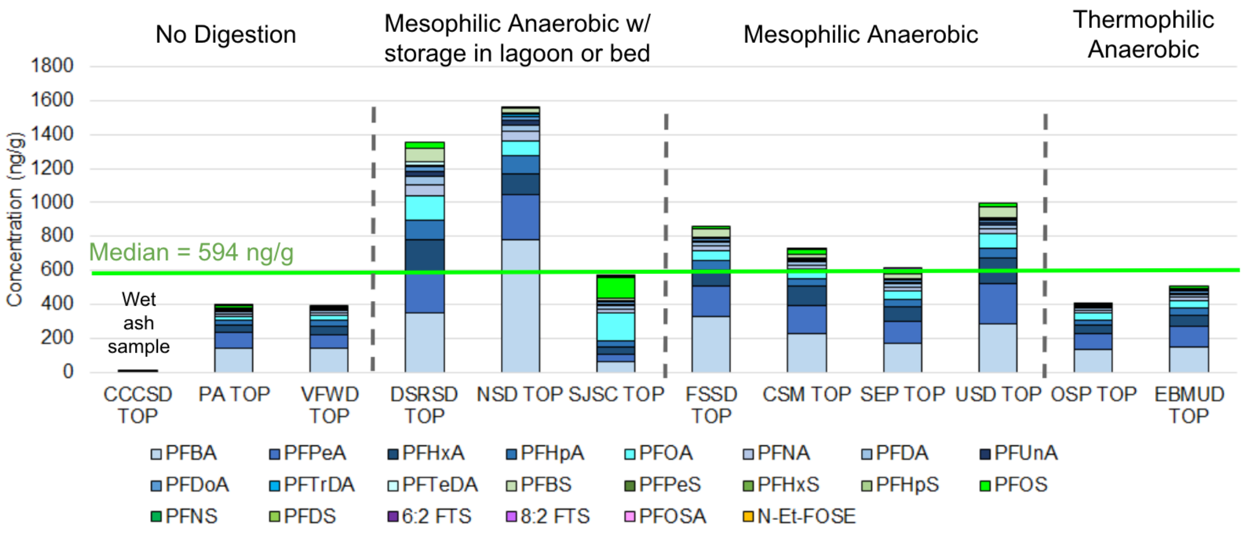

Figure 9. Concentrations of detected PFAS analytes via TOP method in municipal POTW biosolids samples, organized by digestion type.

Table 9. Summary statistics for concentrations of detected PFAS via TOP method in municipal POTW biosolids samples. All values are in ng/g.

Detected Analytes	MDLs (Range)		% Detected in Samples (Total: 12)	Minimum	Max	Median	Mean[1]
PFBA	1.63	15.4	92%	ND	783	160	231
PFPeA	0.815	7.71	92%	ND	55	19	21
PFHxA	0.408	3.85	92%	ND	30	12	13
PFHpA	0.408	3.85	92%	ND	114	44	50
PFOA	0.454	3.85	100%	1	188	75	84
PFNA	0.408	3.85	92%	ND	65	22	25
PFDA	0.408	3.85	92%	ND	162	54	65
PFUnA	0.408	3.85	100%	1	267	125	138
PFDoA	0.408	3.85	92%	ND	16	4	6
PFTrDA	0.408	3.85	83%	ND	13	3	4
PFTeDA	0.408	3.85	92%	ND	26	8	10
PFBS	0.408	3.85	83%	ND	80	16	24
PFHxS	0.408	3.85	25%	ND	7	ND	1
PFOS	0.408	3.85	25%	ND	4	ND	1
PFDS	0.408	3.85	92%	ND	120	15	23
6:2 FTS	1.47	13.9	8%	ND	14	ND	1
8:2 FTS	1.63	15.4	8%	ND	6	ND	1
PFOSA	0.408	3.85	25%	ND	1	ND	ND
N-EtFOSAA	0.408	3.85	8%	ND	2	ND	ND
N-Et-FOSE	3.05	28.8	8%	ND	7	ND	1
Sum of PFAS	-	-	-	2	1,565	594	699

[1]Calculated with all detected values and setting non-detects (NDs) as zero.

4. Recommendations for Phase 2

SFEI joined conversations with BACWA, BACWA members, and State and Regional Water Board representatives to discuss priority objectives for Phase 2. The overall consensus was to better understand the major sources of PFAS entering municipal POTWs in order to inform source control measures. While State Water Board investigation orders have been sent to some industrial dischargers (e.g., bulk fuel terminal/refineries, chrome platers, landfills, and airports), many other industrial and commercial dischargers may be potential sources of PFAS to municipal wastewater. Additionally, a presentation of statewide wastewater results presented by Orange County Sanitary District and Ramboll at the Clean Summit Partners (September 1, 2021) meeting showed the contribution of PFAS concentrations from residential/commercial customers were comparable to industrial customers. These results suggest PFAS sources may be widespread and dispersed among residential and commercial wastewater customers as well.

Based on the findings from Phase 1 and priorities from BACWA members and the Water Boards, we recommend the following priority study questions for Phase 2. Specific study questions and scope will be refined through the development of a Sampling and Analysis Plan for Phase 2.

1) What are concentrations of TOP and target PFAS from residential flows versus total influent (influent received at the facility)?

2) What are concentrations of TOP and target PFAS from specific industrial and commercial dischargers in the sewershed? Potential commercial and industrial operations to investigate for Phase 2 include metalworking (i.e., those not included in previous SWB investigation orders), industrial laundry, dry cleaning, car washes, auto repair shops, hospitals, manufacturing (auto parts, aviation, chemical, pesticide, pharmaceutical, paint, coatings, lens, plastics, semiconductor, electronic components, paperboard), fire stations, composting facilities, jails/prisons, military operations. This list will be narrowed down based on further conversations with BACWA members. How do concentrations from these dischargers compare to concentrations reported to the SWB under previous investigation orders?

3) What are TOP concentrations in the effluent, and how do these compare with TOP in influent and biosolids?

4) Is there a significant presence of other PFAS in influent, effluent, and biosolids that are not captured by TOP analysis? Total organic fluorine analysis, adsorbable organofluorine analysis (for water samples), and extractable organofluorine analysis (solid samples) may be used to respond to this question.

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6. Appendix A: Supplementary Information

All questionnaire responses received from BACWA members are available as a separate excel file. Characteristics of each facility were used to select study participants.

7. Appendix B: Sample Data for Phase 1

All sample data for all facilities and matrices, including field and lab blanks, are included as a separate excel file. The first tab includes notes to help to understand the presented data with subsequent tabs showing data by matrix.