# State Water Resources Control Board

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**SUBJECT**:   Broad-Spectrum Per- and Polyfluoroalkyl Substances (PFAS) Method Comparison Study Results and Selection of Broad-Spectrum Methods to Support Statewide Monitoring for the Class of PFAS

## Executive Summary

Through California Assembly Bill 178 (AB 178; Ting), the Budget Act of 2022, the State Water Resources Control Board (State Water Board) is charged with three primary objectives to address statewide per- and polyfluoroalkyl substances (PFAS) testing including the development and validation of a standard operating procedure for a broad-spectrum test that could be used to monitor all community public water systems in the state for the class of PFAS. In support of this objective, State Water Board developed a method comparison study plan, as documented in the document titled, "Method Comparison Study for the Determination of Appropriate Broad Spectrum Analytical Methods for the Class of Per- and Polyfluoroalkyl Substances (PFAS)" (Method Comparison Study Plan, included as Attachment 1).

The primary objective of the Method Comparison Study Plan is to identify the most appropriate broad-spectrum analytical method for characterizing the occurrence of "total PFAS" in drinking water. The most appropriate broad-spectrum analytical method will be reproducible, robust, with high potential to support feasible ongoing monitoring. A secondary objective of this study is to characterize the chemical space that is captured by available broad-spectrum analytical methods. The broad-spectrum test will be an analytical testing methodology to measure organic fluorine within the broadest chemical space possible using commercially viable technology.

The Method Comparison Study Plan was implemented during the fourth quarter 2023 and analytical results were compiled, processed, and evaluated during the first quarter 2024. Four data evaluation discussion meetings were hosted with several study partners and interested participants from the State Water Board contract laboratory (Babcock Laboratories), University of Notre Dame (Dr. Graham Peaslee), and the U.S. Environmental Protection Agency (USEPA) including participants from USEPA Region 9

Water Division, USEPA Office of Ground Water and Drinking Water, and USEPA Office of Research and Development. These meetings provided the opportunity to receive input and feedback throughout the data evaluation process from many leaders and experts interested in identifying a "total PFAS" analytical method. It is recognized that due to the complex nature of PFAS as a class, there is not currently a single analytical method that captures all PFAS. However, the results of the Method Comparison Study Plan did provide clarity regarding the optimal approach for the broad-spectrum test to be used to monitor all severely disadvantaged communities and disadvantaged communities (SDAC/DAC) public water systems (PWS) in the state for the class of PFAS.

After analyzing the performance of six broad-spectrum PFAS analytical techniques and method preparation procedures and three targeted PFAS analytical techniques and method preparation procedures for this study, the most appropriate and commercially available broad-spectrum analytical method available is adsorbable organic fluorine by combustion ion chromatography (AOF-CIC) modeled after USEPA Method 1621. This broad-spectrum analytical method is recommended to be used along with USEPA 533 to characterize the presence of organic fluorine and targeted PFAS occurring in PWS wells servicing SDAC/DAC. Additionally, the subset of samples to be analyzed by liquid chromatography high resolution mass spectrometry (LC-HRMS) should be conducted on samples that are prepared for PFAS analysis in accordance with Table B-15 of the Department of Defense Quality Systems Manual version 5.3 (DoD QSM) as this extraction process supports a broad-spectrum analysis of PFAS using non-targeted chemical analysis. To further expand the PFAS chemical space characterized in the statewide investigation, it is recommended that the same subset of samples that will be characterized by LC-HRMS be analyzed for presence/absence of ultrashort PFAS (including trifluoroacetic acid, or TFA) using ion chromatography tandem mass spectrometry (IC-MSMS) on samples prepared using the DoD QSM extract.

## Study Plan Implementation

The Method Comparison Study Plan included two key study elements. The primary study focused on the collection and analysis of samples from nine public water supply (PWS) groundwater wells (prior to treatment) to characterize the spectrum of PFAS present in the environment that can be measured using available analytical methods. The study included broad-spectrum organic fluorine methods that are commercially viable (i.e., AOF-CIC and extractable organic fluorine by combustion ion chromatography [EOF-CIC]), and other methods that are primarily available through academic partnerships. In addition to field sample analysis, the study included several laboratory control spike experiments to evaluate the analytical fate of analytical standards that represent a range of inorganic fluorine compounds and ultrashort-chain, volatile, and cationic PFAS over a range of concentrations. The analytical fate study provides important context for interpretation of the field sample results and is therefore described first.

## Analytical Fate Study

The analytical fate study included evaluation of a list of PFAS standards analyzed via combustion ion chromatography (CIC) to evaluate the combustion efficiency of each

standard. Additionally, spiked samples were prepared using one to three spike levels of each standard and samples were processed to assess performance of the compound through the extraction and analysis process. Samples were prepared and analyzed by Babcock Laboratories, as follows:

- AOF-CIC with extraction modeled after USEPA Method 1621.
- EOF-CIC with extraction modeled after USEPA Method 533.
- IC-MSMS using a direct injection (or analyzed as received) sample preparation approach.
- IC-MSMS using the DoD QSM sample preparation approach.
- Liquid chromatography tandem mass spectrometry (LC-MSMS) using the DoD QSM sample preparation approach.

The standards included in the analytical fate study and the associated analyte fate category (analyte groups) are listed in Table 1.

*Table 1. Analytical standards included in analyte fate study and associated analyte category.*

| Analyte Name | Abbreviation | Analyte Fate Category |
|---|---|---|
| Sodium Fluoride | $NaF^-$ | Inorganic Fluorine |
| Hexafluorophosphate | $PF_6^-$ | Inorganic Fluorine |
| Tetrafluoroborate | $BF_4^-$ | Inorganic Fluorine |
| Trifluoroacetic acid | TFA | Ultrashort Chain PFCA |
| Perfluoropropanoic acid | PFPrA | Ultrashort Chain PFCA* |
| Hexafluoroisopropanol | HFIP | Ultrashort chain volatile (likely) PFCA precursor |
| 6:2 Fluorotelomer alcohol | 6:2 FTOH | (Semi) Volatile short chain fluorotelomer (PFCA precursor) |
| 8:2 Fluorotelomer alcohol | 8:2 FTOH | (Semi) Volatile long chain fluorotelomer (PFCA precursor) |
| Trifluoromethanesulfonic acid | TFMS | Ultrashort chain PFSA |
| Perfluoroethane sulfonate | PFetS | Ultrashort chain PFSA* |
| Perfluoropropyl sulfonate | PFPrS | Ultrashort chain PFSA* |
| Perfluorobutyl sulfonate | PFBS | Short chain PFSA* |
| Perfluorohexyl sulfonate | PFHxS | Long chain PFSA* |
| Triflinate | TFMSi | Ultrashort chain sulfinate (likely PFSA precursor)* |
| Bistriflimide | - | Ultrashort chain sulfonamide (likely PFSA precursor) |
| Trifluoromethane sulfonamide | TFMSA | Ultrashort chain sulfonamide (PFSA precursor) |
| Perfluorobutanesulfonamide | PFBSA | Short chain sulfonamide (PFSA precursor)* |

| Analyte Name | Abbreviation | Analyte Fate Category |
|---|---|---|
| Perfluorohexanesulfonamide | PFHxSA | Long chain sulfonamide (PFSA precursor)* |
| Perfluorodecanesulfonamide | PFDSA | Long chain sulfonamide (PFSA precursor)* |
| N-[3-(perfluoro-1-hexanesulfonamido)propan-1-yl]-N,N,N-trimethylammonium | N-TAmP-FHxSA | Cationic long chain sulfonamide (PFSA precursor) |
| N-(3-dimethylaminopropan-1-yl)perfluoro-1-hexanesulfonamide | N-AP-FHxSA | Cationic long chain sulfonamide (PFSA precursor) |
| 6:2 Fluorotelomer sulfonamidoalkyl betaine | N-CMAmP-6:2FOSA/ 6:2 FTAB | Zwitterionic short chain fluorotelomer (PFCA precursor)* |

*Notes: PFCA = perfluorocarboxylic acid or perfluorocarboxylate; PFSA = perfluorosulfonic acid or perfluorosulfonate; * = additional standards not originally included in study design but included in analytical fate study to further evaluate performance of analytes for select analytical methods.*

Additional information regarding the analytical fate of standards is also available through the analysis of laboratory control samples (e.g., blank spikes and blank spike duplicates) analyzed as part of this PWS Well Study.

## PWS Well Study

Field samples were collected from nine PWS wells by State Water Board, Division of Drinking Water (DDW) branch staff and submitted to Babcock Laboratories. Samples were processed and analyzed for laboratory analysis as follows:

- Babcock Laboratories analyzed samples for:
    - AOF-CIC using extraction procedures modeled after USEPA Method 1621.
    - EOF-CIC using extraction procedures modeled after USEPA Method 533.
    - Targeted analysis by LC-MSMS using USEPA Method 533.
    - Non-target analysis (NTA) by LC-HRMS using USEPA Method 533 sample extracts.
    - Targeted analysis by LC-MSMS using the DoD QSM.
    - NTA by LC-HRMS using DoD QSM sample extracts.
    - Targeted analysis by IC-MSMS using a direct inject approach. *Note that due to elevated detection limits observed for target PFAS using a direct inject approach, the study plan was modified to include sample analysis by IC-MSMS using DoD QSM sample extracts.*
- Babcock Laboratories filtered samples and sent filters to University of Notre Dame for adsorbable organic fluorine by particle induced gamma emission (AOF-PIGE) following sample preparation procedures included in Appendix A of the Method Comparison Study Plan. Sample containers and supplies were provided by University of Notre Dame.

- Babcock Laboratories prepared and sent samples to Oregon State University for fluorine nuclear magnetic resonance spectroscopy ($^{19}$F NMR) using extraction procedures modeled after USEPA Method 533. Samples using a modified direct injection (or analyzed as received) sample preparation approach were also sent to Oregon State University for analysis, and samples were analyzed based on the results of the USEPA 533 extracts. *Note that due to elevated detection limits observed for $^{19}$F NMR using a direct inject/ analyze as received approach, samples were only analyzed using sample extracts following procedures modeled after USEPA Method 533.*

Quality control sample types included in the study included laboratory method blanks, laboratory control spikes, analytical duplicates and replicates, field samples, field duplicates, field reagent blanks, and field matrix spikes and matrix spike duplicates. Additionally, a subset of field samples was collected and analyzed in triplicate.

## Study Results

### Analytical Fate Study Results

Figure 1 provides a summary of the analytical test results for the six methods included in the analytical fate study. A table and several charts providing detailed study results for the analytical fate study results are included in Attachment 2.

*Figure 1. Summary of Analytical Fate Study Results*

| | Fluoride | PF6 | BF4 | TFA | PFPrA | TFMS | PFEtS | PFPrS | TFMSA | Bis | TFMSI | PFBSA | PFHxSA | PFDSA | HFIP | 6:2 FTOH | 8:2 FTOH | FHxSA | N-AP-FHxSA | FPBS | PFHxS | 6:2 FOSA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CIC | 4 | 5 | 4 | 3 | 4 | 4 | 4 | 4 | 3 | 4 | 3 | 4 | 3 | 4 | 2 | 1 | 0 | 4 | 4 | 4 | 4 | 4 |
| AOF-CIC (~1621 prep) | 0 | 1 | 1 | 1 | 1 | 0 | 1 | 4 | 0 | 4 | 0 | 4 | 4 | 4 | 2 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| EOF-CIC (~533 prep) | 0 | 5 | 1 | 1 | 3 | 4 | 4 | 4 | 0 | 4 | 2 | ■ | ■ | ■ | 0 | 1 | 0 | 4 | 1 | ■ | ■ | ■ |
| IC-MS/MS (Direct Inject) | ■ | 3 | 0 | 4 | 4 | 4 | 4 | 4 | TIA | 4 | 3 | ■ | ■ | ■ | TIA | TIA | TIA | TIA | TIA | ■ | ■ | ■ |
| IC-MS/MS (DoD QSM) | ■ | 4 | 4 | 4 | 4 | 4 | 5 | 5 | 0 | 4 | 4 | ■ | ■ | ■ | TIA | TIA | TIA | TIA | TIA | 4 | TIA | TIA |
| LC-MSmS (DoD QSM) | ■ | TIA | TIA | 2 | 2 | 2 | 3 | 3 | TIA | TIA | ■ | ■ | ■ | ■ | TIA | TIA | TIA | 0 | 1 | ■ | ■ | 3 |

*Notes: Black boxes to indicate analyte was not assessed; TIA = technique inhibited analysis. Refer to Table 1 for the full analyte name for the abbreviated acronym included in this table.*

0 = No recovery (<5%)
1 = Very poor (5 to 20%)
2 = Poor recovery (20 to 50%)
3 = Acceptable recovery (50 to 70%)
4 = Good Recovery (70 to 130%)
5 = High Recovery (>130%)

The following provides a summary of general observations for each of the CIC-based analytical methods evaluated:

- The CIC evaluation provides information regarding the combustion efficiency of each of the compounds evaluated in the analytical fate study. In general, the compounds evaluated as part of this study have acceptable to good recovery (and combustion efficiency) with the following exceptions.
  - The compound $PF_6^-$ has high combustion efficiency indicating that if $PF_6^-$ is present in an environmental sample analyzed by CIC, the result would potentially be biased high.
  - Volatile PFAS have poor to no recovery by CIC which may not reflect the combustion efficiency of these compounds but instead be attributed to the loss of volatile PFAS prior to combustion as the instrument does not have a trapped vessel for containing volatile PFAS prior to combustion.
- The analytical fate results for AOF-CIC using extraction procedures modeled after USEPA Method 1621 indicate that for the compounds analyzed as part of this study, inorganic fluorine compounds have very poor to no recovery; ultrashort PFCAs, PFSAs, and ultrashort PFSA precursors (i.e., TFMSA and TFMSi), and ultrashort volatile PFAS (i.e., HFIP) generally have very poor to no recovery via AOF-CIC, but most sulfonamides and other volatile PFAS, as well as cationic PFAS have good recovery via AOF-CIC.
- The analytical fate results for EOF-CIC using extraction procedures modeled after USEPA Method 533 indicate that for compounds analyzed as part of this study, inorganic fluorine compounds range from high to no recovery, ultrashort PFCAs, PFSAs, and sulfonamides have very poor to good recovery. Other sulfonamides were not evaluated in the analytical fate study, but it is inferred from other method comparison study results that sulfonamides would have very poor to no recovery (see Figure 3). Volatile PFAS also have very poor to no recovery. Cationic PFAS have good to very poor recovery.

The results from the other three analytical methods included in the analytical fate study are useful for identifying potential opportunities to supplement weaknesses identified with subgroups of PFAS that are not recovered well using either of the AOF-CIC or EOF-CIC methods. The IC-MSMS analyses can provide supplemental information for inorganic fluorine compounds ($PF_6^-$ and $BF_4^-$), and ultrashort PFCAs, PFSAs, and sulfonamides except for TFMSA, which is apparently very challenging to measure using any of the analytical methods evaluated as part of this study. Volatile PFAS like the FTOHs are not conducive to measurement via IC-MSMS and LC-MSMS, and cationic PFAS have very low to no recovery via the DoD QSM extract measured on LC-MSMS likely due to positively charged quaternary nitrogen.

In comparing the chemical space that is captured by AOF-CIC using an extraction procedure modeled after USEPA Method 1621 versus EOF-CIC following a procedure modeled after USEPA Method 533, the findings for inorganic fluorine, many sulfonamides, volatile PFAS, and cationic PFAS demonstrate that AOF-CIC using an extraction procedure modeled after USEPA Method 1621 captures a broader organic

fluorine chemical space while also minimizing interference from inorganic fluorine compounds.

## PWS Well Study Results
### Organic Fluorine Results

Table 2 provides a summary of the maximum and median concentration of organic fluorine measured using the two commercially available broad-spectrum test methods (i.e., AOF-CIC and EOF-CIC), and sum ultrashort PFAS measured via IC-MSMS, as well as the range in reporting limits and detection frequency for each method. Figure 2a provides a visual summary of analytical results summarized in Table 2. Figure 2a also provides the sum of PFAS measured via LC-MSMS and IC-MSMS via the DoD QSM extract to provide a metric for the total measurable PFAS using available analytical methods. Attachment 3 provides a detailed summary of analytical results for the total organic fluorine concentrations measured using laboratory analyses included in the study.

Figure 2b provides a comparison of the sum of PFAS measured via LC-HRMS, reported in abundance per milliliter (abundance/mL) as a means for evaluating the total PFAS measurable using the two extracts evaluated as part of this study. The sum relative abundance of detected PFAS analytes was used to compare the performance of the two extracts (USEPA Method 533 versus DoD QSM). This approach assumes that the ionization potential of detected analytes measured in one extract but not the other is similar, which may or may not be an accurate assumption.

*Table 2. Summary of organic fluorine concentrations observed in environmental samples. Concentrations reported as nanograms organic fluorine per liter (ng OF/L).*

| Analytical Method | Method Type | Maximum Concentration (ng OF/L) | Reporting Limit (ng OF/L) | Detection Frequency |
|---|---|---|---|---|
| AOF-CIC via USEPA 1621M* | Bulk Organic Fluorine | 1,170 | 560 to 800 | 100% \| 89% |
| EOF-CIC via USEPA 533M* | Bulk Organic Fluorine | 687 | 540 to 640 | 33% \| 15% |
| SUM Ultrashort PFAS measured using IC-MSMS via DoD QSM | Targeted Ultrashort PFAS | 1,087 | ~15 | 100% |

*Note: * = samples analyzed in triplicate, summary of analytical results based on the average value of the triplicate sample results, detection frequency values are shown first based on average results and second based on individual samples analyzed (n = 27).*

*Figure 2a. Sum PFAS abundance measured via LC-HRMS for the USEPA 533 extract compared to the DoD QSM Extract.*
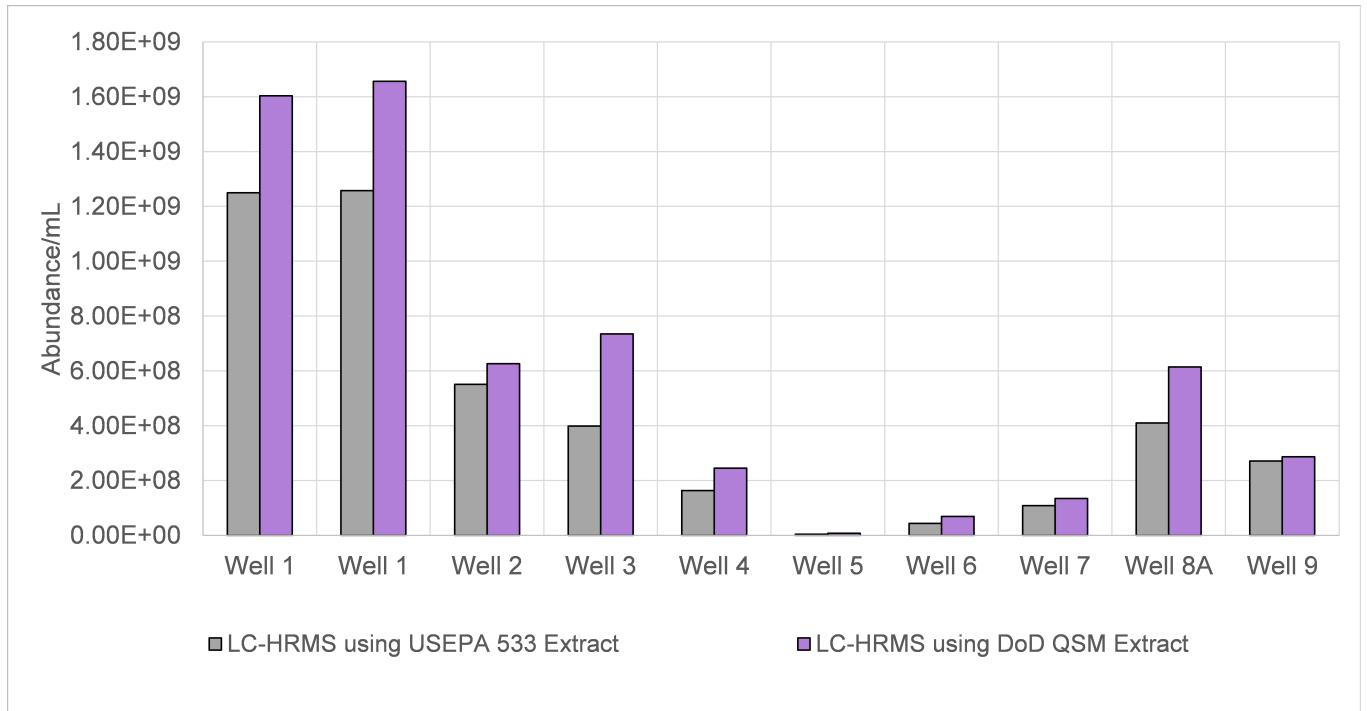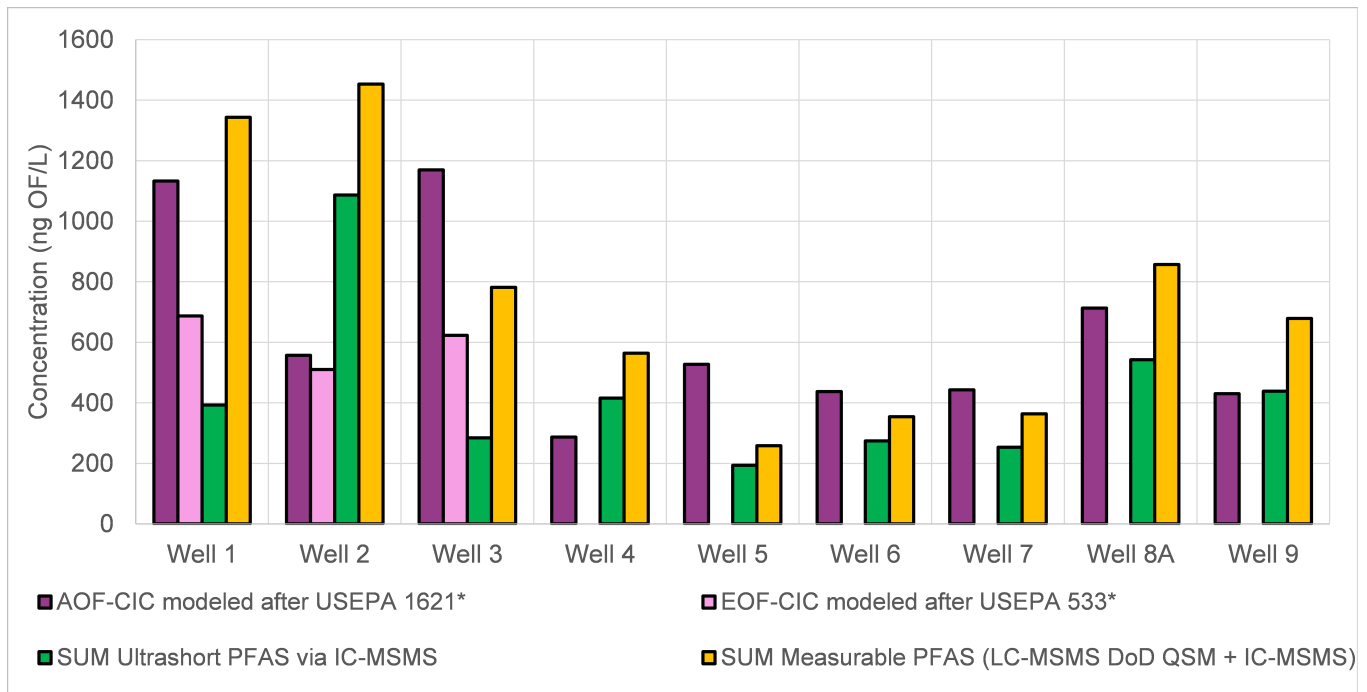


*Figure 2b. Total Organic Fluorine Measured Using AOF-CIC, EOF-CIC, and ultrashort PFAS Analytical Methods Compared to Sum of Measurable PFAS. Note: \* is used to denote average of triplicate sample results.*

The results are summarized as follows:

- Comparison of bulk organic fluorine methods demonstrates that the highest maximum concentration of organic fluorine is measured using AOF-CIC following the extraction procedure modeled after USEPA Method 1621.
- Comparison of the bulk organic fluorine results and the sum ultrashort PFAS and sum ultrashort PFAS plus targeted PFAS indicates that ultrashort PFAS concentrations present in the environmental samples analyzed as part of this study represent a significant portion of the total measurable PFAS.
- Comparison of the USEPA 533 extract versus the DoD QSM extract via LC-HRMS demonstrates that the highest sum PFAS result is measured using the DoD QSM extract.

These results are consistent overall (as shown in Table 2) and based on individual PWS well results (see Figures 2a and 2b and detailed results summarized in Attachment 3).

*Sum PFAS Results for Analyte Groups of Interest*

Figure 3 provides a summary of PFAS analyte groups detected via LC-HRMS using the USEPA Method 533 extract compared to the DoD QSM extract. As shown, there is a significant difference between the sum of C3 and longer sulfonamides that are measured in the nine wells using the DoD QSM extract compared with the USEPA 533 extract.

*Figure 3. Comparison of LC-HRMS results using the DoD QSM extract versus the USEPA 533 extract.*
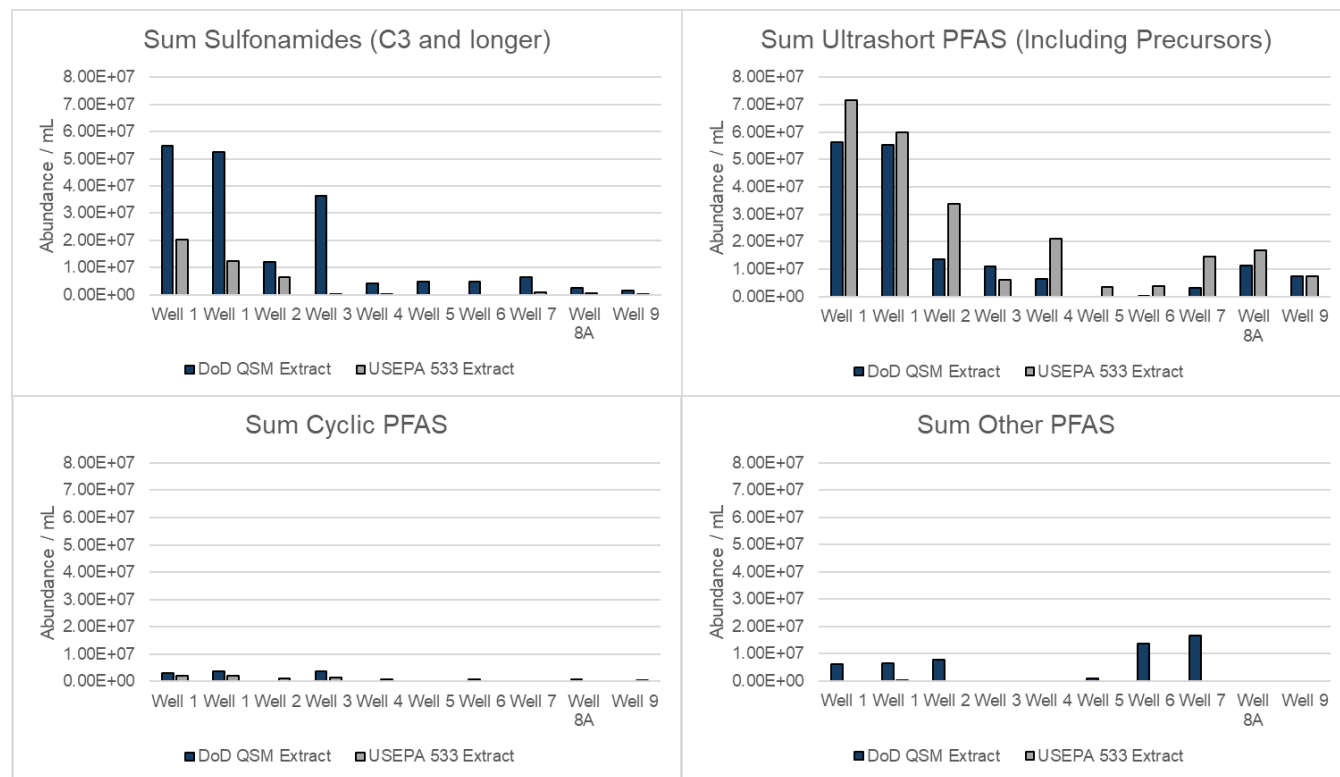


The sum of ultrashort PFAS (including precursors) and other PFAS measured in the nine wells using the USEPA 533 extract are similar to the sum PFAS measured using the DoD QSM, though a closer look at individual analytes indicates that these differences are attributable to differences in the analytes detected in each extract. Although this level of detail has not been fully evaluated at this time, the presence of C3 and longer sulfonamides in environmental samples is significant and should be accounted for in the broad-spectrum method to be used to monitor all SDAC/DAC PWS in the state.

These observations provide insight regarding differences in bulk organic fluorine results measured via EOF-CIC using extraction procedures modeled after USEPA Method 533 compared to the results measured via AOF-CIC using extraction procedures modeled after USEPA 1621. Sulfonamides are generally not retained during the extraction process following procedures modeled after USEPA Method 533 and likely accounts for a portion of the difference between organic fluorine measured using AOF-CIC versus EOF-CIC in the environmental samples measured in this study.

## Evaluation of Broad-Spectrum Method Repeatability

The Method Comparison Study Plan included comparison of two broad-spectrum analytical test methods with the potential to meet the criteria of being reproducible, robust, with high potential to support feasible ongoing monitoring: AOF-CIC using extraction procedures modeled after USEPA Method 1621, and EOF-CIC using

extraction procedures modeled after USEPA Method 533. A multi-laboratory validation of the USEPA methods was conducted as part of the USEPA method development process, however only USEPA Method 1621 is validated for both the extraction and analysis by CIC. USEPA Method 533 extraction protocols have not been validated for use by CIC, although a survey of research methods for EOF-CIC indicates that many researchers do use a similar extraction process to USEPA 533 for EOF-CIC.

Additional validation of the updated procedures modeled after these published methods would be necessary to fully evaluate the robustness and reproducibility of the updated procedures used in this study. Since full method development was not feasible within the scope of this Method Comparison Study, a full evaluation of the robustness and reproducibility of these extraction methods that are modeled after USEPA extraction methods was not conducted. However, samples analyzed by AOF-CIC and EOF-CIC were collected and analyzed in triplicate and provide an overview of the repeatability of each method as performed by the same laboratory using the same measurement procedures and systems, under the same conditions for environmental field samples. Tables 3a and 3b provide a summary of the analytical results for each of the three measurements, the standard deviation, and the coefficient of variation for the sample results for the nine wells included in the method comparison study by AOF-CIC and EOF-CIC, respectively.

*Table 3a. Summary of Replicate Analyses for Commercially Available Broad-Spectrum Test Methods for AOF-CIC Using Extraction Methods Modeled after USEPA 1621*

| Sample Location | Sample Date | S | D | T | Ave | SD | CV |
|---|---|---|---|---|---|---|---|
| Well 1 | 10/30/2023 | 1,200 | 1,200 | 1,000 | 1,133 | 115 | 10% |
| Well 2 | 10/30/2023 | 380 | 650 | 640 | 557 | 153 | 27% |
| Well 3 | 11/1/2023 | 810 | 1,200 | 1,500 | 1,170 | 346 | 30% |
| Well 4 | 11/1/2023 | 300 | 300 | 260 | 287 | 23 | 8% |
| Well 5 | 10/31/2023 | <620 | 530 | 430 | 527 | 95* | 18% |
| Well 6 | 11/1/2023 | <560 | 360 | 390 | 437 | 108* | 25% |
| Well 7 | 11/1/2023 | <560 | 570 | 200 | 443 | 211* | 48% |
| Well 8A | 10/31/2023 | 740 | 300 | 1,100 | 713 | 401 | 56% |
| Well 9 | 10/31/2023 | 560 | 440 | 290 | 430 | 135 | 31% |

*Table 3b. Summary of Replicate Analyses for Commercially Available Broad-Spectrum Test Methods for EOF-CIC Using Extraction Methods Modeled after USEPA 533*

| Sample Location | Sample Date | S | D | T | Ave | SD | CV |
|---|---|---|---|---|---|---|---|
| Well 1 | 10/30/2023 | 820 | 650 | <590 | 687* | 119 | 17% |
| Well 2 | 10/30/2023 | <590 | 360 | <580 | 510* | 130 | 25% |
| Well 3 | 11/1/2023 | <630 | 630 | <610 | 623* | 12 | 2% |
| Well 4 | 11/1/2023 | <540 | <560 | <550 | <550 | NA | NA |
| Well 5 | 10/31/2023 | <610 | <620 | <650 | <627 | NA | NA |
| Well 6 | 11/1/2023 | <550 | <560 | <560 | <557 | NA | NA |
| Well 7 | 11/1/2023 | <560 | <570 | <560 | <563 | NA | NA |
| Well 8A | 10/31/2023 | <580 | <590 | <580 | <583 | NA | NA |
| Well 9 | 10/31/2023 | <600 | <590 | <600 | <597 | NA | NA |

*Note: S = primary sample; D = duplicate sample; T = triplicate sample; Ave = average; SD = standard deviation; CV = coefficient of variation; * = average for samples calculated for analytical results where at least one sample included a detection above the reporting limit and the average is calculated using the reporting limit for sample results that were non-detect; NA = not applicable if all three sample results are non-detect since the observed variation is based entirely on the method reporting limit.*

The coefficient of variation is a ratio of the standard deviation and the overall mean (or average) of the sample results. Note that because both sample methods require the whole sample to be processed, the samples collected in triplicate are from three separate sample bottles and therefore, are not perfectly identical and sample results include environmental variability that is inherent to the sample collection process. More than three measurements of the exact same sample (e.g., nine measurements of a performance standard) would provide a more statistically relevant data set for evaluating repeatability of each method. As such, for the purpose of this evaluation, laboratory control spikes and matrix spikes were also analyzed to provide additional information on the coefficient of variation observed for each method. A total of four or more results are available for each method using these quality control samples and combining the duplicate sample results (e.g., matrix spike and matrix spike duplicates from two analytical batches). Tables 4a and 4b provides a summary of repeatability of spike sample results. Recovery of spiked concentrations for both methods is within the acceptance criteria for the method (i.e., 50% to 150%).

*Table 4a. Summary of Spike Sample Analyses for AOF-CIC Using Extraction Methods Modeled After USEPA 1621*

| Sample Type | Analysis Date | Result | Spike Value | Recovery | Ave | SD | CV |
|---|---|---|---|---|---|---|---|
| LCS | 11/8/2023 | 12,000 | 10,100 | 116% | | | |
| LCS Dup | 11/8/2023 | 11,000 | 10,100 | 111% | 11,250 | 500 | 4% |
| LCS | 11/15/2023 | 11,000 | 10,100 | 107% | | | |

| Sample Type | Analysis Date | Result | Spike Value | Recovery | Ave | SD | CV |
|---|---|---|---|---|---|---|---|
| LCS Dup | 11/15/2023 | 11,000 | 10,100 | 106% | | | |
| Matrix Spike | 11/8/2023 | 9,300 | 743 | 108% | | | |
| Matrix Spike Dup | 11/8/2023 | 9,900 | 743 | 114% | 9,450 | 387 | 4% |
| Matrix Spike | 11/15/2023 | 9,600 | 743 | 111% | | | |
| Matrix Spike Dup | 11/15/2023 | 9,000 | 743 | 105% | | | |

*Table 4b. Summary of Spike Sample Analyses for EOF-CIC Using Extraction Methods Modeled After USEPA 533*

| Sample Type | Analysis Date | Result | Spike Value | Recovery | Ave | SD | CV |
|---|---|---|---|---|---|---|---|
| LCS | 11/17/2023 | 12,000 | 16,200 | 72% | | | |
| LCS Dup | 11/17/2023 | 15,000 | 16,200 | 96% | | | |
| LCS | 11/17/2023 | 15,000 | 16,200 | 92% | 14,400 | 1,342 | 9% |
| LCS | 11/30/2023 | 15,000 | 16,200 | 93% | | | |
| LCS Dup | 11/30/2023 | 15,000 | 16,200 | 92% | | | |
| Matrix Spike | 11/17/2023 | 7,100 | 7,570 | 83% | | | |
| Matrix Spike Dup | 11/17/2023 | 7,700 | 7,710 | 89% | | | |
| Matrix Spike | 11/30/2023 | 6,200 | 7,540 | 73% | 7,125 | 665 | 9% |
| Matrix Spike Dup | 11/30/2023 | 7,500 | 7,240 | 95% | | | |

*Note: S = primary sample; Ave = average; SD = standard deviation; CV = coefficient of variation.*

The repeatability observations are summarized as follows:

- The coefficient of variation for AOF-CIC using an extraction method modeled after USEPA Method 1621 for environmental samples ranged from 8% to 56% with an overall average of 28%. The coefficient of variation for laboratory spiked samples was 4%.
- The coefficient of variation for EOF-CIC using an extraction method modeled after USEPA Method 533 is based on three samples (those with detections) and ranged from 2% to 25% with an overall average of 6%. The coefficient of variation for laboratory spiked samples was 9%.

These results provide a useful metric for data interpretation and highlight the value of using a method such as AOF-CIC using an extraction method modeled after USEPA Method 1621 as it includes the broadest chemical space available with reporting limits that are typically below the organic fluorine concentration present in the environmental samples analyzed in this study. The overall results for triplicate sample analysis for AOF-CIC provide an indication of the variability that could be expected for a single sample result. Given this information, ongoing monitoring of duplicate samples throughout the study is recommended and future data evaluations should consider that

the true sample concentration (which cannot be known except for performance evaluation samples) likely falls within a range of concentrations and the results provide useful information regarding the presence and approximate concentration of organic fluorine detected in PWS wells servicing SDAC/DAC.

## Discussion

A total of six broad-spectrum PFAS analytical techniques and method preparation procedures and three targeted PFAS analytical techniques and method preparation procedures were included in the Method Comparison Study Plan. Fundamentally, this study provided the opportunity to compare various "total PFAS" analyses with the sum PFAS that can be detected using targeted PFAS methods – USEPA 533 and DoD QSM 5.3, as well as targeted analysis of inorganic fluorine compounds and ultra-short PFAS using IC-MSMS following the DoD QSM extraction process. The results summarized herein provide fundamental information to guide the broad-spectrum method selection process. However, the dataset generated from this study supports several additional data evaluations that have not been completed at this time but will further enhance the understanding of the broad-spectrum PFAS methods included in the study.

This study included two broad-spectrum organic fluorine methods that are commercially viable (i.e., AOF-CIC and EOF-CIC) and are the primary focus of the data evaluation conducted to date. The study did not include formal method development so available sample extraction methods were referenced and used as models for preparing samples for analysis – specifically, samples were analyzed for AOF-CIC using an extraction procedure modeled after USEPA Method 1621 and EOF-CIC using an extraction procedure modeled after USEPA Method 533. Primary differences in these two sample extraction procedures combined with the analytical fate study results and observations from targeted and non-targeted PFAS analysis help to explain the observed differences in organic fluorine detected in environmental samples using these two broad-spectrum methods.

The AOF-CIC sample extraction process extracted organic fluorine using a granulated activated carbon (GAC) cartridge and the cartridge was rinsed with nitrate ($NaNO_3$) to remove inorganic fluorine. USEPA Method 1621 includes the use of two GAC cartridges (referred to as carbon tubes) to monitor breakthrough of PFAS during the sample extraction process. For this study, a single carbon tube was used for combustion to lower the detection limit. Following sample preparation, the carbon in the tube was transferred to a combustion boat and combusted at very high temperatures to convert organic fluorine to measure total concentration of fluoride ion in the sample. Since the samples were not further extracted, any PFAS that sorbed to the GAC was retained on the carbon tube, including sulfonamides. Up to 1,000 ng OF/L of ultrashort PFCAs and PFSAs and their precursors could sorb to the carbon tube with acceptable to poor recovery so ultrashort PFAS such as TFA likely breakthrough the carbon tube, and due to competing sorption of other PFAS, this breakthrough could occur at much lower concentrations (e.g., less than 450 ng OF/L of ultrashort PFAS captured via AOF-CIC).

The EOF-CIC extraction process extracted organic fluorine using a weak anion exchange (WAX) solid phase extraction (SPE) cartridge, inorganic fluorine was rinsed off the SPE cartridge using ammonium hydroxide ($NH_4OH$), and organic fluorine was eluted off the SPE cartridge with ammonium hydroxide and methanol solution, and the sample extract was evaporated to dryness and reconstituted in methanol to concentrate the sample prior to analysis. The concentrated extract was transferred to a combustion boat and combusted at very high temperatures to convert organic fluorine to measure total concentration of fluoride ion in the sample. During this process, sulfonamides are apparently not recovered by the USEPA Method 533 extraction process as documented by the comparison of results from USEPA Method 533 extract versus DoD QSM extract via LC-HRMS.

USEPA Method 533 was originally optimized for select target PFAS in drinking water and sulfonamides are not on the target list, so this observation is not considered a limitation of USEPA Method 533 itself but does indicate limited applicability for broad-spectrum analyses and using an extraction method modeled after USEPA Method 533 for EOF-CIC is not preferable. Additionally, as demonstrated by the analytical fate study results, the extraction process retains at least one (and potentially other) inorganic fluorine compounds that are likely sorbed to the WAX SPE cartridge and not rinsed off using ammonium hydroxide prior to eluting and concentrating the sample for analysis on the CIC instrument. The analytical fate of ultrashort PFCAs, PFSAs, and their precursors is similar for both CIC broad-spectrum methods evaluated in this study, and therefore, a portion of the organic fluorine detected via EOF-CIC could be attributed to the presence of TFA measured in the environmental samples, similar to the AOF-CIC organic fluorine results. However, it was observed in the DoD QSM extraction process that TFA is lost significantly (>90%) in matrix samples and most of the loss occurs during the evaporative step.

## Conclusions and Recommendations

At this time, due to observed limitations with the USEPA Method 533 extraction process for broad-spectrum analyses (e.g., losses of sulfonamides and inclusion of at least one inorganic fluorine compound), it is recommended that the selected broad-spectrum method not include those methods that extract organic fluorine using procedures modeled after USEPA Method 533. As such, AOF-CIC following sample extraction procedures modeled after USEPA Method 1621 has been identified as the optimal broad-spectrum method available at this time. This broad-spectrum test method is selected because it measures organic fluorine within the broadest chemical space possible using a commercially viable technology. The broad-spectrum method should be used along with USEPA 533 to characterize the presence of organic fluorine and targeted PFAS occurring in PWS wells servicing SDAC/DAC. Additionally, LC-HRMS analysis to be conducted on a subset of samples should be prepared for PFAS analysis in accordance with the DoD QSM extraction process. Finally, to further expand the PFAS chemical space characterized in the statewide investigation, a subset of samples characterized by LC-HRMS should be analyzed for presence/absence of ultrashort PFAS (including TFA) using IC-MSMS on samples prepared using the DoD QSM extraction process.

E. JOAQUIN ESQUIVEL, CHAIR | ERIC OPPENHEIMER, EXECUTIVE DIRECTOR

Although the AOF-CIC extraction method modeled after USEPA Method 1621 is the optimal commercially available broad-spectrum method available at this time, there are notable challenges with AOF-CIC. One of the primary challenges is the presence of background levels of organic fluorine in the GAC used in the carbon tubes. This challenge results in elevated detection and reporting limits. There may be other sources of background organic fluorine that contribute to elevated detection and reporting limits in the laboratory and therefore, it is recommended that Babcock Laboratories mitigate these issues to the extent feasible to achieve the lowest detection and reporting limits possible for the larger statewide characterization project.

By comparison, EOF-CIC methods have very little background organic fluorine interference from the WAX SPE. Combined with the ability to concentrate the sample through evaporation of the eluted sample provides potential for EOF-CIC to achieve much lower detection and reporting limits compared to AOF-CIC methods. Through further research and method development, it may be possible to identify extraction procedures capable of overcoming the limitations associated with the USEPA 533 extraction process to measure a broader spectrum of organic fluorine in environmental samples. It is recommended that the project team continue to stay abreast of research in "total PFAS" analyses that could provide additional methods that may become available in the future for evaluating the broad-spectrum of PFAS present in the environment.

## Acknowledgements

**ATTACHMENT 1: METHOD COMPARISON STUDY PLAN FOR THE DETERMINATION OF APPROPRIATE BROAD SPECTRUM ANALYTICAL METHODS FOR THE CLASS OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)**

# METHOD COMPARISON STUDY PLAN FOR THE DETERMINATION OF APPROPRIATE BROAD SPECTRUM ANALYTICAL METHODS FOR THE CLASS OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)-

**FINAL - November 2023**

CALIFORNIA
Water Boards

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**Study Plan Revision History**

| Plan Version | Prepared By | Date of Revision | Description of Change |
|---|---|---|---|
| Draft plan sent for USEPA and UND Review | Erica Kalve | 10/02/2023 | Initial version |
| Final, version 1 | Erica Kalve | 11/06/2023 | Accept suggested edits and incorporate final revisions, update sample location, and finalize document |

## 1.0   Overview

California legislature defines per- and polyfluoroalkyl substances (PFAS) as a class of fluorinated organic chemicals containing at least one fully fluorinated carbon atom. The U.S. Environmental Protection Agency (USEPA) has a CompTox Chemicals Dashboard with a PFAS Master List of PFAS Substances that has over 12,000 PFAS itemized and over 10,000 that contain sufficient chemical formula information to confirm that they meet the definition of PFAS in California. A recent analysis of one of the largest open chemical collections, PubChem, with 115 million compounds, contains over seven million PFAS that meet the definition of containing at least one fully fluorinated methyl or methylene carbon atom (Schymanski et al. 2023). A non-exhaustive evaluation of the uses of PFAS (Glüge et al. 2020) identified more than 200 use categories and subcategories for more than 1,400 individual PFAS. By contrast, current laboratory analytical methods for evaluating the significance of PFAS in the environment are limited to 18 to 60 individual PFAS. As a result, and as summarized in the literature (McDonough et al. 2019), the full extent of PFAS contamination at impacted sites is significantly underestimated when surrogate and/or nontargeted methods are *not* employed.

The regulation of thousands of PFAS compounds is not feasible.  As such the State Water Board proposes to develop an approach that uses an inclusive broad-spectrum PFAS analytical method to support a treatment technology-based approach to regulate "total PFAS" in drinking water – both in centralized and point-of-use drinking water systems.  The California legislature agreed and passed California Assembly Bill 178 (Ting), the Budget Act of 2022. Section 124 includes the following three objectives:

1.   Monitor all community public water systems (PWSs) in the state at least once, with state funding directed to accomplish testing of community PWSs serving disadvantaged and severely disadvantaged communities (DAC/SDAC) (*Baseline PFAS Broad Spectrum Testing in Drinking Water*),
2.   Develop standard operating procedures for and validate a broad-spectrum test for the class of PFAS (*Total PFAS Analytical Method Development*), and
3.   Develop a treatment-based regulation for the entire class of PFAS (*Treatment Technology Assessment*).

This method comparison study plan supports these three objectives and will provide the information necessary to select appropriate broad-spectrum PFAS analytical method(s) for evaluating total PFAS at PWSs, and for future validation of a broad-spectrum analytical method for the class of PFAS in support of the treatment technology assessment.

## 2.0   Background Information

Starting in 2019, California's State Water Resources Control Board, Division of Drinking Water (DDW) and Division of Water Quality (DWQ), coordinated targeted sampling efforts to understand and characterize the presence of PFAS in source drinking groundwater wells of PWSs and at suspected industries using PFAS-containing materials or secondary receivers of PFAS-containing waste streams.  Those efforts provided some understanding of the types of PFAS present in waters of California, but the information was limited to the target analyte list of the liquid chromatography tandem mass spectrometry (LC-MSMS) methods used for analyses (i.e., USEPA Method 537.1 for drinking water (18 analytes) and the Department of Defense's Quality System Manual performance method for non-drinking water matrices (up to 35 analytes)).

In 2021, DDW and DWQ conducted a PFAS methods correlation study to assess different analytical methods for their effectiveness in detecting PFAS, particularly those compounds that were not included in the targeted drinking water method used at the time (USEPA Method 537.1). Samples were collected from nine different PWS groundwater wells, and analyzed using traditional targeted analytical methods (USEPA Method 537.1, DoD QSM, and USEPA Method 533) along with more advanced analytical techniques including total oxidizable precursors (TOP) assay followed by targeted analysis by LC-MSMS, adsorbable organic fluorine (AOF) analysis by combustion ion chromatography (CIC) (AOF-CIC), and non-targeted analysis (NTA) suspect screening approach using liquid chromatography high resolution mass spectrometry (LC-HRMS).

The targeted analytical methods identified 14[1] PFAS (out of 18 analytes) that were frequently detected.  However, the summed concentrations of the detected PFAS analytes (converted to organic fluorine mass per volume) from the targeted analyses accounted for a fraction (9% - 42%) of the organic fluorine detected by AOF analysis (see Figure 1). The HRMS NTA suspect screening analysis resulted in identification of 19 additional PFAS that are detected in abundance and frequency with relatively high confidence including short-chain (C4-C6) and ultra-short chain (C1-C3) PFSAs, PFCAs, and their precursors, and other subclasses of PFAS including perfluorinated cyclohexane sulfonates and chlorine substituted sulfonates. These findings demonstrate how limited the current targeted analytical methods are for characterizing PFAS occurrence in the state.

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[1] PFUnDA, PFDA, PFNA, PFOA, PFHpA, PFHxA, PFPeA, PFBA, PFOSA, PFOS, PFHpS, PFHxS, PFPeS, PFBS
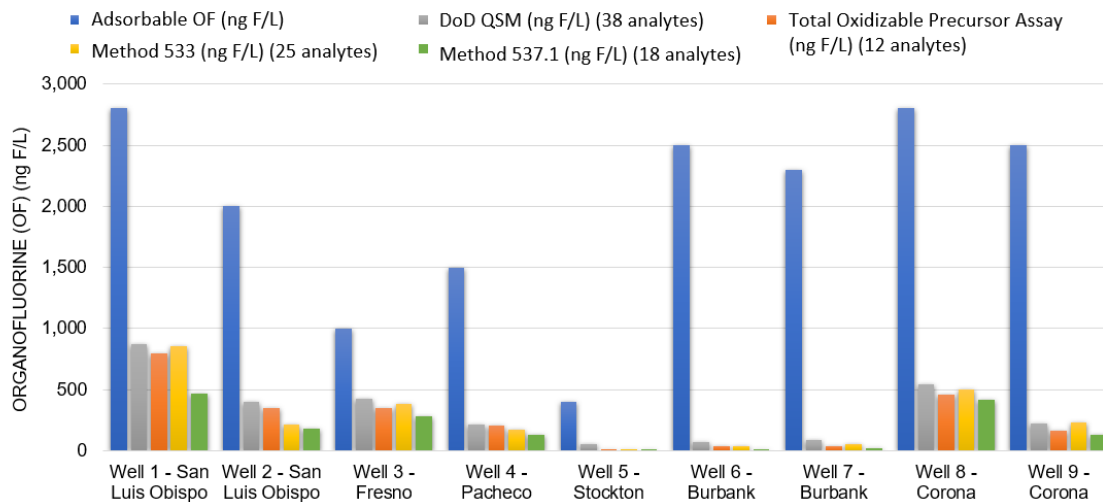
*Figure 1. Summary of sum PFAS by targeted analytical methods compared to AOF-CIC analysis.*

Through California Assembly Bill 178 (AB 178; Ting), the Budget Act of 2022, the State Water Board is charged with three primary objectives to address statewide PFAS testing including the development and validation of a standard operating procedure for a broad-spectrum test that could be used to monitor all community public water systems in the state for the class of PFAS. The broad-spectrum test will be an analytical testing methodology to measure organofluorine within the broadest chemical space possible using commercially viable technology.

Following the selection of an appropriate broad-spectrum analytical method, samples will be collected from PWS wells servicing severely disadvantaged communities and disadvantaged communities (SDAC/DAC), which includes nearly 4,000 wells, to characterize the presence of organofluorine using the broad-spectrum test method and USEPA 533, with LC-HRMS analyzed at approximately 25% of the wells. Additionally, PFAS identified during the baseline testing will be used to guide further testing for PFAS using commercially available drinking water treatment technologies for both centralized and point-of-use drinking water systems.

The benefits of this project will provide an overall landscape of the types of PFAS in California's drinking water, the amount of PFAS 'mass' removed using existing treatment technologies, as well as which PFAS are not removed using available drinking water treatment technologies. Instead of trying to promulgate regulatory limits on thousands of PFAS chemicals, this approach will provide a class-based approach for managing PFAS through a treatment technology regulatory level, as well as provide the information necessary to focus future regulations on those individual PFAS that are found in our state's drinking water supply and have the potential to significantly impact human health.

## 3.0    Study Objectives

The primary objective of this study is to identify the most appropriate broad-spectrum analytical method for characterizing the occurrence of "total PFAS" in drinking water. The most appropriate broad-spectrum analytical method will be reproducible, robust, with high potential to support feasible ongoing monitoring. A secondary objective of this study is to characterize the chemical space that is captured by available broad-spectrum analytical methods.

## 4.0    Decision Inputs and Questions

### 4.1    "Total PFAS" Techniques

There is currently not a single laboratory method that has been proven to provide a "total PFAS" measurement. Most methods have limitations due to the sample preparation process and/or the chemical space that is measured by the instrument. A brief description of the "total PFAS" techniques that are currently available is provided in Table 1 – note that these are referred to as techniques because depending on how samples are processed, multiple methods could be associated with any one of the techniques described.

*Table 1. Summary of "Total PFAS" Techniques for Decision Inputs*

| "Total PFAS" Technique | Description of "total PFAS" technique | Availability |
|---|---|---|
| AOF by CIC (AOF-CIC) | Aqueous samples are prepared for AOF by CIC analysis to isolate the organic fluorine-containing fraction of fluoride by adsorbing organic fluorine onto a granular activated carbon (GAC) cartridge and rinsing with nitrate to remove inorganic fluorine. Following sample preparation, the GAC cartridge is transferred to a combustion boat and combusted at very high temperatures to convert organic fluorine to measure total concentration of fluoride ion in the sample. Higher sample volumes may improve the overall detection limit, but there are limitations due to the potential for PFAS breakthrough on the GAC cartridge. Assuming all inorganic fluorine is removed, the final measured value is inclusive of PFAS mass and other fluorinated organic substances that sorb to the GAC cartridge and are not lost when the sample is heated prior to combustion. Note that sorption of ultrashort (including cationic) and volatile PFAS to GAC is not well characterized. | Academic and Commercial |

| "Total PFAS" Technique | Description of "total PFAS" technique | Availability |
|---|---|---|
| Extractable Organic Fluorine (EOF) by CIC (EOF-CIC) | Aqueous samples are prepared for EOF by CIC analysis to isolate the organic fluorine-containing fraction of fluoride, which is extracted using a solid phase extraction (SPE) cartridge, and the extract is placed in a combustion boat, combusted at very high temperatures to convert organic fluorine to measure total concentration of fluoride ion in the sample. Samples for EOF by CIC may be concentrated prior to analysis, which provides the opportunity to achieve relatively low method detection limits but may also result in losses of ultrashort-chain and volatile PFAS. Depending on the sorbent used during sample extraction, cationic PFAS may also pass through during the extraction process. Assuming all inorganic fluorine is removed, the final measured value is inclusive of PFAS mass and other fluorinated organic substances that are sorbed onto and extracted from the SPE cartridge. | Academic and Commercial |
| AOF by Particle Induced Gamma Emission (AOF-PIGE) | Aqueous samples are prepared for AOF-PIGE by adsorbing organic fluorine onto a granular activated carbon (GAC) filter. The GAC filter may be analyzed for total fluorine (including inorganic fluoride, ultrashort-PFAS, and other organic fluorine compounds). The GAC filter may also be rinsed with methanol to remove PFAS or rinsed with nitric acid to remove inorganic fluorine and the ultra-short PFAS. Under either scenario the GAC filter is dried and then bombarded by protons and the unique gamma ray signature emitted from any fluorine present on the GAC filter is measured — reported as total concentration of absorbed organic fluorine in the sample. Higher sample volumes improve the overall detection limit, and for drinking water samples, there is limited likelihood of PFAS breakthrough on the GAC filter. If using the methanol sample rinse approach, assuming no PFAS were lost when the sample was dried prior to the methanol rinse, and assuming all PFAS are removed following the methanol rinse, the difference between pre-rinsed versus post-rinsed PIGE measurement provides a value for the total absorbed organic fluorine present in the sample. Using the nitric acid rinse, assuming all inorganic fluorine is removed, the | Academic and Limited Commercial |

| "Total PFAS" Technique | Description of "total PFAS" technique | Availability |
|---|---|---|
| | final measured value is a direct measurement of the absorbed organic fluorine mass and other fluorinated organic substances that sorb to the GAC filter. | |
| NTA by LC-HRMS | Aqueous samples are typically prepared for PFAS NTA by LC-HRMS to concentrate the sample and cleanup interfering matrix effects prior to analysis. Samples are commonly extracted by SPE cartridge (usually a weak anion exchange (WAX) cartridge), further concentrated by drying the extract, and reconstituting the sample in an appropriate solvent. The sample extract is then injected into the LC-HRMS to measure the mass, charge, and retention time of the eluted compounds. This information can be used to identify the presence and abundance of suspect PFAS that were not removed during the sample preparation process (e.g., ultrashort, and volatile PFAS, possibly cationic PFAS), are electrospray amenable (e.g., compounds that have acid-base moieties), measurable within the mass range of the instrument (e.g., typically inclusive of a mass to charge range from 100 to 1,400), and can be identified using available spectral libraries and review by experienced chemists. | Academic and Commercial |
| NTA by Gas Chromatography High Resolution Mass Spectrometry (GC-HRMS) | GC-HRMS is currently an underutilized technology for PFAS NTA. Sample preparation for GC-HRMS is not well documented but a workflow has been developed and validated to identify PFAS in samples designed to test the workflow (Casey et al. 2023). In general, samples for gas chromatography methods are processed to separate volatile analytes (including semivolatile analytes) from the nonvolatile components. A processed sample is injected into a GC-HRMS to measure the mass and retention time of the eluted compounds. This information is used to identify the presence and abundance of suspect PFAS that were not removed during the sample preparation process, are thermally stable and volatile and/or have a neutral charge (e.g., semivolatile PFAS), measurable within the mass range of the instrument, and can be identified using available spectral libraries and review by experienced chemists. | Academic |

| "Total PFAS" Technique | Description of "total PFAS" technique | Availability |
|---|---|---|
| TOP Assay followed by LC-MSMS or LC-HRMS | TOP assay is a sample preparation approach to convert oxidizable PFAS precursors into terminal PFAS compounds using a strong oxidation process. Following completion of the TOP assay, the oxidized sample is typically processed using a general method preparation approach such as enrich the sample with surrogates, extract the sample using an SPE cartridge, elute the extract from the SPE cartridge using a solvent, evaporate the eluted sample, and reconstitute the concentrate in solvent. Terminal PFAS are typically measured using a targeted LC-MSMS analytical method and results are inclusive of a relatively small subset of relevant PFAS such as perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs). TOP Assay samples could also be analyzed using LC-HRMS to include a broader suite of terminal PFAS compounds that were not removed during the sample preparation process, are electrospray amenable, and can be identified using available spectral libraries and review by experienced chemists. | Academic and Commercial |
| Fluorine Nuclear Magnetic Resonance ($^{19}$F NMR) | Samples for $^{19}$F NMR can be run with minimal sample processing or can undergo several sample preparation steps to concentrate the sample including the general approach described above. Quantification of organic fluorine is based on the fluorine signal of a fluorinated internal standard. Spectral resolution can be adjusted based on data collection parameters, and the signal to noise ratio can be improved by using a strong magnet, increasing the time for data acquisition (e.g., increasing from 30 minutes to several hours), adding a relaxing agent to the sample, and/or by concentrating the sample prior to analysis. Provided the signal to noise ratio is sufficient to observe chemical shifts of $^{19}$F of the organic fluorine molecules in the sample, it is possible to quantify the presence of fully fluorinated carbons to provide a "total PFAS" measurement. | Academic |

As noted, there are limitations associated with each "total PFAS" technique. These limitations can be generally grouped into three chemical space categories:

- Uncertainty for inorganic fluorine to be removed during the sample preparation step for techniques that are inherently designed to measure total fluorine.
- Potential that ultrashort-chain (C1-C3) PFSAs, PFCAs, and their precursors, volatile, and cationic PFAS have low to no recovery due to limitations with sample preparation methods and/or instrument capabilities.
- Potential that long-chain PFAS and their precursors have low to no recovery due to limitations with sample preparation methods and/or instrument capabilities.

Regarding the "total PFAS" methods that use HRMS, there are also limitations associated with identifying suspect PFAS that are not currently characterized in available spectral libraries.

An additional consideration for the selection of the most appropriate broad-spectrum test is the commercial applicability and economic feasibility for the statewide characterization study. Table 2 summarizes the available techniques with respect to these limitations based on currently available information.

*Table 2. Summary of "Total PFAS" Technique Limitations*

| "Total PFAS" Technique | Inorganic fluorine (other than fluoride) interference? | Ultrashort-chain PFAS likely retained? | Cationic PFAS likely retained? | C15 and longer-chain PFAS likely retained? | Available by contracted laboratory? | Feasible cost to analyze 1000s of samples? |
|---|---|---|---|---|---|---|
| AOF-CIC | Potentially | Potentially, likely low recovery | Potentially, likely low recovery | Yes | Yes | Yes ($$) |
| EOF-CIC | Potentially | Potentially, dependent on sample preparation | Potentially, likely low recovery | No | Pending SOP | Yes ($$) |
| AOF-PIGE | Potentially, but not after nitric acid wash | Yes, likely low recovery, and not after nitric acid wash | Potentially, likely low recovery | Yes | No, but available through partnership | Yes ($) |
| NTA by LC-HRMS | No | Potentially, dependent on sample preparation | Potentially, likely low recovery | No | Yes | No ($$$$) |
| NTA by GC-HRMS | No | Not well characterized | Not well characterized | No | No | No ($$$$) |

| "Total PFAS" Technique | Inorganic fluorine (other than fluoride) interference? | Ultrashort-chain PFAS likely retained? | Cationic PFAS likely retained? | C15 and longer-chain PFAS likely retained? | Available by contracted laboratory? | Feasible cost to analyze 1000s of samples? |
|---|---|---|---|---|---|---|
| TOP Assay by LC-MSMS or LC-HRMS | No | Potentially, likely low recovery, dependent on sample preparation | Potentially, cationic PFAA precursors likely converted to PFAAs | No | No | Yes via LC-MSMS ($$$) <br><br> No via LC-HRMS ($$$$$) |
| $^{19}$F NMR | No | Yes | Yes | Yes assuming longer-chain PFAS are dissolved in solution | Yes (via subcontract) | No ($$$$) |

*Note: Relative per sample cost of analysis indicated with dollar symbols that represent an approximate range of costs not including shipping: $ = in the $100 range; $$ = between $200 to $600 range; $$$ = $600 to $1,200 range; $$$$ = $1,200 to $6,500, $$$$$ = greater than $6,500.*

If inorganic fluorine (including fluoride) is not removed during the sample preparation for AOF-CIC, EOF-CIC, and AOF-PIGE, the sample results for organic fluorine will be biased high. Inorganic fluorine has been shown to be effectively removed using a nitrate wash during the sample preparation process. However, a recent suspect screening study (Neuwald et al. 2021) for 1,310 potentially persistent and mobile chemicals in two German river systems found two inorganic fluorine compounds to be frequently detected – hexafluorophosphate ($PF_6^-$) and tetrafluoroborate ($BF_4^-$). At this time, other potential sources of inorganic fluorine interference have not been evaluated and it is uncertain if compounds like $PF_6^-$ and $BF_4^-$ are removed using a nitrate wash.

By contrast, the loss of ultrashort-chain PFAS during sample preparation for any of the "total PFAS" techniques would bias the results low. A recent study (Neuwald et al. 2022) of ultrashort-chain PFAS in German drinking water sources found ultrashort-chain PFAS trifluoroacetate (also referred to as trifluoroacetic acid (TFA)), perfluoropropanoate (also referred to as perfluoropropanoic acid (PFPS)), and trifluoromethane sulfonate (TFMS) were ubiquitous and present at the highest concentrations, representing 98% of the sum target PFAS concentrations; with detections of novel short-chain PFAS such as hexafluoroisopropanol, bis(trifluoromethylsulfonyl)amide (also referred to as bistriflimide

(TFSI)), and tris(pentafluoroethyl) trifluorophosphate also detected. If these compounds are removed during the sample preparation process (or possibly lost in the instrument prior to combustion), it could result in a large mass of PFAS left uncharacterized.

Cationic and C15 and longer-chain PFAS are of interest but are likely more sorptive and therefore, less likely to be mobilized at long-distances (e.g., 2 miles or more when transported via groundwater) from source areas where PFAS were initially released to the environment. For example, a recent study characterized the presence of zwitterionic and cationic compounds and found that they composed a large percentage (34.5-85.5%) of the total PFAS mass in most surface soil samples in the source zone, with a lower percentage (<20%) in groundwater samples (Liu et al, 2022). The fate and transport of cationic PFAS is not well understood and could be relevant to the PFAS mass balance when considering "total PFAS" analytical techniques. However, existing PWS monitoring data indicates very low to no occurrence of PFAS with chains longer than C11 (based on PFCA analytes), indicating that even longer-chain PFAS may be of low to no concern in drinking water. It would be ideal for C15 and longer-chain PFAS to be captured in any "total PFAS" measurement but in terms of priority, it is higher priority to characterize the analytical fate of ultrashort-chain, volatile, and cationic PFAS over C15 and longer-chain PFAS because of likely incomplete exposure pathways for C15 and longer-chain PFAS to drinking water.

Given the regulatory interest to manage PFAS as a class, and recent observations of inorganic fluorine compounds and ultrashort-chain and volatile PFAS detected in the environment, it is of primary interest to characterize the limitations of "total PFAS" methods as they relate to inorganic fluorine and ultrashort-chain and volatile PFAS. An ion chromatograph tandem mass spectrometer (IC-MSMS) is available by the contracted laboratory and provides a supplemental analytical technique to measure targeted inorganic fluorine species, and ultrashort-chain PFAS; however, volatile PFAS are less likely to be detected using IC-MSMS. Additionally, experiments using laboratory spiked samples over a range of concentrations provides the opportunity to evaluate the analytical fate of inorganic fluorine compounds, and ultrashort-chain, volatile, and cationic PFAS reported in adsorbable and extractable organic fluorine measurements. Additionally, relevant information regarding the analytical fate of different types of PFAS may be inferred by the NTA LC-HRMS results, and/or comparison of results from other analytical techniques and sample extraction methods included in the study.

## 4.2  "Total PFAS" Sample Preparation Methods

This method comparison study does not include method development. As such, the sample preparation methods used in this study must generally align with existing published methods that can be implemented by the state contracted laboratory (Babcock Laboratories). A description of published methods available for use is provided in Table 3.

*Table 3. Summary of Available Sample Preparation Methods for "Total PFAS" Analysis[+]*

| Method Reference | Sample Extraction Description | Limitations/ Concerns |
|---|---|---|
| Direct Inject | A direct inject approach is not a sample extraction method as the sample is not extracted using a process, and there is limited to no preparation involved so samples are nearly analyzed as received. There are existing USEPA methods available that include this type of approach for evaluating low levels of anions using tandem mass spectrometry (e.g., perchlorate by USEPA Method 332). This type of sample processing involves subsampling from the sample container. | Direct injection approaches are a concern for PFAS that have a carbon chain length longer than C4 because C4 and longer chain PFAS stick to the sidewalls of the sample container and therefore result in low bias of the measured sample concentration if the whole sample is not processed for analysis, including a rinse of the container with methanol. Elevated detection limits may also be observed due to sample matrix interferences. |
| USEPA Method 3512/ Solvent Dilution | USEPA Method 3512 is a non-drinking water sample preparation method that includes addition of isotopically labeled analogs of PFAS target analytes and sample dilution with a 1:1 volume of methanol to sample. It does not include the use of an SPE cartridge or other clean-up steps and therefore there are no losses of PFAS due to sample extraction. The whole sample is injected for analysis using this direct inject method. | During method development, some PFAS analytes showed a potential for loss during storage of standard solutions in certain container types so polypropylene containers should be used and subsampling is not appropriate. Elevated detection limits may be observed due to sample matrix interferences. |
| USEPA Draft Method 1621 | USEPA Draft Method 1621 is a non-drinking water method for analyzing AOF by CIC. As described in Table 1, (whole) samples are loaded onto a GAC cartridge and rinsed with a solution of sodium nitrate to remove inorganic fluorine. The method includes many requirements to | USEPA Draft Method 1621 does not achieve relevant detection limits for drinking water. Using USEPA 1621 as a model, a similar approach can be implemented that lowers the limit of detection to a concentration that is relevant for drinking water analyses. |

| Method Reference | Sample Extraction Description | Limitations/ Concerns |
|---|---|---|
| | address background fluoride levels, to minimize interference by inorganic fluoride, and to avoid introduction of cross-contamination of organic fluorine. | |
| USEPA Method 537.1 | Prior to October 2022, USEPA Method 537.1 was the targeted PFAS method used to characterize sources of drinking water in accordance with DDW general orders for monitoring. Whole samples are enriched with surrogates and extracted using an SPE cartridge containing polystyrenedivinyl-benzene (SDVB) single polymer sorbent phase. The cartridge is rinsed with a small amount of methanol and the extract is concentrated to dryness with nitrogen in a heated water bath and then the extract is reconstituted in a solution of water and methanol with addition of internal standards. | USEPA Method 537.1 is likely to result in low to no recovery of ultrashort-chain PFAS such as trifluoroacetic acid (TFA), and other ultrashort-chain and volatile PFAS. The SDVB SPE cartridge is more likely to extract hydrophobic analyte characteristics of long chain alkyl substances, and the methanol rinse is likely capable of recovering long-chain PFAS (including C15 and longer), though these compounds may not easily elute off the SDVB SPE cartridge. The lack of internal standards to evaluate recovery performance for target analytes prior to extraction is concerning. |
| USEPA Method 533 | USEPA Method 533 is the targeted PFAS method currently used to characterize sources of drinking water in accordance with DDW general orders for monitoring PFAS. Whole samples are fortified with isotopically labeled analogues of the method analytes, and then the sample is extracted using a weak anion exchange (WAX) media in the SPE cartridge. The cartridge is rinsed with sequential washes of aqueous ammonium acetate followed by methanol, and compounds are eluted from the SPE cartridge with methanol containing ammonium hydroxide. | USEPA Method 533 is likely to result in low to no recovery of ultrashort-chain PFAS such as trifluoroacetic acid (TFA), and other ultrashort-chain and volatile PFAS because part of the sample process takes the extract to dryness. Additionally, WAX media target sorption of anionic PFAS and therefore, cationic PFAS may pass through the cartridge and result in low recovery. C15 and longer-chain PFAS likely sorb to the WAX SPE cartridge but may not elute off the cartridge due to strong sorptive properties of the WAX media. |

| Method Reference | Sample Extraction Description | Limitations/ Concerns |
|---|---|---|
| | The extract is concentrated to dryness with nitrogen in a heated water bath to settle out PFAS salts, then the extract is reconstituted in a solution of water and methanol and additional (isotopically labeled) internal standards are added. | |
| USEPA Draft Method 1633* | USEPA Method 1633 is finalized and available to use for aqueous samples. Whole samples are fortified with isotopically labeled analogues of the method analytes, and then the sample is extracted using WAX SPE cartridge followed by an SPE carbon cartridge. Samples are eluted off the SPE cartridges and the eluted extract is partially evaporated and brought to a constant final volume. | USEPA Method 1633 is likely to result in low to no recovery of ultrashort-chain PFAS such as trifluoroacetic acid (TFA), and other ultrashort-chain and volatile PFAS because the extraction process involves partial evaporation. Additionally, WAX media target sorption of anionic PFAS and therefore, cationic PFAS may pass through the cartridge and result in low recovery. C15 and longer-chain PFAS likely sorb to the WAX SPE cartridge but may not elute off the cartridge due to strong sorptive properties of the WAX media. |
| Department of Defense, Quality System Manual, Table B-15, version 5.3 (DoD QSM 5.3) | DoD QSM 5.3 or later provides baseline requirements for the establishment and management of quality systems for laboratories performing PFAS analytical services. Quality requirements are met using a laboratory propriety operating procedure that meets the bounds of the quality control limits specified in the DoD QSM Table B-15. A laboratory may or may not process the eluted extract to dryness, as well there is flexibility with the type of isotopically labeled analogues and surrogates and therefore the ability to add analytes to include a longer list of targeted | The sample preparation conditions are more conducive to retaining and measuring ultrashort-chain PFAS because there is not a requirement to take the sample extract to dryness. However, it may be difficult to include a sufficient range of representative internal standards to account for the wide range of potential ultrashort-chain PFAS (e.g., volatile and neutral PFAS) that may be of interest. Additionally, if WAX media are used as the SPE sorbent, the WAX media target sorption of anionic PFAS and therefore, |

| Method Reference | Sample Extraction Description | Limitations/ Concerns |
|---|---|---|
| | PFAS. Following standard operating procedures, low recovery of ultrashort-chain PFAS could be corrected or accounted for using representative internal standards (e.g., isotopically labeled analogues such as TFA, or reference materials such as trifluoromethane sulfonate (TFMS), hexafluoroisopropanol, etc.). | cationic PFAS may pass through the cartridge and result in low recovery. C15 and longer-chain PFAS likely sorb to the WAX SPE cartridge but are not likely eluted off the cartridge due to strong sorptive properties of the WAX media. |

Note: [+] = See Appendix A for sample extraction process for AOF-PIGE analysis; * = USEPA Draft Method 1633 is finalized for aqueous matrices.

Table 4 provides a summary of published PFAS sample preparation methods that are amenable for use with the "total PFAS" techniques summarized in Table 1.

*Table 4. Sample Preparation Methods Applicable to "Total PFAS" and Supplemental Analytical Techniques*

| PFAS Analytical Technique | Direct Inject | USEPA Method 3512 | USEPA Draft Method 1621 | USEPA Method 1633 | DoD QSM 5.3 | USEPA Method 533 | USEPA Method 537.1 |
|---|---|---|---|---|---|---|---|
| AOF-CIC | - | - | X | - | - | - | |
| EOF-CIC | - | - | - | X* | X* | X* | X* |
| AOF-PIGE[#] | - | - | X* | - | - | - | |
| LC-HRMS | - | - | - | X | X | X | X |
| GC-HRMS[+] | - | - | - | - | - | - | - |
| TOP Assay LC-MSMS | - | X | - | X | X | X | X |
| TOP Assay LC-HRMS | - | - | - | X | X | X | X |
| ^{19}F NMR | X* | - | - | X* | X* | X* | X* |
| IC-MSMS | X | X | - | - | - | - | - |

Note: - = method is not amenable; X = method is amenable; X* = key chemical principals of method are useful to model an appropriate extraction method for analysis; [+] = the appropriate sample preparation method for GC-HRMS is not listed; [#] = sample preparation and processing methods for AOF-PIGE are summarized in Appendix A. Shaded boxes indicate sample extraction procedures planned for this study.

Due to budget constraints, it will not be possible to analyze all sample preparation methods with all applicable "total PFAS" analytical techniques. The following provides a

summary of the techniques and methods to be included in this study (also indicated in Table 4):

- AOF-CIC using extraction procedures modeled after USEPA Draft Method 1621.
- EOF-CIC using extraction procedures modeled after USEPA Method 533.
- AOF-PIGE using sample preparation procedures included in Appendix A.
- NTA by LC-HRMS using USEPA Method 533 sample extracts.
- NTA by LC-HRMS using DoD QSM 5.3 sample extracts.
- $^{19}$F NMR using a modified direct injection (or analyzed as received) sample preparation approach.
- $^{19}$F NMR using extraction procedures modeled after USEPA Method 533.

Quality control sample types to be included in the study include laboratory method blanks, laboratory control spikes, analytical duplicates and replicates, field samples, field duplicates, field reagent blanks, and field matrix spikes and matrix spike duplicates. Additionally, a subset of field samples will be collected and analyzed in triplicate. A detailed sample and analysis plan for each method included in this study is provided in Section 5.0.

## 4.3    Summary of Method Comparison Design Questions

This method comparison study is designed to characterize the spectrum of PFAS that can be measured using available analytical methods. Existing targeted methods currently underestimate the occurrence of total PFAS in the environment and could result in lack of identification of locations with PFAS occurrence and limit the ability to identify if PFAS are present above levels of concern. Incorporation of a broad spectrum PFAS measurement provides an inclusive approach that ensures that monitoring would not fail to detect an impact even though one has occurred.

The study includes the use of techniques that are feasible and becoming commercially available (e.g., AOF-CIC, EOF-CIC), as well as those that are not feasible or commercially available (e.g., $^{19}$F NMR). The results of the various "total PFAS" analyses (see Section 5.0) will be used to characterize the uncertainty and/or limitations of the most appropriate "total PFAS" method such that those limitations can be factored into consideration when interpreting the results of the selected broad-spectrum test method used to characterize the occurrence of PFAS at PWS source wells serving SDAC/DAC. Study design questions will be answered by comparing the results of different sample types and sample preparation methods for seven "total PFAS" techniques, two targeted PFAS methods (USEPA Method 533 and DoD QSM 5.3), and one targeted method for inorganic fluorine and ultrashort-chain PFAS.

The study is designed to answer the following questions:

- How well is "total PFAS" characterized using the methods included in this comparison study?

- o How well do the measurements of adsorbable organic fluorine obtained via AOF-CIC and AOF-PIGE correlate?
- o How well do the measurements of adsorbable organic fluorine (AOF-CIC and AOF-PIGE) correlate with the extractable organic fluorine measurement (EOF-CIC)?
- o How well do the measurements of adsorbable and extractable organic fluorine (AOF-CIC, EOF-CIC, and AOF-PIGE) correlate with sum PFAS measured using USEPA Method 533 and DoD QSM 5.3 analyses?
- o How well do the measurements of adsorbable and extractable organic fluorine correlate with sum PFAS measured using semiquantitative LC-HRMS using USEPA Method 533 extract versus the DoD QSM 5.3 extract?
- o How well do the measurements of adsorbable and extractable organic fluorine correlate with total PFAS and other organic fluorinated substances measured by $^{19}$F NMR using a direct injection sample preparation approach? How well do they correlate with $^{19}$F NMR using DoD QSM 5.3 extracts?
- o How well do the $^{19}$F NMR results for the direct injection sample preparation correlate with the $^{19}$F NMR results for the DoD QSM 5.3 extract?
- o Which method provides the measurement of the broadest spectrum of "total PFAS"?
- o Which commercially available method provides the measurement of the broadest spectrum of "total PFAS"?
- o What are the limitations associated with data interpretation of the commercially available "total PFAS" results?
- Do inorganic fluorine compounds interfere with organic fluorine measurements obtained via AOF-CIC, EOF-CIC, or AOF-PIGE?
  - o Are fluoride (as measured by sodium fluoride) and inorganic fluorine compounds such as $PF_6^-$ and $BF_4^-$ removed from AOF-CIC, EOF-CIC, and AOF-PIGE using standard sample preparation steps?
  - o How well do inorganic fluorine measured by $^{19}$F NMR using a direct injection sample preparation approach correlate with $^{19}$F NMR using the DoD QSM 5.3 extract?
  - o Is there additional inorganic fluorine mass that is currently unaccounted for based on a comparison of $^{19}$F NMR inorganic fluorine results in the direct injection sample to the inorganic fluorine compounds measured using IC-MSMS with direct inject sample preparation?
- Which methods do the best job of retaining and reporting ultrashort-chain, volatile, and cationic PFAS?

- o What are the concentrations of ultrashort-chain, volatile, and cationic PFAS present in samples based on targeted IC-MSMS direct inject sample results?
- o Are ultrashort-chain, volatile, and cationic PFAS recovered by adsorbable or extractable organic fluorine measurements (AOF-CIC, EOF-CIC, and AOF-PIGE)? If so, what is the range of recovery?
- o How well are ultrashort-chain and volatile PFAS retained using LC-HRMS for the USEPA Method 533 extract versus the DoD QSM 5.3 extract?
- o What is the range of ultrashort-chain and volatile PFAS present but not measured using USEPA Method 533 and DoD QSM 5.3?
- o How well do organic fluorine measured by $^{19}$F NMR using a direct injection sample preparation approach correlate with $^{19}$F NMR results using the DoD QSM 5.3 extract?
- o How comparable are the differences between the "total PFAS" measurements (e.g., $^{19}$F NMR direct inject minus $^{19}$F NMR using DoD QSM 5.3 extract) to the ultrashort-chain, volatile, and cationic PFAS measured using IC-MSMS with the direct inject sample preparation?

## 5.0   Sampling and Analysis Plan

As noted above, the study plan includes seven "total PFAS" methods and three targeted methods for comparison. Sample types to be included in the study include laboratory method blanks, laboratory control spikes, field samples, field reagent blanks, field matrix spikes, and duplicates and triplicates. Table 5 provides an overview of the sample types and number of samples to be analyzed using the respective analytical methods included in the study plan. A detailed sample and analysis plan for each method included in this study is provided in Section 5.3.

*Table 5. Sample Types to be Analyzed by Analytical Methods Included in Study*

| Analytical Technique/ Method Preparation | Laboratory Quality Control | Field Samples | Field Reagent Blanks | Matrix Spike/ Matrix Spike Duplicates | Field Duplicates/ Triplicates |
|---|---|---|---|---|---|
| Non-Targeted Analyses | | | | | |
| AOF-CIC/ Extraction modeled after USEPA Draft Method 1621 | Minimum of 2 MB per batch<br><br>1 primary LCS and 1 duplicate LCS using | 9 | 9* | 18* | 18+ |

| Analytical Technique/ Method Preparation | Laboratory Quality Control | Field Samples | Field Reagent Blanks | Matrix Spike/ Matrix Spike Duplicates | Field Duplicates/ Triplicates |
|---|---|---|---|---|---|
| | a single PFAS surrogate per batch | | | | |
| EOF-CIC/ Extraction modeled after USEPA 533 | Minimum of 2 MB per batch<br><br>Minimum of 1<br><br>LCS per batch using a single PFAS surrogate per batch | 9 | 9* | 18* | 18+ |
| AOF-PIGE/ Appendix A procedures | 1 MB per batch<br><br>1 primary LCS and 1 duplicate LCS using a single PFAS surrogate per batch<br><br>Extracts analyzed in triplicate | 9 | 1 | 18 | 18+ |
| LC-HRMS/ USEPA Method 533 | Minimum of 2 MB per batch<br><br>Minimum of 2 LCS per batch<br><br>Extracts analyzed in triplicate | 9 | 9* | 18* | 1 |
| LC-HRMS/ DoD QSM 5.3 | Minimum of 2 MB per batch<br><br>Minimum of 1 LCS per batch<br><br>Extracts analyzed in triplicate | 9 | 9* | 18* | 1 |
| $^{19}$F NMR/ Direct Inject | 1 MB | 9 | 1 | 1 | 1 |
| $^{19}$F NMR/ Extraction modeled after USEPA Method 533 | 1 MB | 9 | 1 | 1 | 1 |
| Targeted Analyses | | | | | |

| Analytical Technique/ Method Preparation | Laboratory Quality Control | Field Samples | Field Reagent Blanks | Matrix Spike/ Matrix Spike Duplicates | Field Duplicates/ Triplicates |
|---|---|---|---|---|---|
| LC-MSMS/ USEPA Method 533 | Minimum 2 MB per batch<br><br>Minimum 2 LCS per batch | 9 | 9 | 18* | 1 |
| LC-MSMS/ DoD QSM 5.3 | Minimum 2 MB per batch<br><br>Minimum 2 LCS per batch | 9 | 9 | 18* | 1 |
| IC-MSMS/ Direct Inject | Minimum 1 MB per batch<br><br>Minimum 1 LCS per batch<br><br>Extracts analyzed in triplicate | 9 | 9 | 18* | 1 |

*Note: + = Samples to be analyzed in triplicate; * = A minimum of one quality control sample to be analyzed; remaining samples to be collected and placed on hold for as needed analysis; MB = method blank; LCS = laboratory control spike*

In addition to field sample analysis, several laboratory control spike experiments will be conducted to evaluate the analytical fate of analytical standards that represent a range of inorganic fluorine compounds and ultrashort-chain, volatile, and cationic PFAS over a range of concentrations. Table 6 provides an overview of the laboratory control spike experimental design for AOF-CIC, EOF-CIC, and IC-MSMS.

*Table 6. Summary of Laboratory Control Spike Experiments*

| Analytical Standard | Focus Area | AOF-CIC/ Extraction Modeled After **USEPA Draft Method 1621** | EOF-CIC/ Extraction Modeled After **USEPA Method 533** | IC-MSMS/ **Direct Inject*** | LC-MSMS/ **DoD QSM** |
|---|---|---|---|---|---|
| None | Blank/ Background | One blank | One blank | One blank | One blank |
| Sodium fluoride | Inorganic fluorine | One spike at 2,000 µg/L | One spikes at 2,000 µg/L | NA | NA |
| PF6- | Inorganic fluorine | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | Three spikes at | NA |

| Analytical Standard | Focus Area | AOF-CIC/ Extraction Modeled After **USEPA Draft Method 1621** | EOF-CIC/ Extraction Modeled After **USEPA Method 533** | IC- MSMS/ Direct Inject* | LC- MSMS/ DoD QSM |
|---|---|---|---|---|---|
| | | | | 1, 5, 10 µg/L | |
| BF4- | Inorganic fluorine | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | NA |
| Trifluoroacetic acid (TFA; C2 PFCA) | Ultrashort-chain PFAS | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | One spike at 0.1 ug/L |
| Trifluoromethane sulfate (TFMS; C2 PFCA) | Ultrashort-chain PFAS | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | One spike at 0.1 ug/L |
| Trifluoromethane sulfonamide (TFMSA; C1 PFSA Precursor) | Ultrashort-chain PFAS | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | One spike at 0.1 ug/L |
| bis(trifluoromethane sulfonyl)azanide (C2 PFSA Precursor) | Ultrashort-chain PFAS | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | One spike at 0.1 ug/L |
| Hexafluoro isopropanol (likely C2 PFCA Precursor) | Ultrashort-chain and volatile PFAS | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | One spike at 0.1 ug/L |
| 6:2 Fluorotelomer alcohol (C6 and shorter PFCA precursor) | Volatile PFAS | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | One spike at 0.1 ug/L |
| 8:2 Fluorotelomer alcohol (C8 and shorter PFCA precursor) | Volatile PFAS | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | One spike at 0.1 ug/L |

| Analytical Standard | Focus Area | AOF-CIC/ Extraction Modeled After **USEPA Draft Method 1621** | EOF-CIC/ Extraction Modeled After **USEPA Method 533** | IC-MSMS/ **Direct Inject*** | LC-MSMS/ **DoD QSM** |
|---|---|---|---|---|---|
| N-[3-(perfluoro-1-hexanesulfonamido)propan-1-yl]-N,N,N-trimethylammonium (N-TAmP-FHxSA)N-TAmP-FHxSA | Cationic PFAS | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | One spike at 0.1 ug/L |
| N-(3-dimethylaminopropan-1-yl)perfluoro-1-hexanesulfonamide (N-AP-FHxSA)N-AP-FHxSA | Cationic PFAS | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | Three spikes at 1, 5, 10 µg/L | One spike at 0.1 ug/L |

Notes: *µg/L = microgram per liter. NA = not applicable. * = Spike addition to be conducted using field samples. All spike experiments will be conducted in duplicate.*

## 5.1 Sample Location Selection Rationale

The sample locations selected for the 2021 PFAS methods correlation study provided a wide range of organic fluorine profiles such that between 7% to 62% of organic fluorine could be confirmed as PFAS based on conversion of NTA LC-HRMS abundance results to nanograms organic fluorine per liter (ng OF/L)) as compared to the adsorbable organic fluorine measured by AOF-CIC. These nine wells will be resampled as part of this method comparison study as they provide useful information for a broad range of PFAS profiles at sample locations while also providing the opportunity to compare current results to previous results, except for the City of Corona, District 20 well source identification code 3310037-033-033. This well was reported as off-line due to rehabilitation and cannot be sampled at this time. As such, a nearby well in the same PWS service area was selected for this study (i.e., 3310037-030-030).

The district number and well source identification for the nine PWS source wells to be sampled for this method comparison study are summarized in Table 7. Available well construction information (i.e. total depth, top of the screen, screen length) and the 2021 PFAS concentrations (i.e. AOF, sum PFAS 533, sum PFAS semiquantitative NTA) are provided in Appendix B.

*Table 7. PWSs Groundwater Wells Included in Method Comparison Study*

| Public Water System Name | DDW District Number and Name | Well Source Identification Code |
|---|---|---|
| City of Fresno | District 11-Merced | 1010007-204-204 |
| Waste Connections Water Co | LPA 70- San Luis Obispo County | 4000766-011-011 |
| Strasbaugh, Inc | LPA 70- San Luis Obispo County | 4000777-002-002 |
| Golden Eagle Small Water System | LPA 37 Contra Costa County | 0707625-002-002 |
| City of Corona | District 20-Riverside | 3310037-030-030 |
| City of Corona | District 20-Riverside | 3310037-032-032 |
| Burbank City, Water Dept | District 07-Hollywood | 1910179-029-029 |
| Burbank City, Water Dept | District 07-Hollywood | 1910179-028-028 |
| Mapache Trailer Park | LPA69-San Joaquin County | 3900661-001-001 |

## 5.2 Sample Collection, Quality Control, and Handling Procedures

Sample preparation and handling includes the shipment of the required sample bottles and PFAS-free deionized water for the collection of the field reagent blank at each site. Required bottles and sampling material, including necessary field reagent blank water, and shipping supplies, will be sent to DDW field offices. The University of Notre Dame will ship the necessary sampling material (e.g., GAC filter, water collection bags) for the collection of samples for AOF-PIGE. Babcock Laboratories will provide a bottle kit for all other methods for each sample location, including all necessary quality assurance and quality control sample materials and bottles.

**SAMPLE COLLECTION**

DDW field staff will collect samples following DDW's Drinking Water Sample Collection Guidance for Per- and Poly-fluoroalkyl Substances (PFAS), revised November 2022.

**<u>Samples will be collected from the well before treatment.</u>**

Each PWS well sample will be analyzed by USEPA Method 533, DoD QSM 5.3, IC-MSMS, AOF-CIC, EOF-CIC, and AOF-PIGE, and ^{19}F NMR. The type and number of sample collection bottles for each analysis is summarized in Table 8.

*Table 8. Summary of Sample Collection Bottles*

| Field Sample Type | Babcock | Babcock | Babcock | Babcock | Babcock | OSU | UND |
|---|---|---|---|---|---|---|---|
| | USEPA Method 533[+] | DoD QSM 5.3[+] | IC-MSMS Direct Inject | AOF-CIC Extraction procedure modeled after USEPA 1621 | EOF-CIC Extraction procedure modeled after USEPA 533 | ^{19}F NMR | AOF-PIGE |
| Field Sample | 2 x 250 ml HDPE (ammonium acetate preservative) | 2 x 250 ml HDPE | 22 X 50 ml HDPE | 2 x 250 ml HDPE | 2 x 250 ml HDPE | +++ 2 x 250 ml HDPE | 1 x 3.5L LDPE |
| Duplicate/ Triplicate | 2 x 250 ml HDPE (ammonium acetate preservative) | 2 x 250 ml HDPE | NA* | 4 x 250 ml HDPE | 4 x 250 ml HDPE | +++ 2 x 250 ml HDPE | 2 x 3.5L LDPE |
| Matrix Spikes/ Matrix Spike Duplicates | 2 x 250 ml HDPE (ammonium acetate preservative) | 2 x 250 ml HDPE | NA* | 2 x 250 ml HDPE | 2 x 250 ml HDPE | +++ 2 x 250 ml HDPE | 1 x 3.5L LDPE |
| Field Reagent Blank (FRB) | 1 x 250 ml HDPE (ammonium acetate preservative) | 1 x 250 ml HDPE | 1 x 50 ml HDPE | 1 x 250 ml HDPE | 1 x 250 ml HDPE | +++ 1 x 250 ml HDPE | 1 x 3.5L LDPE |

*Note: Babcock = Babcock Laboratories; OSU = Oregon State University; UND = University of Notre Dame; ml = milliliter; L – liter; HDPE = high-density polyethylene; LDPE = low density polyethylene; + = same extract used for LC-HRMS; NA\* = not applicable, analysis conducted using subsample from primary field sample bottle; +++ = subsample IC-MSMS DI sample bottle for ^{19}F NMR direct inject sample analysis.*

The sample ID system used for these analytical samples is as follows:

*System Number – Facility ID. – Sample/Well No. – Identifying Letter – Analysis*

Where:

Identifying Letter = field sample (S), field duplicate (D), field triplicate (T), field

reagent blank (FB), matrix spike (MS), matrix spike duplicate (MSD).

Analysis = 533_HRMS, QSM_HRMS, IC-DI, AOF-CIC, EOF-CIC, NMR, AOF-PIGE

Examples:

*3310037-032-032-S-533-HRMS*
(System 3310037, Facility ID. 032, Well No. 032, Field Sample, Target analysis)

*3310037-032-032-S-QSM-HRMS*
(System 3310037, Facility ID. 032, Well No. 032, Field Sample, Target DoD QSM 5.3 analysis)

*3310037-032-032-S-IC-NMR-DI*
(System 3310037, Facility ID. 032, Well No. 032, Field Sample, Target IC-MSMS analysis and NMR using the direct inject sample preparation)

*3310037-032-032-D-533-HRMS*
(System 3310037, Facility ID. 032, Well No. 032, Field duplicate, Target USEPA 533 analysis)

*3310037-032-032-T-PIGE*
(System 3310037, Facility ID. 032, Well No. 032, Field triplicate, AOF-PIGE analysis)

*3310037-032-032-FB-QSM-HRMS*
(System 3310037, Facility ID. 032, Well No. 032, Field reagent blank, Target DoD QSM 5.3
analysis)

*3310037-032-032-MS-IC-DI*
(System 3310037, Facility ID. 032, Well No. 032, matrix spike, Target IC-MSMS analysis)

*3310037-032-032-MSD-PIGE*
(System 3310037, Facility ID. 032, Well No. 032, matrix spike duplicate, AOF-PIGE analysis)

The list of sample IDs for this project is provided in Appendix B.

**FIELD QUALITY CONTROL SAMPLES**

Field duplicates and triplicates will be collected at frequency of 10% of the samples except as noted for AOF-CIC, EOF-CIC, and AOF-PIGE, which will include field triplicates for all samples (Table 8). Since there are less than 10 samples to be collected, a minimum of one field duplicate or triplicate will be collected from the nine sample locations for the remaining analyses.

The field reagent blanks are collected to verify that the sampling environment does not introduce PFAS and cross-contaminate samples during the sampling event. One sample location will have field reagent blanks collected and analyzed for all analytical methods. One field reagent blank will be collected at each site for the following methods: AOF-CIC using an extraction procedure modeled after USEPA Method 1621 sample preparation method, EOF-CIC using an extraction procedure modeled after USEPA Method 533 sample preparation method, USEPA Method 533, DoD QSM 5.3, and IC-MSMS. Therefore, a minimum of five field reagent blanks will be collected at each site (Table 8). The field reagent blanks for AOF-CIC and EOF-CIC will be placed on hold, the remaining field reagent blanks will be analyzed using target PFAS analyses, which has lower detection limits compared to the seven "total PFAS" analytical methods included in this study.

The collection of the field duplicate sample (and triplicate samples, as noted) and the field reagent blank will follow the procedure outlined in DDW's Drinking Water Sample Collection Guidance for Per- and Poly-fluoroalkyl Substances (PFAS).

**LABORATORY QUALITY CONTROL SAMPLES**

Matrix spike and matrix spike duplicates are included in the study design to document the accuracy and precision of the method for a randomly chosen sample. Matrix spike and spike duplicates will be collected from all wells, but only 10% (or one sample) of the matrix spike and matrix spike duplicates will be analyzed (except for AOF-PIGE), and the remaining matrix spike and matrix spike duplicate samples will be put on hold and analyzed if needed (Table 8). Matrix spike and matrix spike duplicate samples that are placed on hold but not needed for quality control may be used as backup sample volume for other sample analyses, if appropriate.

**SAMPLE HANDLING**

Refer to the DDW's Drinking Water Sample Collection Guidance for Per- and Poly-fluoroalkyl Substances (PFAS), revised November 2022, regarding samples being shipped to Babcock Laboratories.

Samples should be stored in ice chests at least 1/3 filled with wet ice which do not exceed 10°C (50°F) until analyzed at the laboratory. If immediate delivery to the laboratory is not possible, samples should be stored at 10°C (50°F) while enclosed in

their individual sealed bag but must not be frozen. Use fresh ice for packaging and shipping.

- Samples must arrive at the laboratory within 48 hours of sampling and at a temperature between 10°C (50°F) and 0°C (32°F) but not frozen.

- If samples are received at the laboratory more than 48 hours after sampling, they must be between 6°C (42.8°F) and 0°C (32°F) but not frozen.

An example chain of custody is provided as Appendix C.

## 5.3    Laboratory Sample Preparation, Analysis, and Reporting

**LABORATORY SAMPLE PREPARATION AND ANALYSIS**

Table 5 provides a summary of analytical techniques and the associated sample preparation methods to be included in this method comparison study.

Babcock Laboratories is responsible for preparing samples as follows:

- AOF-CIC sample preparation using extraction procedures modeled after USEPA Draft Method 1621: Whole samples are to be processed for analysis. The extraction procedure updates for this study include use of a single carbon tube for combustion and additional laboratory standards to evaluate inorganic fluorine removal efficiency and ultrashort-chain and volatile PFAS recovery. Another modification is the use of perfluorobutane sulfonate (PFBS) instead of perfluorohexane sulfonate (PFHxS) as the laboratory control spike standard.
- EOF-CIC sample preparation using extraction procedures modeled after USEPA Method 533: Whole samples are to be processed for analysis. The extraction procedure updates for this study include the exclusion of preservatives, exclusion of isotope dilution analogues during sample processing, use of 0.1% ammonium hydroxide in water for the inorganic wash, 0.2% ammonium hydroxide in methanol for the elution, and final extract volume of 200uL. Additionally, matrix spike and matrix spike duplicates are spiked with a single compound (PFBS).
- AOF-PIGE sample preparation following the procedures specified in Appendix A.
- NTA by LC-HRMS sample preparation using USEPA Method 533.
- NTA by LC-HRMS sample preparation using a modified laboratory operating procedure that meets DoD QSM 5.3 requirements. The laboratory SOP will be modified to include an additional isotopically labeled analogue (i.e., TFA) and spike compounds (i.e., TFMS and hexafluoroisopropanol).
- ^{19}F NMR sample preparation using a direct injection sample preparation approach. An aliquot of sample will be transferred from the sample container to the NMR tube. Laboratory spikes will be added directly to the NMR tube. Samples will also be prepared with trifluoroethane (TFE) as the standard for quantification, and a strongly paramagnetic complex to reduce

fluorinerelaxationion rates (i.e., gandolinium with diethylenetriaminepentaacetic acid (GD-DTPA)). Additional details regarding sample preparation for $^{19}$F NMR analysis are provided in Appendix D.

- $^{19}$F NMR sample preparation using extraction procedures modeled after USEPA Method 533. Whole samples are to be processed for analysis. The extraction procedure updates for this study include the exclusion of preservatives, exclusion of isotope dilution analogues during sample extraction, and the use of deuterated methanol when reconstituting the dried SPE sample extract. Samples will also be prepared with TFE as the standard for quantification, and GD-DTPA. Additional details regarding sample preparation for $^{19}$F NMR analysis are provided in Appendix D.

Babcock Laboratories is also responsible for preparing samples for the following targeted analyses:

- USEPA Method 533 per the method.
- DoD QSM 5.3 per the laboratory operating procedures with the modifications noted above.
- IC-MSMS following sample preparation by direct inject per the laboratory operating procedure, which aligns with USEPA Method 332 with modifications to the internal standards.

Following sample preparation, Babcock Laboratories is responsible for analyzing the prepared samples as follows:

- AOF-CIC on the sample prepared using the extraction procedures modeled after Draft USEPA 1621 procedure.
- EOF-CIC on the sample prepared using the extraction procedures modeled after USEPA 533 procedure.
- LC-HRMS on the sample prepared using the USEPA 533 procedure.
- LC-HRMS on the sample prepared using the modified DoD QSM 5.3 compliant laboratory procedure.
- LC-MSMS on the sample prepared using the USEPA 533 procedure.
- LC-MSMS on the sample prepared using DoD QSM 5.3 compliant laboratory extraction procedure.
- IC-MSMS on the sample prepared using the direct inject procedure.

Targeted analytes and reporting limits for the USEPA Method 533 and the DoD QSM 5.3 analyses are provided in Table 9.

*Table 9. Target PFAS Analyte List and Reporting Limits (ng/L)*

| Analyte | DOD QSM 5.3 Compliant | USEPA Method 533 |
|---|---|---|
| Perfluorobutanoate (PFBA) | 5.0 | 2.0 |
| Perfluoropentanoate (PFPeA) | 5.0 | 2.0 |
| Perfluorohexanoate (PFHxA) | 5.0 | 2.0 |
| Perfluoroheptanoate (PFHpA) | 5.0 | 2.0 |
| Perfluorooctanoate (PFOA) | 5.0 | 2.0 |
| Perfluorononanoate (PFNA) | 5.0 | 2.0 |
| Perfluorodecanoate (PFDA) | 5.0 | 2.0 |
| Perfluoroundecanoate (PFUnA) | 5.0 | 2.0 |
| Perfluorododecanoate (PFDoA) | 5.0 | 2.0 |
| Perfluorotridecanoate (PFTrDA) | 5.0 | NA |
| Perfluorotetradecanoate (PFTeDA) | 5.0 | NA |
| Perfluorohexadecanoic acid (PFHxDA) | 5.0 | NA |
| Perfluorooctadecanoic acid (PFOcDA) or (PFODA) | 5.0 | NA |
| Perfluorobutanesulfonate (PFBS) | 5.0 | 2.0 |
| Perfluoropentanesulfonate (PFPeS) | 5.0 | 2.0 |
| Perfluorohexanesulfonate (PFHxS) | 5.0 | 2.0 |
| Perfluoroheptanesulfonate (PFHpS) | 5.0 | 2.0 |
| Perfluorooctanesulfonate (PFOS) | 5.0 | 2.0 |
| Perfluorononanesulfonate (PFNS) | 5.0 | NA |
| Perfluorodecanesulfonate (PFDS) | 5.0 | NA |
| 4:2 fluorotelomersulfonate (4:2 FTS) | 5.0 | 2.0 |
| 6:2 fluorotelomersulfonate (6:2 FTS) | 5.0 | 5.0 |
| 8:2 fluorotelomersulfonate (8:2 FTS) | 5.0 | 5.0 |
| 10:2 fluorotelomersulfonate (10:2 FTS) | 8.0 | NA |
| N-Methylperfluorooctanesulfonamidoacetic acid (N-MeFOSAA) | 8.0 | NA |
| N-Ethylperfluorooctanesulfonamidoacetic acid (N-EtFOSAA) | 8.0 | NA |
| Perfluorooctanesulfonamide (PFOSA) or (FOSA) | 8.0 | NA |
| N-Methylperfluorooctanesulfonamide (N-MeFOSA) | 8.0 | NA |
| N-Ethylperfluorooctanesulfonamide (N-EtFOSA) | 8.0 | NA |
| N-Methylperfluorooctanesulfonamidoethanol | 8.0 | NA |

| Analyte | DOD QSM 5.3 Compliant | USEPA Method 533 |
|---|---|---|
| (N-MeFOSE) | | |
| N-Ethylperfluorooctanesulfonamidoethanol (N-EtFOSE) | 8.0 | NA |
| Hexafluoropropylene oxide dimer acid (HFPO-DA) | 5.0 | 2.0 |
| 4-dioxa-3H-perfluorononanoate (ADONA) | 5.0 | 2.0 |
| 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (9Cl-PF3ONS) | 5.0 | 2.0 |
| 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS) | 5.0 | 2.0 |
| 3:3 perfluorohexanoic acid (3:3 FTCA) | 5.0 | NA |
| 5:3 perfluorooctanoic acid (5:3 FTCA) | 8.0 | NA |
| 7:3 perfluorodecanoic acid (7:3 FTCA) | 8.0 | NA |
| Perfluoro(2-ethoxyethane) sulfonic acid (PFEESA) | 8.0 | 2.0 |
| Perfluoro-4-methoxybutanoate (PFMBA) | 8.0 | 2.0 |
| Perfluoro-3-methoxypropanoate (PFMPA) | 8.0 | 2.0 |
| Perfluoro-3,6-dioxaheptanoate (NFDHA) | 8.0 | 2.0 |

*Note: Reporting for samples analyzed by DoD QSM 5.3 will also include TFA, TFMS, and hexafluoroisopropanol. These analytes do not currently have reporting limits.*

Once samples for $^{19}$F NMR are prepared by Babcock Laboratories, they will be shipped to Oregon State University under chain of custody protocol. Note that for the samples prepared using the direct inject method (e.g., analyzed as received), Oregon State University will analyze samples with the highest organic fluorine concentration first to determine if the analysis will achieve a sufficient detection limit for the analysis.

Following filtration of field samples for AOF-PIGE by Babcock Laboratories, the GAC SPE filters will be shipped to University of Norte Dame under chain of custody protocol where the samples will undergo additional sample preparation for AOF-PIGE analysis.

**LABORATORY SAMPLE REPORTING**

Laboratory analytical reporting shall include communication of results via e-mail to the State Water Board. Analytical results will be submitted as soon as they are available in electronic data deliverables (EDDs).

Babcock Laboratories will provide Excel files to the State Water Board containing essential information, including sample identification, compound formula, mass in the appropriate unit for each analytical method (e.g., nanogram per liter, abundance, nanogram of organic fluorine per liter, etc.), and generated confidence level for the NTA

results. Excel files will also be provided to summarize the results of the laboratory control spike experiments.

Analyses performed will also be reported via standard Level 2 Laboratory Report, as outlined below, in PDF format.

a) Case narrative
b) Requestor
c) Project Code/Region
d) COC form
e) Sample ID/number
f) Date and time samples were collected
g) Date and time samples were received by the laboratory
h) Analytical, extraction/preparation methods (include United States Environmental Protection Agency or Standard Method numbers where applicable)
i) Analytical results for all laboratory determinations
j) Dilution factors, if used
k) Sample matrix and fraction (total or dissolved)
l) Date and time samples were prepared/extracted and analyzed
m) Names and initials of analysts
n) Analytical results (including detections between the RL and MDL)
o) RL and MDL
p) Quality Control Samples and results:
- Method Blank
- Laboratory Control Sample (LCS)
- Laboratory Control Duplicate
- Matrix Spike (MS) & Duplicate (MSD), where appropriate
- Sample Replicate, where appropriate
- Field Quality Control Samples (when included)
q) Quality Control Performance Criteria
r) Result qualifiers/flags and definitions (where applicable)
s) Discussion of any deviations from approved methods
t) Subcontractor laboratory reports (when applicable).

Additionally, all data and records used to generate the laboratory reports and EDDs must be retained by Babcock Laboratories and made available to the State Water Board upon request.

Oregon State University and University of Notre Dame will provide sample results in electronic format using Excel. The Excel file will contain sample meta data including the sample ID/number, date and time samples were collected, date and time samples were received by Oregon State University, date and time the samples were analyzed, and analytical results. The electronic deliverable will also include a pdf copy of the spectra for each sample with sample identification information clearly identified for each spectra.

## 6.0 Field Implementation Schedule

The project is planned for fourth quarter 2023 (October to December). The sample collection schedule is summarized in Table 10.

*Table 10. Sample Collection Schedule*

| Public Water System Name | Public Water System No. | Well Source Identification Code | Sample Date |
|---|---|---|---|
| WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | October 2023 |
| STRASBAUGH, INC | 4000777 | 4000777-002-002 | October 2023 |
| CITY OF FRESNO | 1010007 | 1010007-204-204 | November 2023 |
| GOLDEN EAGLE SMALL WATER SYSTEM | 707625 | 0707625-002-002 | November 2023 |
| MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | October 2023 |
| BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | November 2023 |
| BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | November 2023 |
| CORONA, CITY OF | 3310037 | 3310037-030-030 | October 2023 |
| CORONA, CITY OF | 3310037 | 3310037-032-032 | October 2023 |

## 7.0 Data Analysis and Reporting

Of the many "total PFAS" techniques and method preparation procedures described in Section 4, AOF-CIC by modified USEPA Draft Method 1621, EOF-CIC by DoD QSM 5.3, LC-HRMS by two sample preparation methods (i.e., USEPA Method 533 and DoD QSM 5.3), AOF-PIGE by modified USEPA Draft Method 1621, and $^{19}$F NMR by two sample preparation methods (i.e., modified direct inject and DoD QSM 5.3) will be included in this method comparison study. This provides the opportunity to compare two total PFAS methods that are adsorbable on GAC (AOF-CIC and AOF-PIGE) – one that is commercially available and economically feasible (AOF-CIC) and one that is not broadly commercially available but is economically feasible (AOF-PIGE). This study will also provide the opportunity to compare these results with one method that is commercially available (LC-HRMS), not economically feasible but for which the potential

exists to identify suspect targeted PFAS, and another method that is not commercially available, economically feasible, but for which the potential exists to estimate the fraction of total organic fluorine attributable to "total PFAS" ($^{19}$F NMR).

This study includes multiple sample preparation methods that provide either direct comparison of a single "total PFAS" technique (e.g., LC-HRMS analysis of a USEPA 533 extract versus a DoD QSM 5.3 extract) or direct comparison of multiple "total PFAS" techniques using one sample preparation approach (e.g., EOF-CIC, LC-HRMS, and 19F NMR using the DoD QSM 5.3 extract). This study also provides the opportunity to compare the various "total PFAS" analyses with the sum PFAS that can be detected using targeted PFAS methods – USEPA 533 and DoD QSM 5.3, as well as targeted analysis of inorganic fluorine compounds, and ultra-short and volatile PFAS.

Ultimately, the analytical results for this study will be used to answer the decision questions summarized in Section 4.3, support incorporation of an inclusive approach that ensures that monitoring would not fail to detect an impact even though one has occurred, and help to characterize the chemical space captured by the available "total PFAS" techniques and associated sample preparation methods (see Figure 2 for example of how chemical space could be illustrated following an example in the literature (McDonough et al. 2019)). Analytical results will be summarized to provide advantages and disadvantages associated with each approach (including confidence with the method, as well as economic and commercial feasibility), and characterize uncertainty associated with results using the appropriate "total PFAS" method such that those limitations can be factored into consideration when evaluating the results of the selected broad-spectrum test method used to characterize the occurrence of PFAS at PWS source wells serving SDAC/DAC. Finally, information gathered by comparing targeted sample results with the suspect PFAS detected using LC-HRMS will support initial efforts to identify lists of frequently and abundantly detected suspected PFAS compounds that may require additional consideration when implementing the b*aseline PFAS b*road s*pectrum t*esting in d*rinking w*ater* at PWS groundwater wells serving DAC/SDAC.

The data analysis and recommendations for selecting the most appropriate broad-spectrum method will be summarized in a draft memorandum and distributed for DDW management review and comment. The draft memorandum will be finalized following review of comments and suggestions, and the selected broad-spectrum method will be single lab validated, and appropriate updates will be incorporated in the quality assurance project plan.
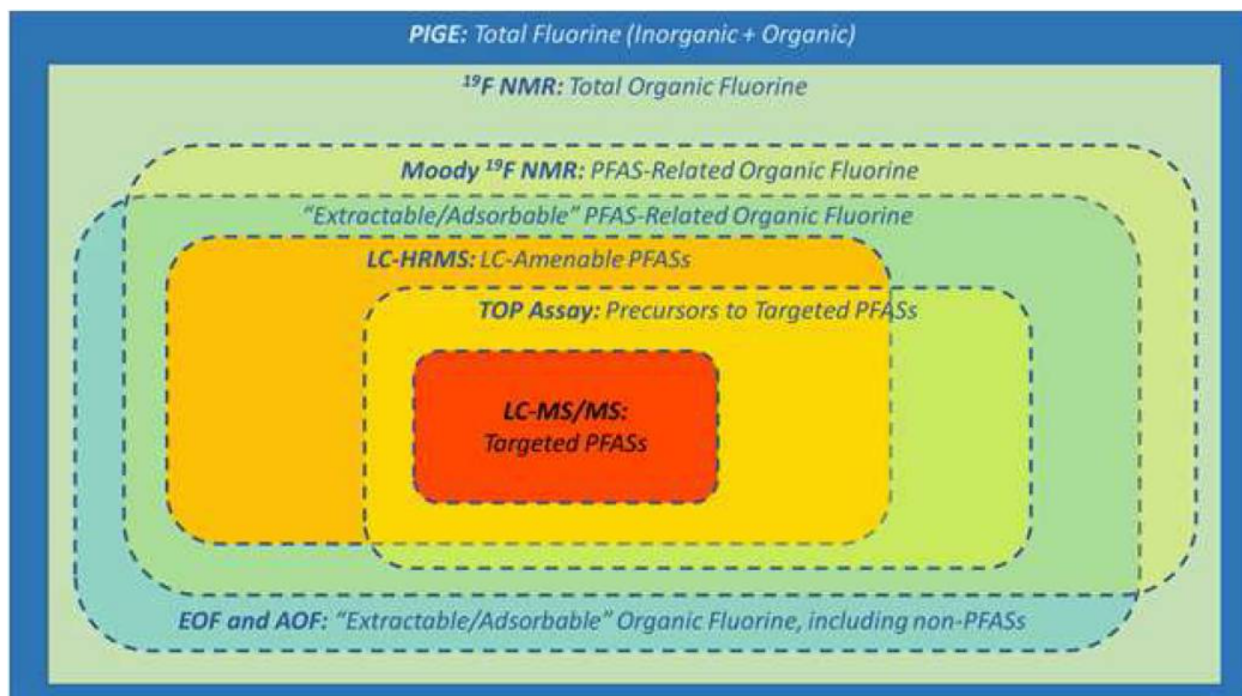
*Figure 2. Example for depicting chemical space reported by various "total PFAS" methods (McDonough et al. 2019).*

## 8.0   References

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# Appendix A: Adsorbable Organic Fluorine Particle Induced Gamma Emission (AOF-PIGE) Sample Processing Procedures

### SAMPLE PREPARATION PROCEDURE FOR PIGE ANALYSIS

1. Samples must be processed within 72 hours of sampling.  Refrigerate
2. Measure and **record** the mass of the entire sample bag using a scale with an appropriate range (4000g).
3. Spike any QC samples with 7uL of 1000ug/mL Organic Fluoride sourced from PFBS.  For a 3.5 liter nominal sample volume, this provides a spike level of 2.0ugL OF in the sample.  Regardless of the sample volume the amount of OF on the ACF will be nominally at 7.0ug.
4. Label the solid sample cap with a numerical identifier.
5. Replace the solid sample cap with the ACF Filter cap and do not discard the small plastic bag (used later for shipping).
6. Invert and suspend the sample bag and allow to drain.  The sample bag should hang freely and not have too much pressure on the sides.  Ideally it does not touch anything.
7. Measure the pH of the water coming out and **record**.
8. Filtration may take 10 to 15 minutes.  Some sample may even take 30 minutes.  As the sample passes through the filter, make sure the sample bag folds correctly.  Kinks may slow down the flow.
9. Once the sample has passed through the filter, remove the ACF lined cap and place back into the provided bag.  **Label** the plastic bag.
10. Place the solid sample cap back on the sample bag and obtain the "Tare" mass of the empty sample bag.  The volume of water passed through the ACF is the initial mass minus the final (empty) mass.
11. Optional: Sign the form and ship back to FAS (Notre Dame)


Calculations:  The ug F reported from Notre Dame can be divided by the actual volume used per sample to obtain the ug/L OF.


*This procedure was adapted from the procedure provided to Babcock Labs by Notre Dame University by Hunter MacMillan (hmacmill@fasanalytical.com)*

# Appendix B: Well Information and Summary of Sample Identifications

*Table B-1. Well Construction Information*

| System Name | System No. | Well Source ID Code | Latitude | Longitude | Total Depth (ft) | Top of Screen (ft) | Screen Length (ft) |
|---|---|---|---|---|---|---|---|
| CITY OF FRESNO | 1010007 | 1010007-204-204 | 36.76462 | -119.71794 | N/A | 150 | 250 |
| WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 35.23948 | -120.65199 | N/A | N/A | N/A |
| STRASBAUGH, INC | 4000777 | 4000777-002-002 | 35.23349 | -120.64 | N/A | 60 | 40 |
| GOLDEN EAGLE SMALL WATER SYSTEM | 707625 | 0707625-002-002 | 38.01233 | -122.05563 | N/A | 0 | 0 |
| CORONA, CITY OF | 3310037 | 3310037-030-030 | 33.873369 | -117.557378 | N/A | N/A | N/A |
| CORONA, CITY OF | 3310037 | 3310037-032-032 | 33.87731 | -117.57457 | N/A | 113 | 77 |
| BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 34.19168 | -118.34819 | N/A | 125 | 180 |
| BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 34.19104 | -118.34498 | N/A | 109 | 180 |
| MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 37.91496 | -121.22256 | N/A | 0 | 10 |

*Table B-2. 2021 PFAS Concentrations and Estimated Suspect Ultrashort PFAS Compounds in Nanograms of Organic Fluorine per Liter (ng OF/L)*

| System Name | Well Source ID Code | AOF | Sum PFAS 533 | Sum PFAS semi-quant NTA | TFA | PFPrA | PFPeA | PFPrS | PFPrSA |
|---|---|---|---|---|---|---|---|---|---|
| CITY OF FRESNO | 1010007-204-204 | 1000 | 381 | 729 | 6 | 5 | 30 | 9 | 6 |
| WASTE CONNECTIONS WATER CO | 4000766-011-011 | 2800 | 853 | 1548 | 130 | 6 | 110 | 21 | 7 |

| System Name | Well Source ID Code | AOF | Sum PFAS 533 | Sum PFAS semi-quant NTA | TFA | PFPrA | PFPeA | PFPrS | PFPrSA |
|---|---|---|---|---|---|---|---|---|---|
| STRASBAUGH, INC | 4000777-002-002 | 2000 | 213 | 731 | 230 | 6 | 25 | 7 | 5 |
| GOLDEN EAGLE SMALL WATER SYSTEM | 0707625-002-002 | 1500 | 170 | 523 | 0 | 5 | 2 | 8 | 5 |
| CORONA, CITY OF | 3310037-033-033 | 2800 | 504 | 913 | 480 | 6 | 21 | 10 | 5 |
| CORONA, CITY OF | 3310037-032-032 | 2500 | 228 | 511 | 160 | 5 | 8 | 8 | 4 |
| BURBANK-CITY, WATER DEPT. | 1910179-029-029 | 2500 | 40 | 343 | 75 | 5 | 5 | 5 | 4 |
| BURBANK-CITY, WATER DEPT. | 1910179-028-028 | 2300 | 50 | 374 | 95 | 5 | 6 | 5 | 4 |
| MAPACHE TRAILER PARK | 3900661-001-001 | 400 | 13 | NM | NM | NM | NM | NM | NM |

*Table B-3. Field and Quality Control Sample IDs*

| District No. - Name | System Name | System No. | Well Source ID Code | Sample ID | Analytical Test | Container Count, Volume, Type | Preservative | Laboratory |
|---|---|---|---|---|---|---|---|---|
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-S-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-FB-AOF-CIC | AOF-CIC (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-MSD-AOF-CIC | AOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-D-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-T-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-S-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-FB-EOF-CIC | EOF-CIC (hold) | 11 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-MSD-EOF-CIC | EOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-D-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-T-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-S-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-MSD-PIGE | AOF-PIGE | 2 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-D-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-T-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-S-533-HRMS | EPA 533/ LC-HRMS | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-FB-533-HRMS | EPA 533/ LC-HRMS (hold) | 1 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-MSD-533-HRMS | EPA 533 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-S-QSM-HRMS | DOD QSM 5.3/ LC-HRMS | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-FB-QSM-HRMS | DOD QSM 5.3/ LC-HRMS (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-MSD-QSM-HRMS | DOD QSM 5.3 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-S-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI | 2 X 50 ml HDPE | N/A | Babcock Labs |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-FB-IC-NMR- DI | IC-MSMS DI/ 19F NMR DI (hold) | 1 x 50 ml HDPE | N/A | Babcock Labs |

| District No. - Name | System Name | System No. | Well Source ID Code | Sample ID | Analytical Test | Container Count, Volume, Type | Preservative | Laboratory |
|---|---|---|---|---|---|---|---|---|
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-S-NMR-533M | 19F NMR 533M | 2 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| 11 - MERCED | CITY OF FRESNO | 1010007 | 1010007-204-204 | 1010007-204-204-FB-NMR-533M | 19F NMR 533M (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| | | | | | | | | |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-S-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-FB-AOF-CIC | AOF-CIC | 1 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-MSD-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-D-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-T-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-S-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-FB-EOF-CIC | EOF-CIC | 11 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-MSD-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-D-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-T-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-S-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-FB-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-MSD-PIGE | AOF-PIGE | 2 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-D-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-T-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-S-533_HRMS | USEPA 533/ LC-HRMS | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |

| District No. - Name | System Name | System No. | Well Source ID Code | Sample ID | Analytical Test | Container Count, Volume, Type | Preservative | Laboratory |
|---|---|---|---|---|---|---|---|---|
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-FB-533_HRMS | USEPA 533/ LC-HRMS | 1 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-MSD-533_HRMS | USEPA 533/ LC-HRMS | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-D-533_HRMS | USEPA 533/ LC-HRMS | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-S-QSM_HRMS | DOD QSM 5.3/ LC-HRMS | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-FB-QSM_HRMS | DOD QSM 5.3/ LC-HRMS | 1 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-MSD-QSM_HRMS | DOD QSM 5.3/ LC-HRMS | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-D-QSM_HRMS | DOD QSM 5.3/ LC-HRMS | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-S-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI | 2 X 50 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-FB-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI | 1 x 50 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-S-NMR-533M | 19F NMR 533M | 2 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-FB-NMR-533M | 19F NMR 533M | 1 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-MSD-NMR-533M | 19F NMR 533M | 2 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| LPA70 - SAN LUIS OBISPO COUNTY | WASTE CONNECTIONS WATER CO | 4000766 | 4000766-011-011 | 4000766-011-011-D-NMR-533M | 19F NMR 533M | 2 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| | | | | | | | | |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-S-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-FB-AOF-CIC | AOF-CIC (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-MSD-AOF-CIC | AOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-DFD-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-TFT-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |

| District No. - Name | System Name | System No. | Well Source ID Code | Sample ID | Analytical Test | Container Count, Volume, Type | Preservative | Laboratory |
|---|---|---|---|---|---|---|---|---|
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-S-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-FB-EOF-CIC | EOF-CIC (hold) | 11 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-MSD-EOF-CIC | EOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-DFD-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-TFT-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-S-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-D-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-T-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-S-533_HRMS | USEPA 533/ LC-HRMS | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-FB-533_HRMS | USEPA 533/ LC-HRMS (hold) | 1 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-MSD-533_HRMS | USEPA 533 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-S-QSM_HRMS | DOD QSM 5.3/ LC-HRMS | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-FB- QSM_HRMS | DOD QSM 5.3/ LC-HRMS (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-MSD-QSM_HRMS | DOD QSM 5.3 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-S-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI | 1 X 50 ml HDPE | N/A | Babcock Labs |
| LPA70 - SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-FB-IC-NMR-DI | IC-MSMS DI 19F NMR DI (hold) | 1 x 50 ml HDPE | N/A | Babcock Labs |
| LPA70 – SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-S-NMR-533M | 19F NMR 533M | 2 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| LPA70 – SAN LUIS OBISPO COUNTY | STRASBAUGH, INC | 4000777 | 4000777-002-002 | 4000777-002-002-FB-NMR-533M | 19F NMR 533M (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| – | | | | | | | | |

| District No. - Name | System Name | System No. | Well Source ID Code | Sample ID | Analytical Test | Container Count, Volume, Type | Preservative | Laboratory |
|---|---|---|---|---|---|---|---|---|
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-S-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-FB-AOF-CIC | AOF-CIC (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-MSD-AOF-CIC | AOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-DFD-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-TFT-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-S-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-FB-EOF-CIC | EOF-CIC (hold) | 11 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-MSD-EOF-CIC | EOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-DFD-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-TFT-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-S-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-D-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-T-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-S-533_HRMS | USEPA 533/ LC-HRMS | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-FB-533_HRMS | USEPA 533/ LC-HRMS (hold) | 1 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-MSD-533_HRMS | USEPA 533 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-S-QSM_HRMS | DOD QSM 5.3/ LC-HRMS | 2 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-FB- QSM_HRMS | DOD QSM 5.3/ LC-HRMS (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-MSD-QSM_HRMS | DOD QSM 5.3 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |

| District No. - Name | System Name | System No. | Well Source ID Code | Sample ID | Analytical Test | Container Count, Volume, Type | Preservative | Laboratory |
|---|---|---|---|---|---|---|---|---|
| LPA37 – CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-S-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI | 2 X 50 ml HDPE | N/A | Babcock Labs |
| LPA37 - CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-FB-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI (hold) | 1 x 50 ml HDPE | N/A | Babcock Labs |
| LPA37 - CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-S-NMR-533M | 19F NMR 533M | 2 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| LPA37 - CONTRA COSTA COUNTY | GOLDEN EAGLE SMALL WATER SYSTEM | 0707625 | 0707625-002-002 | 0707625-002-002-FB-NMR-533M | 19F NMR 533M (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs to OSU |
|  |  |  |  |  |  |  |  |  |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-S-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-FB-AOF-CIC | AOF-CIC (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-MSD-AOF-CIC | AOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-D--FD-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-T--FT-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-S-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-FB-EOF-CIC | EOF-CIC (hold) | 11 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-MSD-EOF-CIC | EOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-D--FD-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-T--FT-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-S-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-D-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-T-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-S-533_HRMS | USEPA 533/ LC-HRMS | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-FB-533_HRMS | USEPA 533/ LC-HRMS (hold) | 1 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-MSD-533_HRMS | USEPA 533 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-S-QSM_HRMS | DOD QSM 5.3/ LC-HRMS | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-FB-QSM_HRMS | DOD QSM 5.3/ LC-HRMS (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |

| District No. - Name | System Name | System No. | Well Source ID Code | Sample ID | Analytical Test | Container Count, Volume, Type | Preservative | Laboratory |
|---|---|---|---|---|---|---|---|---|
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-MSD-QSM_HRMS | DOD QSM 5.3 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-S-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI | 2 X 50 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-FB-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI (hold) | 1 x 50 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-S-NMR-533M | 19F NMR 533M | 2 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-030-030 | 3310037-030-030-FB-NMR-533M | 19F NMR 533M (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| | | | | | | | | |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-S-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-FB-AOF-CIC | AOF-CIC (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-MSD-AOF-CIC | AOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-DFD-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-TFT-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-S-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-FB-EOF-CIC | EOF-CIC (hold) | 11 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-MSD-EOF-CIC | EOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-DFD-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-TFT-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-S-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-D-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-T-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-S-533_HRMS | USEPA 533/ LC-HRMS | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-FB-533_HRMS | USEPA 533/ LC-HRMS (hold) | 1 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-MSD-533_HRMS | USEPA 533 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-S-QSM_HRMS | DOD QSM 5.3/ LC-HRMS | 2 x 250 ml HDPE | N/A | Babcock Labs |

| District No. - Name | System Name | System No. | Well Source ID Code | Sample ID | Analytical Test | Container Count, Volume, Type | Preservative | Laboratory |
|---|---|---|---|---|---|---|---|---|
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-FB- QSM_HRMS | DOD QSM 5.3/ LC-HRMS (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-MSD-QSM_HRMS | DOD QSM 5.3 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-S-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI | 2 X 50 ml HDPE | N/A | Babcock Labs |
| 20 – RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-FB-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI (hold) | 1 x 50 ml HDPE | N/A | Babcock Labs |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-S-NMR-533M | 19F NMR 533M | 2 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| 20 - RIVERSIDE | CORONA, CITY OF | 3310037 | 3310037-032-032 | 3310037-032-032-FB-NMR-533M | 19F NMR 533M (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| | | | | | | | | |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-S-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-FB-AOF-CIC | AOF-CIC (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-MSD-AOF-CIC | AOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-DFD-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-TFT-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-S-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-FB-EOF-CIC | EOF-CIC (hold) | 11 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-MSD-EOF-CIC | EOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-DFD-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-TFT-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-S-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-D-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |

| District No. - Name | System Name | System No. | Well Source ID Code | Sample ID | Analytical Test | Container Count, Volume, Type | Preservative | Laboratory |
|---|---|---|---|---|---|---|---|---|
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-T-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | University of Notre Dame |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-S-533_HRMS | USEPA 533/ LC-HRMS | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-FB-533_HRMS | USEPA 533/ LC-HRMS (hold) | 1 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-MSD-533_HRMS | USEPA 533 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-S-QSM_HRMS | DOD QSM 5.3/ LC-HRMS | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-FB- QSM_HRMS | DOD QSM 5.3/ LC-HRMS (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-MSD-QSM_HRMS | DOD QSM 5.3 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-S-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI | 2 X 50 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-FB-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI (hold) | 1 x 50 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-S-NMR-533M | 19F NMR 533M | 2 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-029-029 | 1910179-029-029-FB-NMR-533M | 19F NMR 533M (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs to OSU |
|  |  |  |  |  |  |  |  |  |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-S-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-FB-AOF-CIC | AOF-CIC (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-MSD-AOF-CIC | AOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-DFD-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-TFT-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-S-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-FB-EOF-CIC | EOF-CIC (hold) | 11 x 250 ml HDPE | N/A | Babcock Labs |

| District No. - Name | System Name | System No. | Well Source ID Code | Sample ID | Analytical Test | Container Count, Volume, Type | Preservative | Laboratory |
|---|---|---|---|---|---|---|---|---|
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-MSD-EOF-CIC | EOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-DFD-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-TFT-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-S-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | UND |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-D-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | UND |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-T-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | UND |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-S-533_HRMS | USEPA 533/ LC-HRMS | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-FB-533_HRMS | USEPA 533/ LC-HRMS (hold) | 1 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-MSD-533_HRMS | USEPA 533 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-S-QSM_HRMS | DOD QSM 5.3/ LC-HRMS | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-FB- QSM_HRMS | DOD QSM 5.3/ LC-HRMS (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-MSD-QSM_HRMS | DOD QSM 5.3 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-S-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI | 2 X 50 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-FB-ICNMR-DI | IC-MSMS DI/ 19F NMR DI (hold) | 1 x 50 ml HDPE | N/A | Babcock Labs |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-S-NMR-533M | 19F NMR 533M | 2 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| 07 - HOLLYWOOD | BURBANK-CITY, WATER DEPT. | 1910179 | 1910179-028-028 | 1910179-028-028-FB-NMR-533M | 19F NMR 533M (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| | | | | | | | | |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-S-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-FB-AOF-CIC | AOF-CIC (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-MSD-AOF-CIC | AOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-DFD-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |

| District No. - Name | System Name | System No. | Well Source ID Code | Sample ID | Analytical Test | Container Count, Volume, Type | Preservative | Laboratory |
|---|---|---|---|---|---|---|---|---|
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-TFT-AOF-CIC | AOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-S-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-FB-EOF-CIC | EOF-CIC (hold) | 11 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-MSD-EOF-CIC | EOF-CIC (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-DFD-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-TFT-EOF-CIC | EOF-CIC | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-S-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | UND |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-D-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | UND |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-T-PIGE | AOF-PIGE | 1 x 3.5 Liter LDPE Bag | N/A | UND |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-S-533_HRMS | USEPA 533/ LC-HRMS | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-FB-533 and HRMS | USEPA 533/ LC-HRMS (hold) | 1 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-MSD-533_HRMS | USEPA 533 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | Ammonium Acetate | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-S-QSM_HRMS | DOD QSM 5.3/ LC-HRMS | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-FB- QSM_HRMS | DOD QSM 5.3/ LC-HRMS (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-MSD-QSM_HRMS | DOD QSM 5.3 (hold)/ LC-HRMS (hold) | 2 x 250 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-S-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI | 2 X 50 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-FB-IC-NMR-DI | IC-MSMS DI/ 19F NMR DI (hold) | 1 x 50 ml HDPE | N/A | Babcock Labs |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-S-NMR-533M | 19F NMR 533M | 2 x 250 ml HDPE | N/A | Babcock Labs to OSU |
| 10 - STOCKTON | MAPACHE TRAILER PARK | 3900661 | 3900661-001-001 | 3900661-001-001-FB-NMR-533M | 19F NMR 533M (hold) | 1 x 250 ml HDPE | N/A | Babcock Labs to OSU |

# Appendix C: Example Chain of Custody

**BABCOCK LABORATORIES**

6100 Quail Valley Court
Riverside, CA 92507
T: (951) 653-3351

**Chain of Custody Record
& Sample Information**

Page ___1_____ of ____6____

| Sample Collection Agency: | Agreement No.: | Sample Matrix (See Codes Below) | Sample Type (G = Grab; C = Composite; O = Other) | Container Size (ml) | Container Type (P = Plastic; G = Glass; O = Other) | Preservation Code (See Codes Below) | # of Containers | Analyses Requested | | | | Field Quality Meter Readings (last measurement before sample collection) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Collection Agency Address: | Project Code: | | | | | | | | | | | | | | |
| | Project Name: GeoTracker Global ID: | | | | | | | | | | | | | | |
| Project Lead: | Field Lead: | | | | | | | | | | | | | | |
| Name: | Name: | | | | | | | | | | | | | | |
| Phone: | Phone: | | | | | | | | | | | | | | |
| Email: | Email: | | | | | | | | | | | | | | |

| | Sample ID | Date | Time | Location | | | | | | | | | | | | | Notes |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1) | | | | | | | | | | | | | | | | | |
| 2) | | | | | | | | | | | | | | | | | |
| 3) | | | | | | | | | | | | | | | | | |
| 4) | | | | | | | | | | | | | | | | | |
| 5) | | | | | | | | | | | | | | | | | |
| 6) | | | | | | | | | | | | | | | | | |
| 7) | | | | | | | | | | | | | | | | | |
| 8) | | | | | | | | | | | | | | | | | |
| 9) | | | | | | | | | | | | | | | | | |
| 10) | | | | | | | | | | | | | | | | | |

**Samples Relinquished By:** / **Samples Received By:**

| | Name (Print) and Agency | Signature | Date | Time | Name (Print) and Agency | Signature | Date | Time |
|---|---|---|---|---|---|---|---|---|
| 1) | | | | | | | | |
| 2) | | | | | | | | |
| 3) | | | | | | | | |
| 4) | | | | | | | | |

| Sample Matrix | Preservation Codes | Sample Receipt - Completed by Laboratory personnel: | Laboratory Notes: | Special Instructions: | |
|---|---|---|---|---|---|
| SFW = Surface Fresh Water; SSW = Surface Salt Water; DW = Drinking Water; GW = Groundwater; SW = Stormwater; WW = Wastewater; OL = Other Liquids; SO = Soil / Sediment; SL = Sludge / Slurry; OS = Other Solids; O = Other _____ | 1. Cool, ≤ 6 °C 2. HNO3 3. HCl 4. H2SO4 5. Na2S2O3 6. NaOH 7. NaOH/ZnAcetate 8. NH4Cl 9. Trizma 10. Filtered 11. Freeze, ≤ -10 °C 12. None required 13. Ammonium Acetate | Total Number of Sample Containers Received: | | Evidence sample handling required? | ☐ |
| | | Sample(s) Properly Cooled: Y / N / NA Temperature: ____°C | | Return Shipping Containers? | ☐ |
| | | Sample(s) Intact: Y / N / NA | | Turn Around Time: / Routine | ☐ |
| | | Custody Seal(s) Intact: Y / N / NA | Send Results to: | *3-5 Day (Rush) | ☐ |
| | | Sample(s) Accepted: Y / N | | *48-Hr (Rush) | ☐ |

Distribution: Original copies accompany sample shipment to laboratory; Electronic copy emailed to aguerra@babcocklabs.com & dwq-pfas@waterboards.ca.gov

Original: v5.0.SWAMP IQ_2021.02.23

# Appendix D: Supplemental NMR Extraction Procedures

# Procedure for NMR Sample Preparation

**REAGENTS/SUPPLIES**

1. $D_2O$, NMR Grade, Sigma 1034280100
2. Methanol-D4, NMR grade (MeOH-D4), Sigma 1060280026
3. Gd-DTPA (Diethylenetriaminepentaacetic acid gadolinium(III) Dihydrate ), Sigma 381667-25G
4. Chromium Ac-Ac (Chromium(III) acetylacetonate), Fisher Sci AC192130050
5. Trifluoroethanol (TFE), Sigma T63002-25G
6. NMR Tubes, 7" x 5mm, NMRTubes.com 502-7

**FINAL PROCEDURE FOR AQUEOUS SAMPLES**

1. Prepare 10mL stock solution of 100mM TFE in <u>$D_2O$</u> by dissolving 0.118g TFE into 10mL of $D_2O$.

$$\frac{0.1\ mol\ TFE}{1.0L\ D2O} * \frac{118g\ TFE}{1mol\ TFE} * 0.01\ L = 0.118g\ TFE$$

2. Working Relaxant/Standard Solution - 10mg/mL Gd-DTPA + 1mM TFE in 10mL $D_2O$.
   a. Dissolve 100mg of Gd-DTPA in 5mL D2O
   b. Add 100uL of 100mM TFE ($D_2O$ stock solution)
   c. Add 4.9mL $D_2O$
3. Add 60uL of Relaxant/standard to 540uL of water sample in an NMR tube
4. Mix Well – Final sample to be analyzed will contain 10% $D_2O$, 100uM TFE, and 1.0mg/mL Gd-DTPA

**FINAL PROCEDURE FOR METHANOLIC EXTRACTS**

1. Prepare 10mL stock solution of 100mM TFE in <u>MeOH-D4</u> by dissolving 0.118g TFE into 10mL of MeOH-D4.

$$\frac{0.1\ mol\ TFE}{1.0L\ MeOH - D4} * \frac{118g\ TFE}{1mol\ TFE} * 0.01\ L = 0.118g\ TFE$$

2. Working Relaxant/Standard Solution - 40mg/mL Cr Ac-Ac + 1mM TFE in 10mL MeOH-D$_4$.
    a. Dissolve 400mg of Cr Ac-Ac in 5mL MeOH-D$_4$
    b. Add 100uL of 100mM TFE (MeOH-D4 stock solution)
    c. Add 4.9mL MeOH-D$_4$
3. Add 60uL of Relaxant/standard to 540uL of methanol extract in an NMR tube
4. Mix Well – Final sample to be analyzed will contain 10% MeOH-D$_4$, 100uM TFE, and 4.0mg/mL Cr Ac-Ac.

# ATTACHMENT 2: SUMMARY OF ANALYTICAL FATE STUDY RESULTS

**Table A2.1. Summary of Analytical Fate Study Results**

| Analyte | Abbreviation | CIC | AOF-CIC (Extraction Procedures Modeled After USEPA 1621) | | | EOF-CIC (Extraction Procedure Modeled After USEPA 533) | | | IC-MS/MS (250 -> 8mL) | | | IC-MS/MS (DOD QSM) | LC-MS/MS (DOD QSM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Spike Level* | | *NA* | *1.0 µg/L* | *5.0 µg/L* | *10.0 µg/L* | *1.0 µg/L* | *5.0 µg/L* | *10.0 µg/L* | *0.05 µg/L* | *0.10 µg/L* | *0.4 µg/L* | *0.10 µg/L* | *0.10 µg/L* |
| Sodium Fluoride | NaF⁻ | NP | 0.08% | NP | NP | 0.09% | NP | NP | NP | NP | NP | NP | NP |
| Hexafliuorophosphate | PF₆⁻ | 156% | 3.8% | 17% | 8.6% | 132% | 137% | 99% | 63% | 59% | 70% | 76% | TIA |
| Tetrafluoroborate | BF₄⁻ | 123% | <1.0% | <1.0% | <1.0% | 44% | 15% | 6.6% | 0% | 0% | 60% | 116% | TIA |
| Trifluoroacetic Acid | TFA | 61% | 45% | 0.0% | 0.0% | 33.6% | 6.4% | 3.2% | 74% | 83% | 73% | 96% | 23% |
| Perfluoropropanoic Acid | PFPrA | 105% | 101% | 11% | 5.0% | NP | NP | 68% | 70% | 85% | 77% | 109% | 38% |
| Hexafluoroisopropanol | HFIP | 35% (V) | 22% | 45% | 44% | 3.6% | 0.7% | 2.2% | TIA | TIA | TIA | TIA | TIA |
| 6:2 Fluorotelomer Alcohol | 6:2 FTOH | 5.1% (V) | 101% | 91% | 86% | 9.0% | 6.1% | 5.1% | TIA | TIA | TIA | TIA | TIA |
| 8:2 Fluorotelomer Alcohol | 8:2 FTOH | 0.0% (V) | 82% | 63% | 74% | 3.2% | 2.5% | 2.4% | TIA | TIA | TIA | TIA | TIA |
| Trifluoromethanesulfonic Acid | TFMS | 116% | <1.0% | 2.2% | 3.3% | 106% | 81% | 93% | 85% | 89% | 81% | 128% | 42% |
| Perfluoroethane Sulfonate | PFetS | 106% | 6.5% | NP | NP | NP | NP | 108% | 81% | 79% | 86% | 140% | 64% |
| Perfluoropropyl Sulfonate | PFPrS | 108% | 90% | NP | NP | NP | NP | 100% | 87% | 81% | 88% | 135% | 66% |
| Perfluorobutyl Sulfonate | PFBS | 128% | 109% | NP | NP | NP | NP | NP | NA | NA | NA | 118% | NA |
| Perfluorohexyl Sulfonate | PFHxS | 105% | 105% | NP | NP | NP | NP | NP | TIA | TIA | TIA | NA | NA |
| Bistriflimide | Bistrif | 77% | 106% | 116% | 97% | 87% | 92% | 71% | 85% | 79% | 99% | 115% | TIA |
| Triflinate | TFMSi | 59% | 2.7% | NP | NP | NP | NP | 39% | 72% | 66% | 65% | 113% | NA |
| Trifluoromethane Sulfonamide | TFMSA | 69% | <1.0% | 3.2% | 1.8% | 8.0% | <1.0% | <1.0% | TIA | TIA | TIA | 0% | TIA |
| Perfluorobutane Sulfonamide | PFBSA | 108% (V) | 95% | NP | NP | NP | NP | NP | NP | NP | NP | NP | NP |
| Perfluorohexane Sulfonamide | PFHxSA | 85% (V) | 106% | NP | NP | NP | NP | NP | NP | NP | NP | NP | NP |
| Perfluorodecane Sulfonamide | PFDSA | 53% | 100% | NP | NP | NP | NP | NP | NP | NP | NP | NP | NP |

| Analyte | Abbreviation | CIC | AOF-CIC (Extraction Procedures Modeled After USEPA 1621) | | | EOF-CIC (Extraction Procedure Modeled After USEPA 533) | | | IC-MS/MS (250 -> 8mL) | | | IC-MS/MS (DOD QSM) | LC-MS/MS (DOD QSM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Spike Level* | | *NA* | *1.0 µg/L* | *5.0 µg/L* | *10.0 µg/L* | *1.0 µg/L* | *5.0 µg/L* | *10.0 µg/L* | *0.05 µg/L* | *0.10 µg/L* | *0.4 µg/L* | *0.10 µg/L* | *0.10 µg/L* |
| N-[3-(perfluoro-1-hexanesulfonamido)propan-1-yl]-N,N,N-trimethylammonium | N-TAmP-FHxSA | 107% | 133% | 83% | 83% | 102% | 108% | 105% | TIA | TIA | TIA | TIA | 3.2% |
| N-(3-dimethylaminopropan-1-yl)perfluoro-1-hexanesulfonamide | N-AP-FHxSA | 123% | 127% | 96% | 97% | 14% | 8.2% | 16% | TIA | TIA | TIA | TIA | 7.5% |
| 6:2 Fluorotelomer sulfonamidoalkyl betaine | N-CMAmP-6:2FOSA/ 6:2 FTAB | 108% | 86% | NP | NP | NP | NP | NP | TIA | TIA | TIA | NA | 57% |

Notes: µg/L = microgram per liter, NA = not applicable, NP = not performed, TIA = technique inhibited analysis

**Figure A2.1. Charts illustrating recovery of analytical fate of (a) inorganic fluorine, (b) ultrashort PFCAs, (c) volatile PFCA precursors, (d) ultrashort PFSAs, and (e) ultrashort sulfonamides.**

**(a) Inorganic Fluorine**
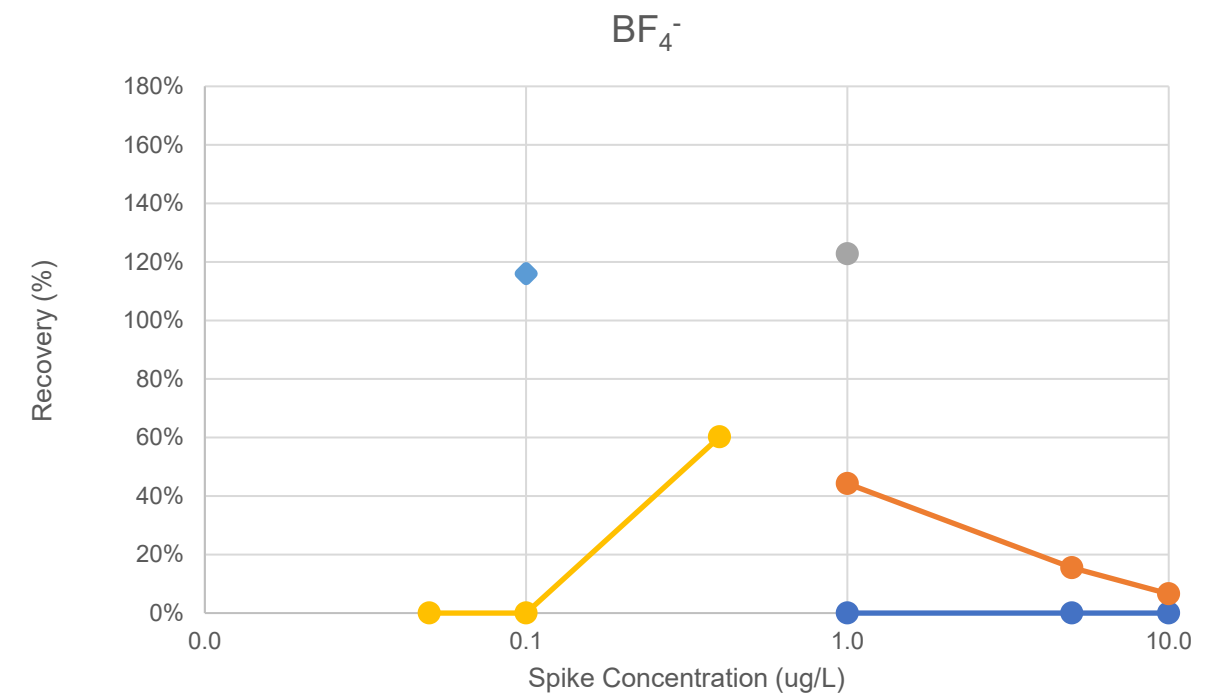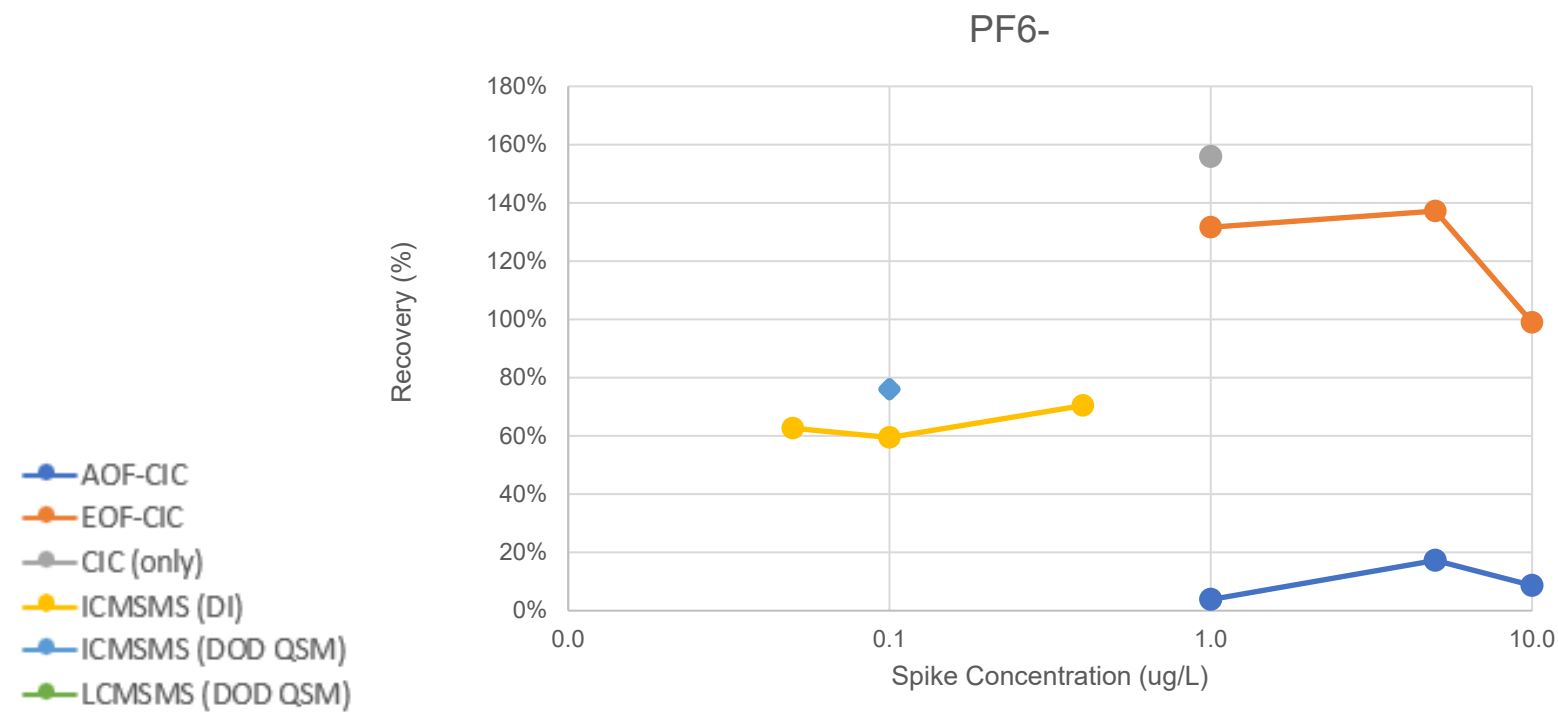


**(b) Ultrashort PFCAs**

**(c) Volatile PFCA Precursors**



HFIP

6:2 FTOH

8:2 FTOH
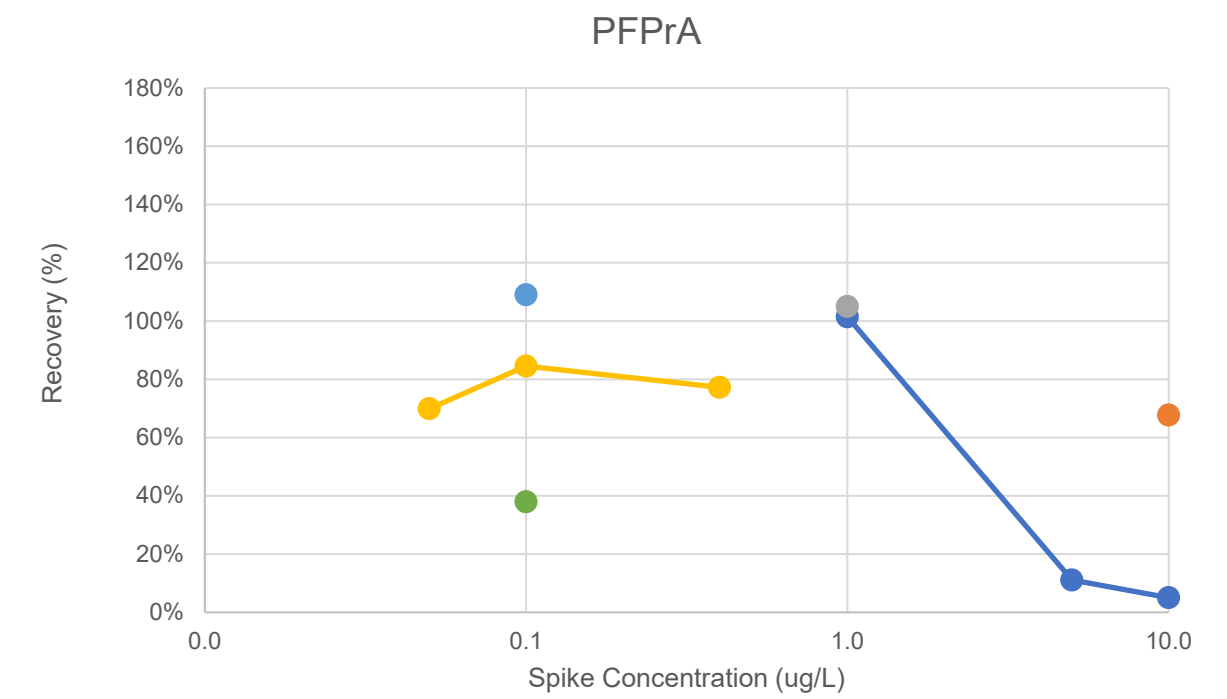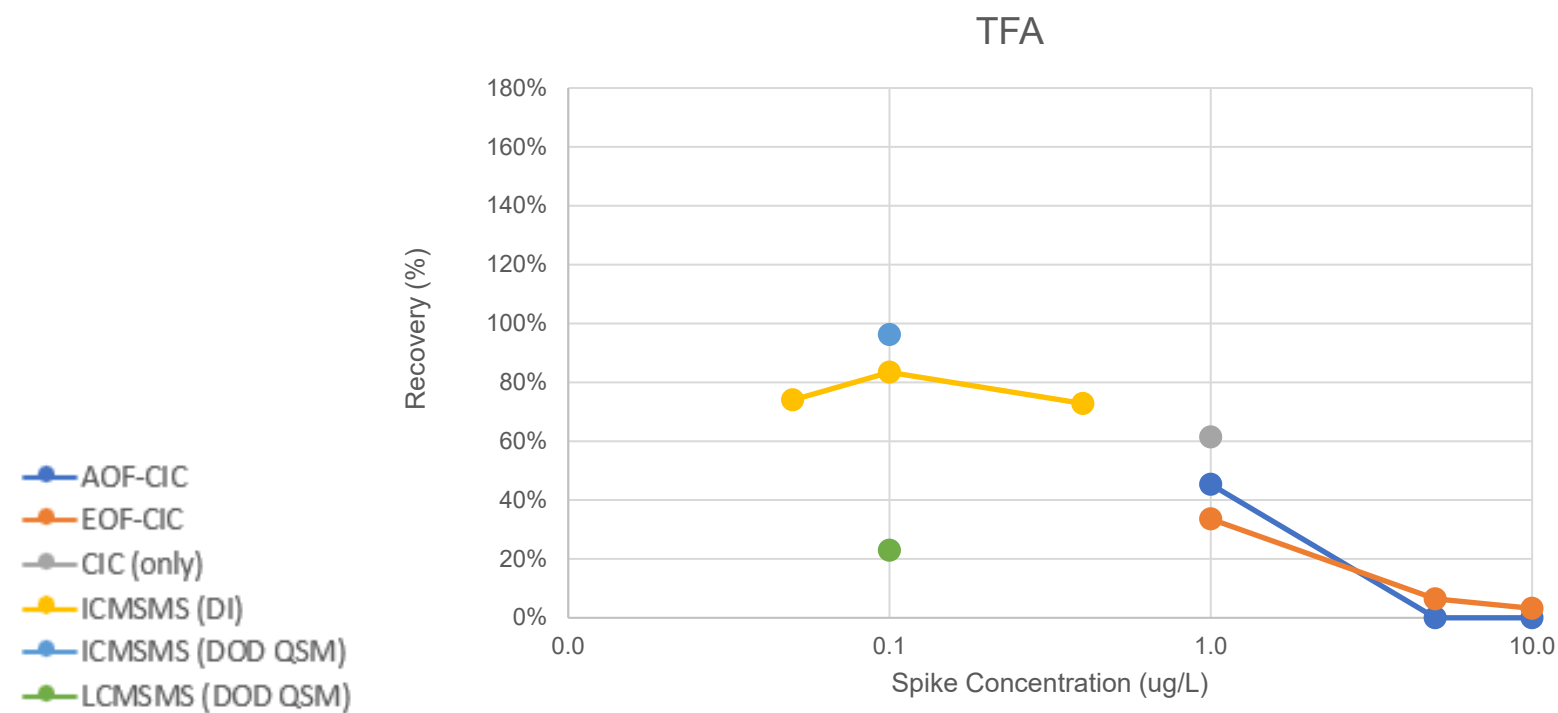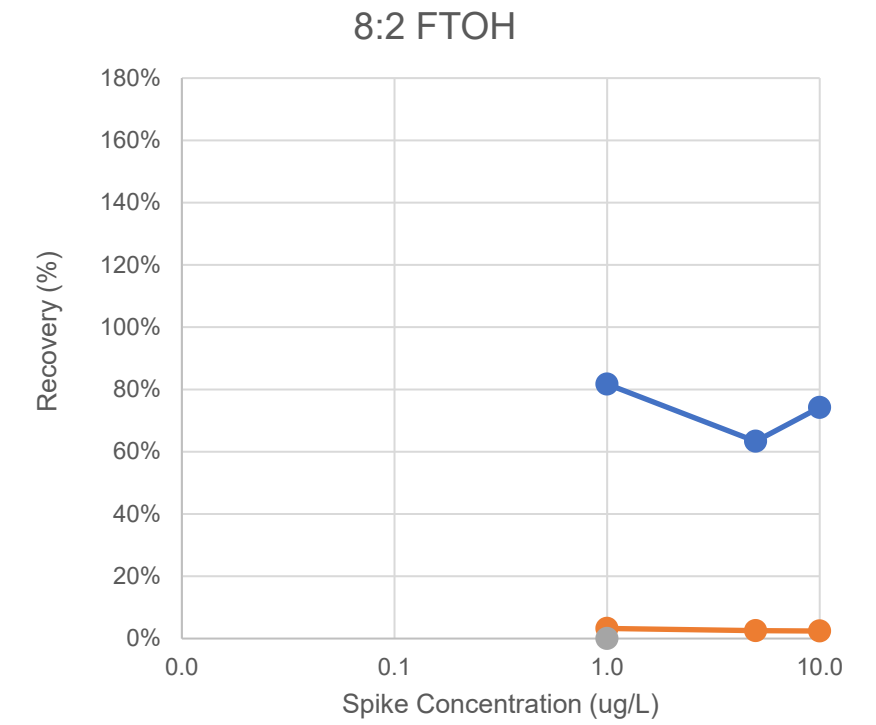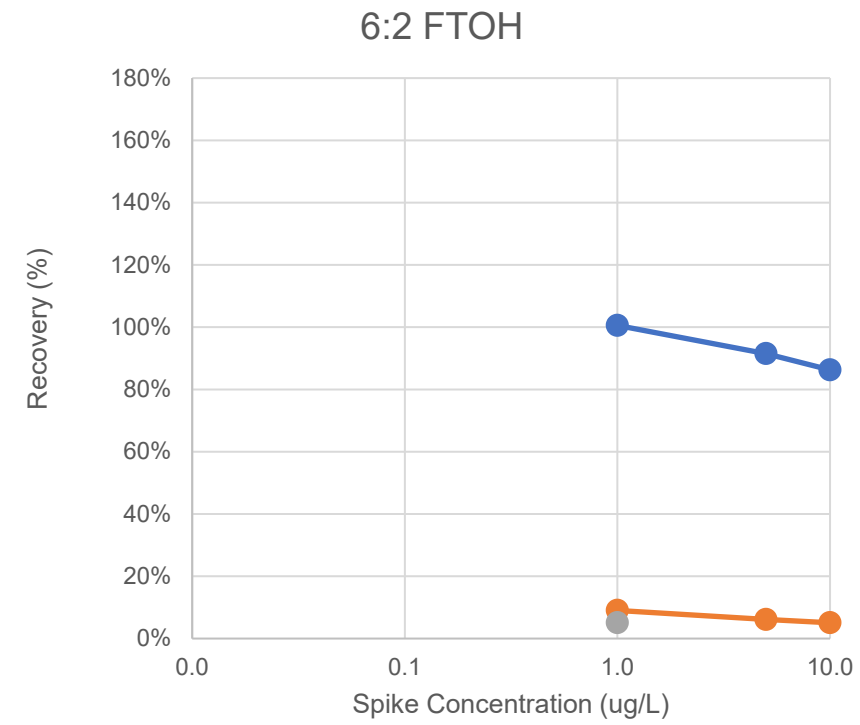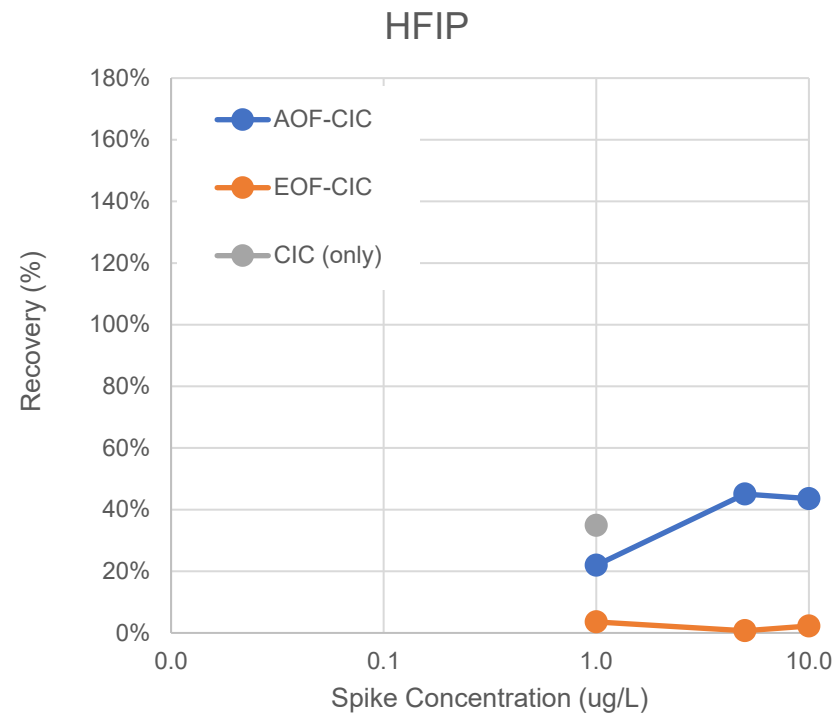
Legend (left side):
- AOF-CIC
- EOF-CIC
- CIC (only)
- ICMSMS (DI)
- ICMSMS (DOD QSM)
- LCMSMS (DOD QSM)

**(d) Ultrashort PFSAs**



PFPrS

TFMS

PFEtS
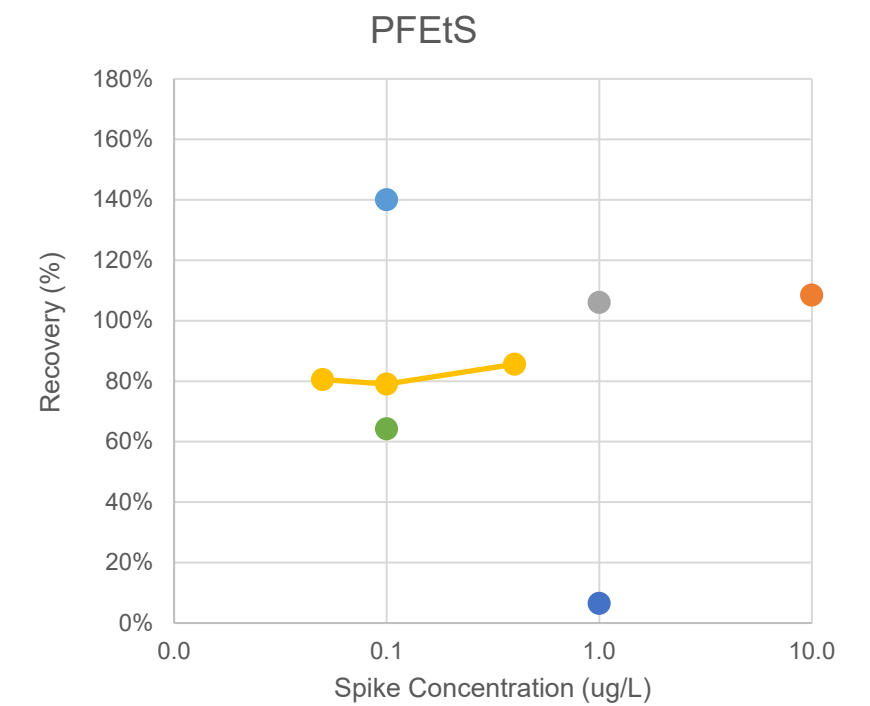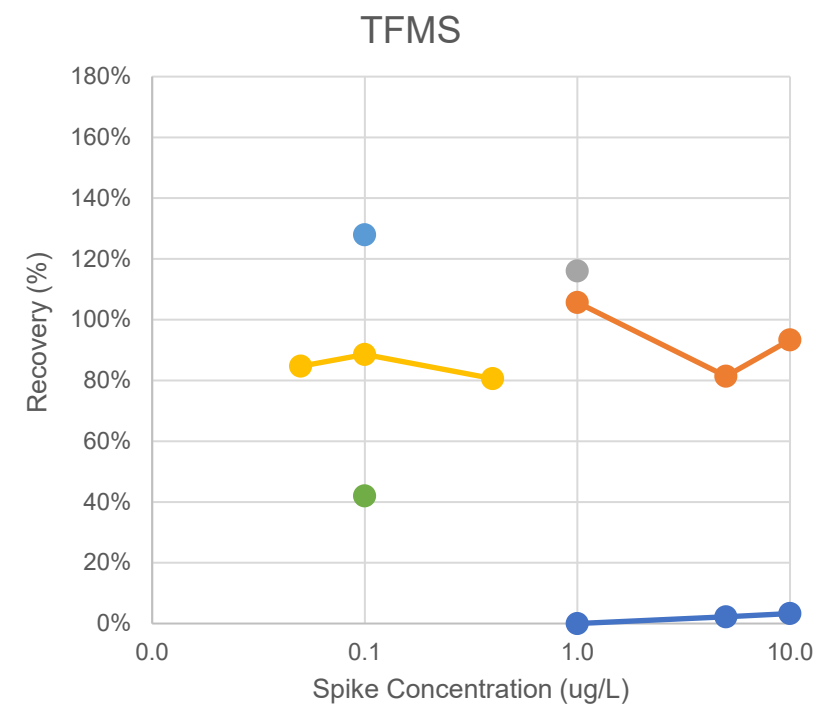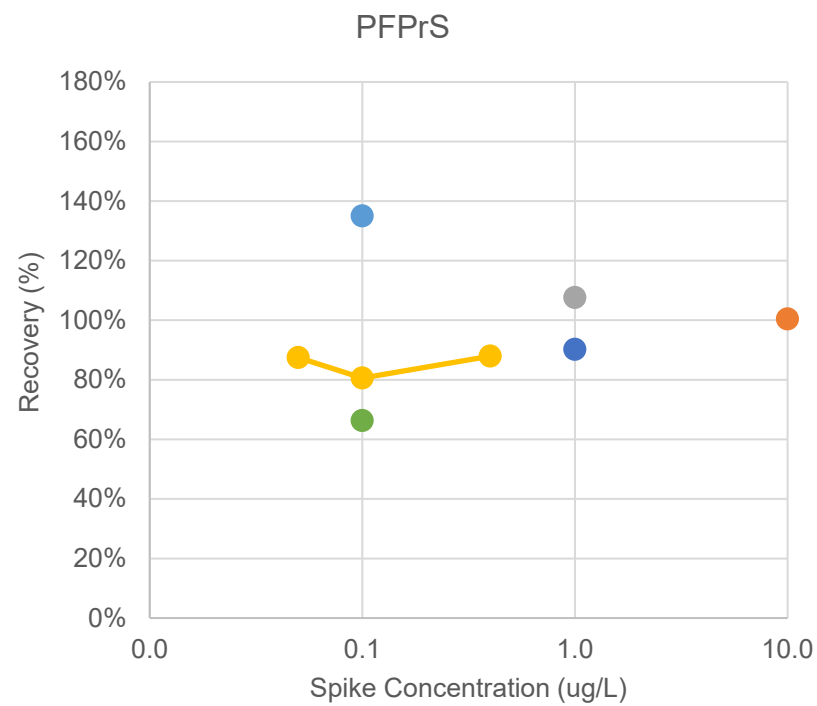
Legend (left side):
- AOF-CIC
- EOF-CIC
- CIC (only)
- ICMSMS (DI)
- ICMSMS (DOD QSM)
- LCMSMS (DOD QSM)

**(e) Ultrashort Sulfonamides**



TFMSA

Bistriflimide

Triflinate (TFMSi)

Legend:
- AOF-CIC
- EOF-CIC
- CIC (only)
- ICMSMS (DI)
- ICMSMS (DOD QSM)
- LCMSMS (DOD QSM)
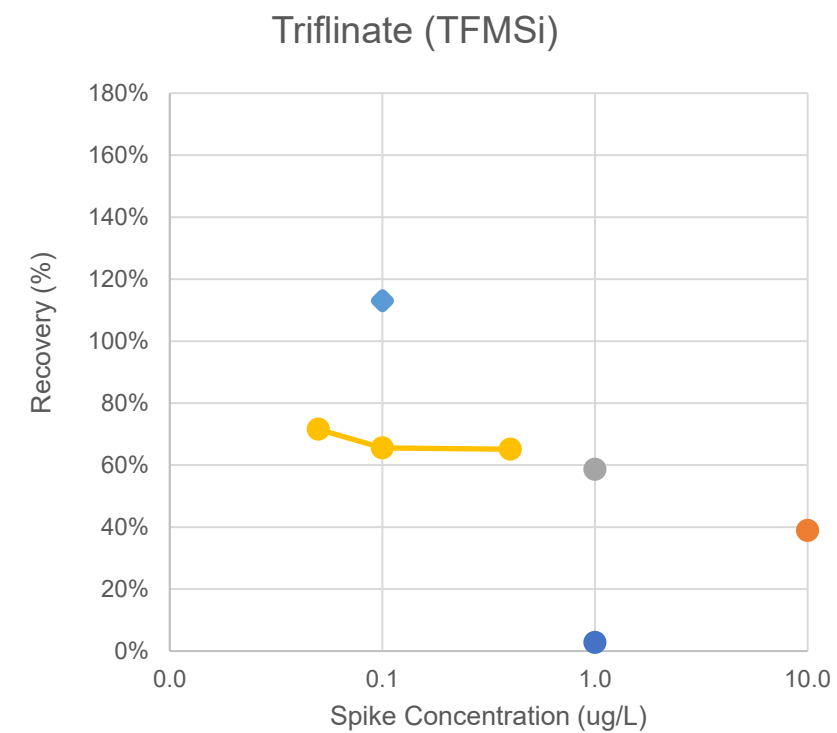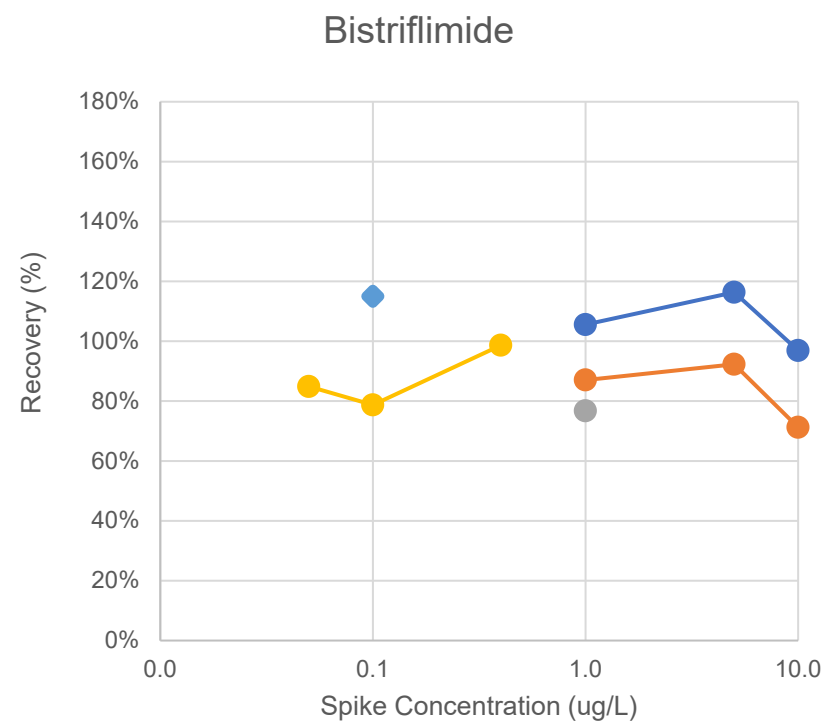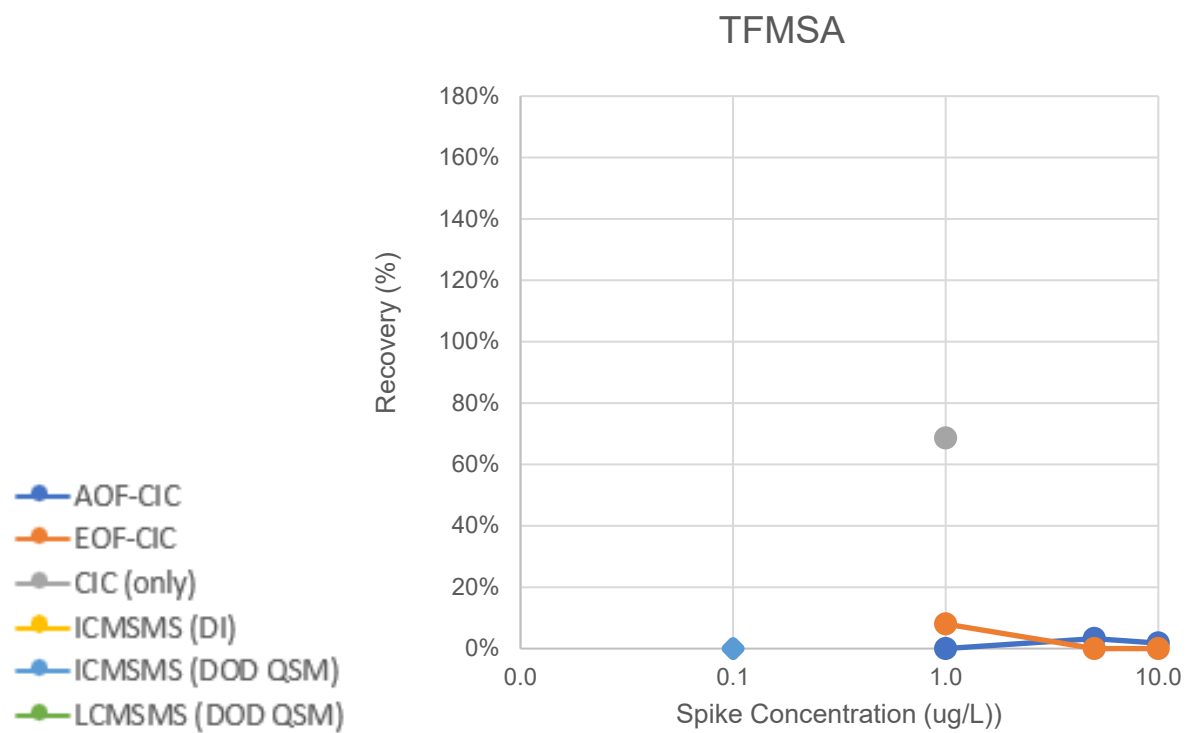
# ATTACHMENT 3: SUMMARY OF PWS WELL STUDY RESULTS

**Figure A3.2. Charts illustrating the results for replicate environmental samples analyzed by AOF-CIC using sample extraction procedures modeled after USEPA 1621, EOF-CIC using sample extraction procedures modeled after USEPA 533, and PIGE using extraction procedures described in the Method Comparison Work Plan. ND = not detected above lab reporting limit.**
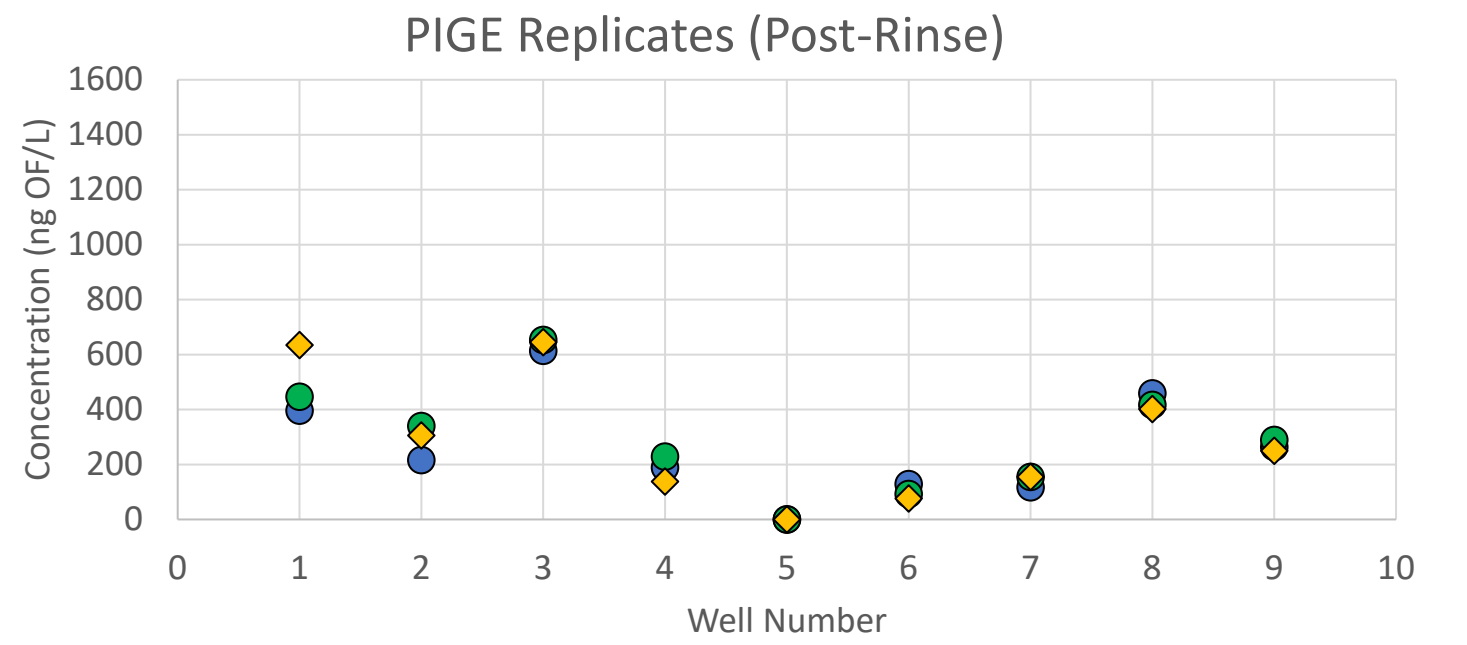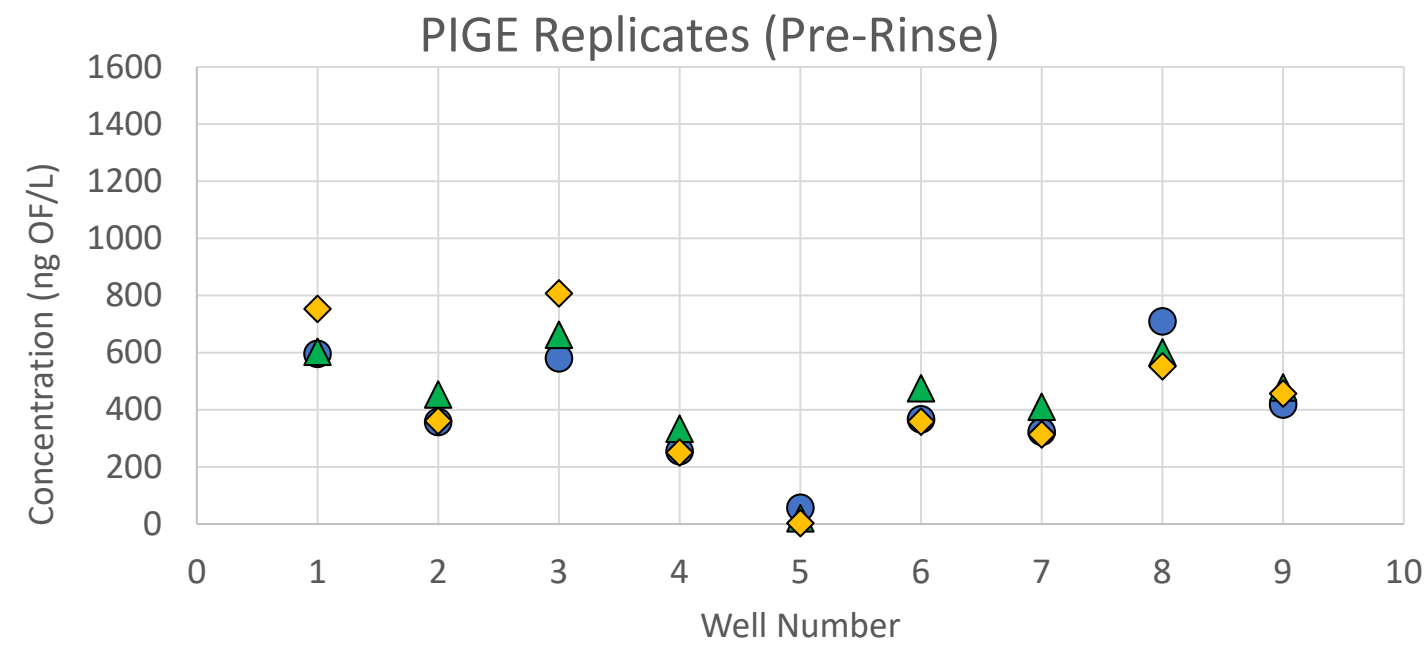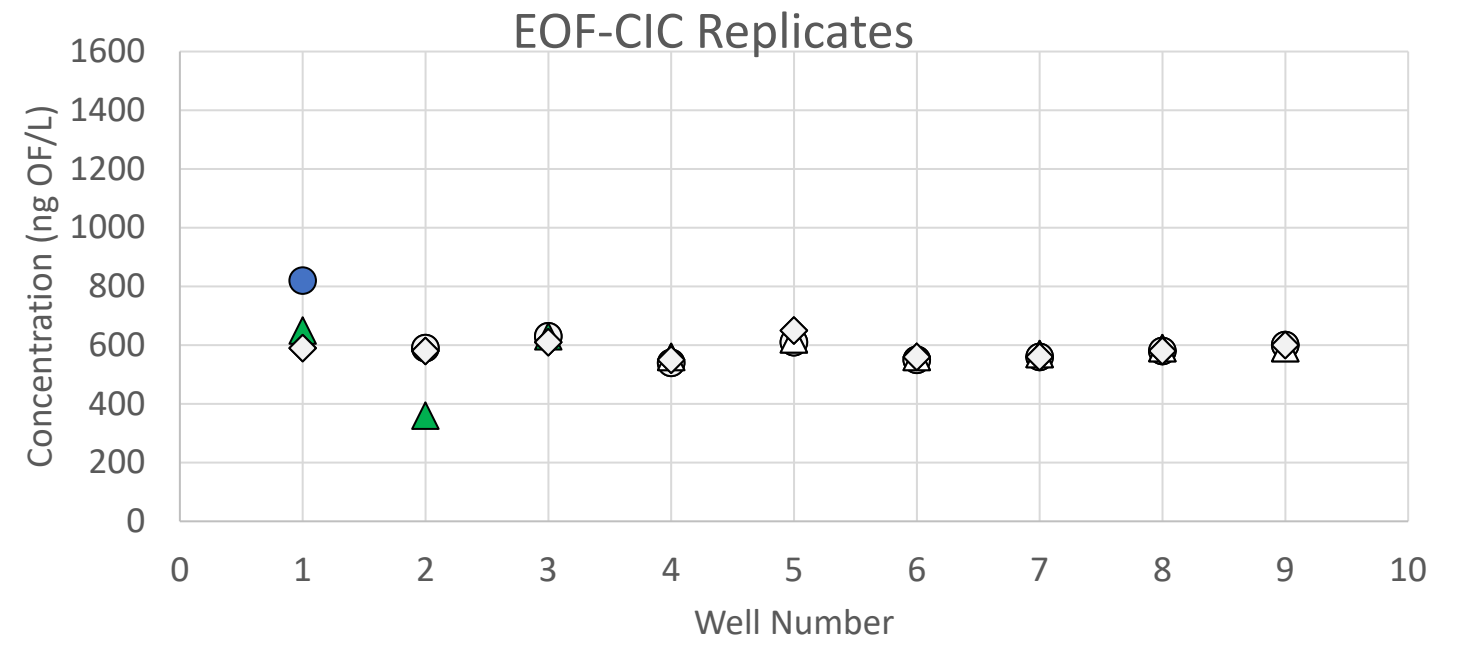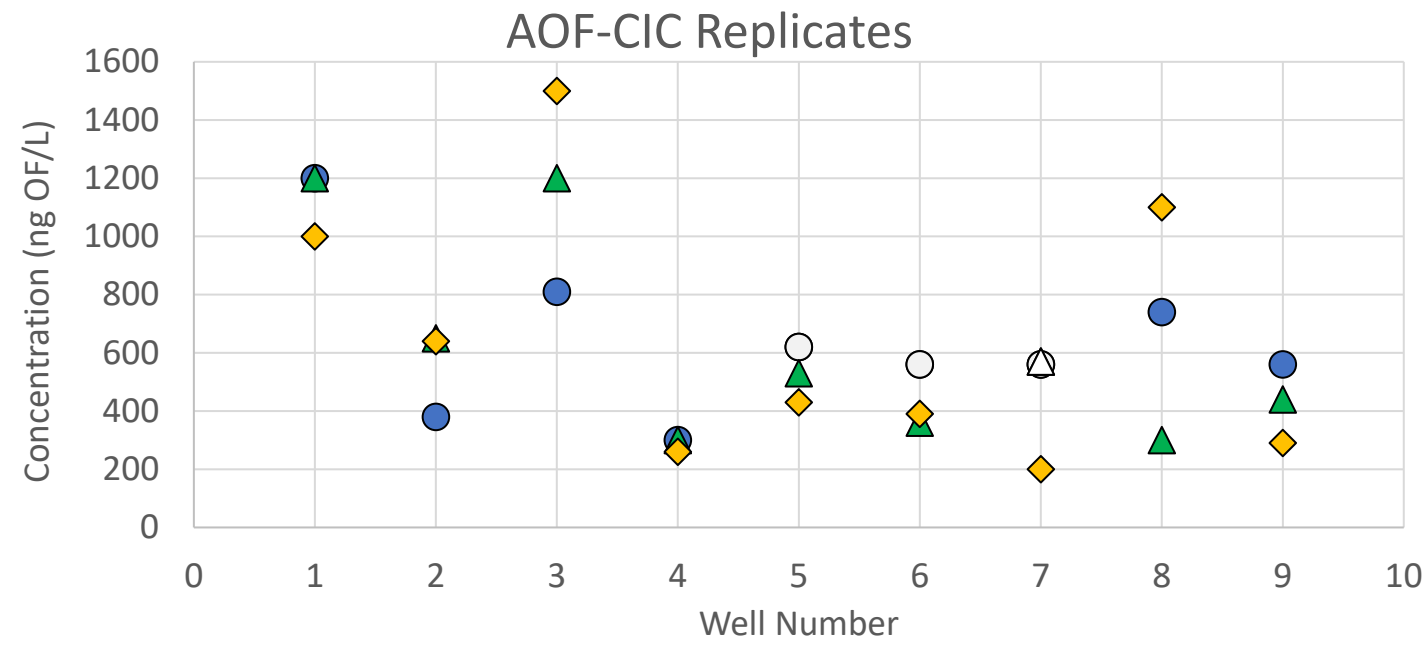
**Table A3.2. Organic fluorine concentrations detected at each sample location for all "total PFAS" methods included in the Method Comparison Study Plan. Concentrations reported in ng OF/L.**

| Analytical Method | Well 1 | Well 2 | Well 3 | Well 4 | Well 5 | Well 6 | Well 7 | Well 8A | Well 9 |
|---|---|---|---|---|---|---|---|---|---|
| | 10/30/2023 | 10/30/2023 | 11/1/2023 | 11/1/2023 | 10/31/2023 | 11/1/2023 | 11/1/2023 | 10/31/2023 | 10/31/2023 |
| AOF-CIC modeled after USEPA 1621* | 1133 | 557 | 1170 | 287 | 527 | 437 | 443 | 713 | 430 |
| EOF-CIC modeled after USEPA 533* | 687 | 510 | 623 | <550 | <627 | <557 | <563 | <583 | <597 |
| PIGE post-rinse* | 492 | 287 | 637 | 185 | 0 | 99 | 142 | 426 | 267 |
| $^{19}$F NMR via USEPA 533M | 682 | 183 | 182 | 7 | 0 | 0 | 53 | 121 | 21 |
| SUM PFAS via LC-MSMS and USEPA 533 | 901 | 385 | 392 | 112 | 9 | 40 | 70 | 311 | 177 |
| SUM PFAS via LC-MSMS and DoD QSM | 950 | 366 | 497 | 148 | 65 | 80 | 110 | 314 | 240 |
| SUM Ultrashort PFAS via IC-MSMS and DoD QSM | 393 | 1087 | 284 | 416 | 194 | 274 | 254 | 543 | 439 |
| Maximum Organic Fluorine Concentration Observed | 1133 | 1087 | 1170 | 416 | 527 | 437 | 443 | 713 | 439 |
| Analytical Method | AOF-CIC | IC-MSMS | AOF-CIC | IC-MSMS | AOF-CIC | AOF-CIC | AOF-CIC | AOF-CIC | IC-MSMS |

**Table A3.3 Summary of minimum, maximum, and median organic fluorine concentrations measured in environmental samples and detection frequency for each method. Note that the detection frequency for AOF-CIC, EOF-CIC, and PIGE results includes an overall summary and summary based on samples analyzed in triplicate (n = 9 | n = 27).**

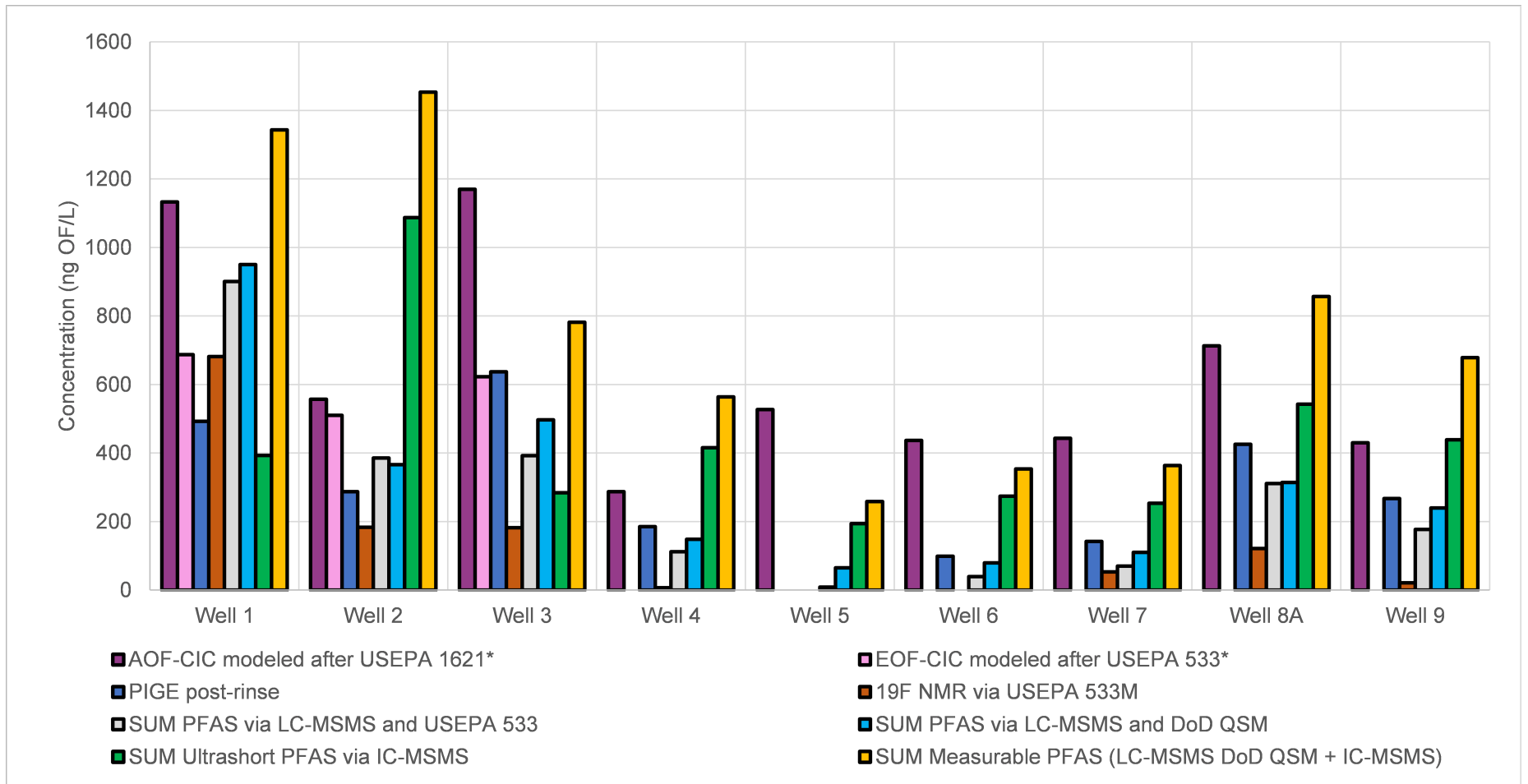| Analytical Method | Minimum Concentration | Maximum Concentration | Median Concentration | Detection Frequency |
|---|---|---|---|---|
| AOF-CIC via USEPA 1621M* | 287 | 1170 | 527 | 100% \| 89% |
| EOF-CIC via USEPA 533M* | 510 | 687 | 583 | 33% \| 15% |
| PIGE post-rinse* | 0 | 637 | 267 | 89% \| 89% |
| $^{19}$F NMR via USEPA 533M | 0 | 682 | 53 | 78% |
| SUM PFAS via LC-MSMS and USEPA 533 | 16 | 901 | 177 | 100% |
| SUM PFAS via LC-MSMS and DoD QSM | 65 | 950 | 240 | 100% |
| SUM Ultrashort PFAS via IC-MSMS and DoD QSM | 194 | 1087 | 393 | 100% |

**Figure A3-2. Total Organic Fluorine Measured Using Various PFAS Analytical Methods. Note: * is used to denote average concentration of triplicate sample results.**