Measuring PFAS: What's happening on Methods?

So much jargon, so little time ☹

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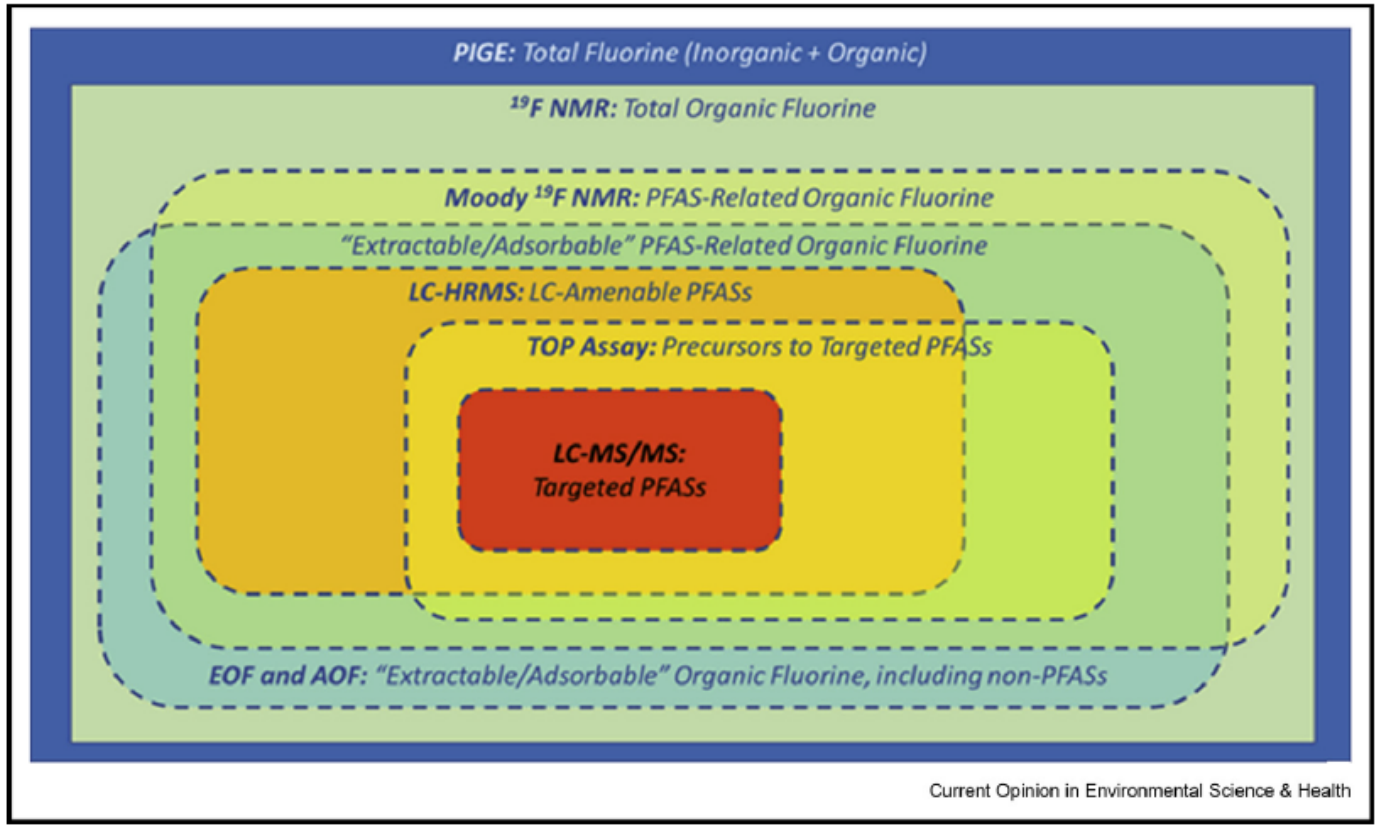
MEASURING PFAS: SELECTIVITY VERSUS INCLUSIVITY

Figure 2



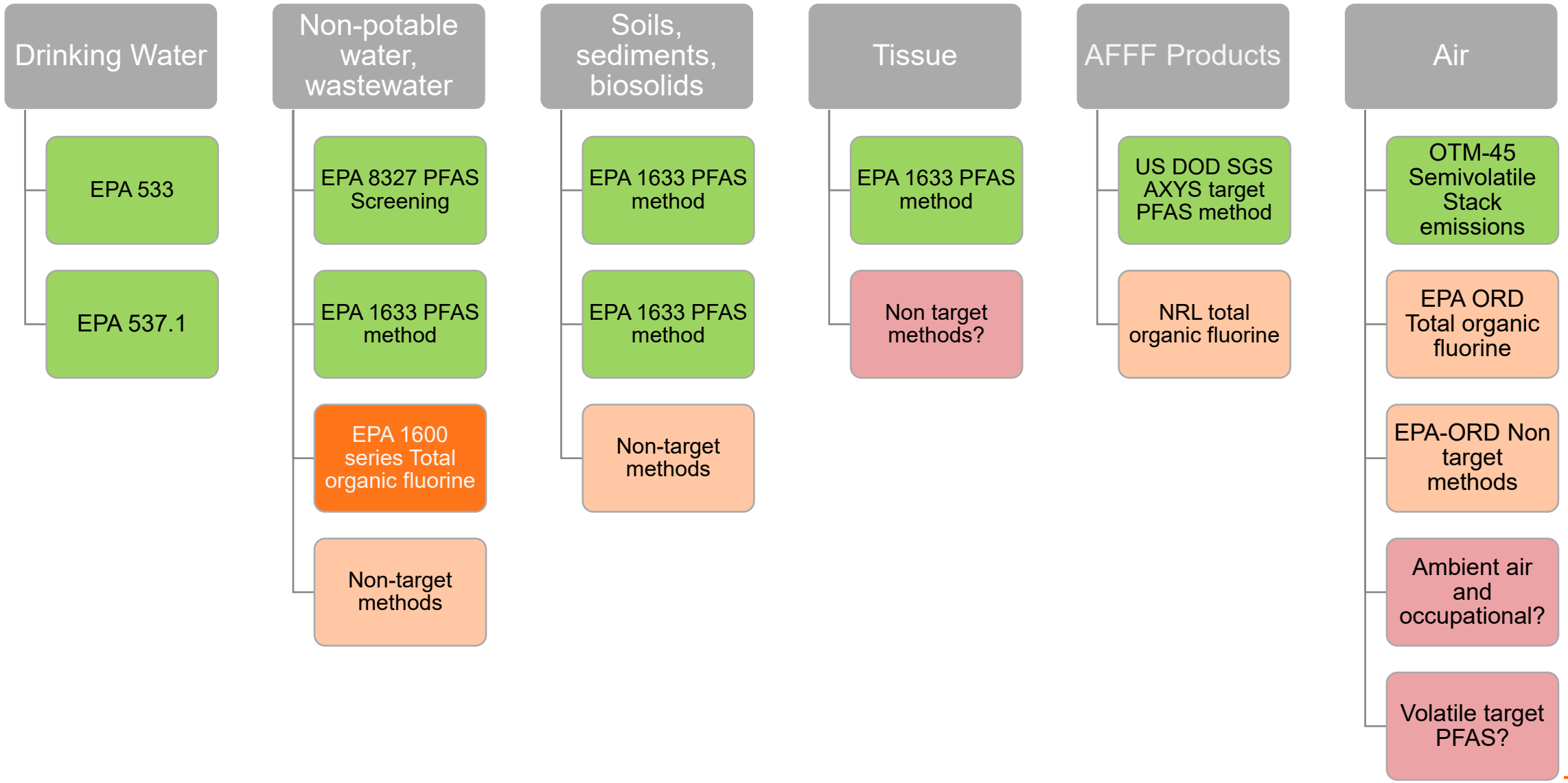
Selectivity and inclusivity associated with total organofluorine methods. Methods for total organofluorine analysis and the fraction of total fluorinated species each method is associated with. Sizes of boxes are meant only to recognize more specific and more general fractions and do not represent the actual relative abundance of each fraction.

McDonough et al. 2019

MEASURING PFAS: THE ONE SLIDE (MOSTLY) SUMMARY

Organic fluorine	Target LC-MS/MS	Total Oxidizable Precursor	Target GC-MS (or MS/MS)	Non-Target Analysis (NTA)
• Reporting of fluorine presence • Extractable? Adsorbable? Total? Preparation defines result • No chemical or structural information • Reporting limits now in the -500 ng F/L range	• Reporting specific PFAS of interest • Most common approach for 2-100 specific PFAS • Multiple EPA methods finished and in progress • Reporting limits in the sub ng/L range	• Add-on to target LC-MS/MS methods • Provides estimates of “precursors” – Subset of PFAS that can be source of perfluorinated alkyl acids • Reporting limits similar to LC-MS/MS • Provides chain length information, data relatively hard to interpret	• Measures volatile and neutral PFAS • Relatively no standardization • Most uncertainty is in sample capture	• Expands world of addressable PFAS by high-resolution mass spectrometry • Provides information “suspects” without standards, true characterization • Multiple applications including source • Relatively inaccessible due to instrument costs and complexity of data

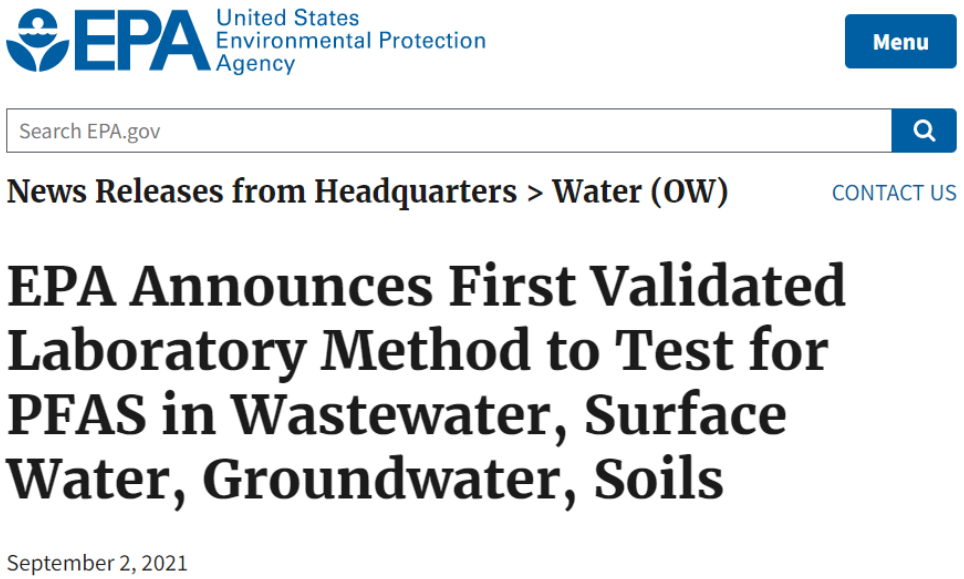
EPA and US Federal Methods Status March 2022



Target PFAS Methods Before September 2021

Method	Targets	Matrices	Isotope Dilution	Weak anion exchange	Multiple Transitions/Ratios	Branched/linear isomer total
EPA 537.1	18 (starts with C6 PFCA)	Drinking water only				
EPA 533	25, but doesn't include 4 EPA 537.1 targets	Drinking water only				
LAB SOP EPA537Mod DoD QSM Table B15 compliant inhouse methods	Not standardized	Drinking water, non-potable water, solids		Only for aqueous		
EPA 8327/3512 (direct injection screening method)	24 (does not include ether PFAS)	Water, wastewater		Data for several analytes not satisfactory		

EPA 1633 STANDARDIZES PFAS METHODS



This draft method can be used in various applications, including National Pollutant Discharge Elimination System (NPDES) permits. The method will support NPDES implementation by providing a consistent PFAS method that has been tested in a wide variety of wastewaters and contains all the required quality control procedures for a Clean Water Act (CWA) method. While the method is not nationally required for CWA compliance monitoring until EPA has promulgated it through rulemaking, it is recommended now for use in individual permits.

Draft Method 1633 complements existing validated methods to test for PFAS in drinking water and non-potable water.

US EPA

ORIGIN OF 1633

Lack of PFAS measurement Standardization flagged as major concern

EPA starts internal development process with 8000 series methods 8327 and 8328

Isotope dilution method 8328 stalls and EPA Office of Water takes over

SGS AXYS selected for validation by EPA and DoD team due to long history of work on isotope dilution mass spectrometry methods for the EPA

EPA 1633 PROGRESS

SGS AXYS Phase1
- Validation and method detection limits in aqueous, solids and tissue

SGS AXYS Phase2
- Analysis of spiked and unspiked samples, 3 each of groundwater, surface water, wastewater, leachate, soil, sediment, biosolid, and tissue
- Holding time studies

Draft 1633 publication
- For review and recommended use in all applications including NPDES

Multi-lab validation
- Starting Q4 2021 and into 2022

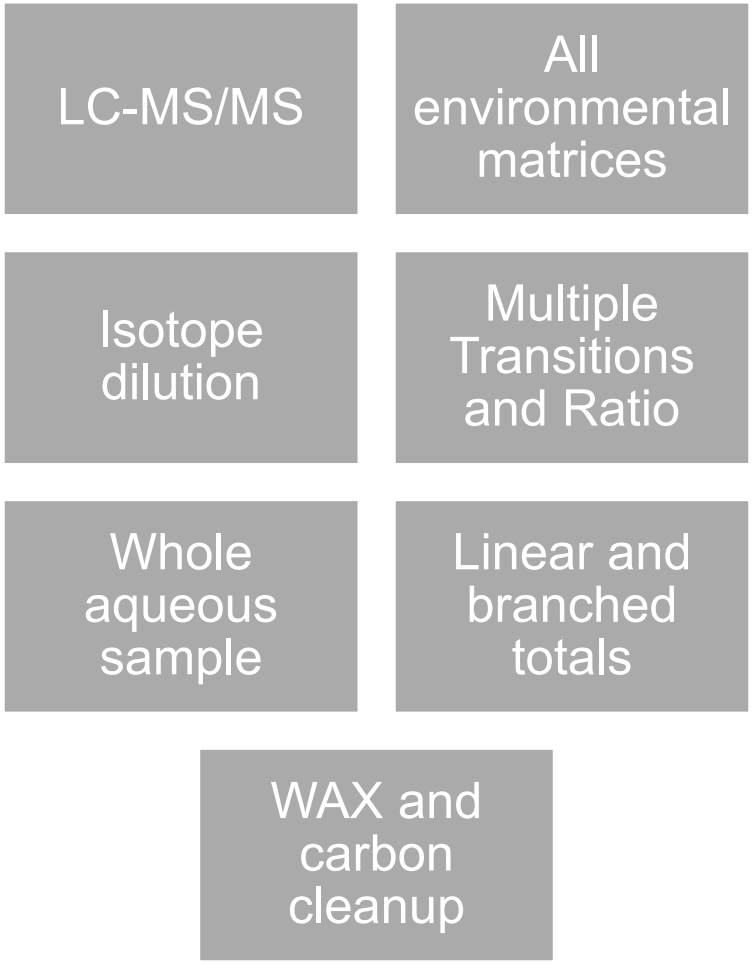
Final validation report and comments period

Promulgation

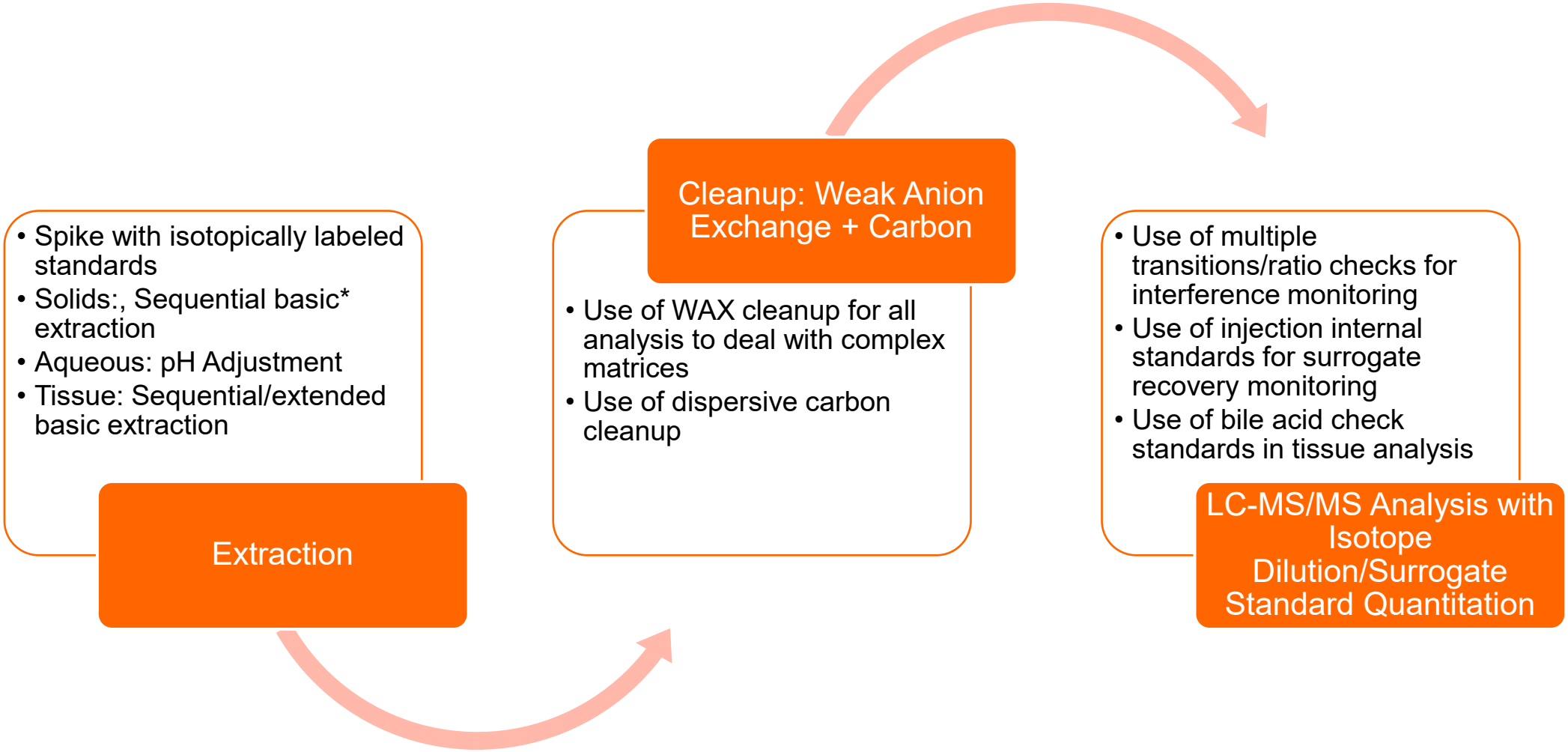
[EPA Announces First Validated Laboratory Method to Test for PFAS in Wastewater, Surface Water, Groundwater, Soils | US EPA]

What is EPA 1633?

- Isotope dilution target LC-MS/MS analytical method
- Standardizes measurement of 40 PFAS in non-potable water, leachates, solids, wastewater treatment plant matrices and tissue
- Typical reporting limit at 1.6 ng/L PFOS/PFOA and upwards (we report to a 0.4 ng/L DL)
- Incorporates all PFAS target analyses best practices building on the DoD QSM 5.4 Table B15



EPA 1633: BEST PRACTICE UNIVERSAL PFAS METHOD



PFAS targets in EPA 1633 (Covers 537.1, 533 and 8327)

Analyte groups
Perfluoroalkyl carboxylates (C_4-C_{14}, C_{16})
Perfluoroalkyl sulfonates (C_4-C_{10}, C_{12})
Fluorotelomer sulfonates (4:2, 6:2 and 8:2)
Fluorotelomer carboxylates (3:3, 5:3 and 7:3)
Perfluorooctane sulfonamides (FOSA, MeFOSA and EtFOSA)
Perfluorooctane sulfonamidoacetic acids (MeFOSAA and EtFOSAA)
Perfluorooctane sulfonamide ethanols (MeFOSE and EtFOSE)
Per- and polyfluoroether carboxylates (HFPO-DA, ADONA, PFMBA, PFMPA, NFDHA)
Ether sulfonates (F-53B, PFEESA)

Target PFAS Methods After September 2021

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LAB SOP EPA537Mod DoD QSM Table B15 compliant inhouse methods	Not standardized	Drinking water, non-potable water, solids		Only for aqueous		
EPA 1633 Draft	40: Includes all EPA 537.1 and 533 targets, more precursors and some neutral PFAS	Water, wastewater, leachate, soils, biosolids, tissue and more		For all matrices		
EPA 8327/3512 (direct injection screening method)	24 (does not include ether PFAS)	Water, wastewater		Data for several analytes not satisfactory		

EPA 1633 Draft differences from a EPA537 Mod method

Scope and Application

- Standard list of 40 targets
- Standard procedures for ALL environmental matrices including WWTP matrices and leachates, fish tissue

Sample sizes and storage

- Default aqueous sample size 500 mL as opposed to 250 mL with 533/537
- Freezing of all samples at ≤ -20 ºC upon receipt (Refrigeration also acceptable for shorter lists/shorter time)

Sample/Extract Processing

- Use of weak anion exchange mandated for ALL samples, not just aqueous
- Use of dispersive carbon mandated for all samples through validation. Labs will revalidate carbon columns as necessary post validation. But carbon is mandatory

EPA 1633 Draft differences from a EPA537 Mod method

Instrumental Analysis

- Use of non-extracted internal standard (NIS) for measuring recovery of surrogates
- List of PFAS with branched isomers includes PFOA, PFNA, PFOSA, NMeFOSA, NEtFOSA, NEtFOSE, and NMeFOSE (Qualitative) and PFOS, PFHxS, NMeFOSAA, and NEtFOSAA (Quantitative)
- Regular use of bile acids to confirm separation of PFOS from taurine-conjugated bile acids prior to tissue analysis

QA/QC

- Initial specifications established from single lab validation different from typical DoD QSM specs (50-150)
- Labs will generate internal specifications. “Floor” needs clarification
- Extra LCS at 2x LOQ level (LLOPR)

METHOD FLEXIBILITY AND PROSPECTS FOR CHANGE?

9.1.2 In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options to improve separations or lower the costs of measurements. These options include alternative extraction, concentration, and cleanup procedures, and changes in sample volumes, columns, and detectors. Alternative determinative techniques and changes that degrade method performance, are *not* allowed without prior review and approval.

- Post multi-laboratory validation, labs are likely to align existing procedures under the EPA 1633 performance-based modifications as much as practicable
- EPA 1633 lists a number of non-changeable aspects such as isotope dilution, use of NIS, performance specifications, MRM – MS/MS, WAX and carbon cleanup
- Labs start with method specifications and generate in-house limits
- Depending on results from laboratories through multi-lab validation and comments period, minor changes are expected

1633 DRAFT CORRECTIONS TO NOTE: STORAGE TEMP

Maintain solid samples protected from light (in HDPE containers) at 0 - 6 ºC from the time of collection until receipt at the laboratory. The laboratory must confirm that the sample temperature is 0 - 6 ºC upon receipt. Once received by the laboratory, the samples may be stored at ≤ -20 ºC, or at 0 - 6 ºC, until sample preparation. However, the allowable holding time for samples depends on the storage temperature, as described in Section 8.5.

Revised Errata Sheet for Draft Method 1633 (epa.gov)

Matrix	Storage Temp	Notes
Aqueous	90 days at -≤ -20ºC, 28 at 0 - 6ºC	CAVEAT: Perfluorooctane sulfonamide PFAS subject to interconversion after 7 days at 0-6
Solids and tissue	90 days either at 0-6ºC or ≤ -20 ºC	NFDHA stability is an issue
Biosolids	90 days either at 0-6ºC or ≤ -20 ºC	Frozen preferred due to odor issues
Extracts	90 days at 0 - 4ºC	Elevation of ether sulfonates after 28 days, issues with NFDHA

EPA RELEASES SINGLE LAB VALIDATION REPORT

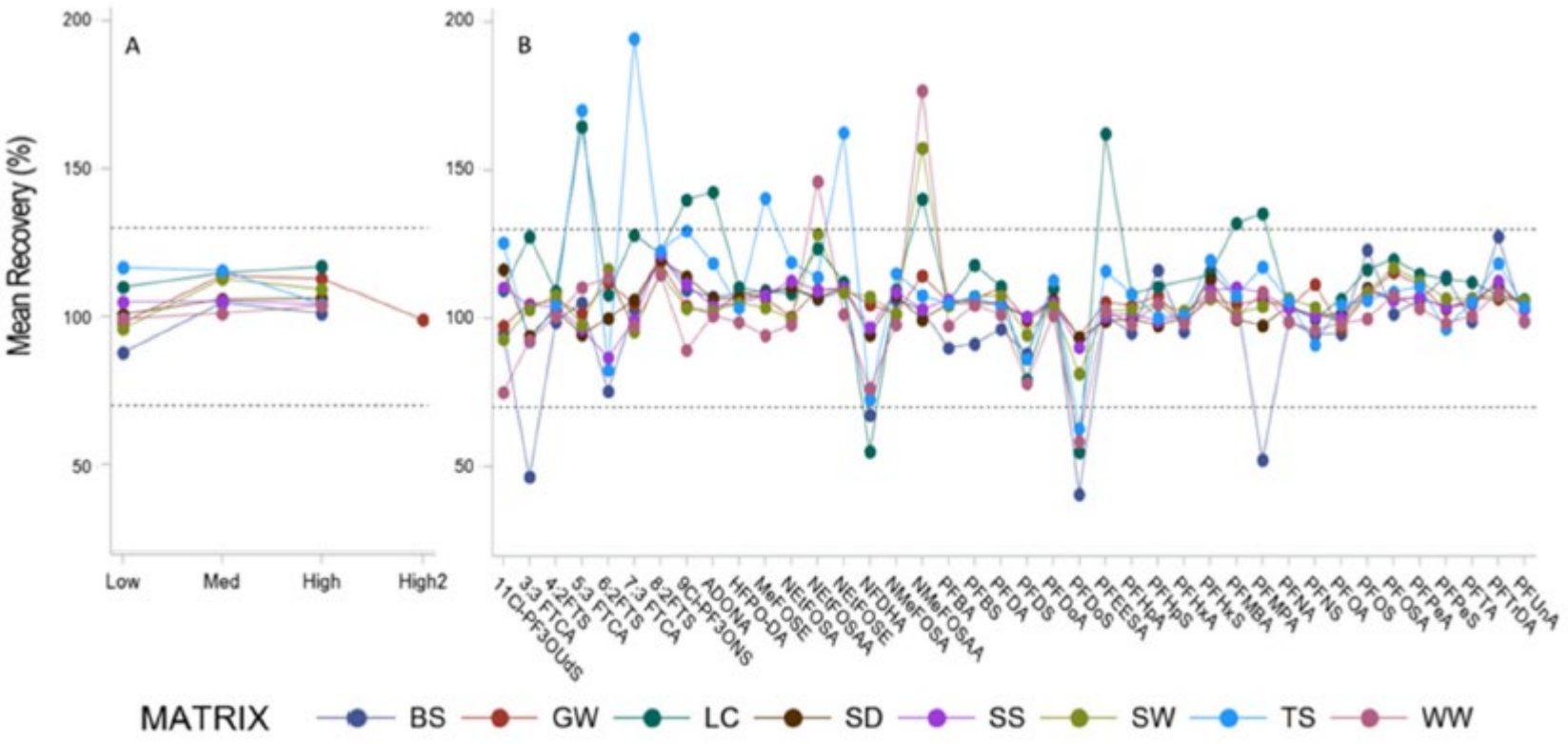


Figure ES-1. Accuracy Analysis

- “The vast majority of the PFAS method analyte and matrix combinations (>93%) were within the accuracy and precision control limits“
- "Given the success of the method in this SLVS, the EPA published the method as draft EPA Method 1633 in September 2021"

EPA.Gov

MDLS ACHIEVED BY THE SINGLE LAB VALIDATION

Table 6-1. Aqueous Method Detection Limit Study Results

Target Analyte	MDL_S (ng/L)	MDL_b (ng/L)	Initial MDL (ng/L)
PFBA	0.330	0.249	0.330
PFPeA	0.184	0.196	0.196
PFHxA	0.318	0.118	0.318
PFHpA	0.221	0.146	0.221
PFOA	0.211	0.302	0.302
PFNA	0.221	0.082	0.221
PFDA	0.333	0.084	0.333
PFUnA	0.264	0.104	0.264
PFDoA	0.379	0.073	0.379
PFTrDA	0.238	0.137	0.238
PFTeDA	0.264	0.228	0.264
PFBS	0.245	0.048	0.245
PFPeS	0.204	0.011	0.204
PFHxS	0.217	0.118	0.217
PFHpS	0.137	0.008	0.137
PFOS	0.327	0.118	0.327
PFNS	0.303	0.025	0.303
PFDS	0.334	0.039	0.334
PFDoS	0.179	0.052	0.179
4:2FTS	2.281	0.056	2.281
6:2FTS	3.973	0.848	3.973
8:2FTS	1.566	0.036	1.566
PFOSA	0.227	0.200	0.227
NMeFOSA	0.196	0.045	0.196
NEtFOSA	0.585	0.102	0.585
NMeFOSAA	0.586	0.029	0.586
NEtFOSAA	0.324	0.000	0.328
NMeFOSE	1.191	1.072	1.191
NEtFOSE	0.914	1.022	0.914
HFPO-DA	0.406	0.000	0.406
ADONA	0.779	0.045	0.779
PFEESA	0.137	0.000	0.137
PFMPA	0.177	0.028	0.177
PFMBA	0.117	0.026	0.117
NFDHA	1.384	0.000	1.384
9Cl-PF3ONS	0.871	0.037	0.871
11Cl-PF3OUdS	0.819	0.086	0.819
3:3FTCA	0.721	0.000	0.721
5:3FTCA	5.066	2.913	5.066
7:3FTCA	5.942	1.221	5.942

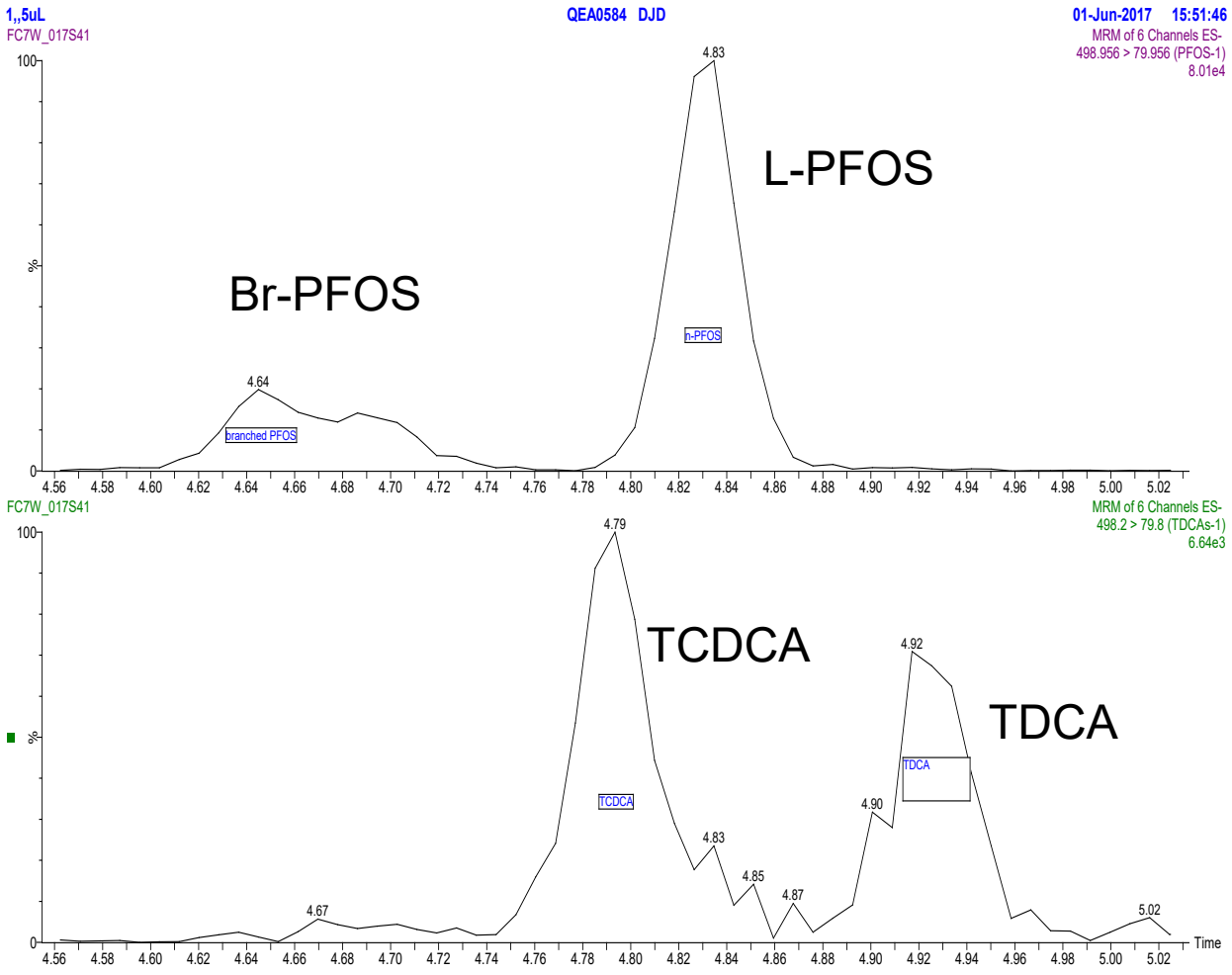
1633 DRAFT CORRECTIONS TO NOTE: DILUTIONS

EIS cannot drop below 5% in the diluted sample. So, if original recovery was 50%, no more than a 10X dilution is allowed

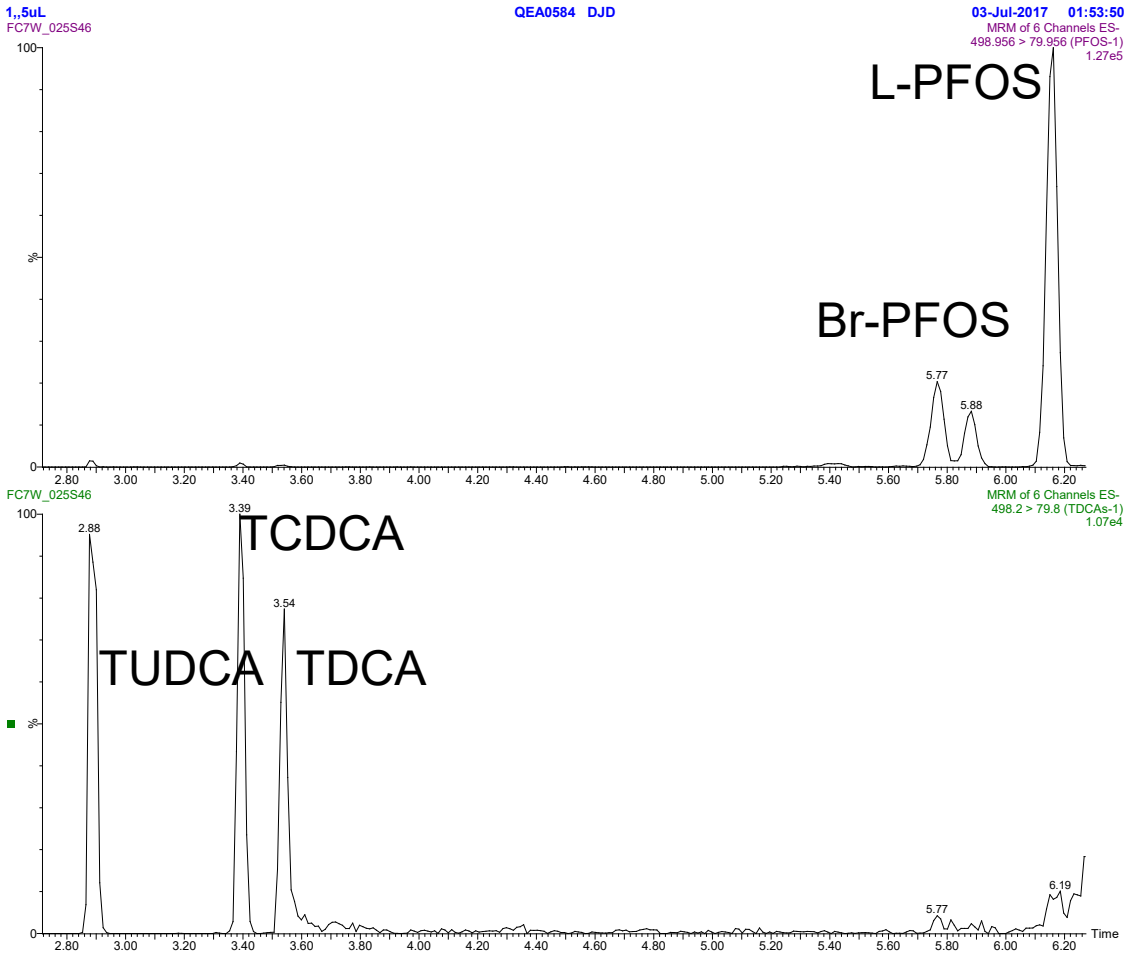
If dilution more than 10X is indicated, repeat with a smaller aliquot of sample

1633 DRAFT CORRECTIONS TO NOTE: BILE ACIDS

Methanol



Acetonitrile



[Revised Errata Sheet for Draft Method 1633 (epa.gov)]

THE DOD QSM 5.4 TABLE B-24

The DoD Environmental Data Quality Workgroup has determined that draft method 1633 meets the precision, accuracy, and limits of quantitation needed to support sound decision-making. All new contracts and task orders after December 31, 2021, shall require the use of Draft Method 1633 for the analysis for PFAS in matrices other than drinking water using a laboratory accredited to the method/matrix/analyte by the DoD Environmental Laboratory Accreditation program (ELAP). All existing projects are encouraged to use Draft Method 1633 for PFAS analysis in matrices other than drinking water when ELAP-accredited laboratories become available.

DoD Memorandum dated 07-Dec-2021

- Major change announced by the DoD that accelerates the use of EPA 1633 draft starting Q1 of 2022

Parting thoughts

- Target PFAS methods are more standardized than ever, but there are still differences to be seen between labs, 1633 may fix that, but PFAS measurement has many variables, so quality still matters
- Organic fluorine methods are next on the list for standardization
- TOP will remain a niche application useful in certain circumstances
- Non-Target Analysis has a long way to go on standardization, especially on data analysis and interpretation.