Automating Solid Phase Extraction: A Game Changer for Efficient PFAS Sample Preparation in Wastewater

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Purpose

- Sample Preparation Workflows and tools for EPA method 1633
- New Fluidics Design
- EPA Method 1633 results

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Target Analytes

Method	533	537.1	1633	ISO21675
PFBA	x		x	x
PFPeA	x		x	x
PFHxA	x	x	x	x
PFHpA	x	x	x	x
PFOA	x	x	x	x
PFNA	x	x	x	x
PFDA	x	x	x	x
PFUnA	x	x	x	x
PFDoA	x	x	x	x
PFTrDA		x	x	x
PFTeDA		x	x	x
PFBS	x	x	x	x
PFPeS	x		x	
PFHxS	x	x	x	x

Target Analytes

Method	533	537.1	1633	ISO21675
PFHpS	x		x	x
PFOS	x	x	x	x
PFNS			x	
PFDS			x	x
PFDoS			x	
4:2FTS	x		x	
6:2FTS	x		x	x
8:2FTS	x		x	x
PFOSA			x	x
NMeFOSA			x	x
NEtFOSA			x	x
NMeFOSAA		x	x	x
NEtFOSAA		x	x	x
NMeFOSE			x	

Target Analytes

Method	533	537.1	1633	ISO21675
NEtFOSE			x	
HFPO-DA	x	x	x	x
ADONA	x	x	x	x
PFMPA	x		x	
PFMBA	x		x	
NFDHA	x		x	
9Cl-PF3ONS	x	x	x	x
11Cl-PF3OUdS	x	x	x	
PFEESA	x		x	
3:3 FTCA			x	
5:3 FTCA			x	
7:3 FTCA			x	
PFOcDA				x
PFHxDA				x
8:2 FTUCA				x
8:2 diPAP				x

Optimizing the PFAS Analysis Workflow

- Automate the Sample Prep Workflow
  - Automate the Solid Phase Extraction Step
  - Automate the Concentration/Evaporation Step

- Automated SPE extractions and Concentration
  - Decreases Human Error
  - Reduces Outside contamination and background
  - Decreases Solvent Usage
  - Reduces Labor

- Use SPE solutions to deliver consistent, reproducible results
- Different configurations to handle Matrix type and Budget
- No Teflon Components

Comparison of Manual SPE vs. Automated SPE Methods

Manual	Automated
Manually Separate Waste	Separates Aqueous and Organic Waste
<10 mls solvent evaporate	<10 mls solvent to evaporate
Run times are ~ 30 to 90 minutes	Run times are ~20 to 50 minutes or less
Technician Time 25 minutes	Technician time 5 minutes
Physical transfer and Concentration steps	Automatic and Direct to Concentratio delivery and completion
Concentration steps 70 to 200 minutes	Concentration step 70 minutes ready for injection

Critical Factors

- Closed System
- Ability to load samples by vacuum or positive pressure consistently.
- Handle Difficult Matrices
- Ability to dry cartridges by vacuum and positive Nitrogen gas pressure.
- Easily handle various cartridge designs and sizes without cumbersome modifications.
- Easy, Simple Sample delivery
- Bottle Rinse

Automated Solid Phase Extraction front end for LC/MS

EconoTrace® PFC

TurboTrace® PFC

TurboTrace®
Parallel
Sequential

LC/MS

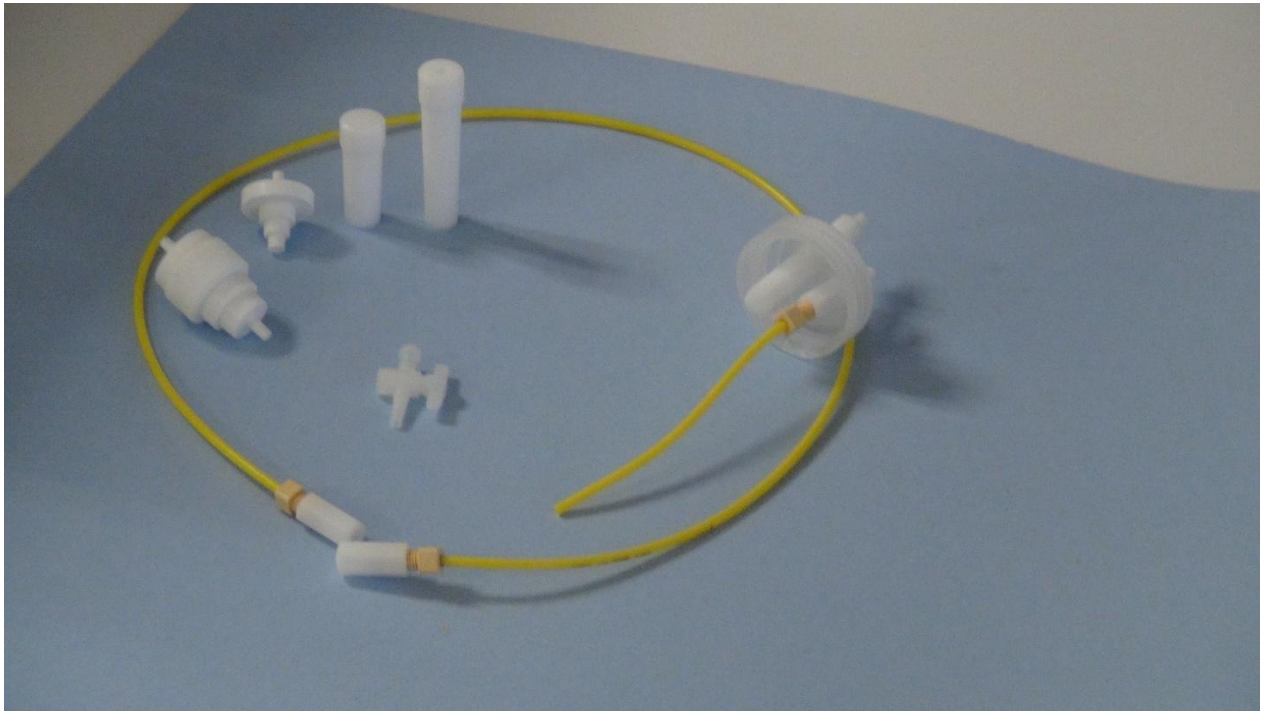
System Components

No Teflon

Tubing - High Density Polyethylene

Fittings – Delrin

Cartridge Adapters – Medical Grade Polypropylene



Can this Handle Dirty Samples?

Typical Cartridge can have problems!

- **6ml cartridge**
  - **Doesn't do well**
  - **Frit Surface Area is to small**

Yes, A Cartridge will work

- **25ml cartridge**
  - **Does well**
  - **3X the Frit Surface Area**

FMS, Inc. Plastic Filtration Wool

Glass/Plastic Wool

- Irregular random stranding
- Slows Particles to the Uniform Frit
- Prevents Clogging

Prepping the 6ml Cartridge with Plastic Filtration Wool

6ml Cartridge with Plastic Wool

- Take a little and push it into the barrel of the syringe until it touches the cartridge Frit

- The Sample will not clog, it will take longer to process

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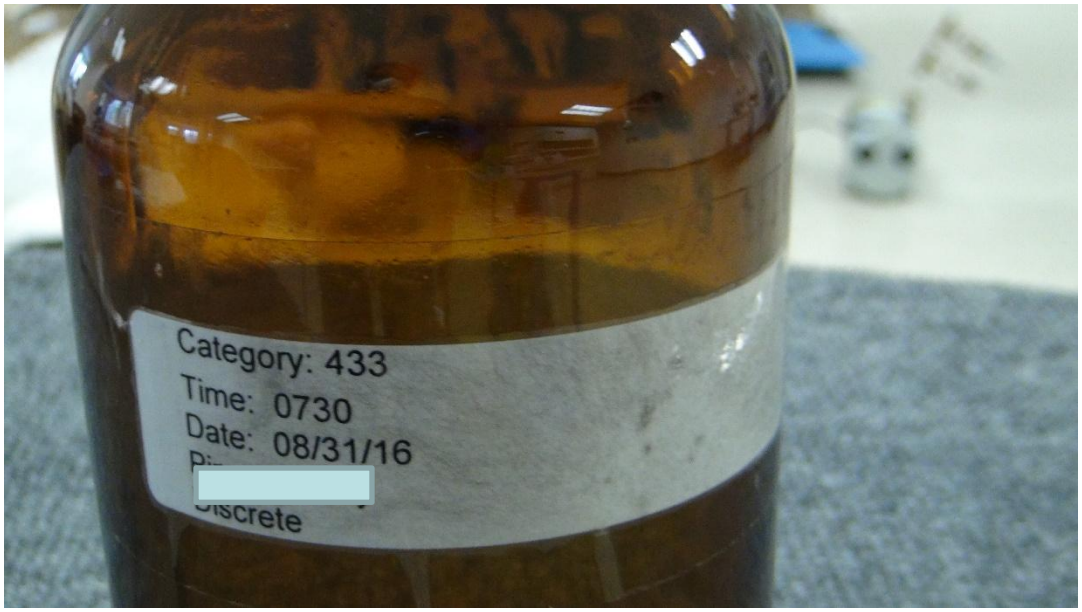
Sample Bottle Filter

Dirty Sample from a Customer



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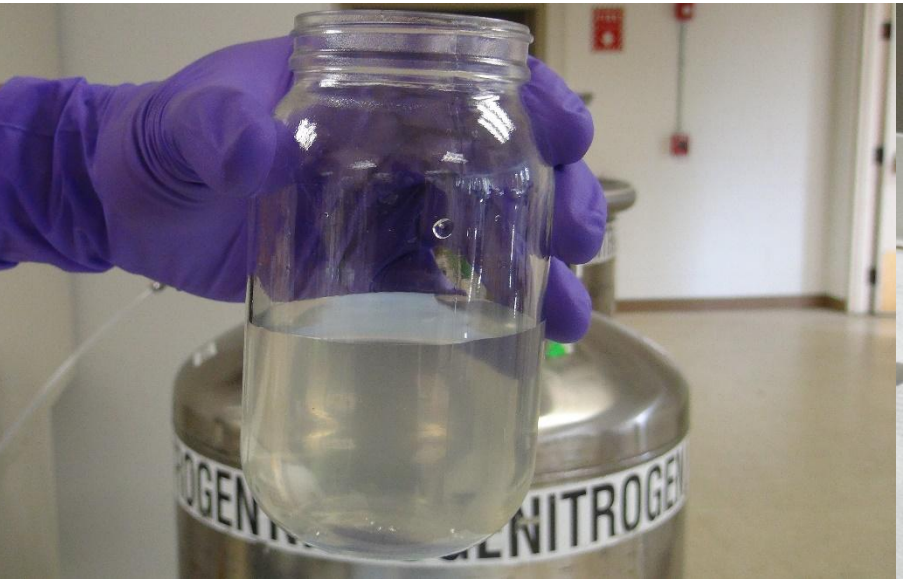
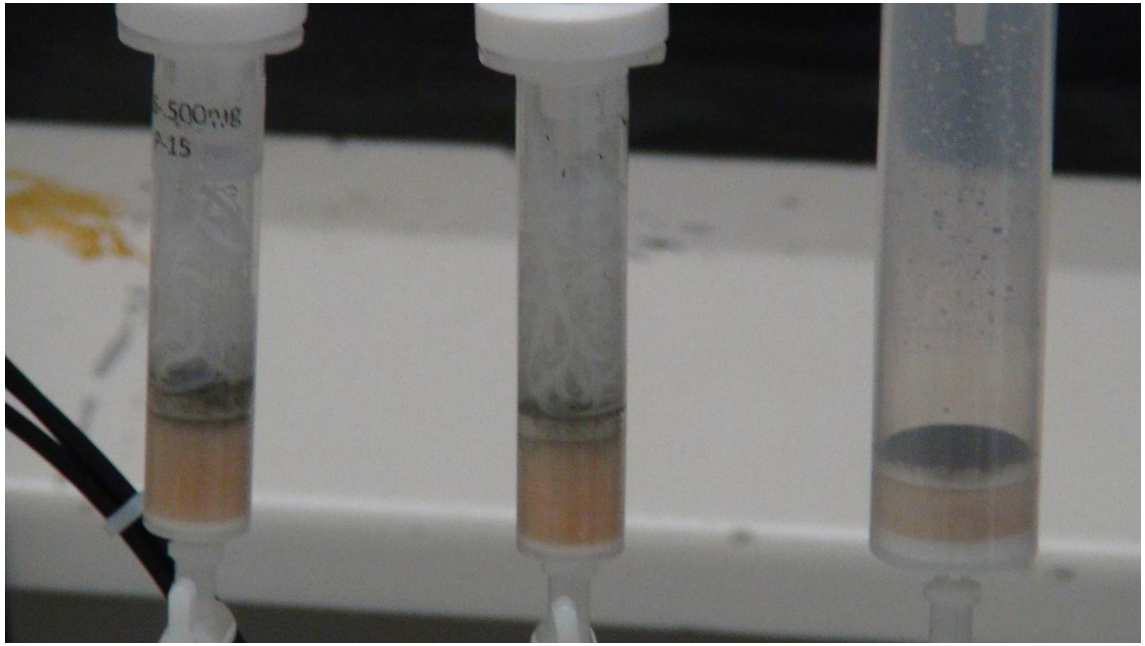
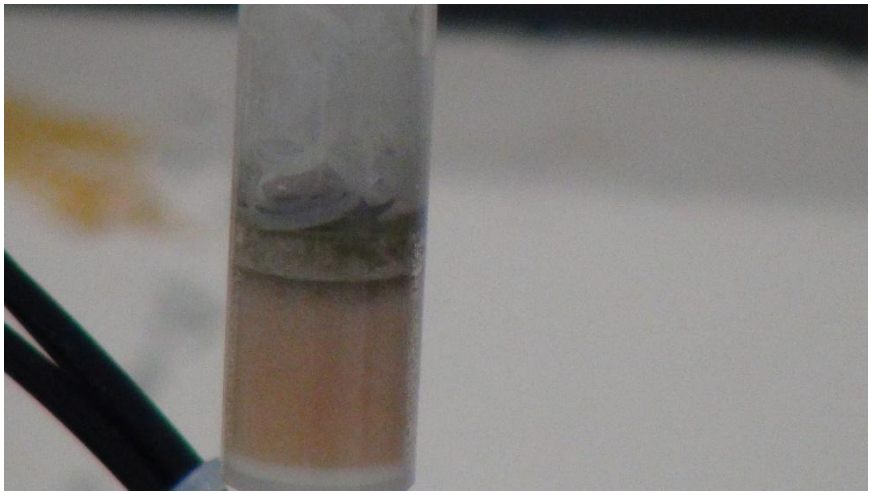
Industrial 433 Matrix 250ml

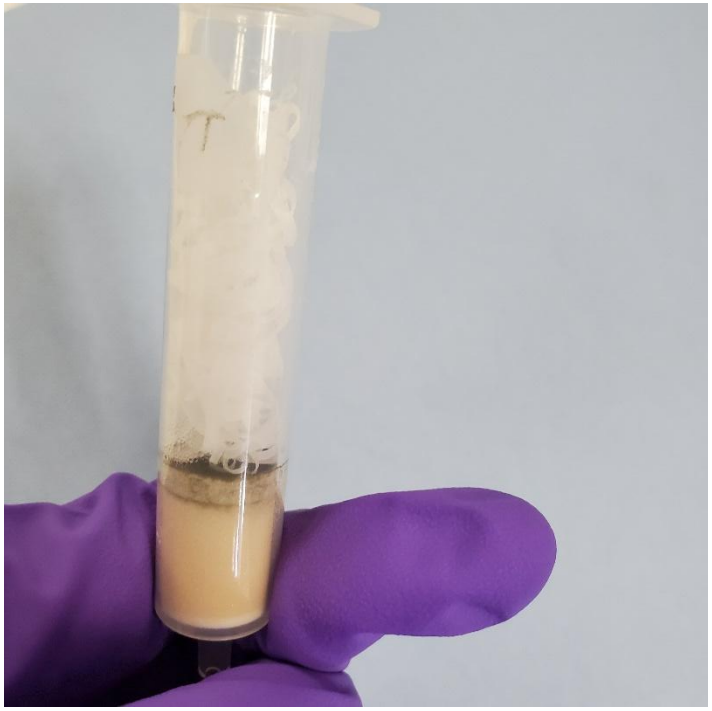


6ml and 25ml Cartridges

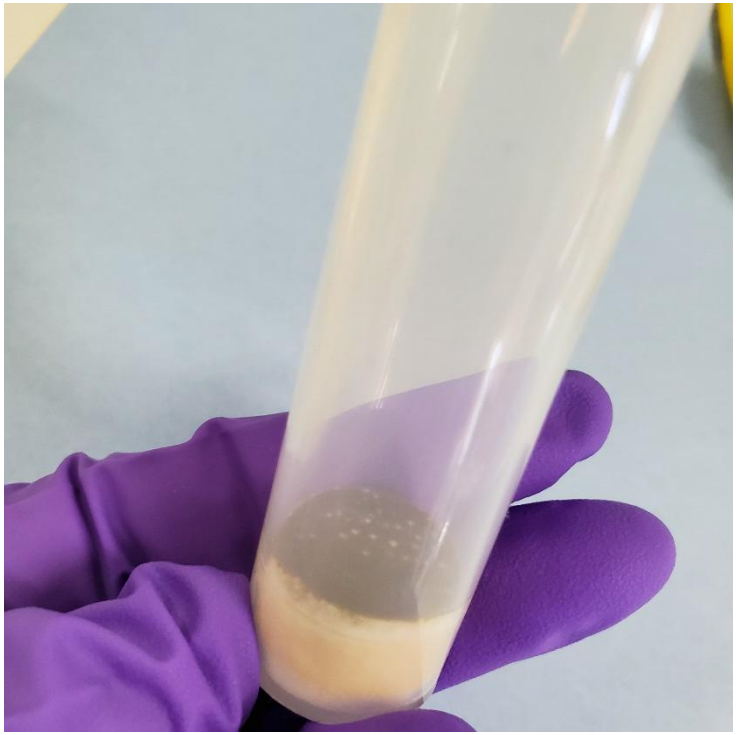


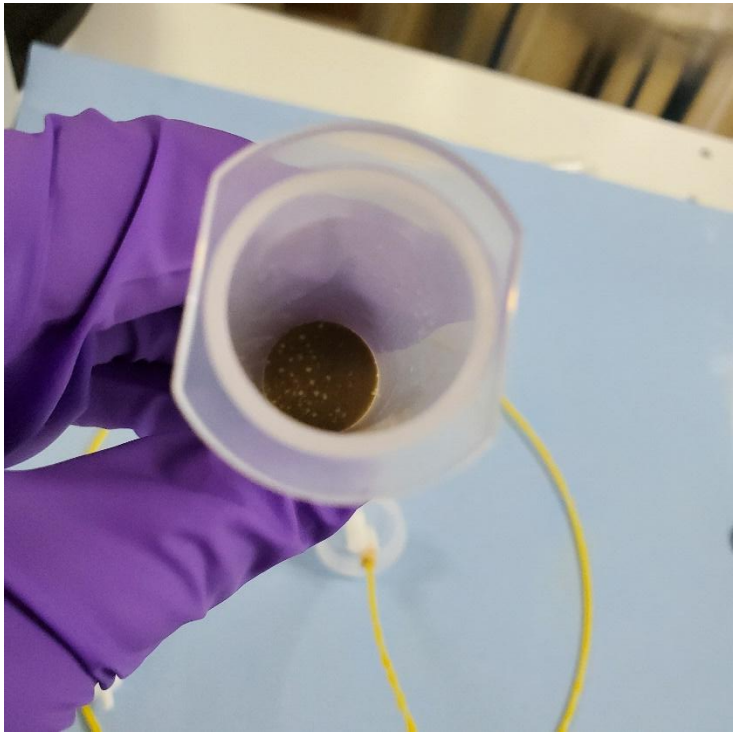
250 ml run to completion on 6 ml cartridge with Plastic Wool





250ml run to completion
25ml cartridge





TurboTrace PFC Automated Extraction and Concentration for PFAS/PFOS in Drinking Water and WasteWater

TurboTrace® PFC

- Wastewater, Particulate Laden Samples
- Drinking water Samples
- Vacuum Pump or Positive Pressure for loading samples
- Positive Pressure Pumping for conditioning, rinsing and elution
- Direct to SuperVap Concentrator

LC/MS

TurboTrace for Extraction and Concentration of PFAS/PFOS in Drinking/WasteWater

Fluid Management Systems

Fully Automated from start to finish

Modular and Scalable expandable from 1 to 4 Modules

Run 2 to 8 samples

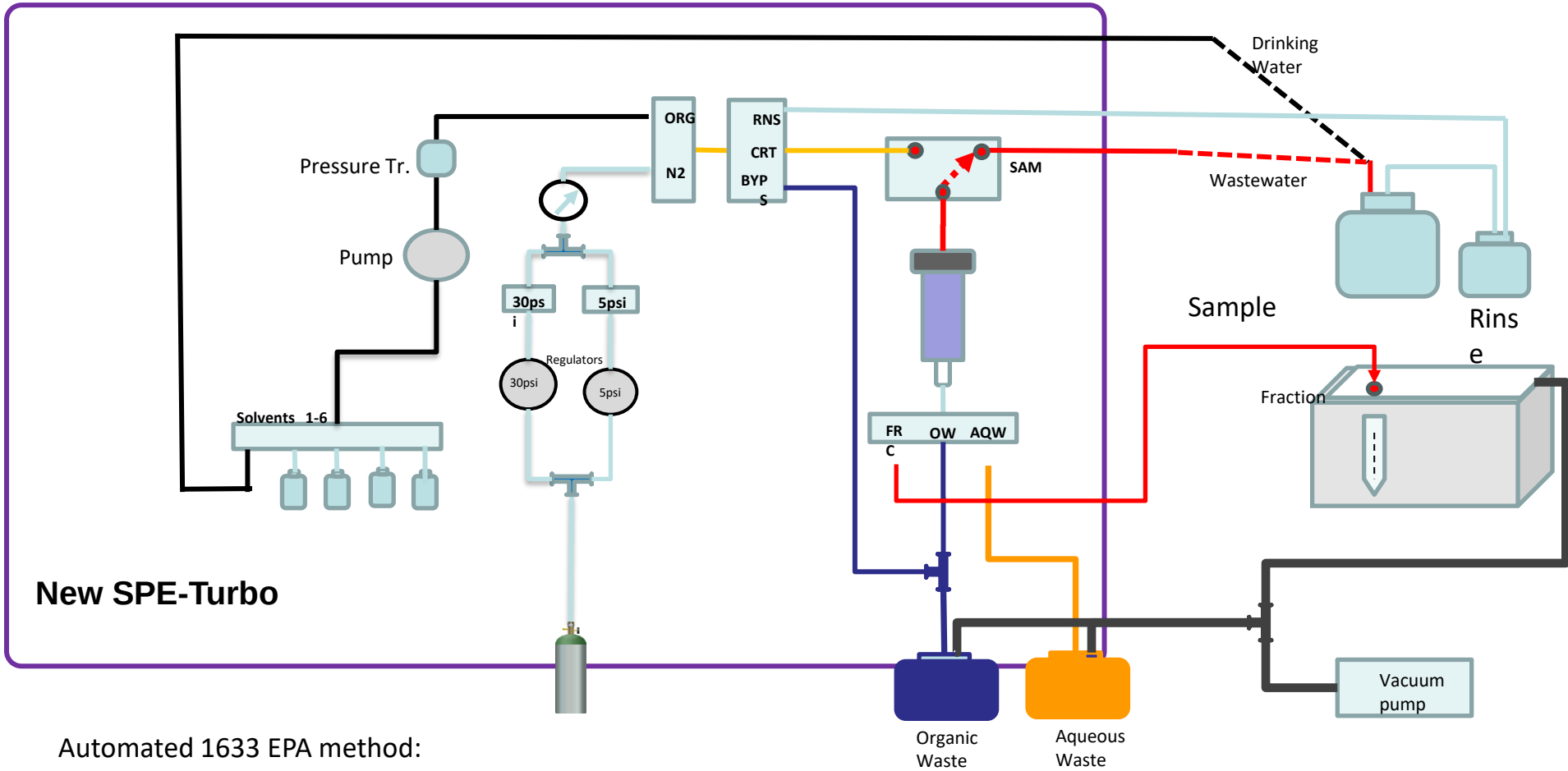
Each Module can Run 2 Samples in parallel

Uses Positive Pressure Pumping for Precise delivery of Elution and Wash Solvent

One valve pathway to the cartridge

Uses a Vacuum with liquid sensor to Load Dirty Samples and detect when finished

Direct Extract delivery to Concentrator for Evaporation



Automated 1633 EPA method:

Automated Concentration for PFAS

- SuperVap PFC
  - 24 positions
  - 15ml Conical vials
  - Dry Bath

Automated Concentration for PFAS

- SuperVap PFC
  - 12 positions
  - 50 ml Conical vials
  - Dry Bath

Concentration Functionality

- Self Installable
  - Video unpacking, installation and training video
- Preprogrammed with most common temperature settings
- Direct to 15ml Centrifuge Tubes
- Dry bath heating element
- Time based endpoint
- Savable temperature log
- No Teflon Components

TurboTrace PFC SPE Conditions

- Eight synthetic wastewater samples (500 mL) spiked with native PFAS standards and relevant internals
- Load sample bottles onto system and install cartridges
- Rinse bottles are automatically filled during procedure
- Use positive pressure (nitrogen) for pumping solvents and mixes through the system and use vacuum to load the samples
- Condition cartridges with 15 mL 1% methanolic ammonium hydroxide followed by 5 mL of 0.3M formic acid
- Load samples across the cartridges at 5-10 mL/min (vacuum ~ 8-inch Hg)

TurboTrace PFC SPE Conditions

- Sample bottles rinsed with 5 mL reagent water (twice) followed by 5 mL of 1:1 0.1M formic acid/methanol and load rinses across the cartridges
- Dry 2.5 min
- Rinse sample bottles with 5 mL 1% methanolic ammonium hydroxide
- Load rinses across cartridges and collect in polypropylene tubes
- Cleanup over 10 mg of loose carbon
- As per the method no further concentration is carried out
- Further relevant standards were added prior to LC/MS analysis

LC/MS Analysis 1633

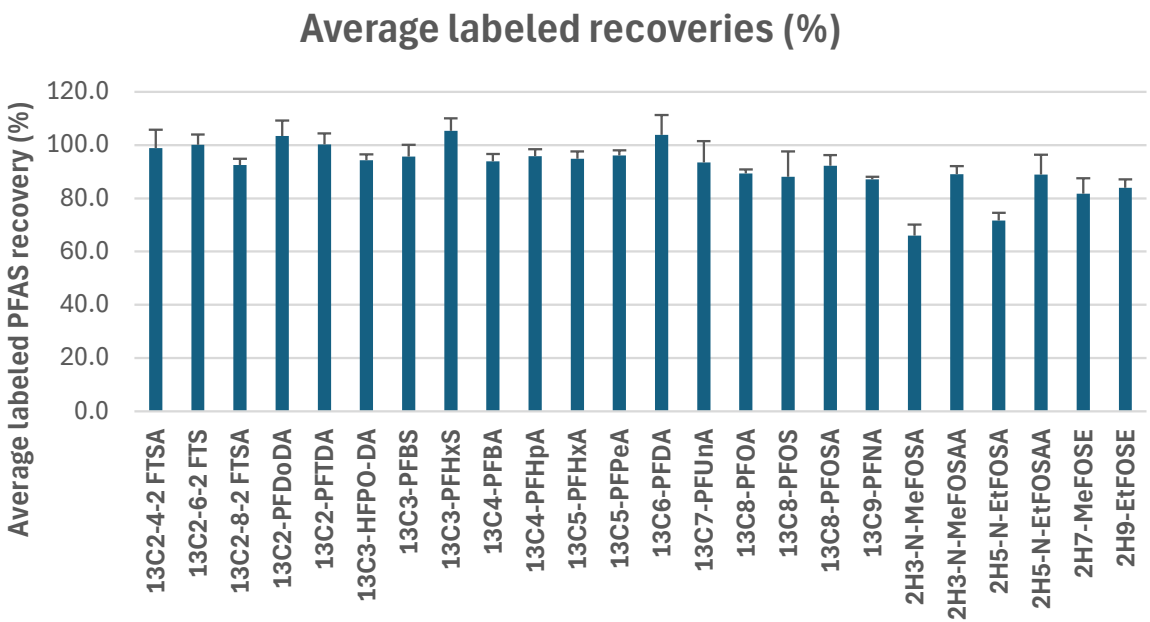
Analysis

- Take aliquot from final 5 mL extract (Method 1633 does not require volume reduction of final extract)
- Agilent 1290 Infinity II LC System
- Agilent 6475 Triple quad LC/MS
- Agilent Zorbax Eclipse Plus C18 column 3.0 x 50 mm, 1.8 um
- Column temperature 40 ^{o}C
- Injection 5.0 uL

LC/MS Analysis 1633

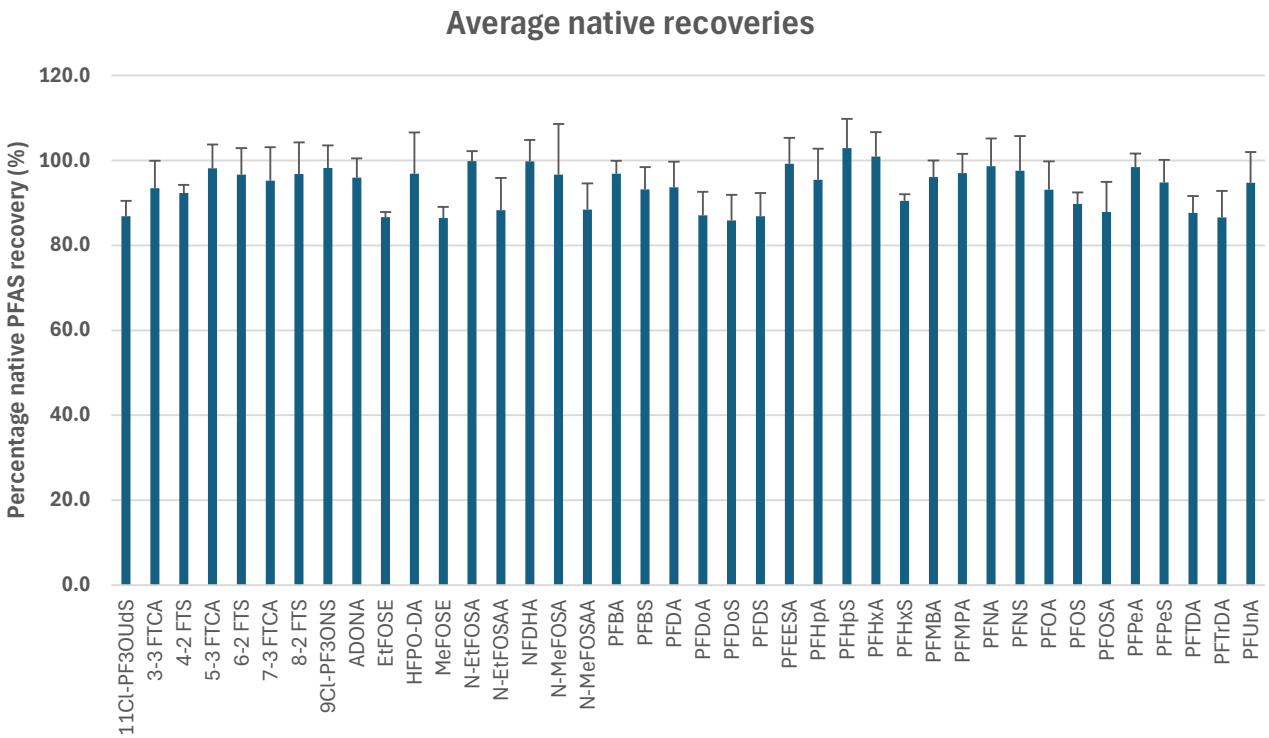
- **Mobile phase 5 mM ammonium acetate in 95% water, 5% acetonitrile (A) and methanol (B) Gradient**
- 0 min 98% A 2% B
- 0.2 min 98% A 2% B
- 10 min 5% a 95% B
- **Stop time 12.2 min**
- **Dynamic MRM negative electrospray**
- T (gas) = 230 ^{o}C

IDC Data for Labeled



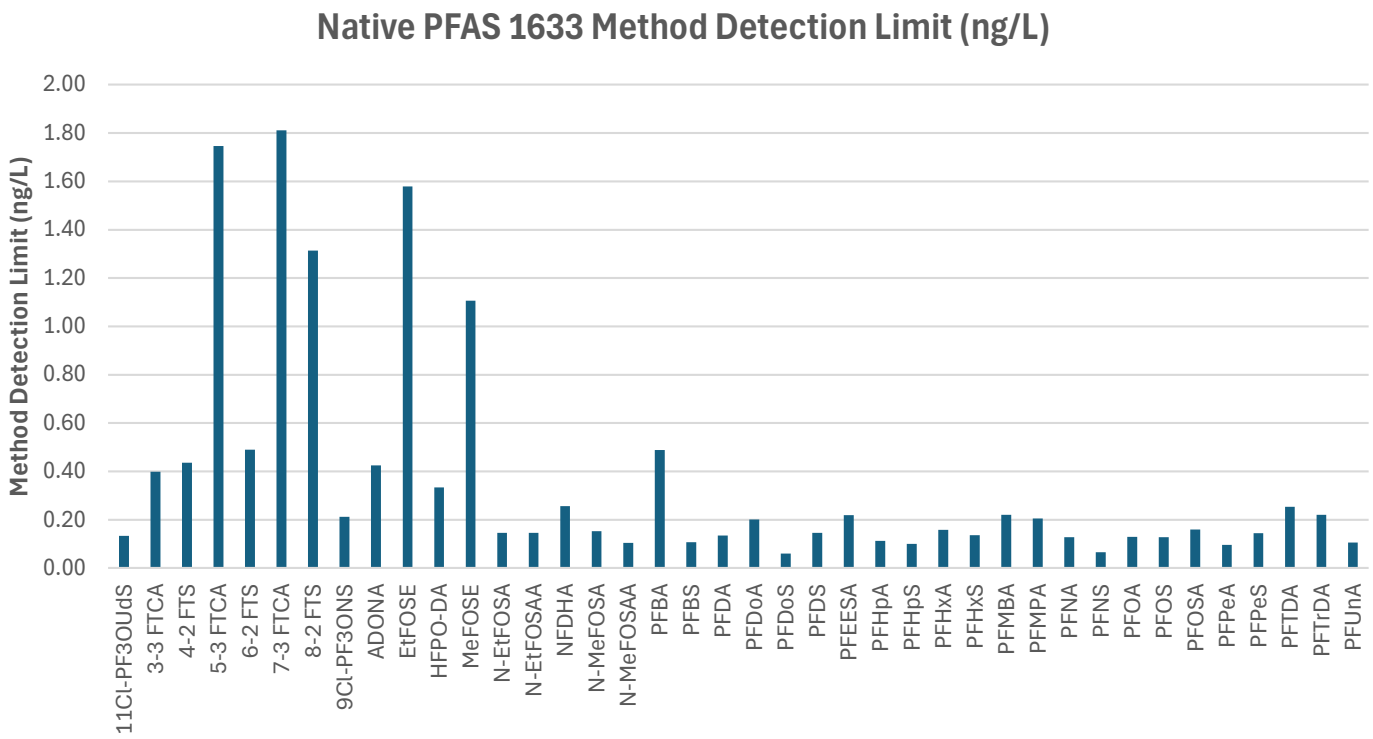
Average labeled recoveries (% , n=4)

IDC Data for Natives



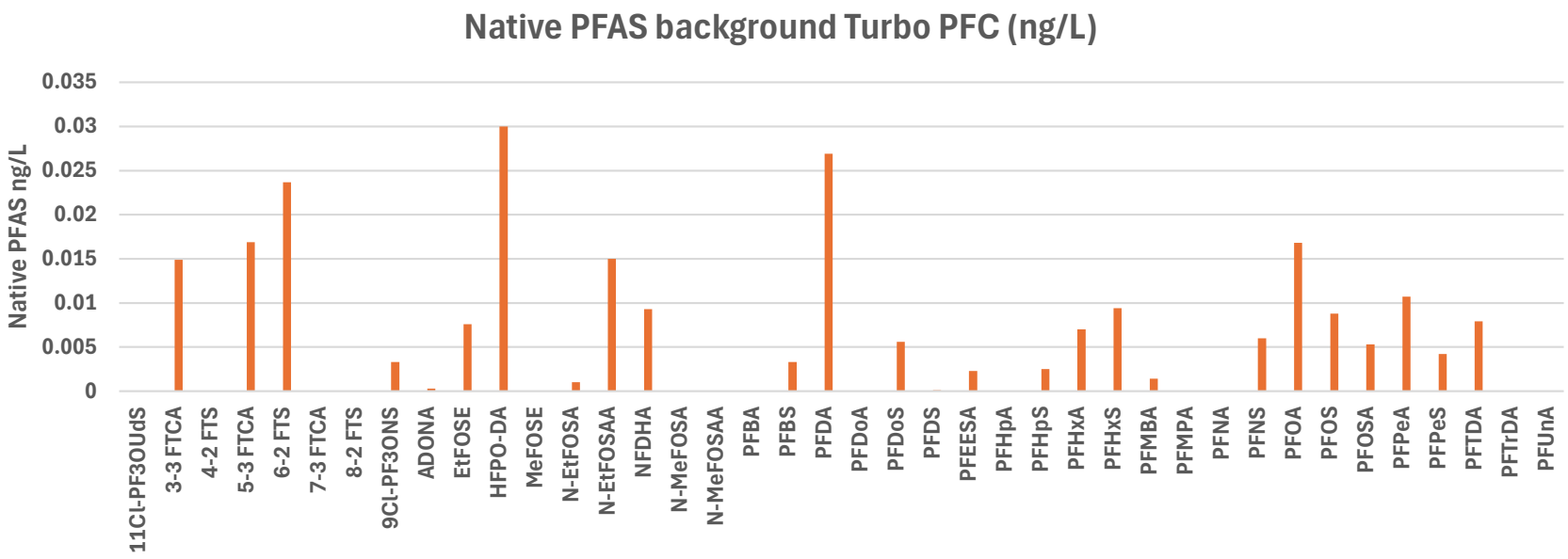
Initial Demonstration of Capability (1-38 ng/L, n=4)

MDL



Method Detection Limit (0.2-6 ng/L, n=7)

System Blank



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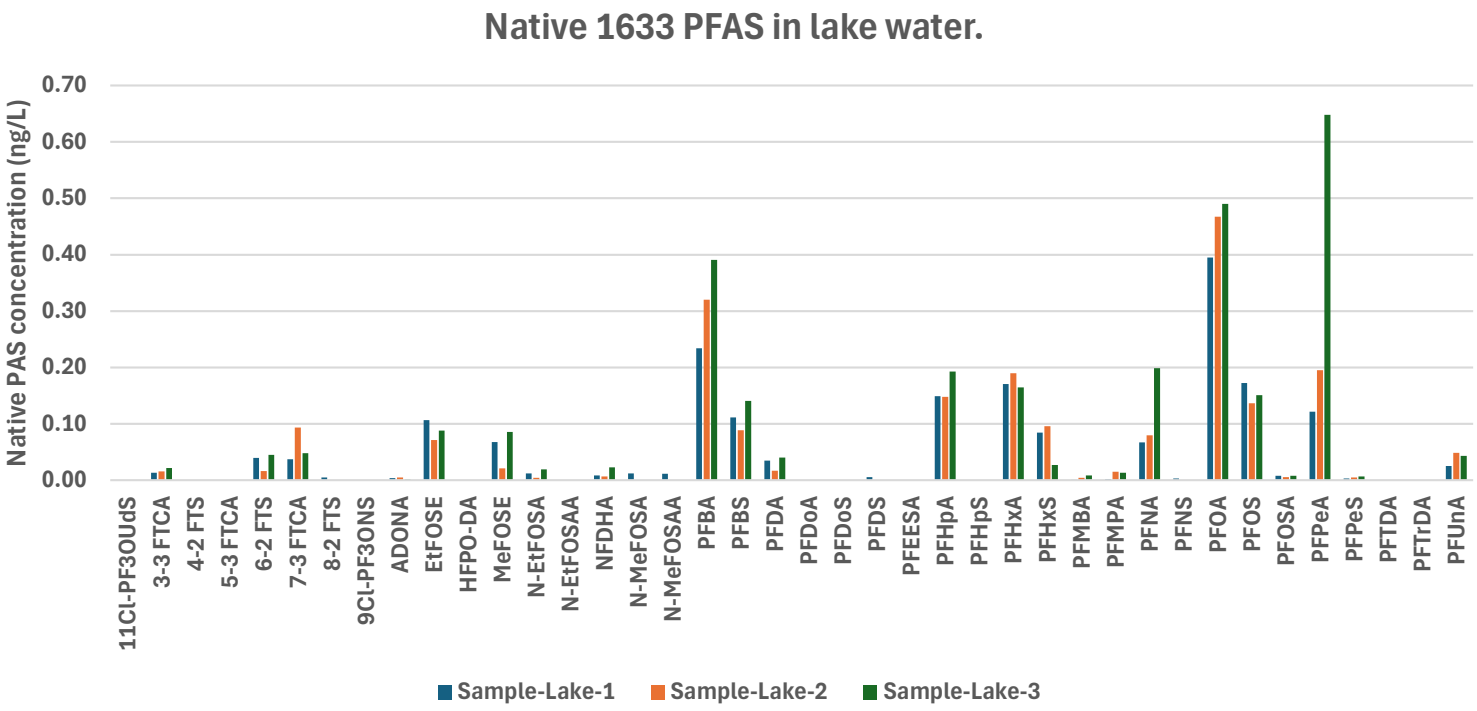
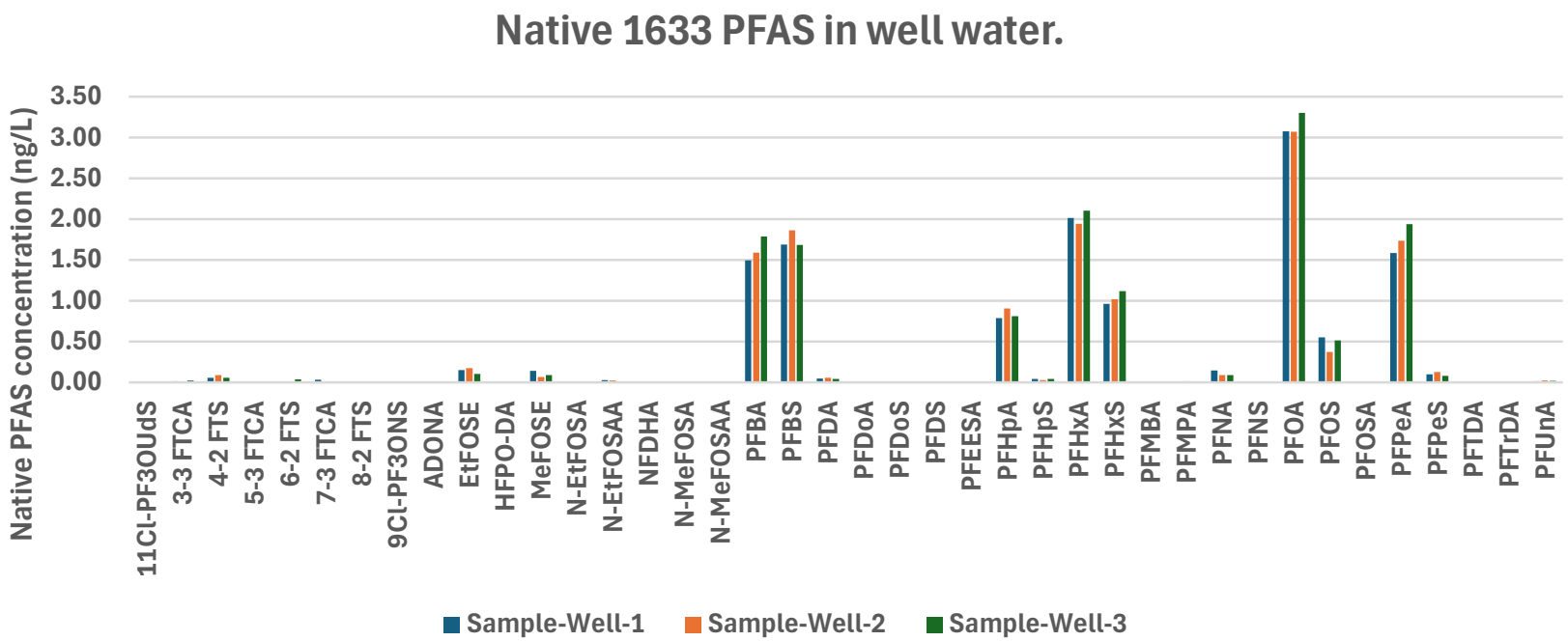
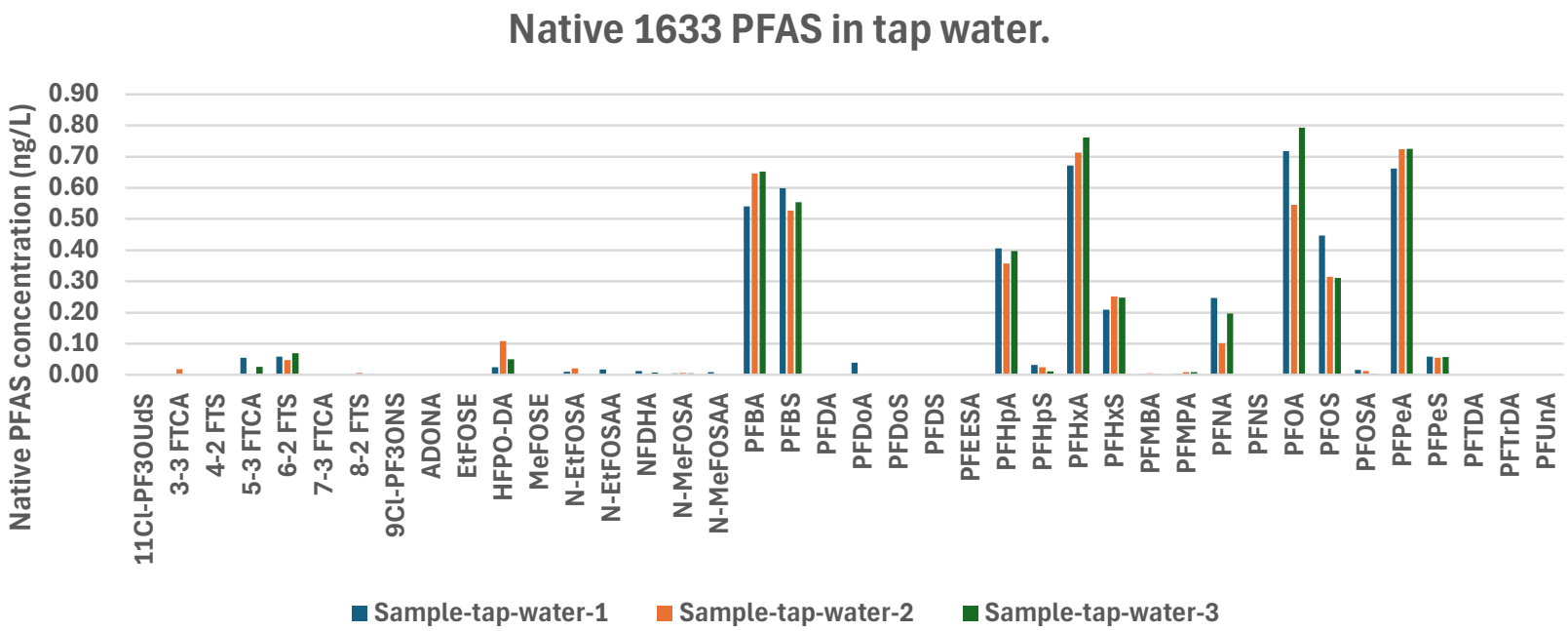
Lake Water


Native 1633 PFAS in lake water.
Native PAS concentration (ng/L)
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
11Cl-PF3OUdS
3-3 FTCA
4-2 FTS
5-3 FTCA
6-2 FTS
7-3 FTCA
8-2 FTS
9Cl-PF3ONS
ADONA
EtFOSE
HFPO-DA
MeFOSE
N-EtFOSA
N-EtFOSAA
NFDHA
N-MeFOSA
N-MeFOSAA
PFBA
PFBS
PFDA
PFDoA
PFDoS
PFDS
PFEESA
PFHpA
PFHpS
PFHxA
PFHxS
PFMBA
PFMPA
PFNA
PFNS
PFOA
PFOS
PFOSA
PFPeA
PFPeS
PFTDA
PFTrDA
PFUnA
Sample-Lake-1
Sample-Lake-2
Sample-Lake-3

Well Water


Native 1633 PFAS in well water.
Native PFAS concentration (ng/L)
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
11Cl-PF3OUdS
3-3 FTCA
4-2 FTS
5-3 FTCA
6-2 FTS
7-3 FTCA
8-2 FTS
9Cl-PF3ONS
ADONA
EtFOSE
HFPO-DA
MeFOSE
N-EtFOSA
N-EtFOSAA
NFDHA
N-MeFOSA
N-MeFOSAA
PFBA
PFBS
PFDA
PFDoA
PFDoS
PFDS
PFEESA
PFHpA
PFHpS
PFHxA
PFHxS
PFMBA
PFMPA
PFNA
PFNS
PFOA
PFOS
PFOSA
PFPeA
PFPeS
PFTDA
PFTrDA
PFUnA
Sample-Well-1
Sample-Well-2
Sample-Well-3

Tap Water


Native 1633 PFAS in tap water.
Native PFAS concentration (ng/L)
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
11Cl-PF3OUdS
3-3 FTCA
4-2 FTS
5-3 FTCA
6-2 FTS
7-3 FTCA
8-2 FTS
9Cl-PF3ONS
ADONA
EtFOSE
HFPO-DA
MeFOSE
N-EtFOSA
N-EtFOSAA
NFDHA
N-MeFOSA
N-MeFOSAA
PFBA
PFBS
PFDA
PFDoA
PFDoS
PFDS
PFEESA
PFHpA
PFHpS
PFHxA
PFHxS
PFMBA
PFMPA
PFNA
PFNS
PFOA
PFOS
PFOSA
PFPeA
PFPeS
PFTDA
PFTrDA
PFUnA
Sample-tap-water-1
Sample-tap-water-2
Sample-tap-water-3

Summary

Automated SPE for PFAS

- TurboTrace
  - Fully automated, Vacuum pump for loading “dirty samples”, automated bottle rinse,
  - Direct delivery to SuperVap Concentrator

Semi Automated SPE for PFAS

- EZPFC
  - 2 EZPFC 12 position systems and the SuperVap PFC Concentrator for 24 samples
  - Run a batch of 24 in 2 hours

Questions

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