Automation of Solid Phase Extraction following EPA Method 533

PROMOCHROM
TECHNOLOGIES

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PFAS SPE Methods

Matrices	Methods
Drinking Water	**EPA Method 537.1** 18 compounds **EPA Method 533** 25 compounds
Non-Potable Water	**DoD QSM Table B-15** **Proprietary Methods** >40 compounds **ISO 21675 (water)** >30 compounds
Solids/Tissues/Soil	**SPE Clean Up** > 40 compounds

PFAS SPE Methods

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Non-Potable Water	**DoD QSM Table B-15** **Proprietary Methods** >40 compounds **ISO 21675 (water)** >30 compounds
Solids/Tissues/Soil	**SPE Clean Up** > 40 compounds

PFAS SPE Methods

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Non-Potable Water	**DoD QSM Table B-15** **Proprietary Methods** >40 compounds **ISO 21675 (water)** >30 compounds
Solids/Tissues/Soil	**SPE Clean Up** > 40 compounds

Significance of EPA Method 533

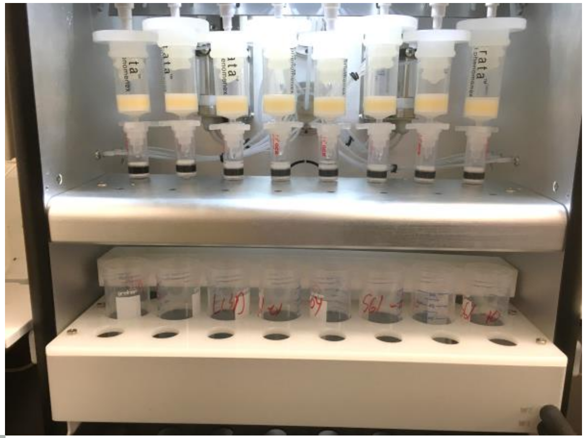
1. UCMR 5
    - EPA Method 537.1 + 533 (29 PFAS)
    - >10,000 PWSs
    - Sampling period 2023-2025
    - UCMR_Lab_Approval@epa.gov

Significance of EPA Method 533

1. UCMR 5
   - EPA Method 537.1 + 533 (29 PFAS)
   - >10,000 PWSs
   - Sampling period 2023-2025
   - UCMR_Lab_Approval@epa.gov

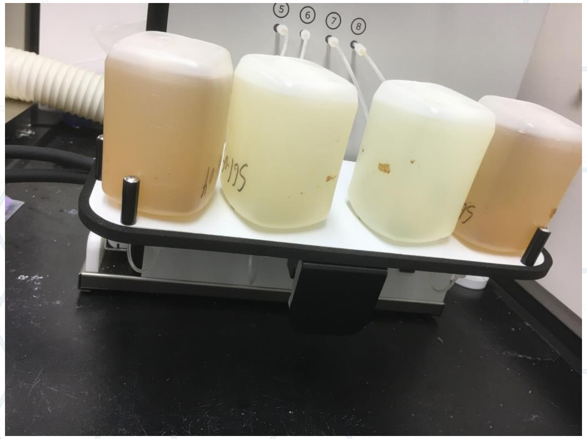
2. Similarity to many PFAS methods
   - Non-drinking water methods
   - Solids/Tissue/Soil extract clean up

DoD QSM 5.3
Table B-15



Proprietary Methods

Extract cleanup



EPA Method 533 and 537.1

- EPA Method 533
  - 25 compounds
  - Weak Anion Exchange
  - Isotope Dilution
- EPA Method 537.1
  - 18 compounds
  - Reverse Phase SPE

Both	EPA 533	EPA 537.1
PFBS	PFBA	NMeFOSAA
PFHxA	PFMPA	NEtFOSAA
PFHpA	PFPeA	PFTA
PFHxS	PFMBA	PFTrDA
PFOA	PFEESA	
PFOS	NFDHA	
PFNA	PFPeS	
PFDA	FPHpS	
PFUnA	4:2 FTS	
PFDoA	6:2 FTS	
9 Cl-PF3ONS	8:2 FTS	
11 Cl-PF3OUdS		
HFPO-DA (GenX)		
ADONA		

Extraction Procedure

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Conditioning

- 10mL MeOH
- 10 mL of 0.1 M phosphate buffer
- 2-3mL of 0.1 M phosphate buffer
- Fill with water

*Do not allow cartridge to go dry

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Sample loading

250mL sample at 5mL/min

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- 250mL sample at 5mL/min

*Do not allow cartridge to go dry

Bottle rinsing and cartridge wash
- 10 mL of 1 g/L ammonium acetate
- 1 mL of MeOH

Extraction Procedure

Conditioning	10mL MeOH 10 mL of 0.1 M phosphate buffer 2-3mL of 0.1 M phosphate buffer Fill with water
Sample loading	250mL sample at 5mL/min
Bottle rinsing and cartridge wash	10 mL of 1 g/L ammonium acetate 1 mL of MeOH
Cartridge drying	5 mins

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Extraction Procedure

Conditioning	10mL MeOH 10 mL of 0.1 M phosphate buffer 2-3mL of 0.1 M phosphate buffer Fill with water	*Do not allow cartridge to go dry
Sample loading	250mL sample at 5mL/min	*Do not allow cartridge to go dry
Bottle rinsing and cartridge wash	10 mL of 1 g/L ammonium acetate 1 mL of MeOH	
Cartridge drying	5 mins	
Bottle rinsing and elution	5 mL of 2% Basic MeOH 5 mL of 2% Basic MeOH	*Drop-wise

Evolution of SPE-03

2018

Considerations
for PFAS

Present

Considerations of PFAS Automation

1. Size and Efficiency
    - Compact footprint
    - 8 samples in parallel

Valves in conventional design

Patented multi-channel valve

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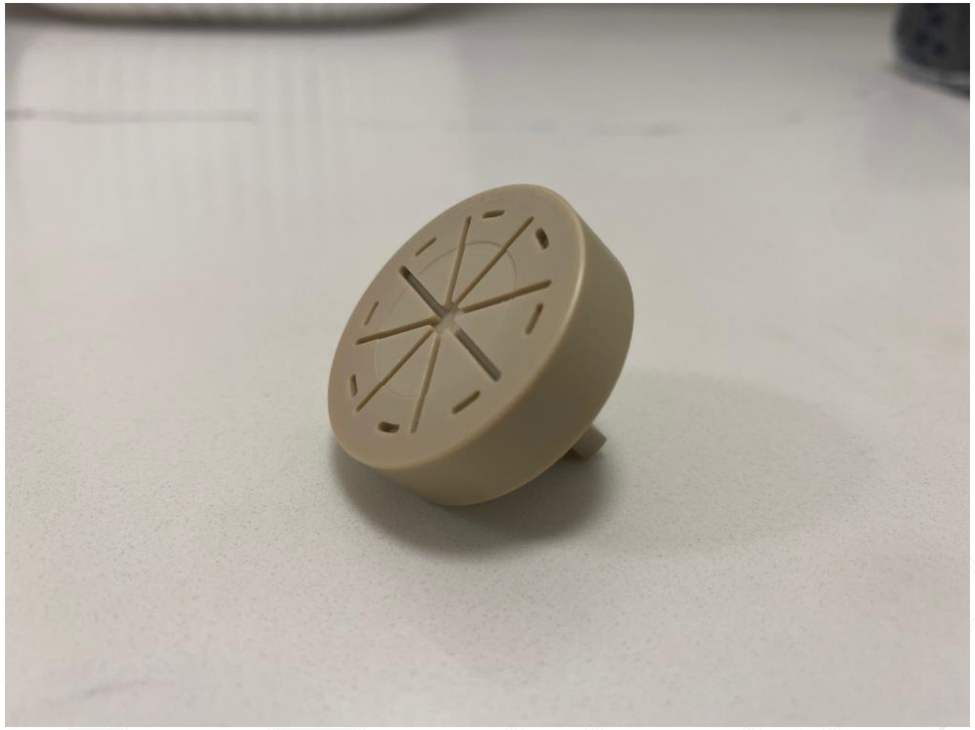
2. PFAS Background
    - Replace PTFE lines
    - Replace PTFE valve rotor



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3. Bottle Rinsing
   - Integrated rack

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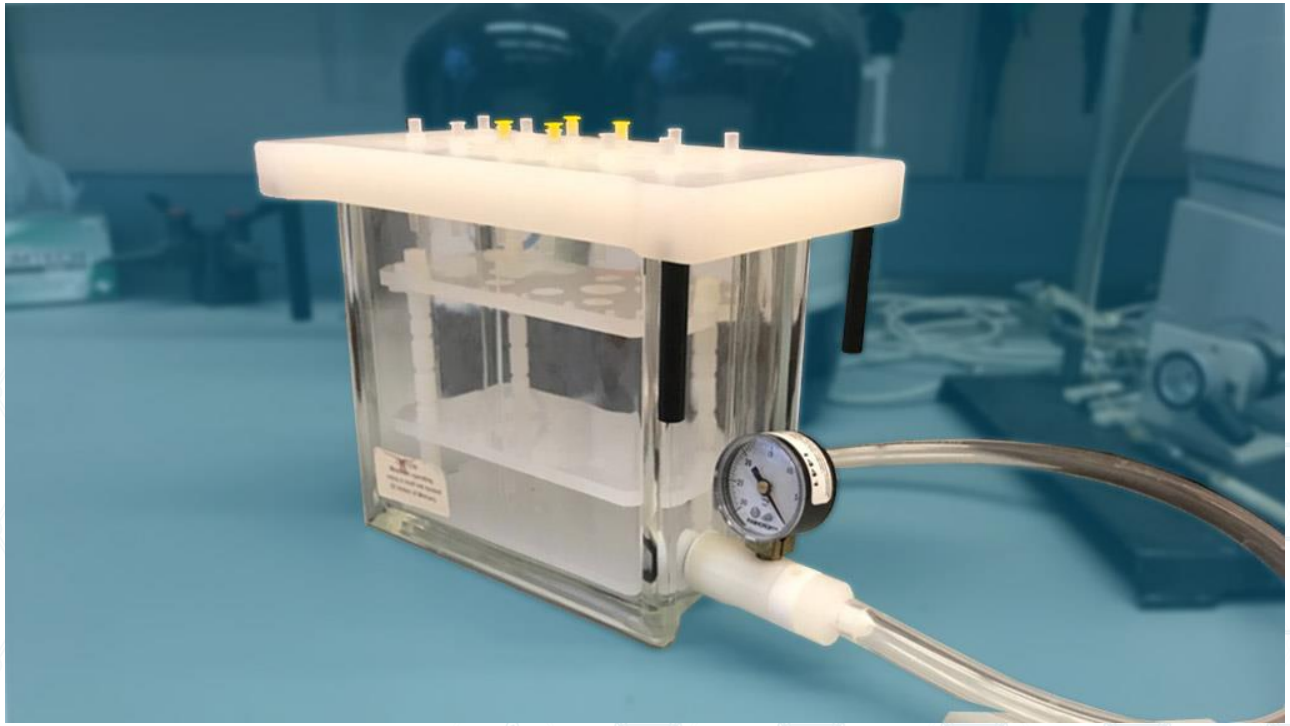
4. Flow control

Vacuum Manifold

- One shared vacuum source
- Non-uniform flow
- Constant supervision
- Clogs easily



Considerations of PFAS Automation

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2. PFAS Background
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3. Bottle Rinsing
   - Integrated rack
   - Built-in resonators

4. Flow control

SPE-03 Pumps

- Positive pressure
- Uniform flow across all samples
- Sorbent does not go dry
- Resistant to clogging

Multi-lab Validation of 533

- Most of the aforementioned features validated in 2018 for EPA Method 537

- EPA Method 533 Multi-lab validation study at **Merit Labs**, Michigan, September 2019

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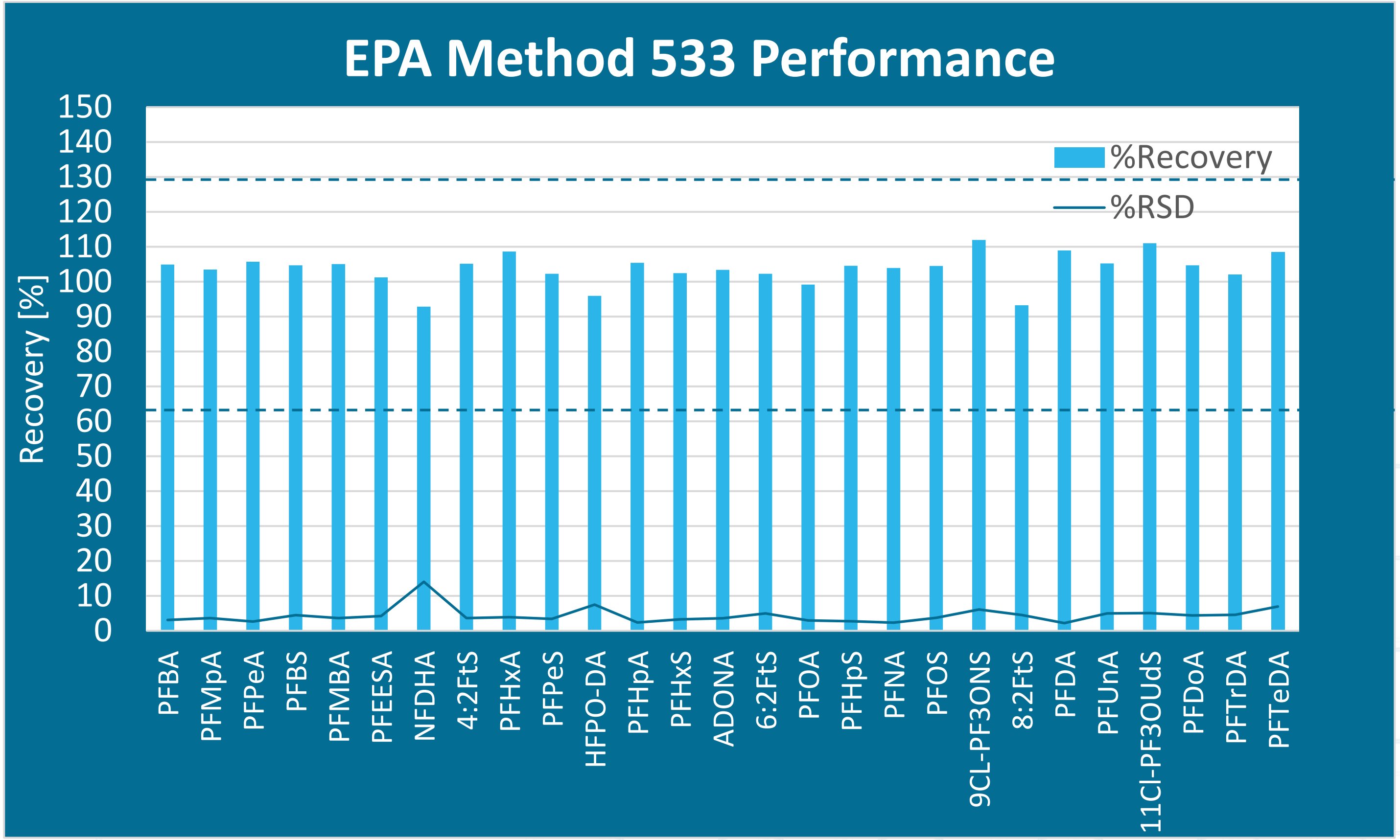
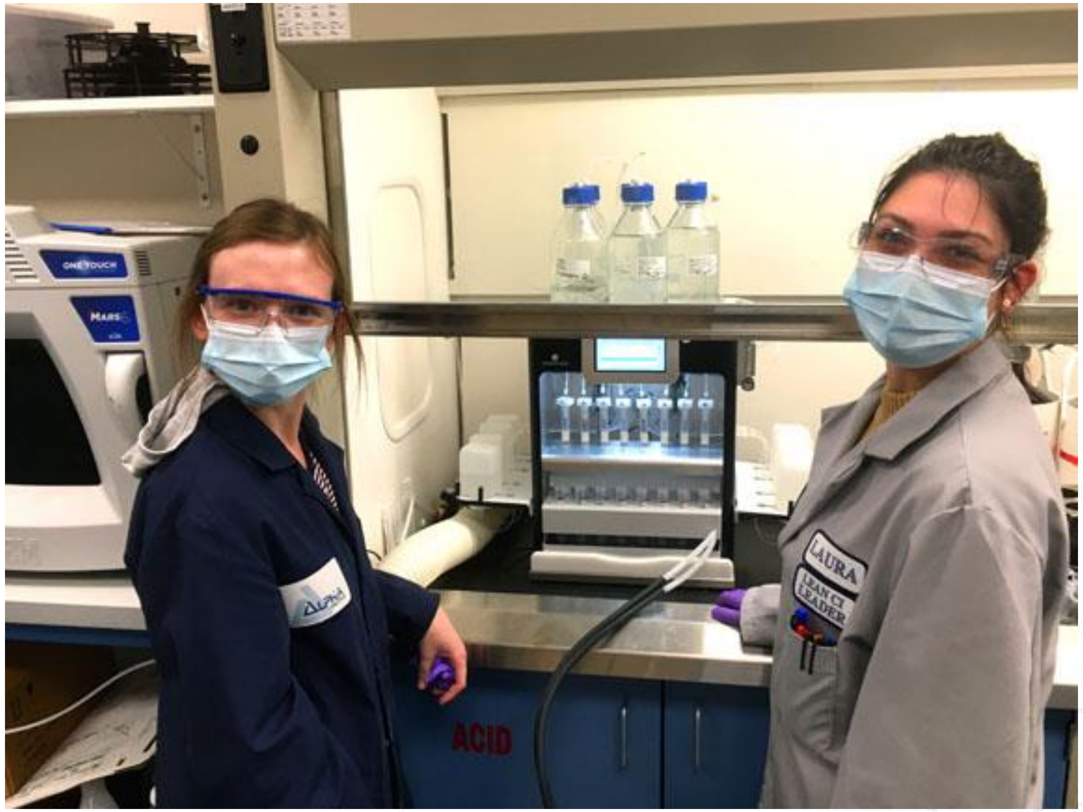
- Most of the aforementioned features validated in 2018 for EPA Method 537
- EPA Method 533 Multi-lab validation study at **Merit Labs**, Michigan, September 2019
- First look at 533 performance
  - N = 4 x 40 ppt spikes



Data Collection

- Field extraction data from **Alpha Analytical**, Massachusetts, March to April 2021
- Including both **SPE-03** and **manual extraction**



Data Collection

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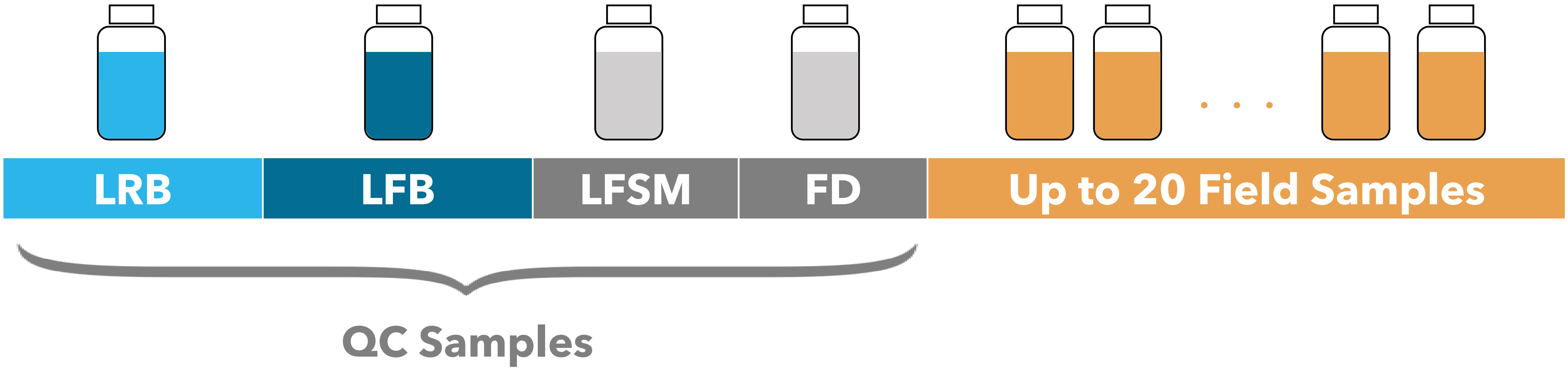
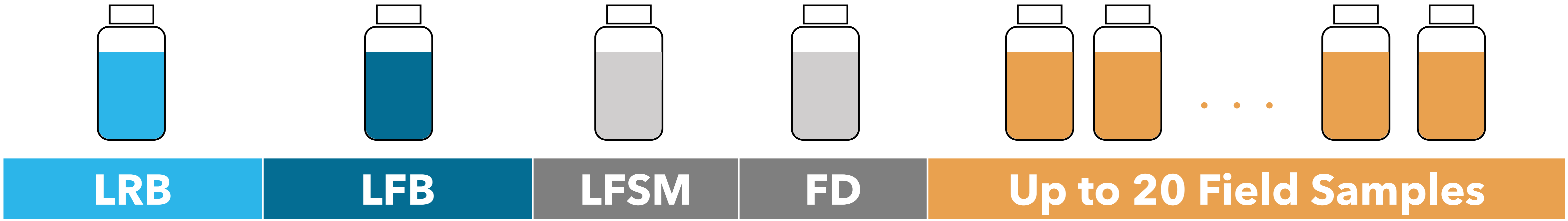
- **Materials:**
  - PromoChrom SPE-03 with MOD-004 (sample bottle rinsing) and MOD-005 (minimal-Teflon option)
  - Phenomenex Strata™-X-AW 33 µm Polymeric Weak Anion, 500 mg/6 mL SPE cartridge
  - SCIEX 4500 LC/MS/MS using ExionLC UHPLC

Sample Batch



Sample Batch



- Used for background check

Sample Batch

LRB	LFB	LFSM	FD	Up to 20 Field Samples
• Used for background check	• Used for recovery validation • Rotated between low/mid/high			

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- 15-minute cleaning cycle between extractions

SPE-03 Method

	Action	Inlet	Flow	Volume
Conditioning	Elute W2	Solvent 1	10 mL/min	10 mL
	Elute W1	Solvent 3	10 mL/min	10 mL
	Elute W1	Solvent 3	10 mL/min	3 mL
	Elute W1	Solvent 5	10 mL/min	3 mL
Sample loading	Add Samp W1	Sample	5 mL/min	270 mL
Bottle rinsing and cartridge wash	Rinse W1	Solvent 4	5 mL/min	10 mL
	Shake	Time based		30 s
	Clean	Solvent 1	5 mL/min	1 mL
	Add Samp W2	Sample	5 mL/min	9 mL
Nitrogen drying	Blow N2	Time based		5 min
Bottle rinsing and elution	Rinse 1	Solvent 5	2 mL/min	5 mL
	Rinse 1	Solvent 5	2 mL/min	5 mL
	Shake	Time based		10 s
	Collect 1	Sample	2 mL/min	4.5 mL

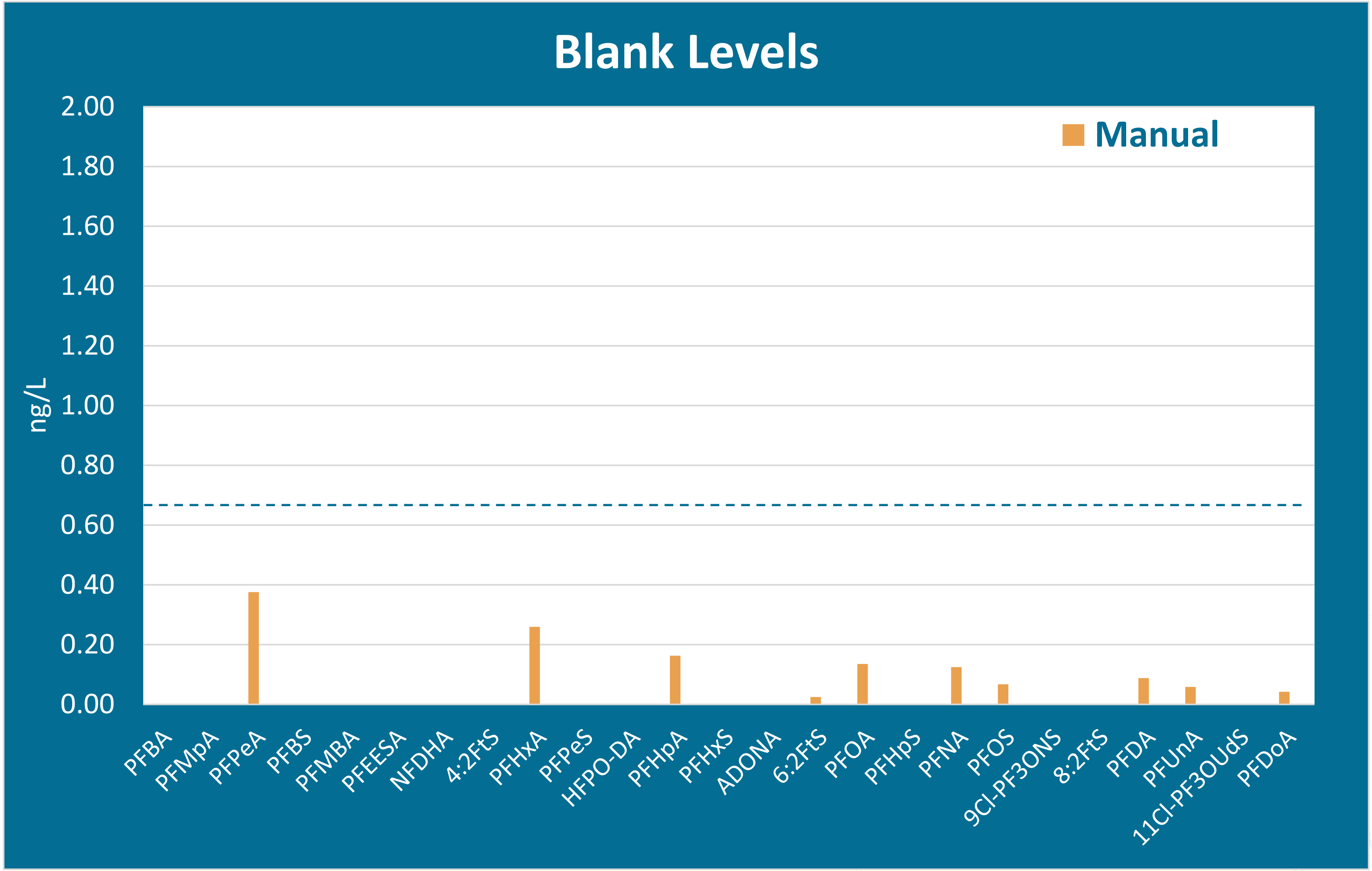
Results – Detection Limit

Compound	Measured Concentration [ng/mL]								Std	MDL
	#1	#2	#3	#4	#5	#6	#7	#8	Dev	[ng/L]
PFBA	1.00	1.00	0.97	1.16	1.00	0.98	0.83	1.00	0.10	0.29
PFMpA	1.00	1.06	0.98	1.12	1.13	1.05	1.00	0.97	0.07	0.20
PFPeA	1.00	1.44	1.37	1.44	1.32	1.26	1.42	1.36	0.07	0.20
PFBS	0.88	0.97	0.92	1.32	0.91	0.94	0.83	0.93	0.16	0.48
PFMBA	1.00	1.09	0.98	1.10	0.99	0.87	1.04	1.17	0.09	0.27
PFEESA	0.88	0.90	0.82	0.89	0.95	0.88	0.81	0.86	0.05	0.14
NFDHA	1.00	1.11	1.08	1.22	1.03	0.94	0.96	1.08	0.09	0.26
4:2FtS	0.92	0.96	0.83	0.98	1.00	0.75	1.03	0.98	0.11	0.34
PFHxA	1.00	1.05	0.95	1.27	1.07	1.21	0.98	1.04	0.13	0.39
PFPeS	0.96	0.74	1.01	0.92	1.27	0.96	0.81	1.06	0.19	0.56
HFPO-DA	1.00	1.18	1.04	0.89	0.90	0.72	0.95	1.12	0.15	0.44
PFHpA	1.00	1.05	1.06	1.14	0.86	1.14	0.94	0.90	0.11	0.34
PFHxS	0.92	1.03	0.75	0.96	1.01	0.84	0.72	0.90	0.15	0.44
ADONA	0.96	1.05	1.14	1.13	1.14	0.84	0.93	0.96	0.11	0.33
6:2FtS	0.96	0.80	1.88	1.56	1.12	1.30	1.43	1.20	0.32	0.95
PFOA	1.00	0.98	1.14	1.12	0.96	1.00	0.89	1.27	0.12	0.37
PFHpS	0.96	1.04	0.84	0.78	1.09	0.97	0.79	0.75	0.14	0.41
PFNA	1.00	1.14	1.12	0.81	1.07	1.04	1.02	1.23	0.14	0.43
PFOS	0.92	0.95	0.84	1.04	1.14	0.92	0.91	0.70	0.14	0.42
9Cl-PF3ONS	0.92	0.95	0.83	0.81	0.85	0.81	1.00	0.79	0.08	0.23
8:2FtS	0.96	0.99	0.88	1.09	1.34	1.18	0.97	1.00	0.15	0.44
PFDA	1.00	1.18	1.04	1.14	1.09	1.02	0.97	1.11	0.10	0.30
PFUnA	1.00	1.09	1.10	1.22	1.17	0.98	1.04	1.04	0.07	0.22
11Cl-PF3OUdS	0.96	0.75	0.73	0.74	0.98	0.76	0.80	0.72	0.09	0.26
PFDoA	1.00	1.22	1.09	1.12	1.11	1.05	1.00	1.07	0.07	0.22

MDL

- 8 x 1 ng/L spikes
- All MDL < 1 ng/L
- MRL set at 2 ng/L

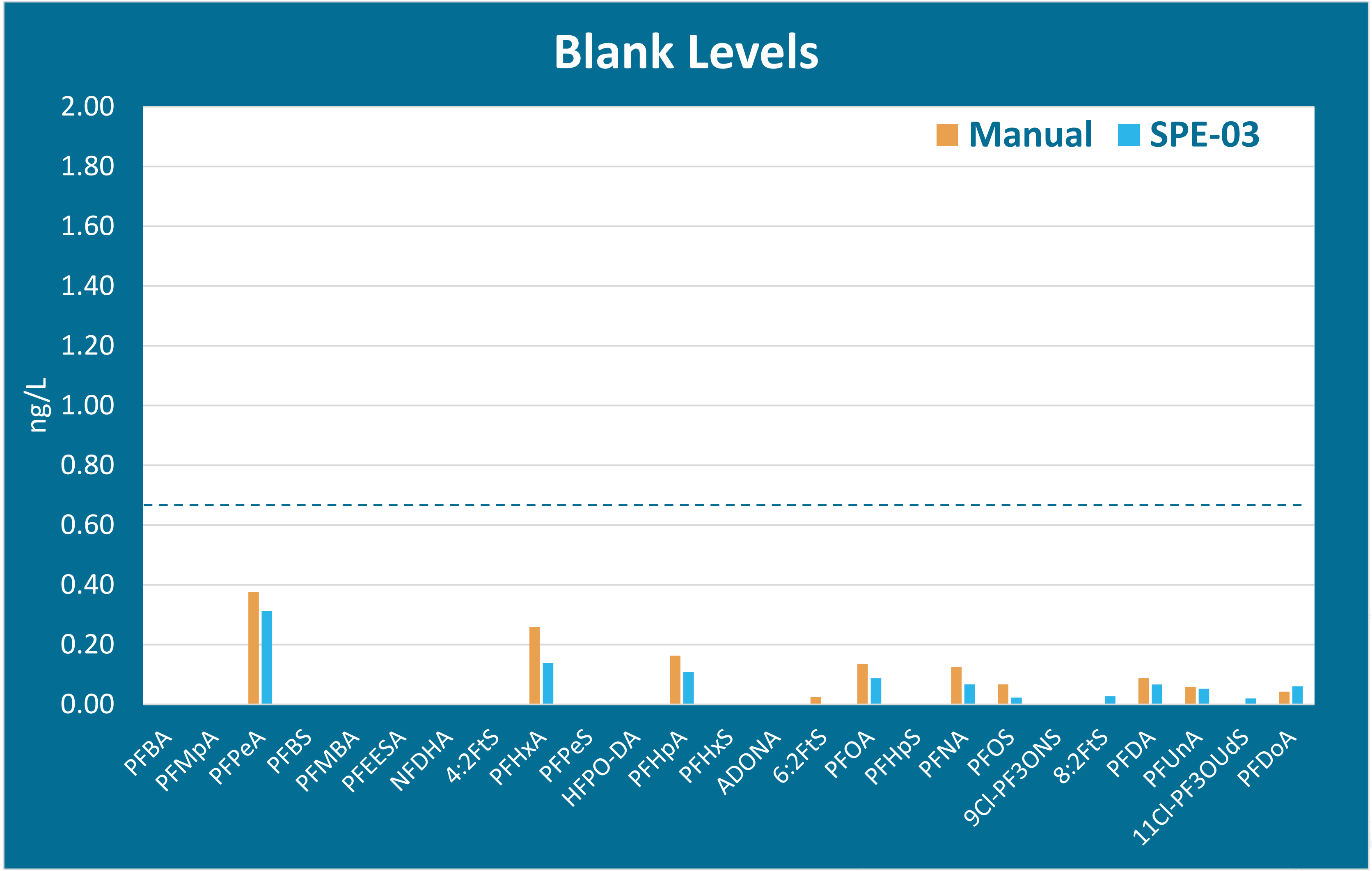
Results – Background



Manual LRB Levels

- N = 7 LRBs
- MRL = 2 ng/L
- < 1/3 MRL, 0.67 ng/L

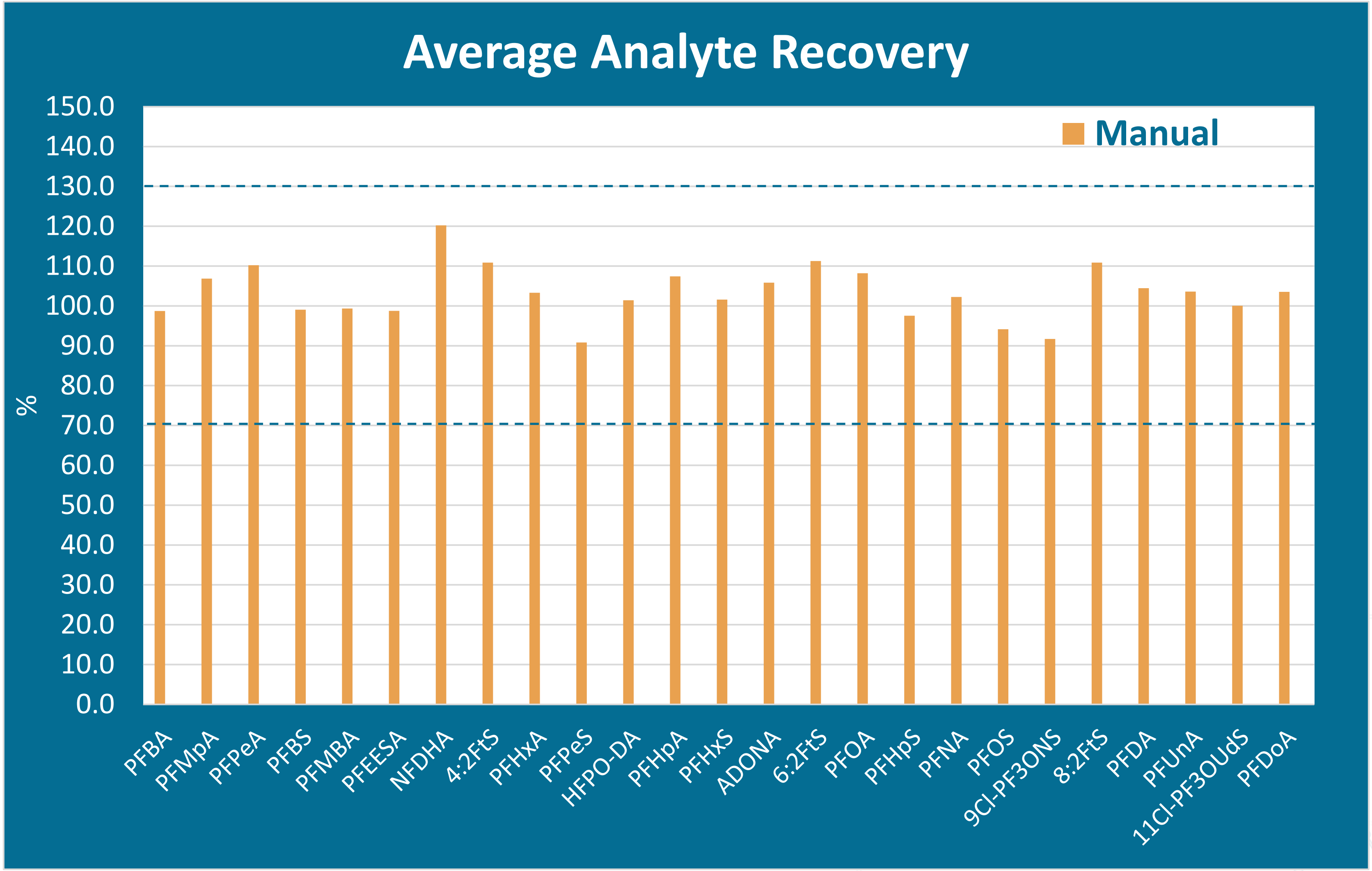
Results – Background



Manual and SPE-03 LRB Levels

- Similar analyte traces on both
- Contamination likely outside of extraction system

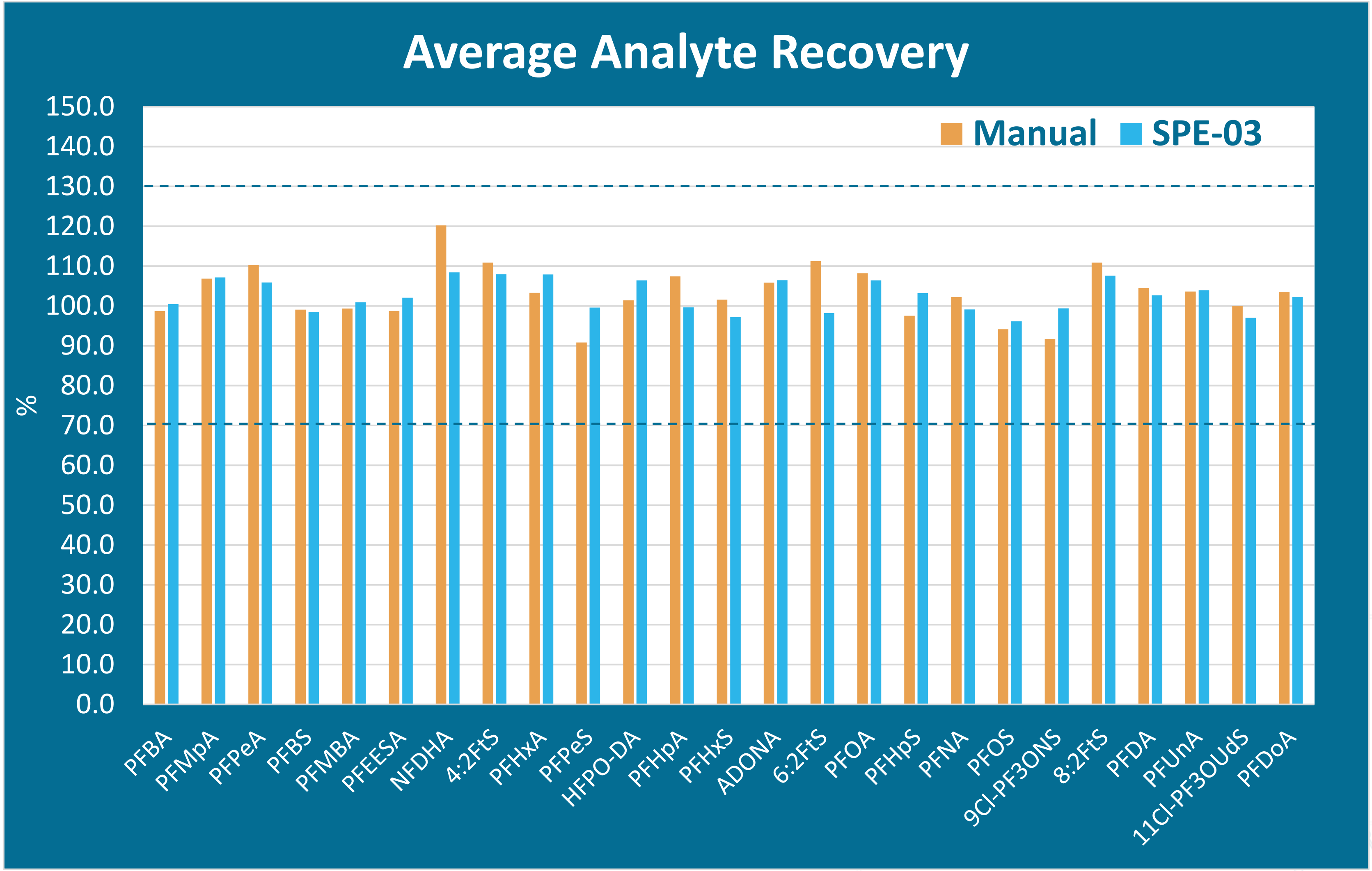
Results – Accuracy



Manual LFB Recovery

- N = 8 x LFBs
  - 2 low (2 ng/L)
  - 4 mid (40 ng/L)
  - 2 high (160 ng/L)
- Method requires 70% to 130%
- All recoveries within 90% to 120%

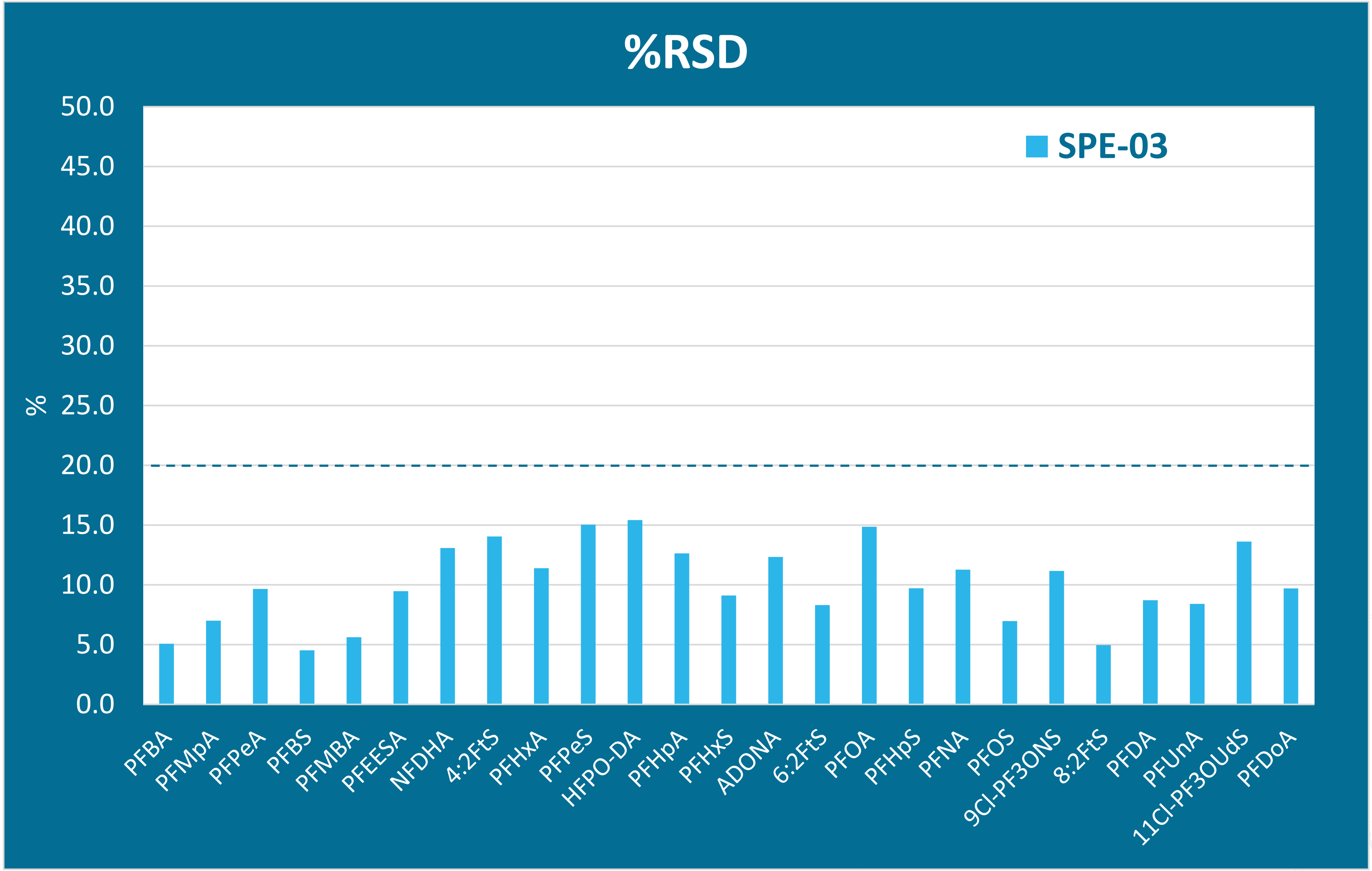
Results – Accuracy



Manual and SPE-03 LFB Recovery

- All SPE-03 recoveries within 95% to 110%
- Well within method limits

Results – Reproducibility



SPE-03 %RSD of LFBs

- Across different:
  - sample batches
  - dates
  - concentrations
  - extractor positions
  - lab personnel
- < ~15%

Results – Matrix Tolerance

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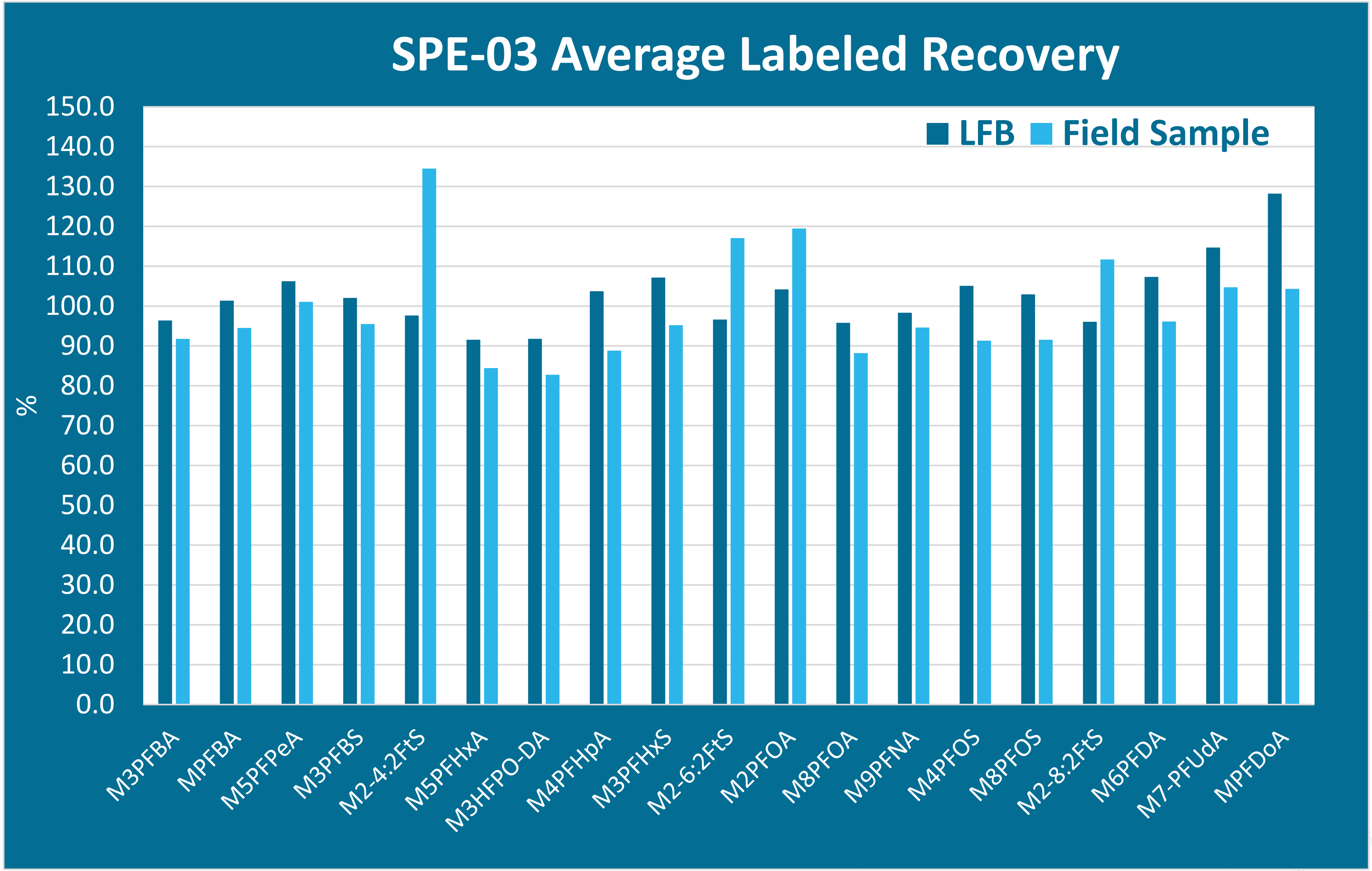
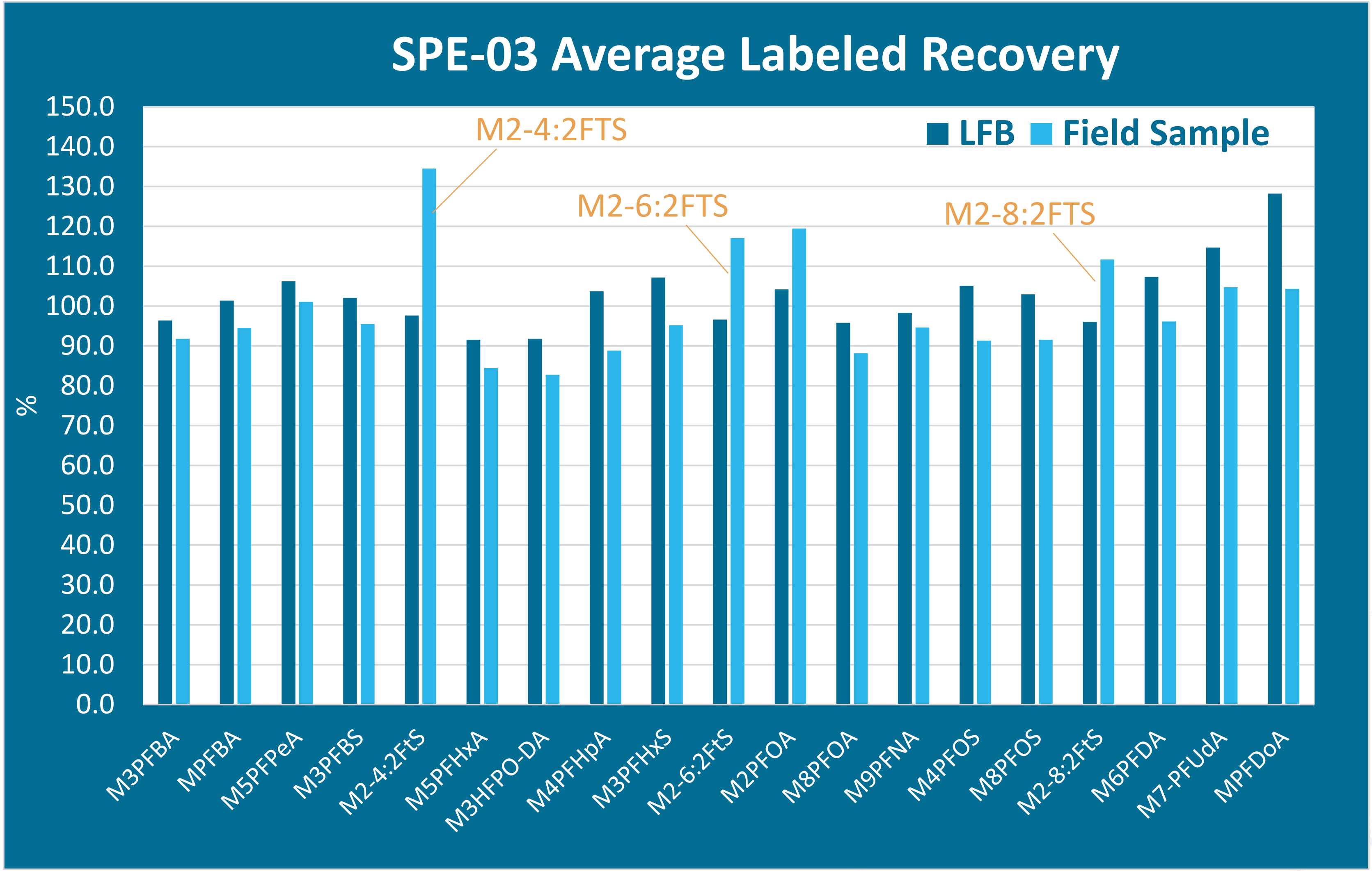


LFB vs Field Sample Labeled Recovery on SPE-03

- N = 24 field samples

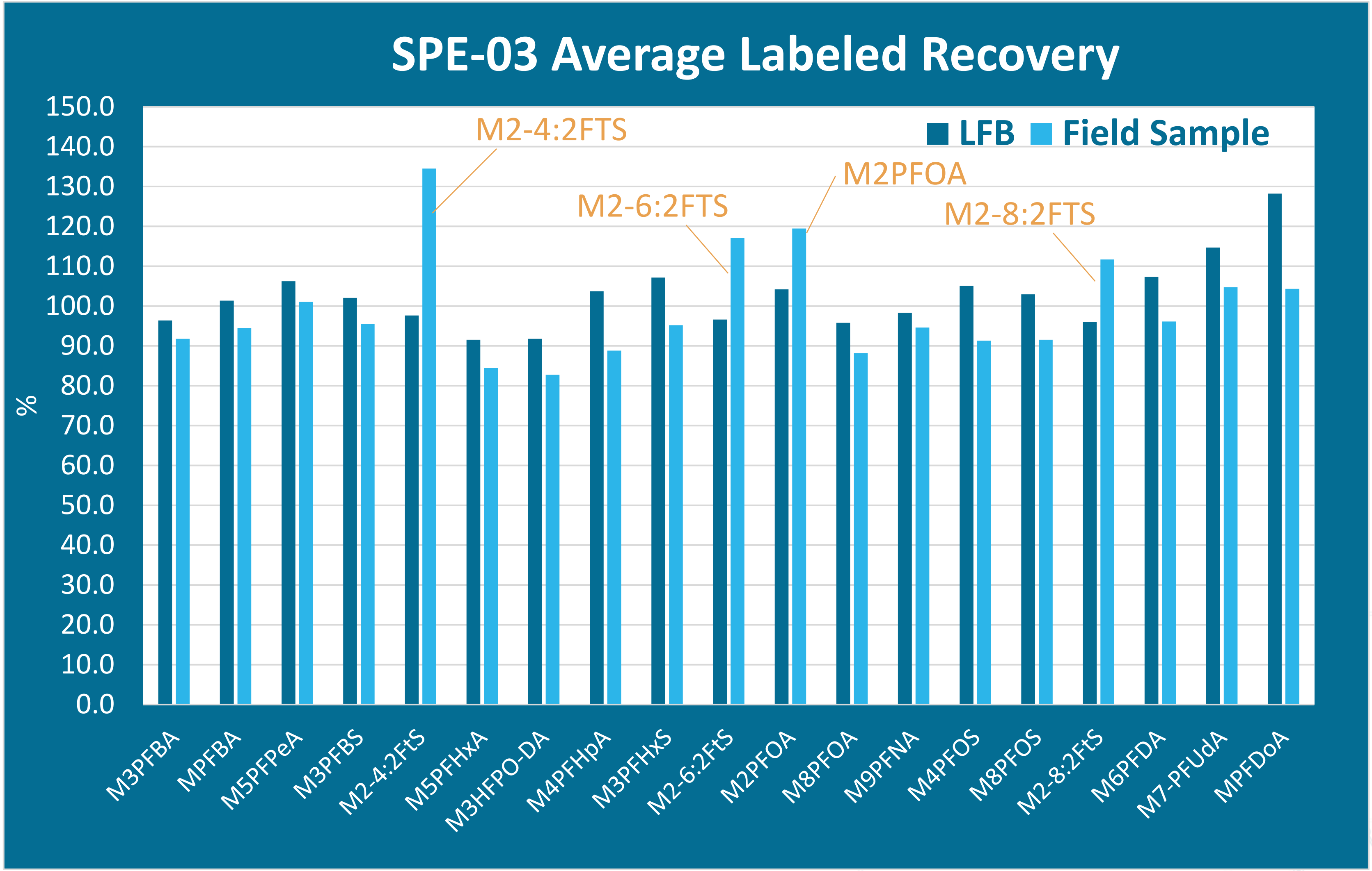
Results – Matrix Tolerance



LFB vs Field Sample Labeled Recovery on SPE-03

- N = 24 field samples
- Matrix enhancement on FTS and M2 isotopes

Results – Matrix Tolerance



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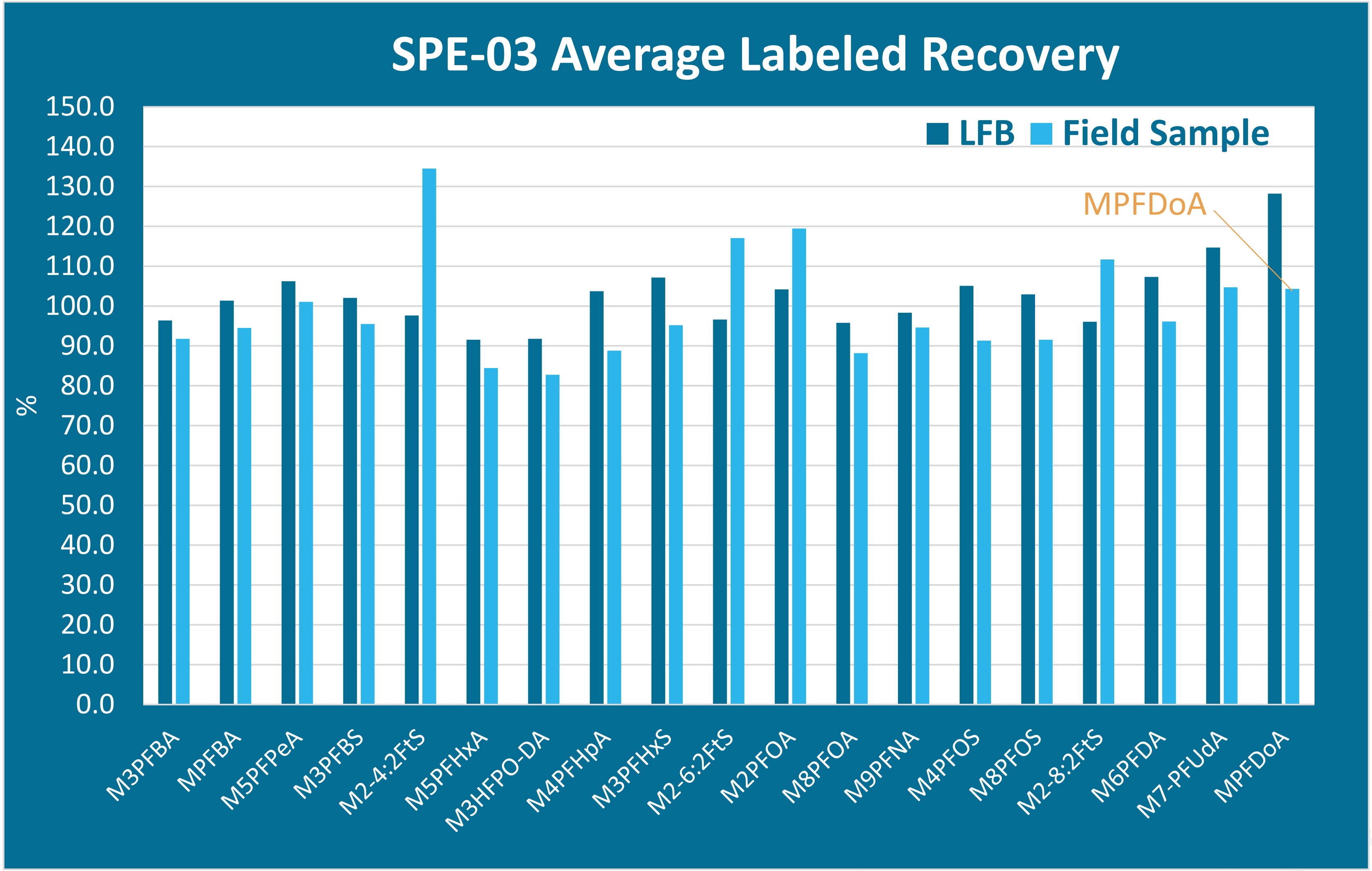
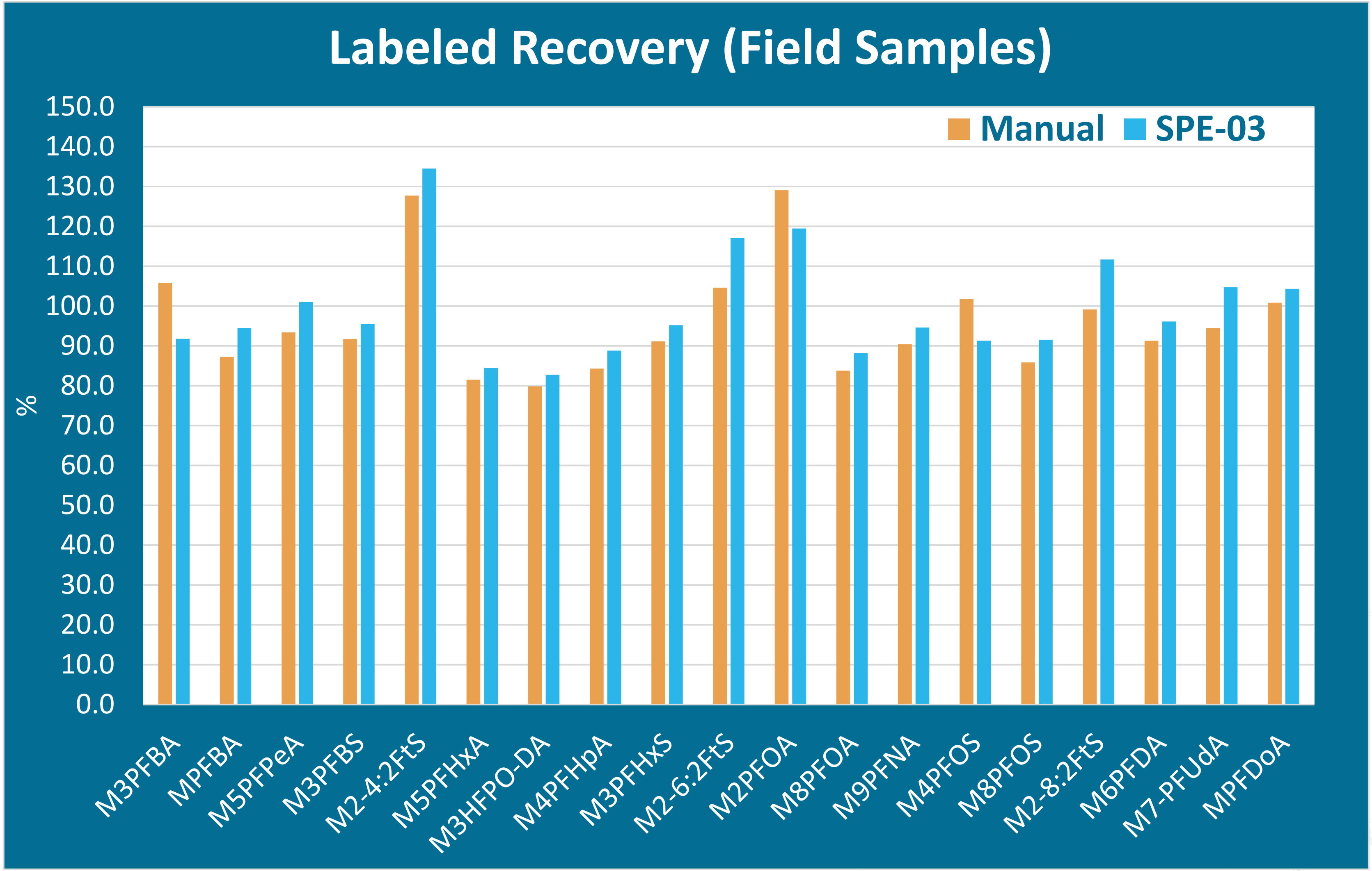


LFB vs Field Sample Labeled Recovery on SPE-03

- N = 24 field samples
- Matrix enhancement on FTS and M2 isotopes
- Lower recoveries for isotopes with longer retention time, e.g. MPFDoA

Results – Matrix Tolerance

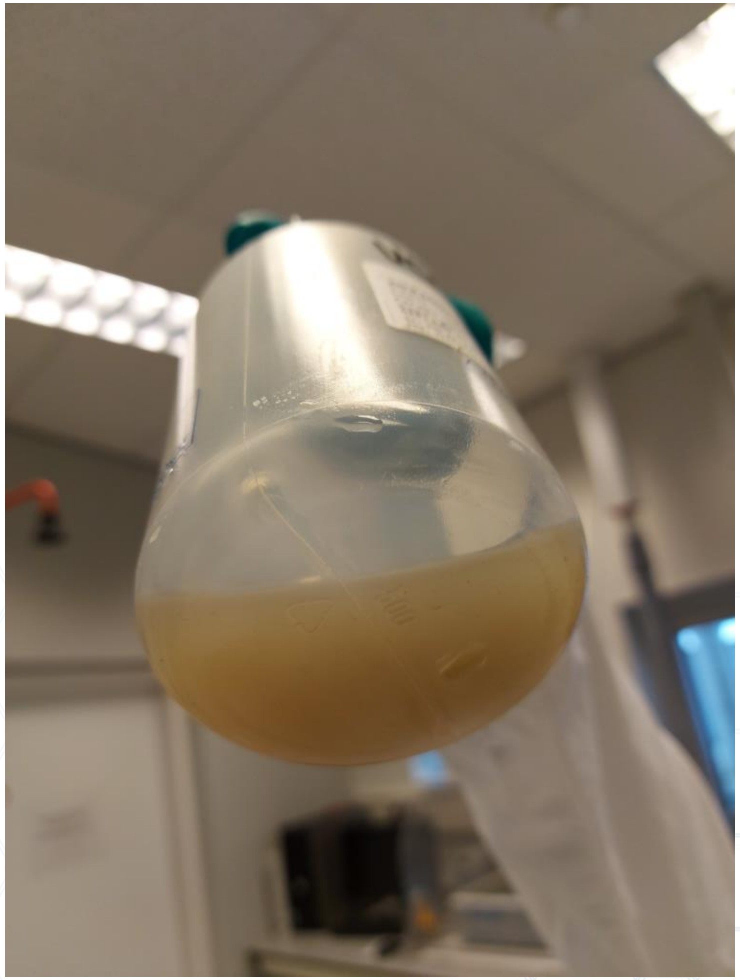


Manual vs SPE-03
Labeled Recovery

- Similar matrix effects

Field Sample Tolerance

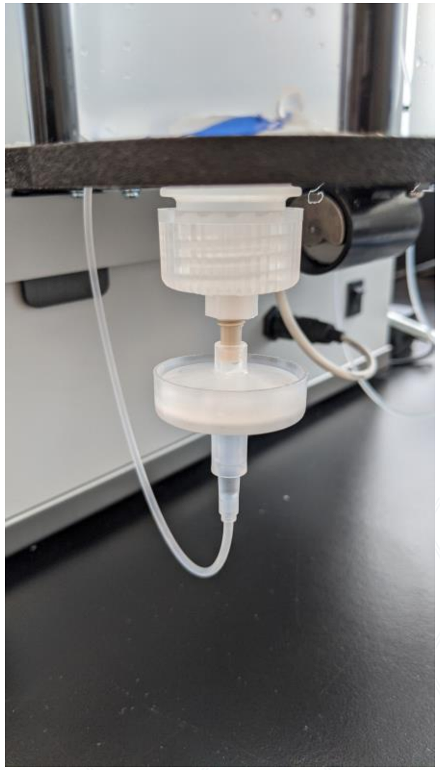
- Drinking water with particulates
- Surface/Waste water



Field Sample Tolerance

1. Inline filters

Direct Connection

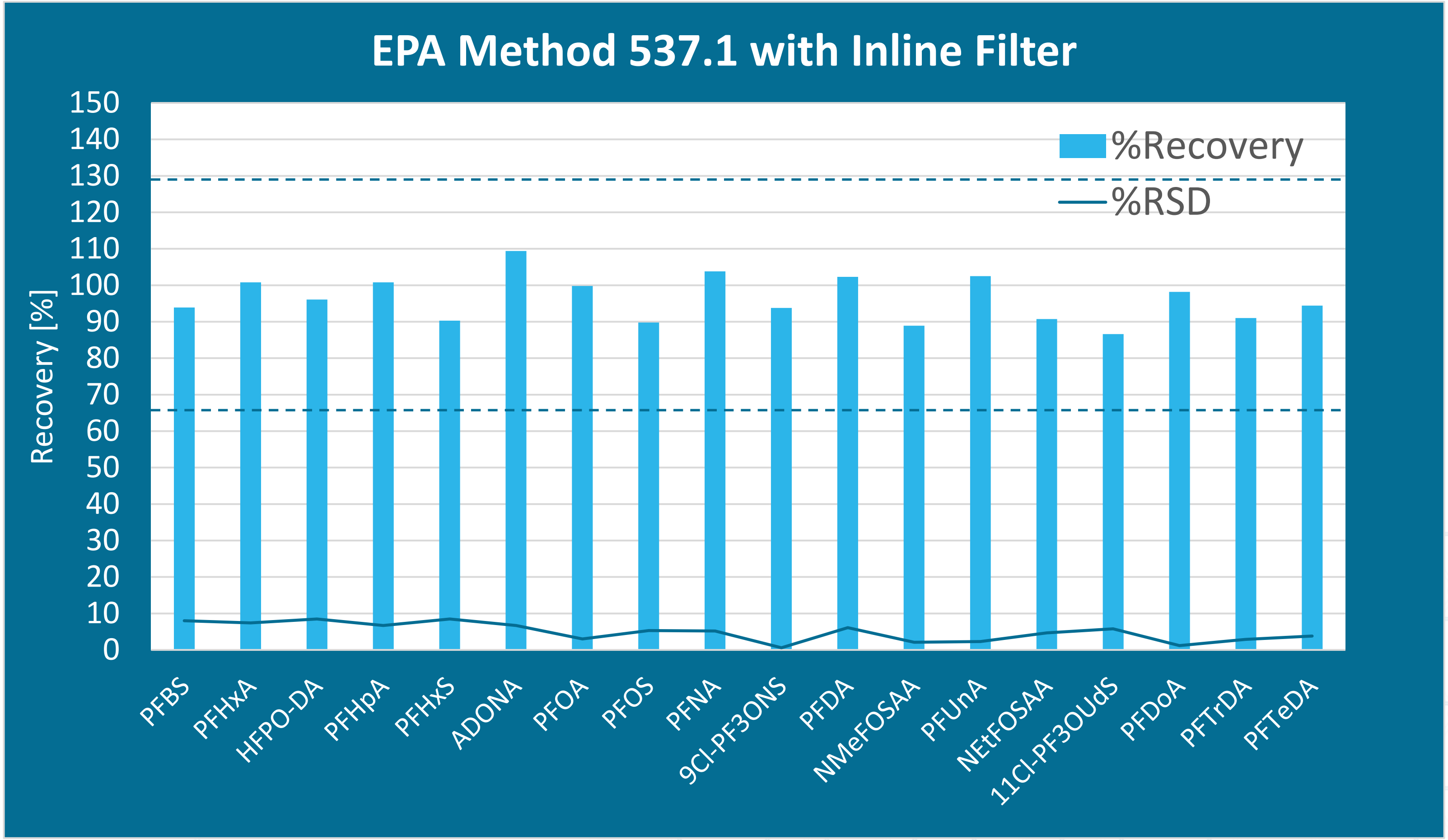


High Capacity

Field Sample Tolerance

1. Inline filters

- EPA Method 537.1 using inline filters (OCWD)
- N = 4 x 20 ppt spikes



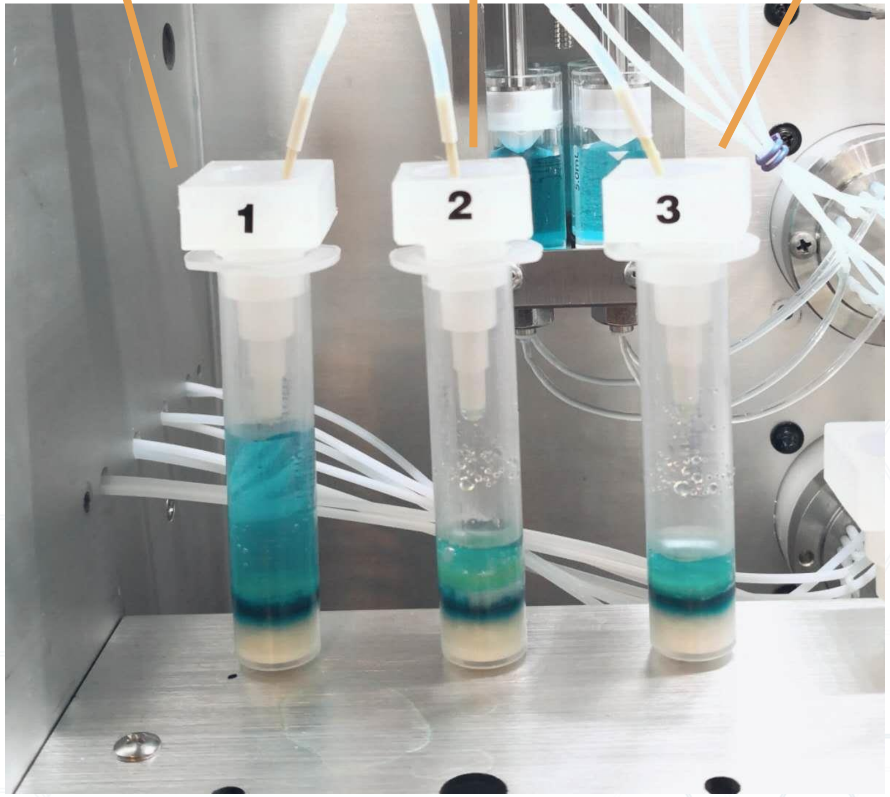
Field Sample Tolerance

1. Inline filters
2. Anti-clogging frits

Regular cartridge

Anti-clogging frit added on top

Original frit replaced with anti-clogging frit



Conclusion

1. PFAS applications call for specific features
    - Sample bottle rinsing
    - High efficiency
    - Clean background
    - Handling particulates

2. **Full automation** with good performance can be achieved following EPA Method 533

Acknowledgements

Alpha Analytical

Merit Labs

Orange County Water District

NEMC

Questions?

- ian_wan@promochrom.com
- www.promochrom.com/pfas-extractions

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