A Simple, Rapid Method for the Analysis of Perfluorocarboxylic Acids in Drinking, Ground and Waste Waters Using GC/MS/MS

Megan Pennington-Boggio, PhD

Catherine Svingos, Eva Doty, Gary Schafran, PhD

August 2025

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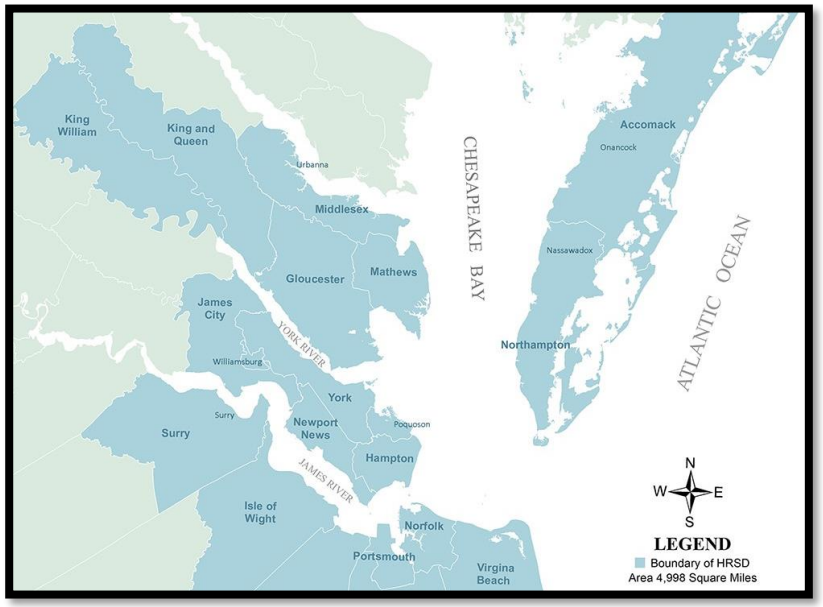
Hampton Roads Sanitation District

Nation's 14th largest wastewater utility
Population served: 1.9 million

Political Subdivision created in 1940
Serves 20 cities and counties

Combined treatment capacity:
225 million gallons per day



Sustainable Water Initiative for Tomorrow (SWIFT): Indirect Potable Reuse

Central Environmental Laboratory:
Annually ~230k results, 75k samples, 389 fields of accreditation

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Potomac Aquifer Recharge Monitoring Laboratory (PARML)

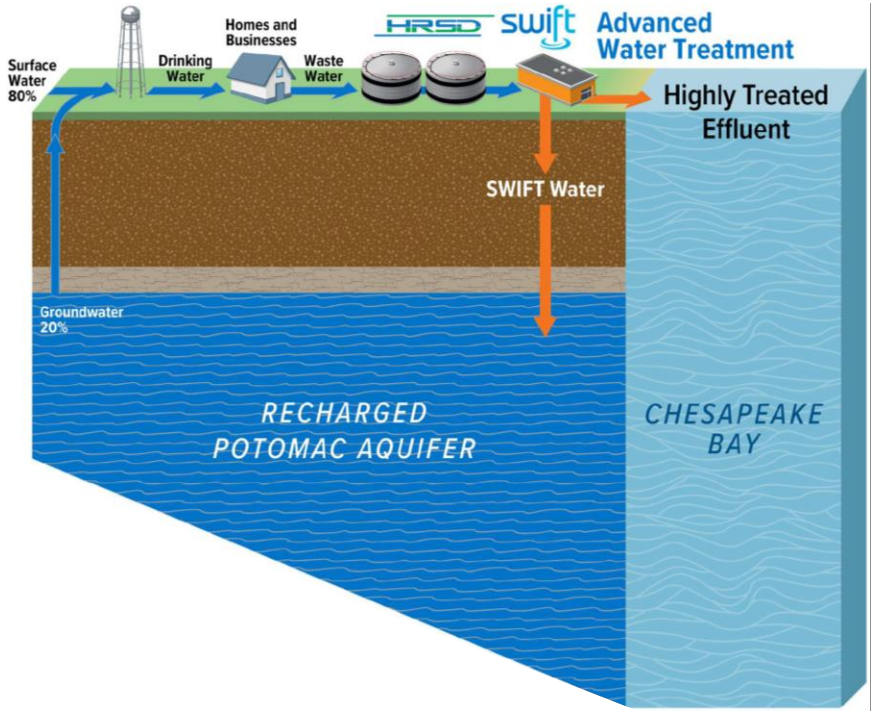
Established by Virginia Legislation in 2019

Jointly operated by Old Dominion University and Virgina Tech

Independent oversight of HRSD's SWIFT

Monitors: Quality of recharge water
Response of the aquifer

Conducts research to advance the field of water reuse



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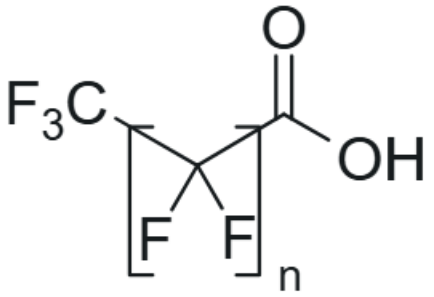
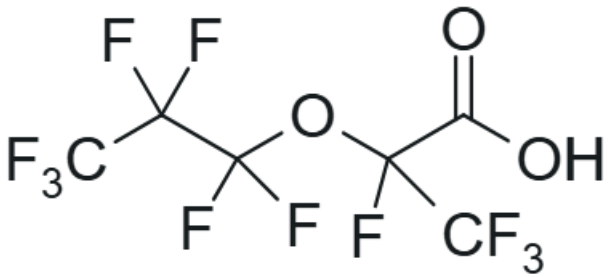
Obligatory PFAS Slide

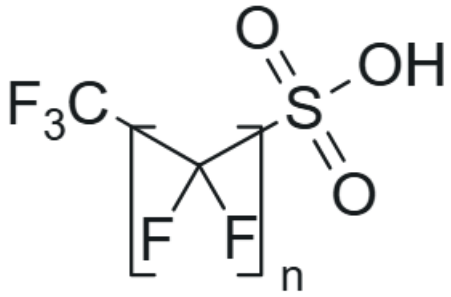
- PFAS – Per- and Polyfluoroalkyl Substances
  - — Persistent in the environment
  - — Cause cancer, hormone disruption, reproductive issues, etc.



PFCAs



HFPO-DA (GenX)



PFSAs

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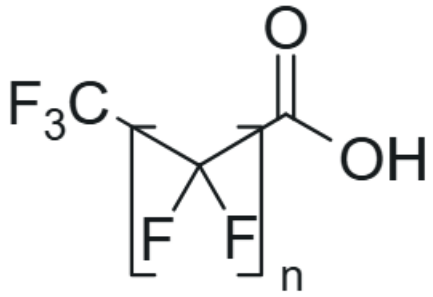
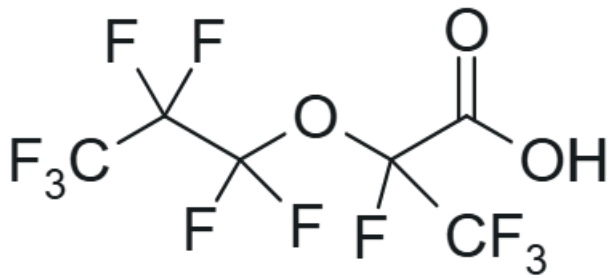


PFCAs



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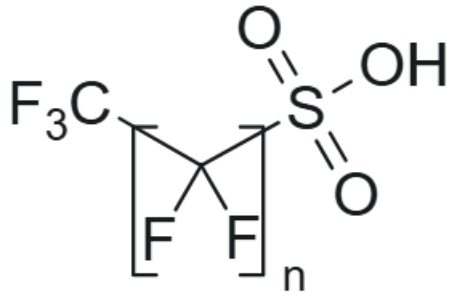

PFSAs

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EPA Methods

- EPA 533, EPA 537.1, EPA 1633
  - — Solid Phase Extraction
  - — Analysis by LC/MS/MS
  - — LLOQ's ≈ 1-5 ng/L
- EPA 8327
  - — Dilute & Shoot
  - — LLOQ's ≈ 10 ng/L

Media	Method	Scope
Potable Water	Method 537.1	18 PFAS Drinking water
	Method 533	25 PFAS Drinking water
Non-Potable Water	Method 8327	24 PFAS Non-drinking water aqueous
	Method 1633	40 PFAS Wastewater Surface water Groundwater Landfill leachate

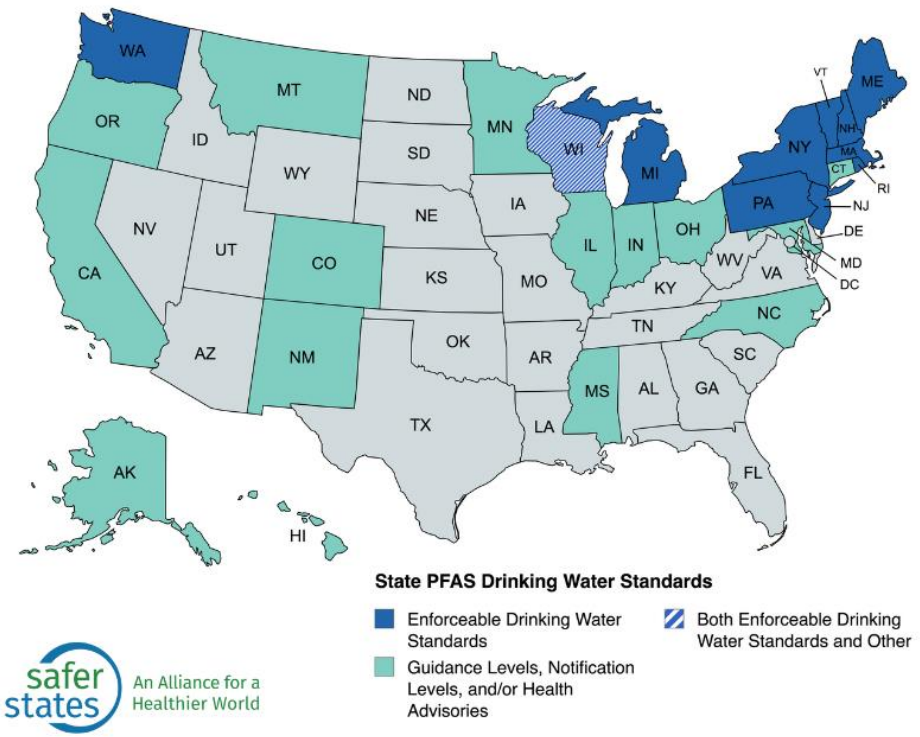
Treatment and Monitoring

Expanding regulation ->

Treatment is increasingly important

Effective treatment requires frequent monitoring

Long turnaround times are not conducive to decision making



https://www.saferstates.org/priorities/pfas/; 7/1/2025

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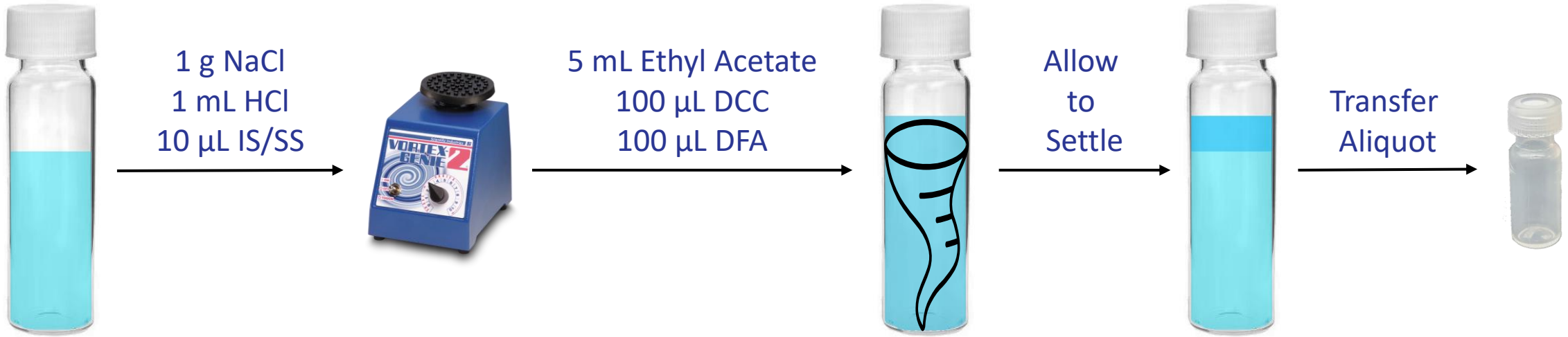
Simple, Rapid Monitoring Method

- Quick, Easy, Cheap, Effective, and Rugged
  - Quick: Turnaround in < 1 hour is possible
  - Easy: Room temperature derivatization and micro-extraction
  - Cheap*: Affordable reagents
    - *GC/MS/MS not included
  - Effective: Most recoveries within 70-130%
  - Rugged: Drinking Water to Industrial Waste
  - 13 Analytes: C2-C13 PFCAs and HFPO-DA
  - Sensitive: LOQs as low as 1 ng/L

Derivatization Procedure



IS/SS: 100 ug/L PFOA-$^{13}C_{8,}$ 50 ug/L PFBA-$^{13}C_4$ in H_2O
DCC: 100 mg/mL N,N'-dicyclohexylcarbodiimide in Ethyl Acetate
DFA: 5% v/v 2,4-difluoroaniline in Ethyl Acetate

Adapted from Scott et al., Environ. Sci. Technol., 2006, 40, 6405–6410

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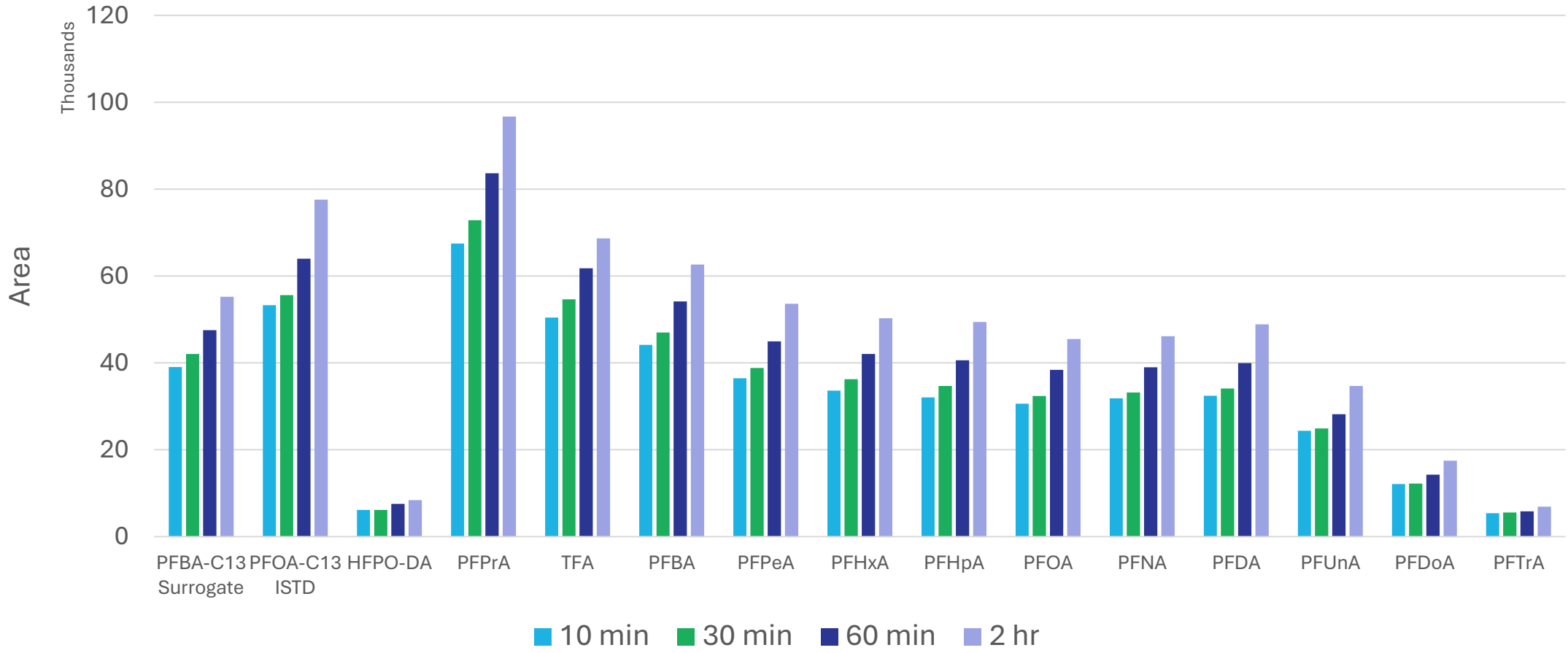
Settling Time



(TFA response divided by 100 for scaling)

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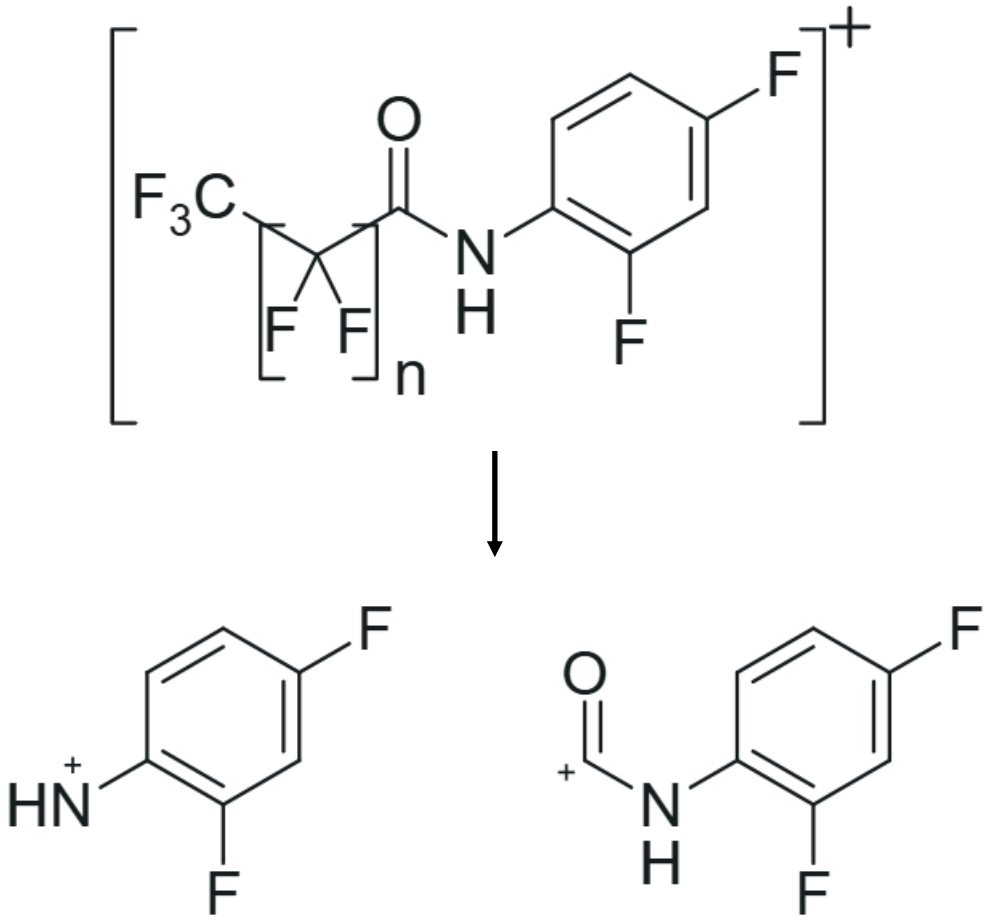
Analysis

- Analyzed by MRM
  - GC/MS/MS: Agilent 7890B/7010B
  - Column: Agilent J&W DB-1701
- 14-minute run time
- 2 transitions per target
  - $M^+ \rightarrow$ m/z 128
  - $M^+ \rightarrow$ m/z 156



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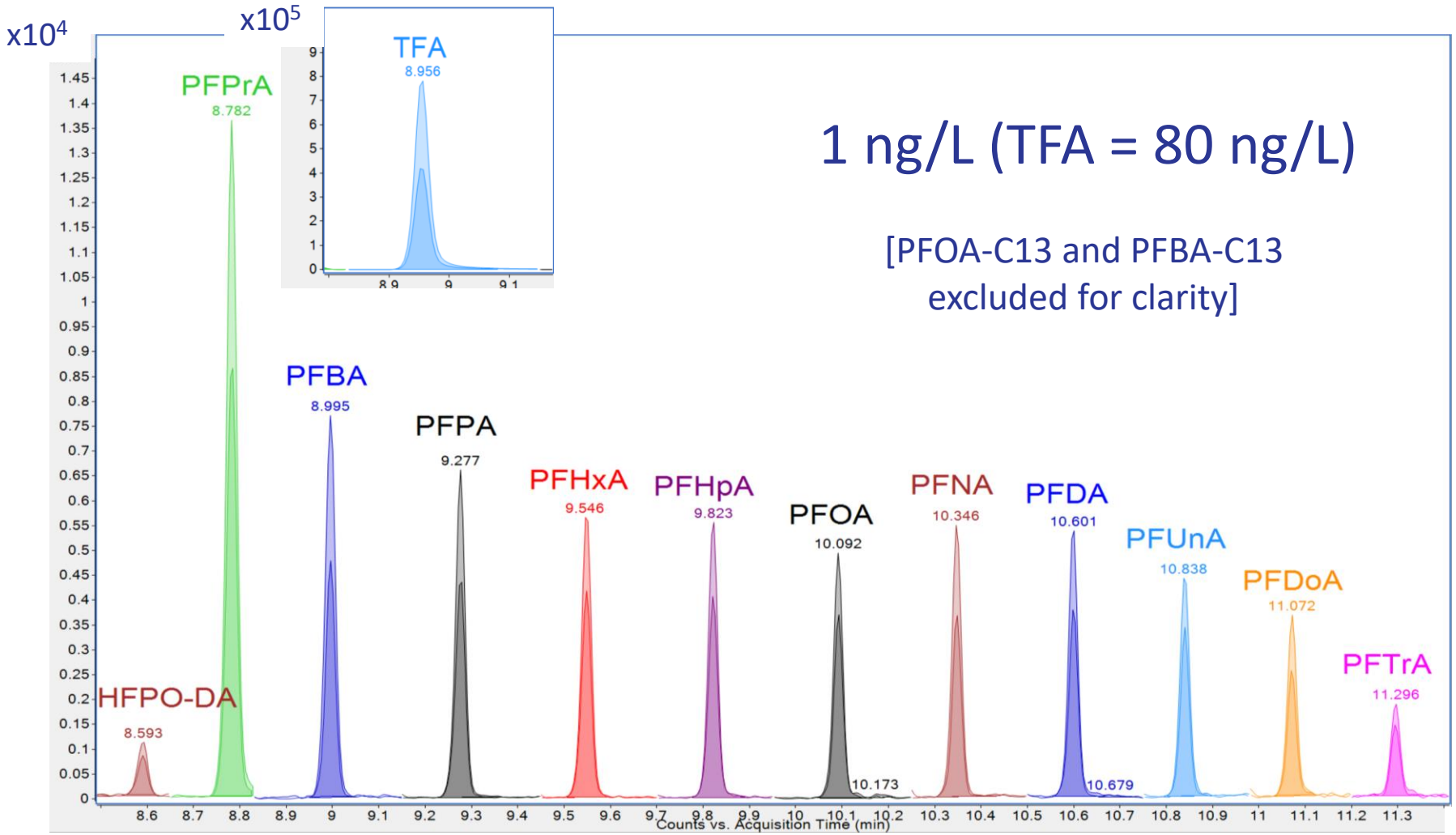
Chromatogram



1 ng/L (TFA = 80 ng/L)

[PFOA-C13 and PFBA-C13 excluded for clarity]

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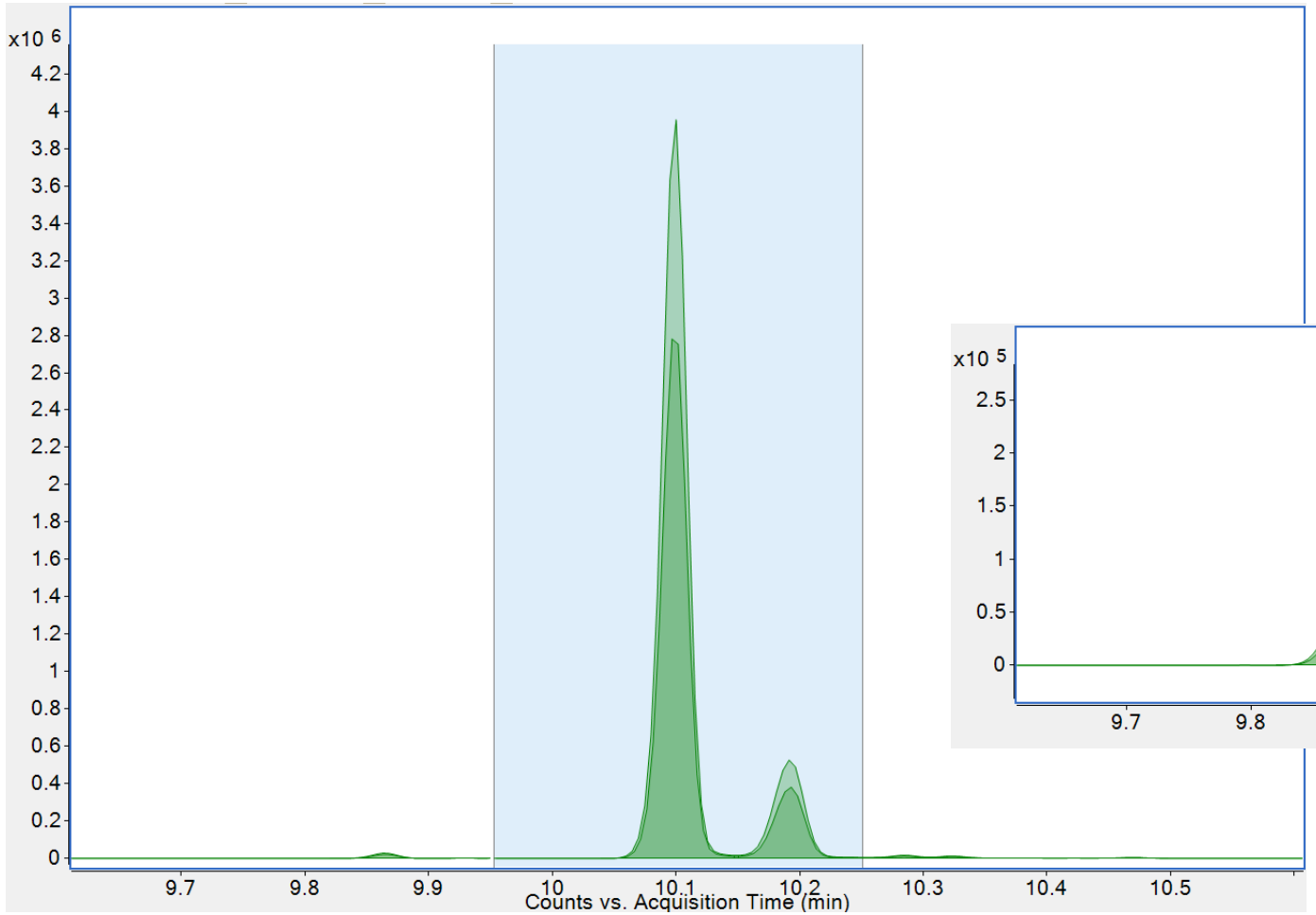
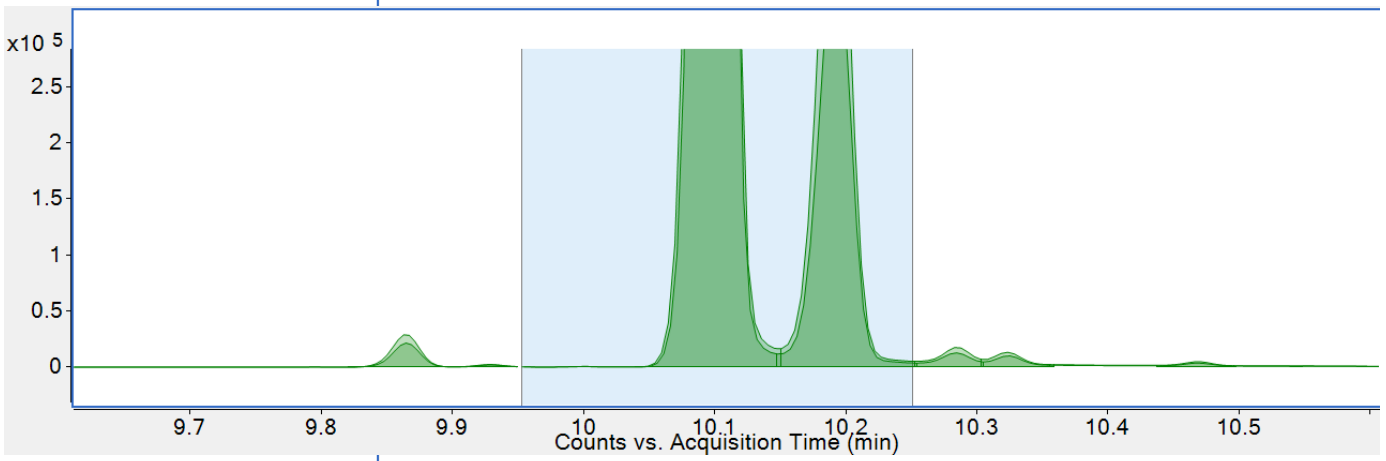
PFOA Isomers





Current method captures ~98% of PFOA isomers

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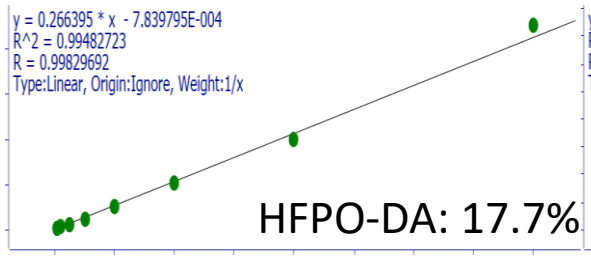
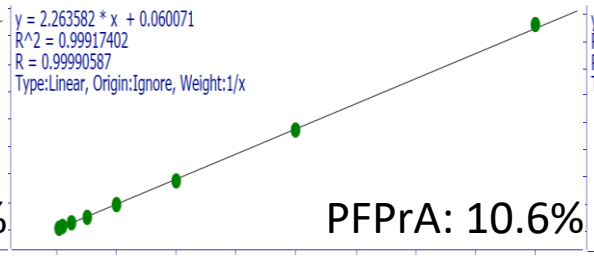
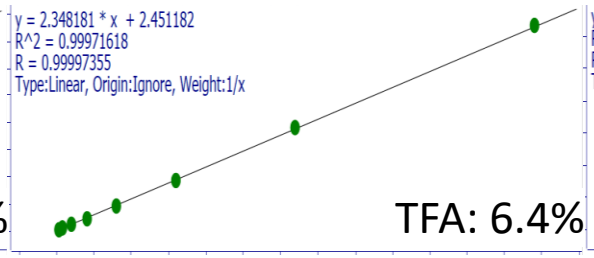
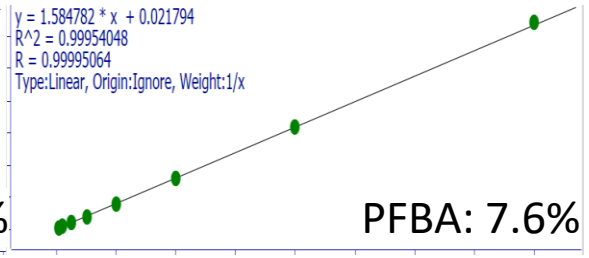
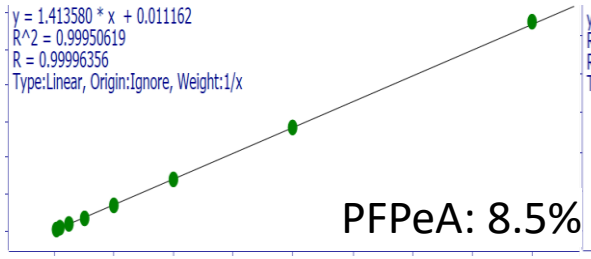
Calibration - %RSE

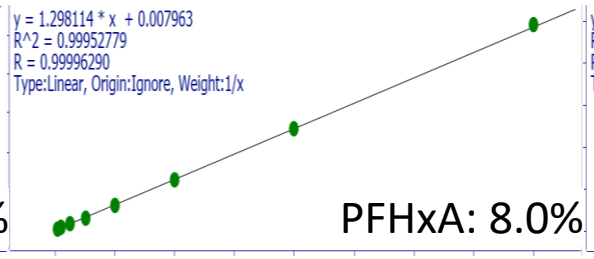


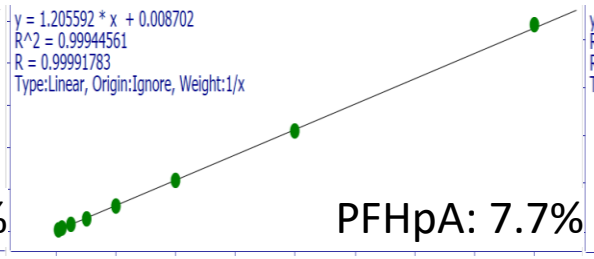


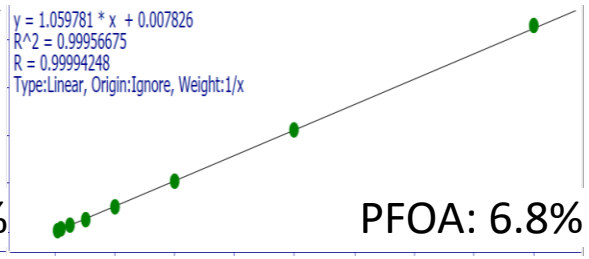


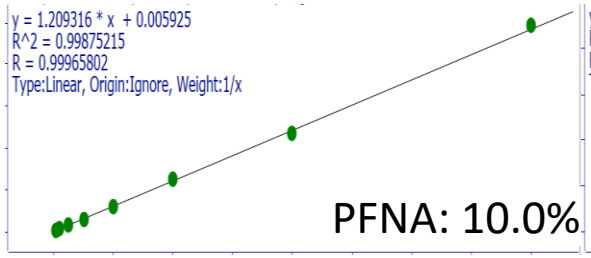


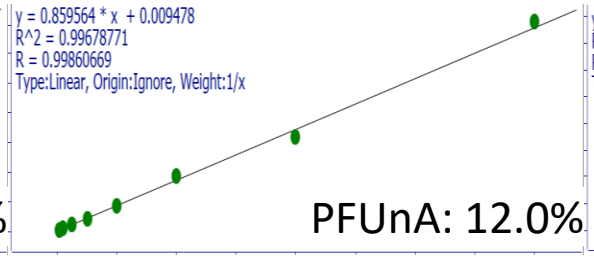


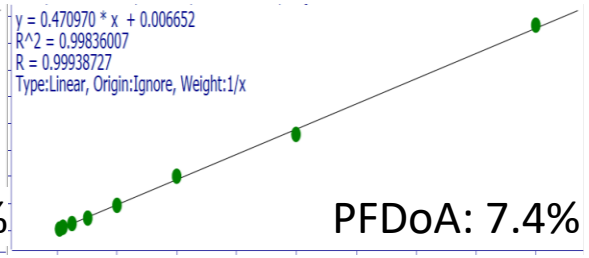


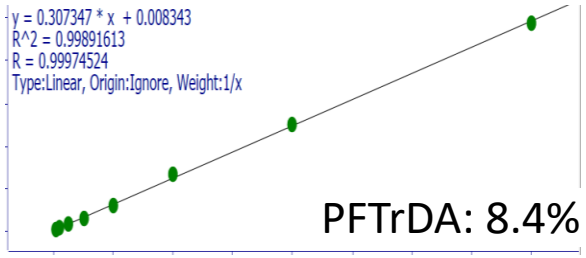












1 – 200 ng/L
(TFA: 80 – 16,000 ng/L)

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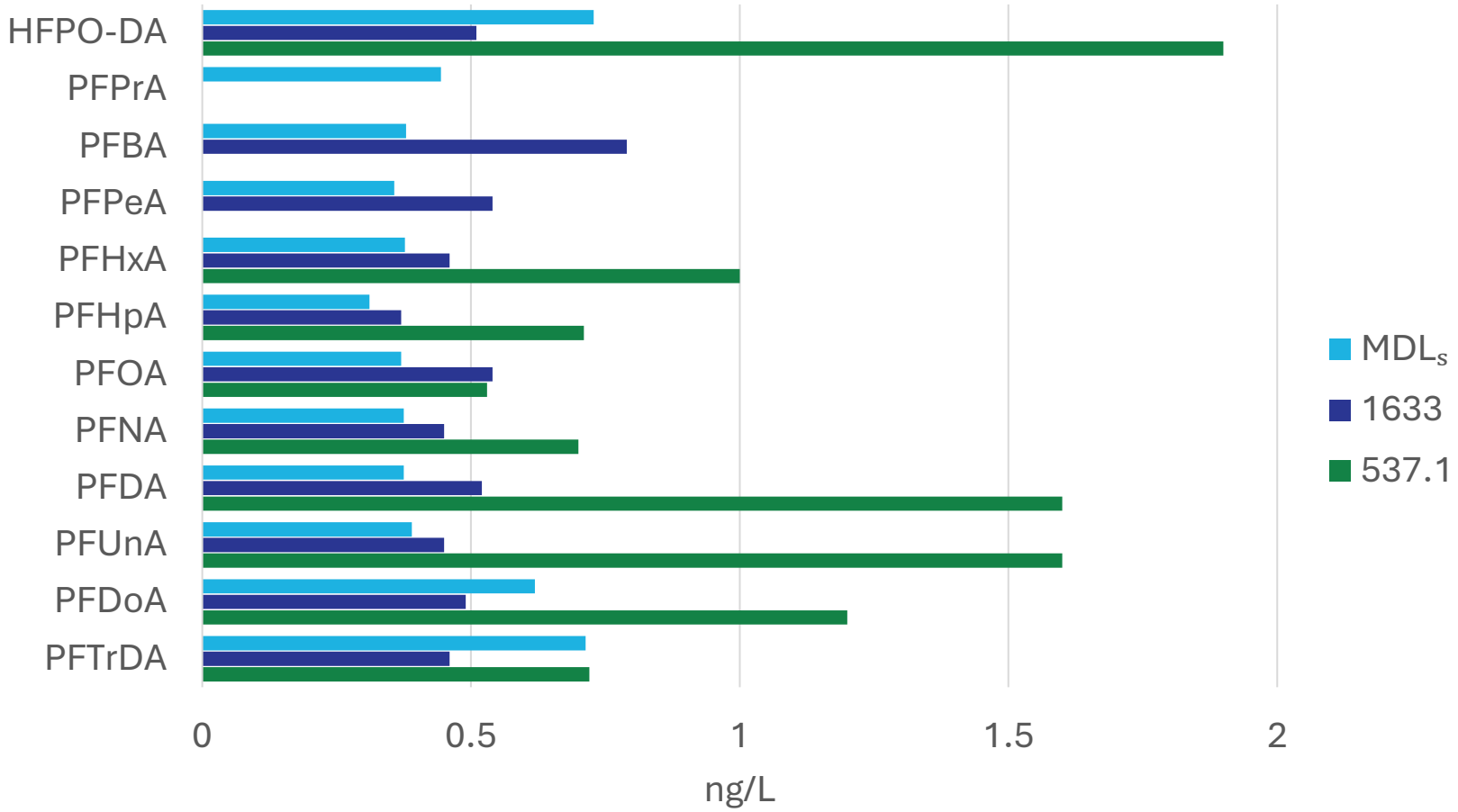
Spike MDL



Spiked at 1 ng/L

TFA:
Spiked at 80 ng/L
MDL_s= 32.9 ng/L

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Blank MDL

Compound	MDL_b (ng/L)
HFPO-DA	0.379
PFPrA	0.129
TFA	36.0
PFBA	0.027
PFPeA	-
PFHxA	0.001
PFHpA	-
PFOA	-
PFNA	0.072
PFDA	-
PFUnA	-
PFDoA	0.118
PFTrDA	-

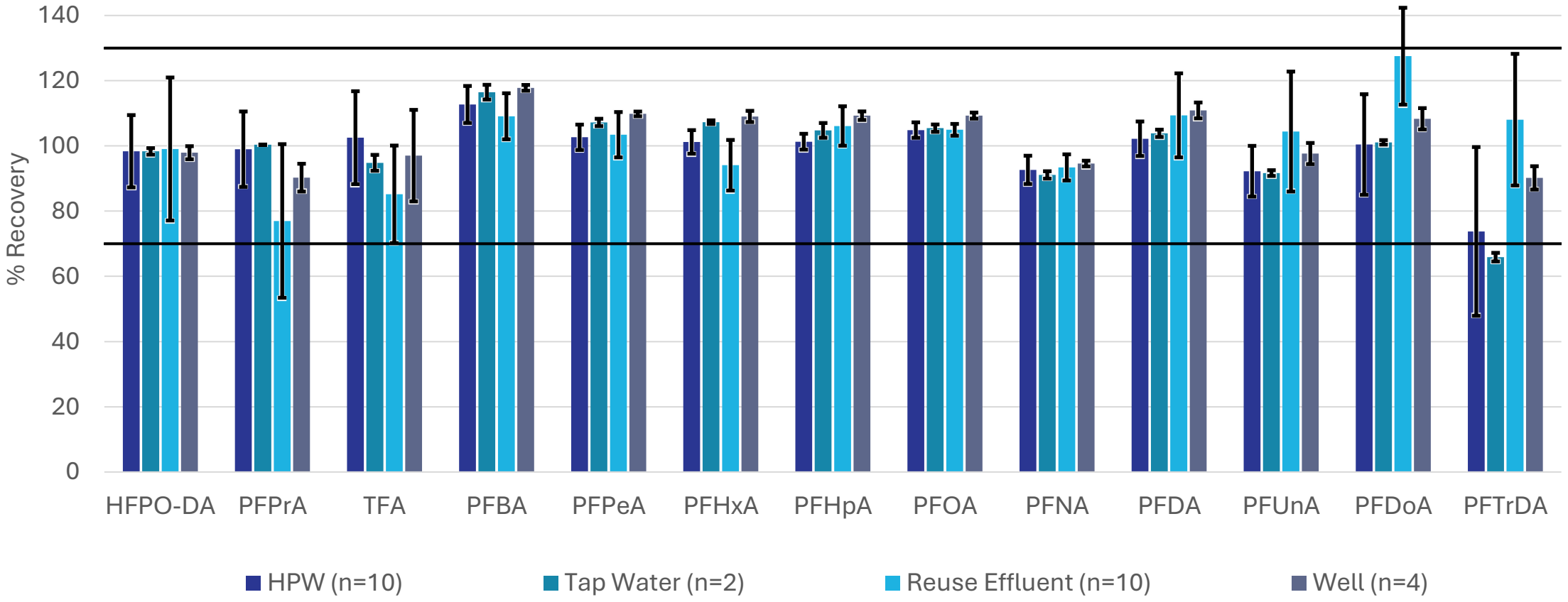
We do:

- Reuse sample bottles
- Use PTFE capped vials
- Use sharpies

We don't:

- Rinse pipette tips
- Wipe down surfaces
- Lot check reagents
- Have a dedicated prep area

Drinking Water and Groundwater



Error bars represent ± 1 SD

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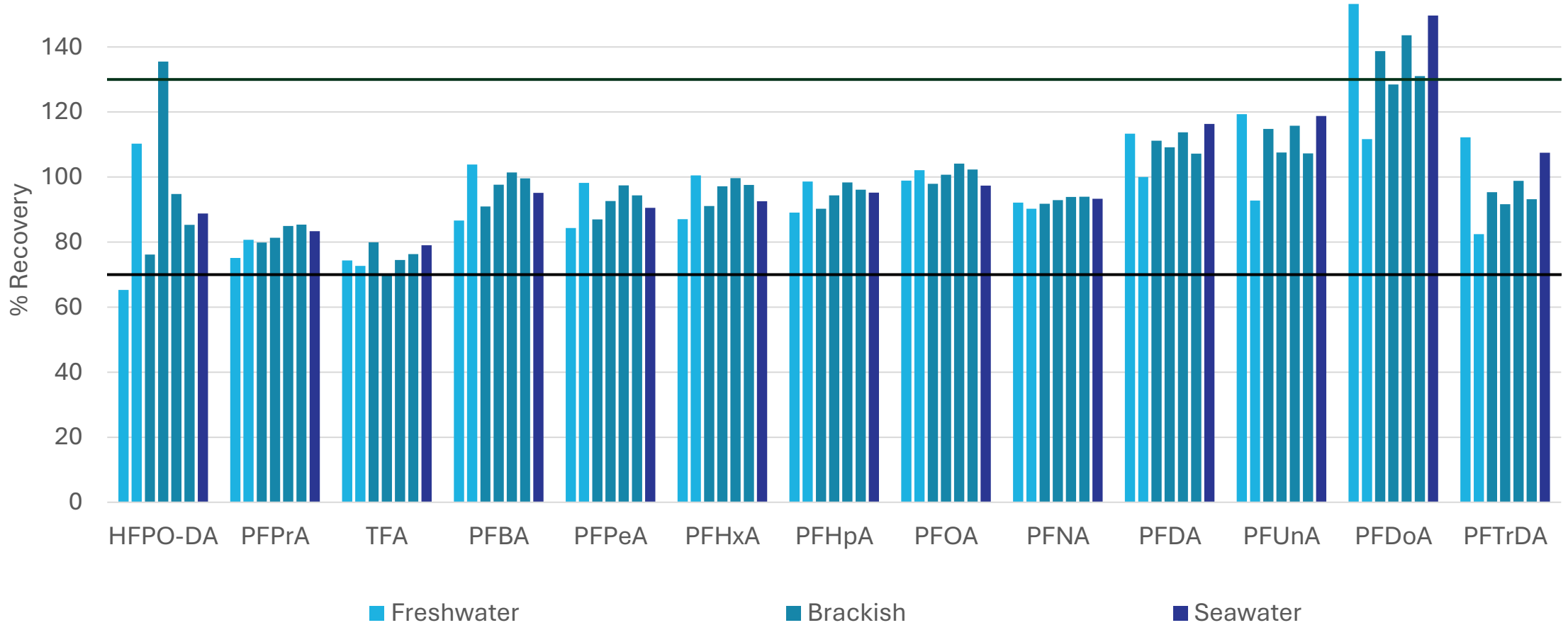
Surface Water



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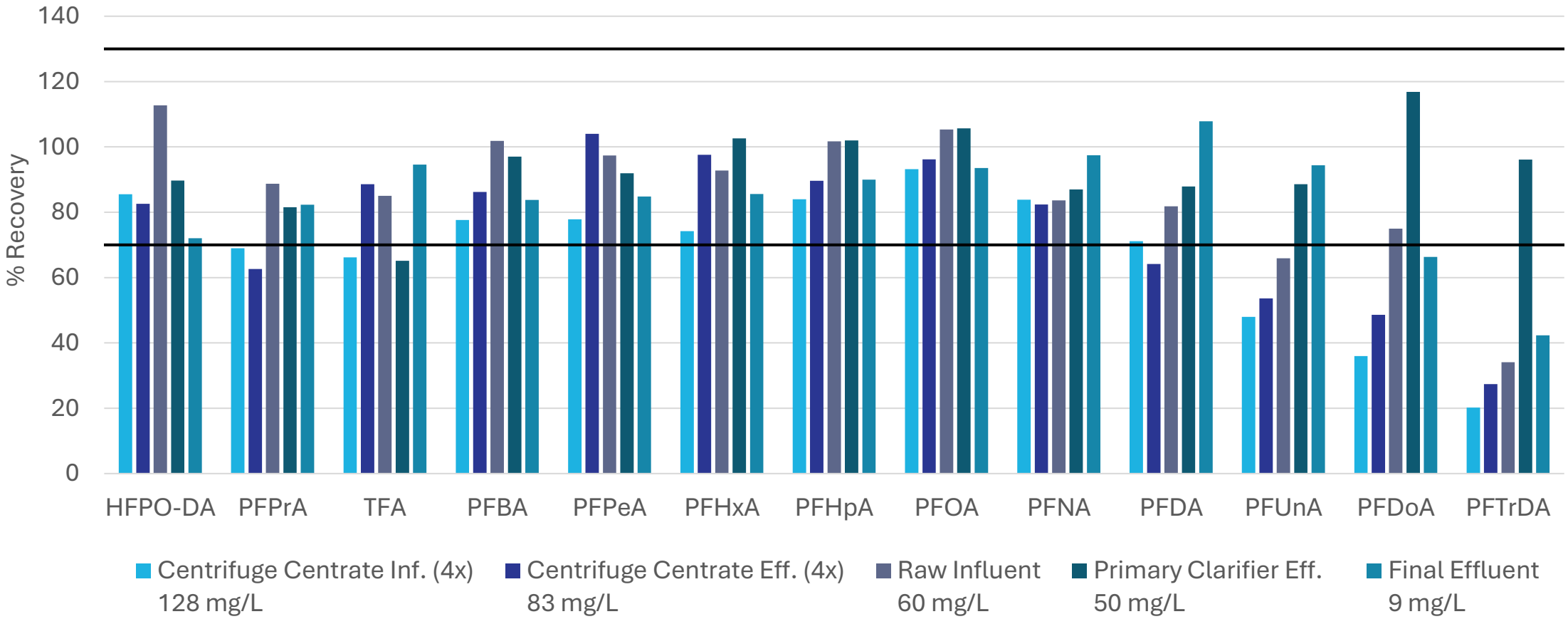
Wastewater Treatment and TOC



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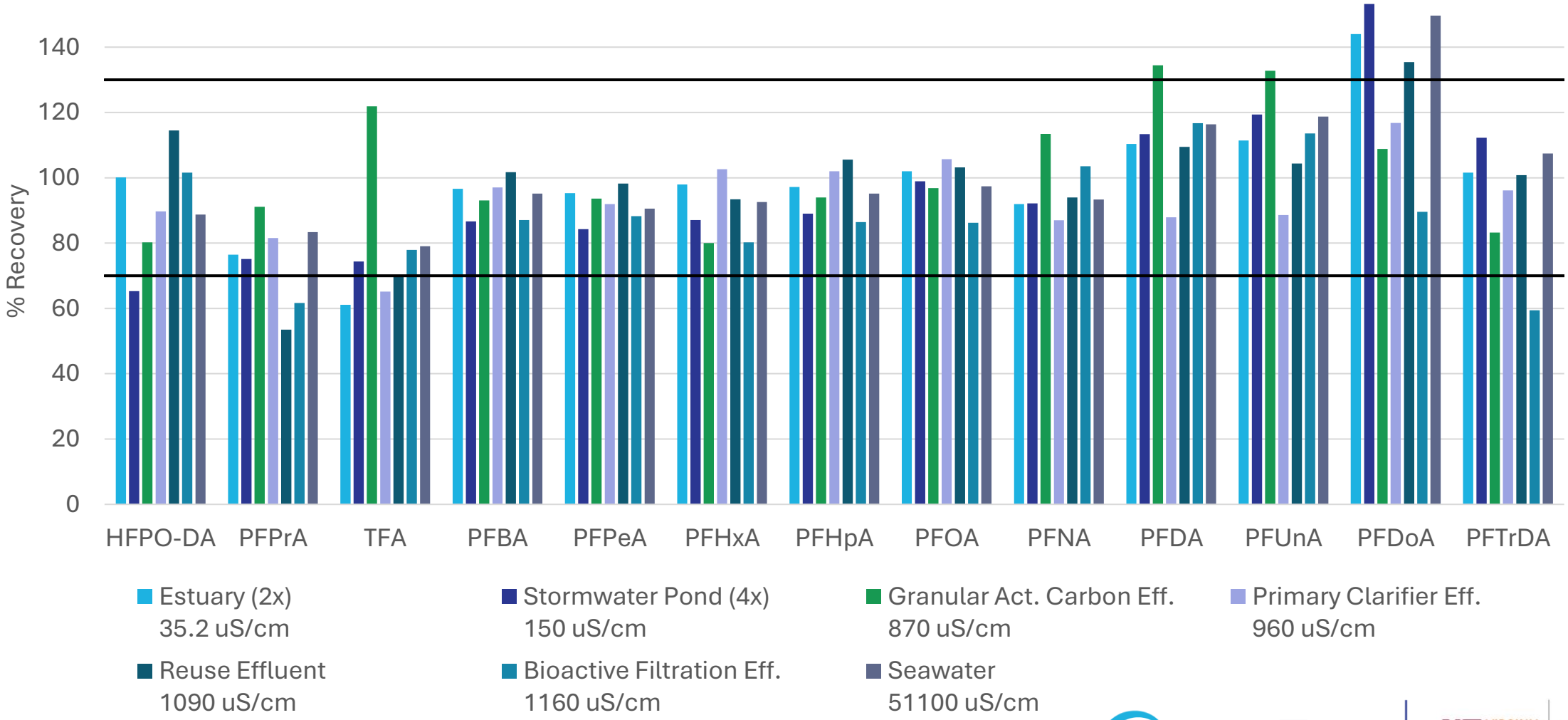
Conductivity



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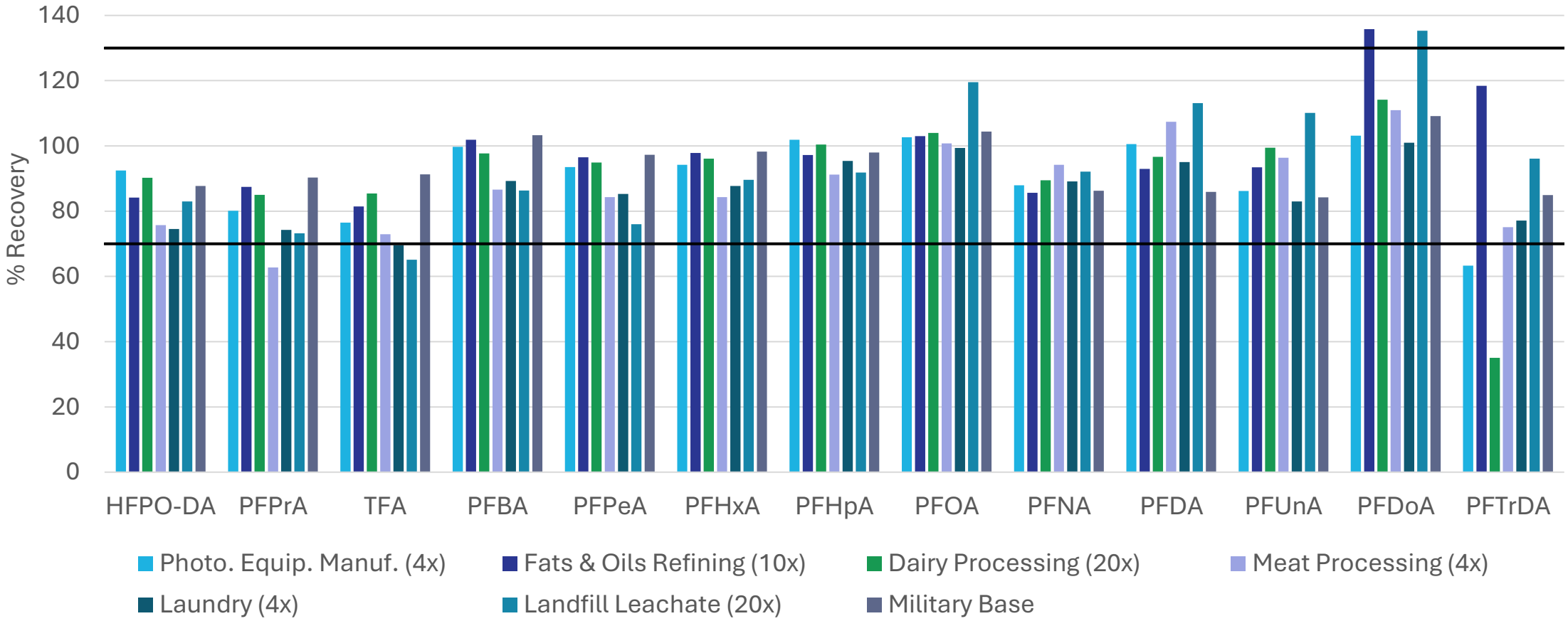
Industrial Waste



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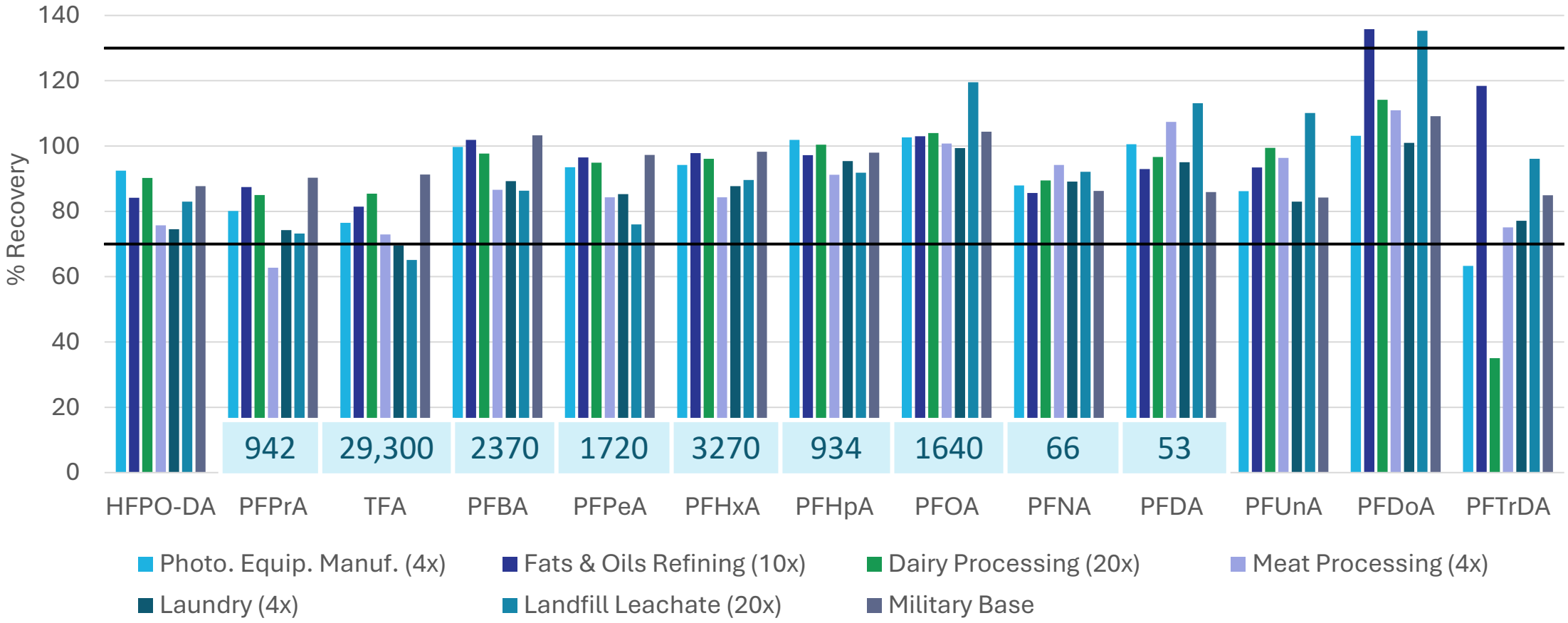

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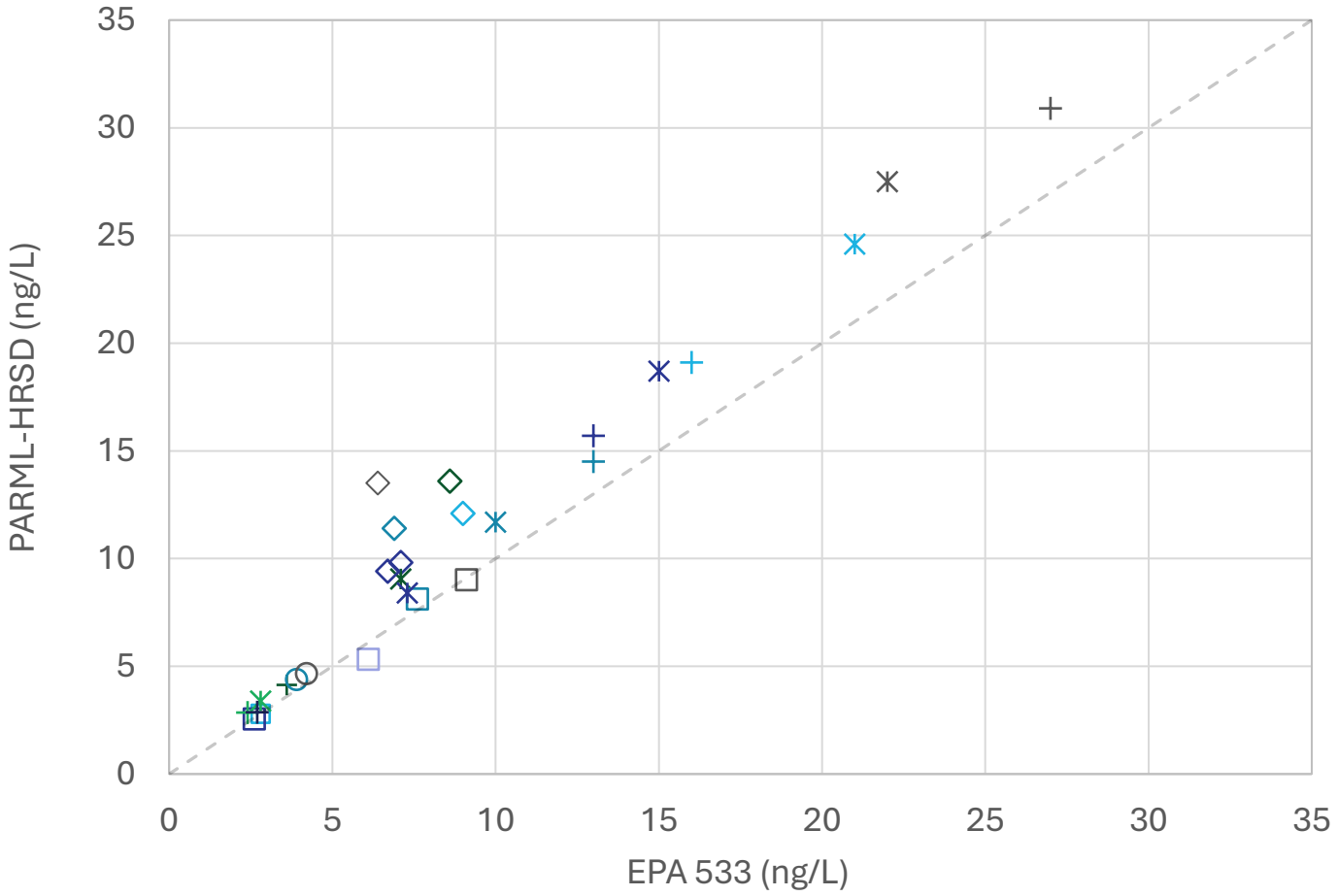
Comparison to EPA data – 533



RPD < 30% except PFBA

- ◇ PFBA
- ✳ PFPeA
- \+ PFHxA
- ○ PFHpA
- □ PFOA

Well #1
Well #2
Well #3
Reuse Effluent
Raw Influent
Secondary Clarifier Eff.
Bioactive Filtration Eff.
Granular Act. Carbon Eff.

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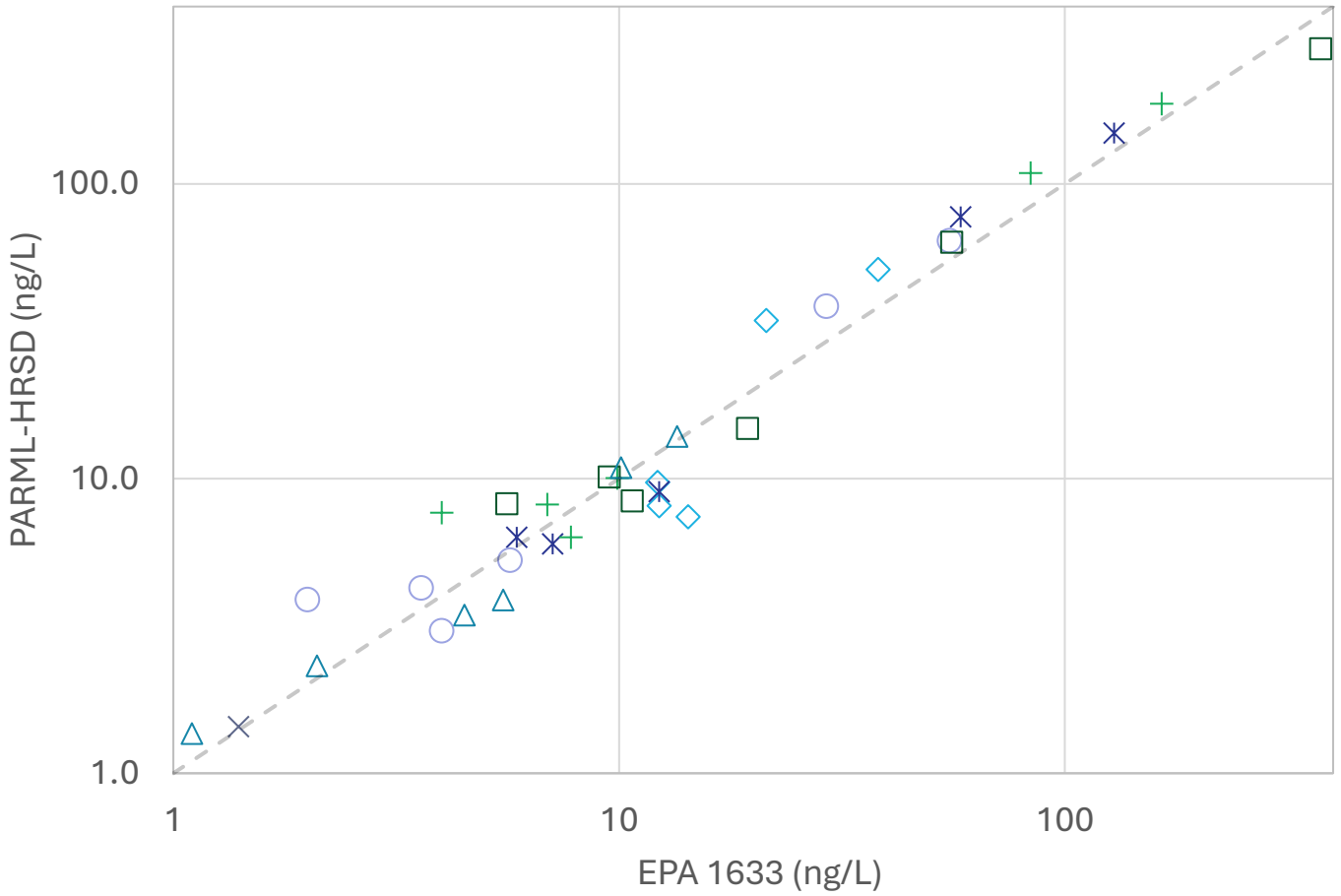
Comparison to EPA data - 1633



6 Sites
Military Base

Most RPD <30%

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Conclusions

- Simple, Rapid Analysis for PFCAs
- Compatible with many matrices
- Not susceptible to contamination
- Not a replacement for approved EPA methods

A useful tool for process monitoring to enable near real-time decision making

Acknowledgements

- PARML – Dr. Hadi Khatami
- CEL Organics
  - — Especially Cat Svingos!
- HRSD Water Quality Division

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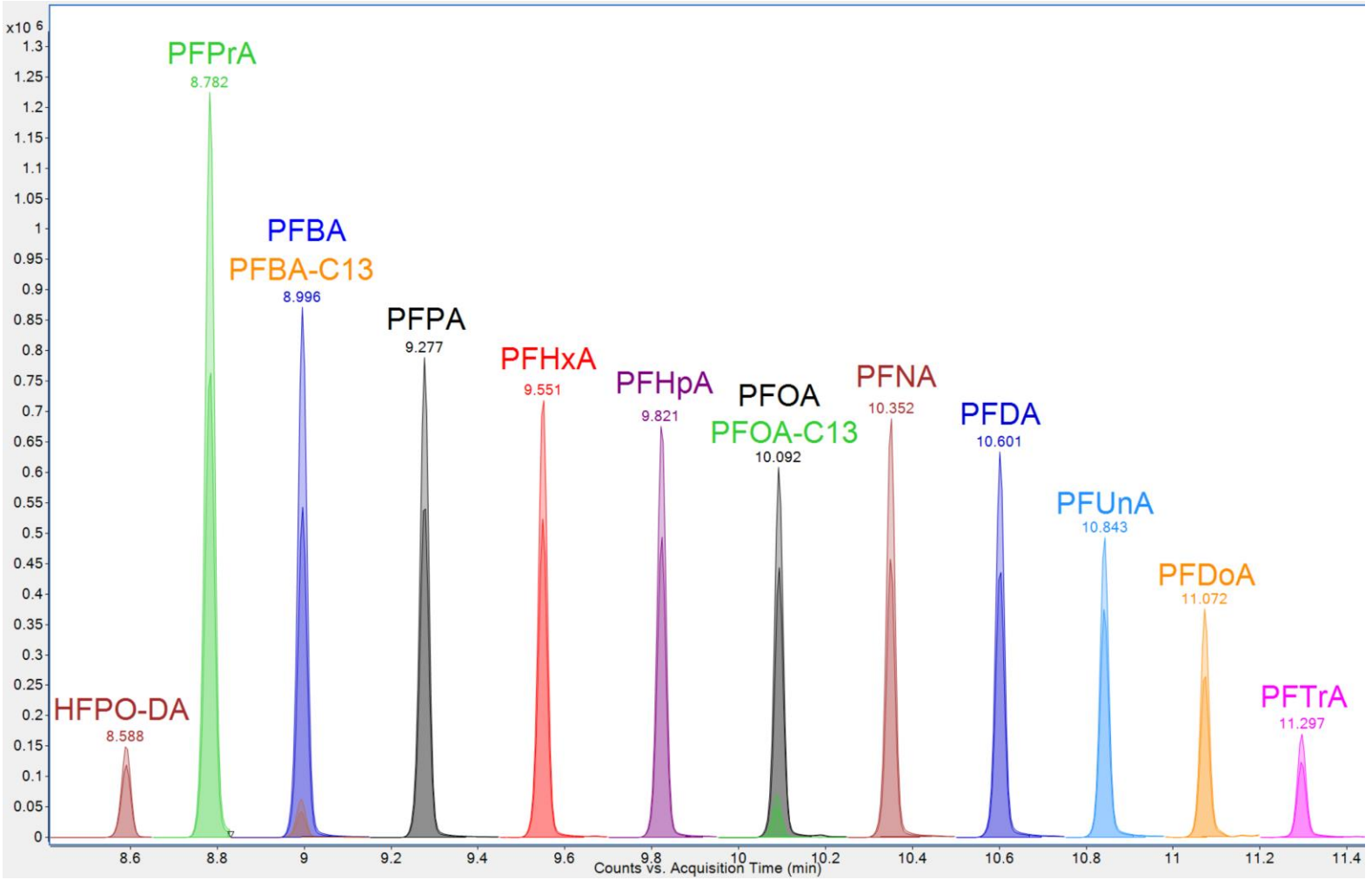
Bonus Slides

200 ng/L Chromatogram



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MRL Verification

Compound	Lower PIR Limit	Upper PIR Limit
HFPO-DA	81	148
PFPrA	97	117
TFA	98	116
PFBA	85	129
PFPeA	82	128
PFHxA	72	139
PFHpA	77	134
PFOA	76	140
PFNA	78	141
PFDA	65	150
PFUnA	82	145
PFDoA	67	145
PFTrDA	59	144

Spiked at 1 ng/L
(TFA = 80 ng/L)