Interlaboratory Validation of ASTM D8421, Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Matrices by Co-solvation followed by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

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Brief Overview Topics

- Appreciation of Volunteers and Sponsors
- Overview ASTM D8421
- Sporadic PFAS contamination issue
- Brief Collaborative Study Results
- What do you need?

Thank You

Consumables, columns, filters, syringes and Standards….

- USEPA OW/OST/EAD (Adrian) and OLEM ORCR MRWMD (Troy)
- Accustandard
- Agilent
- Waters
- Shimadzu

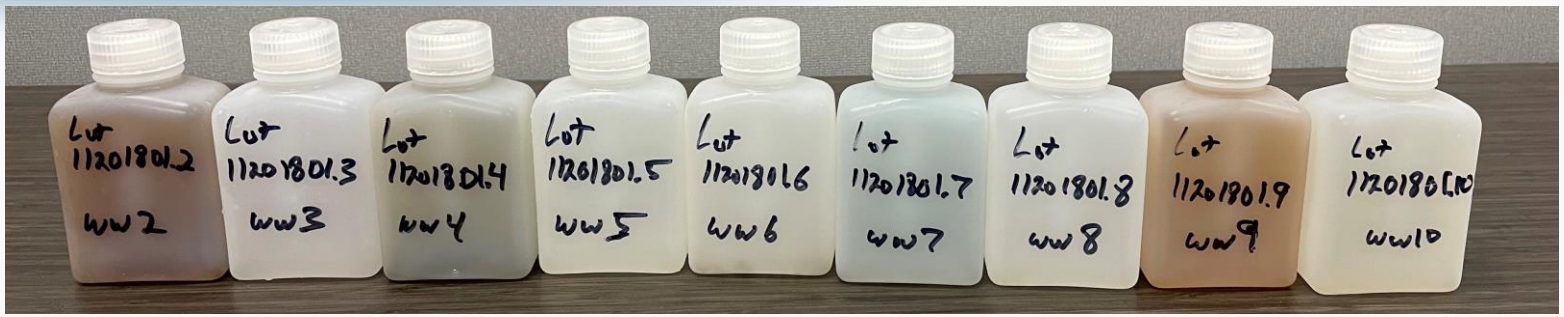
Volunteer Laboratories

- US EPA Region 5
- Rhode Island State Health Laboratories
- Waters
- Agilent
- Pace
- Minnesota Department of Health, Public Health Laboratory
- EPA NEIC- Lakewood, CO…"Denver"
- Merit Laboratories
- US Consumer Product Safety Commission
- BSK Associates
- HydroAnalytical Laboratory
- Manchester Environmental Laboratory
- Pacific Rim Laboratories
- RJ Lee Group
- SGS North America
- Utah Public Health Laboratories
- Weck Laboratories
- ORD-WID PFAS Analytical Lab- Cincinnati

ASTM Method D8421

- Multi-lab Study- 8 Usable Sets of Data
- Eleven Environmental Waters
- Co-solvation/Filter/”Direct” Injection
- Analysis by LC/MS/MS
- Target Analytes:
  - Includes all analytes from EPA 533, 537.1, 1633, and 8327- Plus four additional.
- Isotopically labeled surrogates:
  - Twenty-four (24), more can be added as available.
  - Used to monitor analytical method performance/quality
  - Evaluated and developed not to “correct” the data. Optional to use for Isotope Dilution Correction.
- Uses confirmation ion ratios to identify compounds and minimize false positives

Eleven Matrices



Nine sources supplied by OW/OST/EAD

- Landfill Leachate
- Metal Finisher
- POTW Effluent 1
- Hospital
- POTW Influent
- Bus Washing Station
- Powerplant
- Pulp and Paper
- POTW Effluent 2
- Ground Water
- Surface Water

ASTM D8421 Standard for Water

5 ml sample

Surrogate

5 mL MeOH

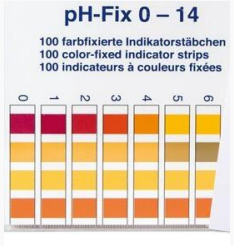
Mix

Filter

LC/MS/MS

10 µL Acetic Acid

Mix



Check pH

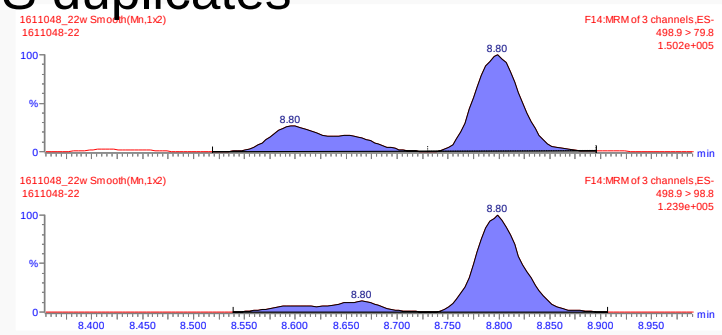
Transfer ~1mL sample in vial (pour)

Run time 21 min
Plus 2 minute recovery

Based on schematic by William Lipps, Shimadzu

Analytical Method Quality Controls

- Analyte Identification based on
  - Each batch: Initial calibration, Calibration check, and Second source check
  - Each analyte: Retention time, Primary and Confirmation ion masses, and Ion ratio
  - Need good chromatography
- Accuracy –
  - Surrogate spiking - All samples and QC
  - Matrix spike samples – MS and MS duplicates
  - Spiked blanks
  - Method reporting limit checks
- Precision –
  - All samples in duplicate
    - (sporadic contamination)
  - Matrix spike duplicates
- Laboratory Contamination – Method/Reagent blanks – 2/batch



Reporting Limits

- ASTM D8421 validated the method to 10 ng/L for all except for PFBA, PFPeA and PFPrA (50 ng/L)
- There is nothing stopping anybody from reporting lower!
- Need to eliminate sporadic hits and control the PFAS background in consumables.
- We require all samples to be taken as duplicates in order to evaluate precision and to “identify” any sporadic hits.

Random Sporadic PFAS Contamination

- This is Establishing Reporting Limit in many cases.
- At this time, no commercial vendors of PFAS consumables provide certified, trace level PFAS free products.
- Must lot check all supplies
- Must pre-rinse filter units and syringes
- PFAS are everywhere! They are widely used, vendors/suppliers don't know their processes are using them.
- Analytical Methods are designed for low level analysis, requires sensitive optimized LC/MS/MS.
- Requires Chromatography

Sporadic Contamination
Various Lab Examples

[RL Spike]	8:2 FTS	Method Blanks
ng/L	ng/L	ng/L
10	4.51	0.00
10	9.21	0.00
10	10.64	0.00
10	961.23	0.94
10	11.51	0.00
10	9.64	0.00
10	10.79	0.00
10	3.77	0.00
10	7.91	0.00
Std Dev.	317.59	
MDL	1065.51	

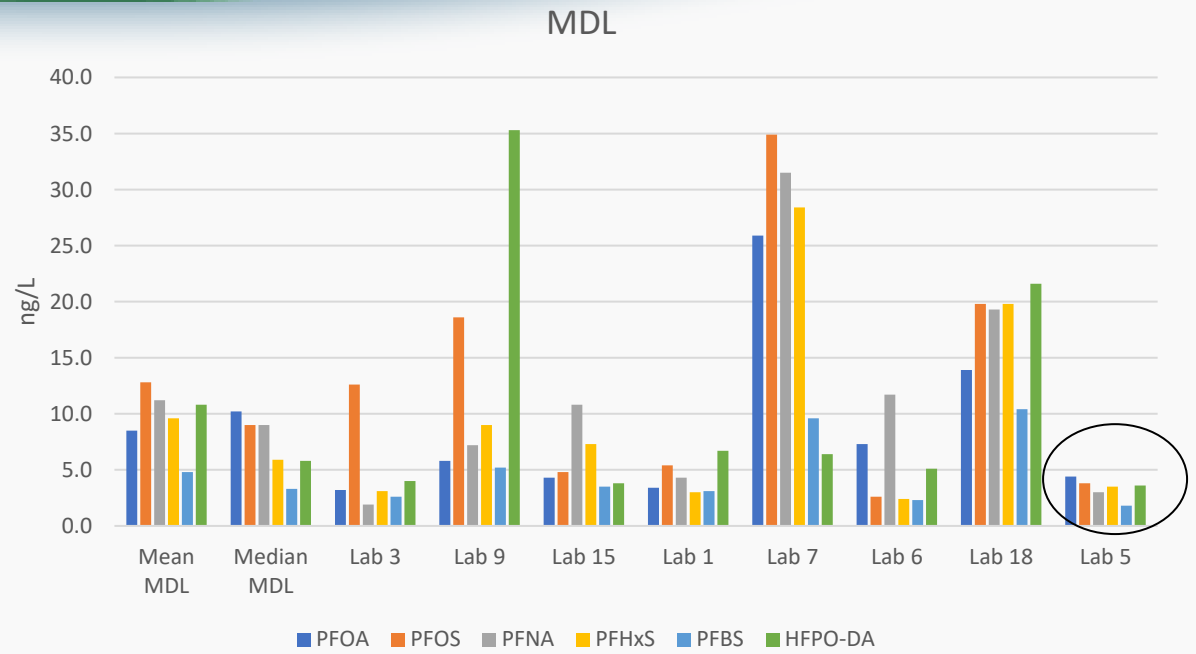
[RL Spike]	PFTreA	Method Blanks
ng/L	ng/L	ng/L
10	MBI	104.2
10	MBI	78.2
10	MBI	76.4
10	MBI	162
10	MBI	135.4
10	MBI	112.6
10	MBI	142.2
10	MBI	127.8
10	MBI	103.6
10	15.6	17.2
10	18.8	15.2
10	0	0
10	0	0

[RL Spike]	6:2 FTS	Method Blanks
ng/L	ng/L	ng/L
10	10.43	8.54
10	10.84	8.06
10	12.45	6.87
10	8.20	0.00
10	9.73	0.00
10	9.63	0.00
10	3.07	0.00
10	6.50	0.00
10	5.65	0.00
10	28.90	100.10
10	47.20	9.20
10	11.90	0.00
10	16.70	6.70
Std Dev.	11.82	
MDL	36.12	

[RL Spike]	PFOS	Method Blanks
ng/L	ng/L	ng/L
10.00	9.00	0.30
10.00	8.62	0.30
10.00	9.56	1.58
10.00	9.70	1.80
10.00	9.64	0.56
10.00	9.58	0.00
10.00	9.86	6.20
10.00	9.76	12.60
10.00	9.34	3.23
Std Dev.	0.40	3.78
MDL	1.35	

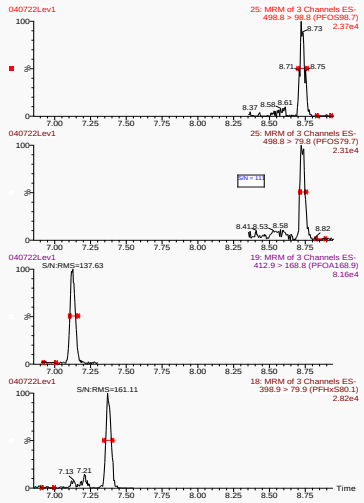
[RL Spike]	4:2 FTS	Method Blanks
ng/L	ng/L	ng/L
10	11.56	0.00
10	10.51	0.00
10	12.62	0.00
10	1330.96	2.20
10	11.99	0.00
10	11.10	0.00
10	13.19	0.00
10	11.47	0.00
10	12.62	1.45
Std Dev.	439.69	
MDL	1475.17	

Method Reporting Limit/ MDL



- These all at 5 ng/L On Column
- RL and MDL Lab Dependent

PFOA S/N 137 for primary



PFOS S/N 158 for primary and 111 for confirmatory

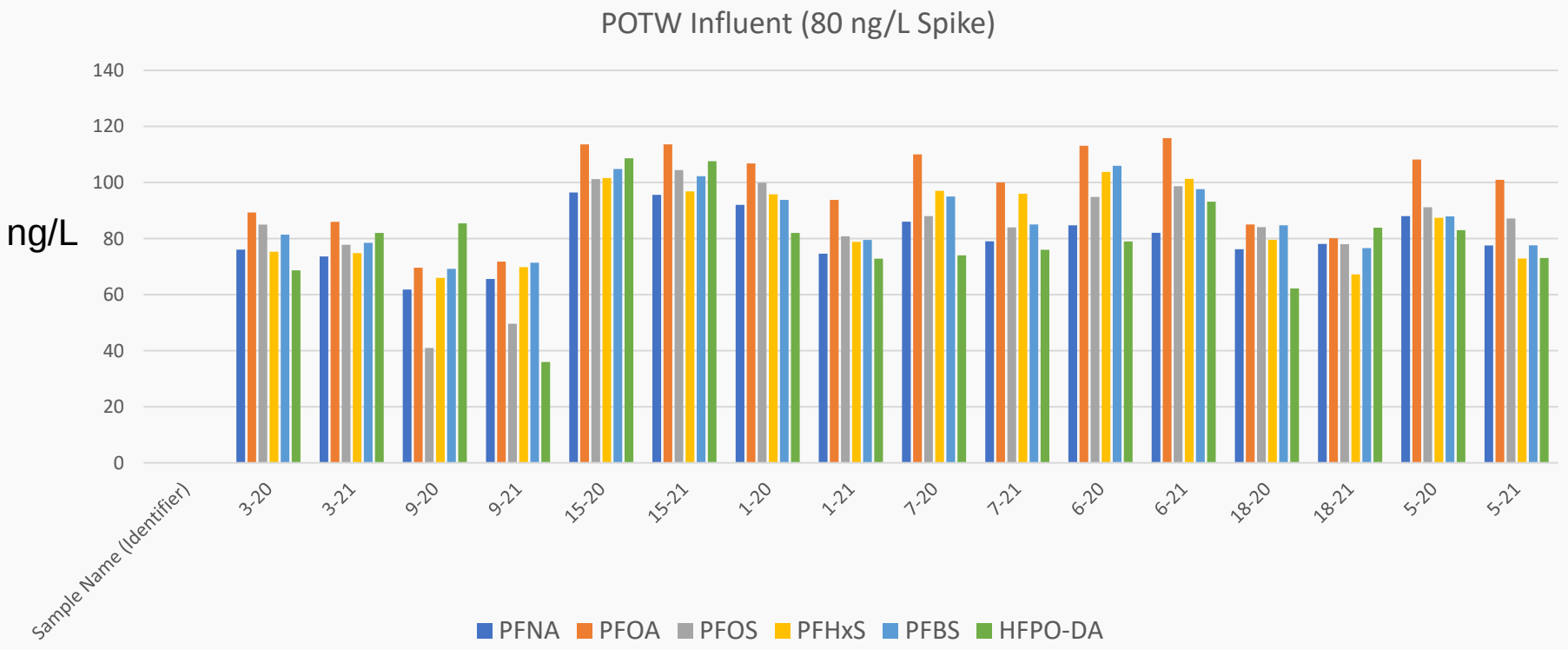
PFHxS S/N 161 for primary

How Data are Evaluated

- All unknown Spikes in Duplicate to obtain precision. ASTM calculates Precision in the lab and then between labs.
  - Nine labs submitted data, eight data sets were usable.
  - Concentrations from 20-800 ng/L
- All Unspiked analyzed individually for EPA to obtain percent recoveries. EPA SW-846 calculates recoveries.

Precision Between Duplicates and Labs

(Not accounting for PFAS already present in Matrix)



Precision Between Duplicates and Labs

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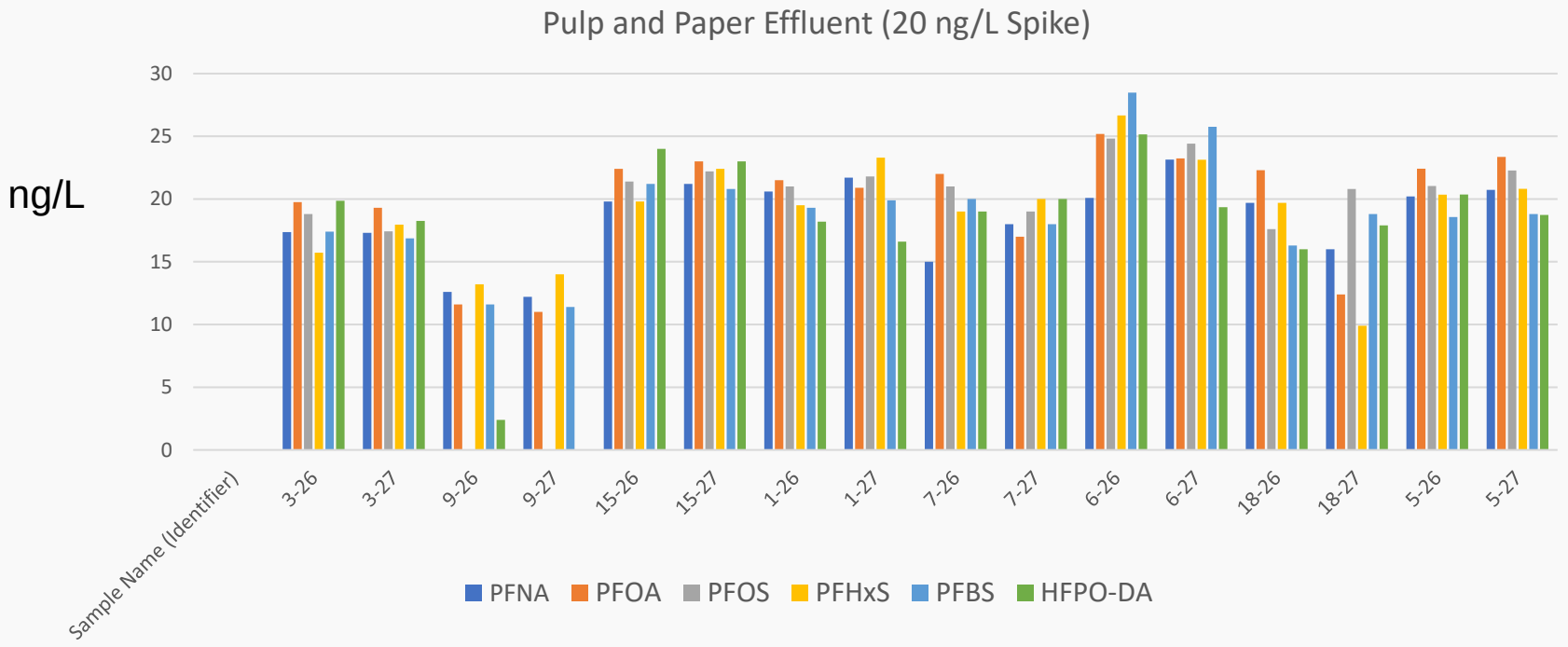
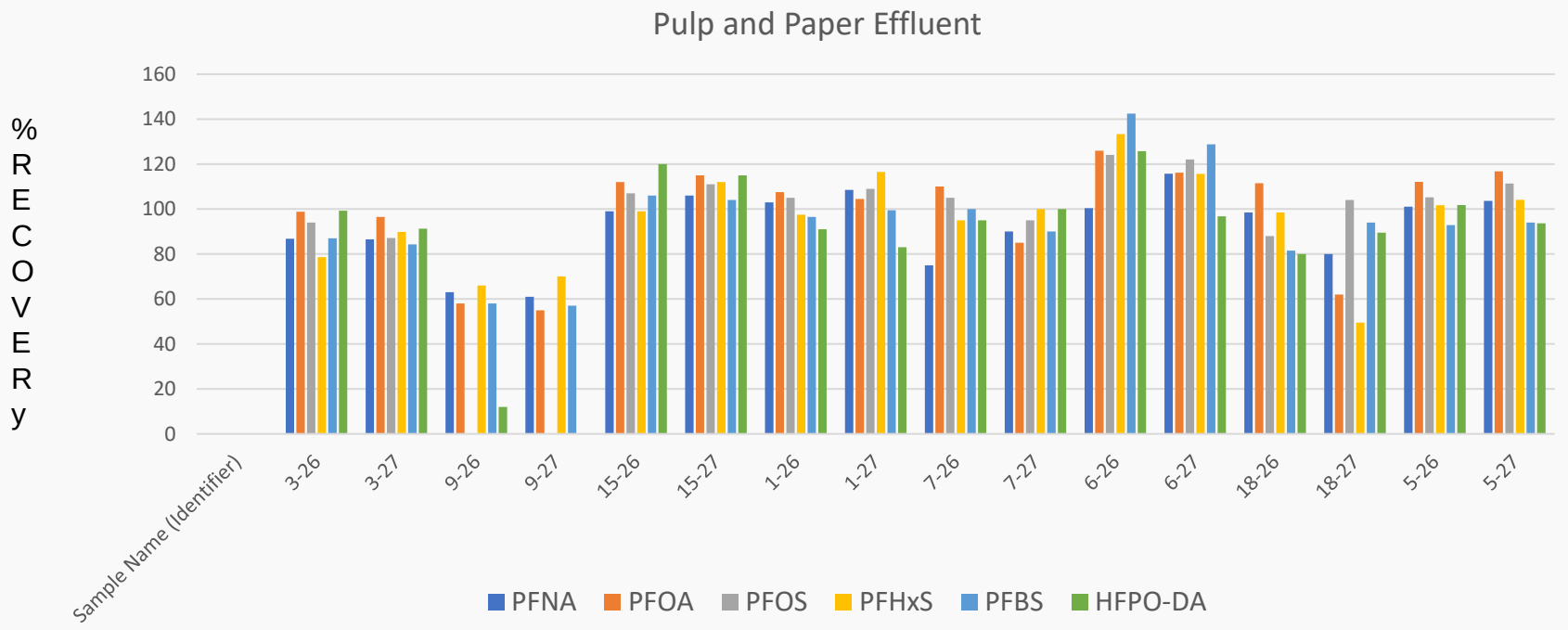


Percent Recovery- Duplicates and Labs

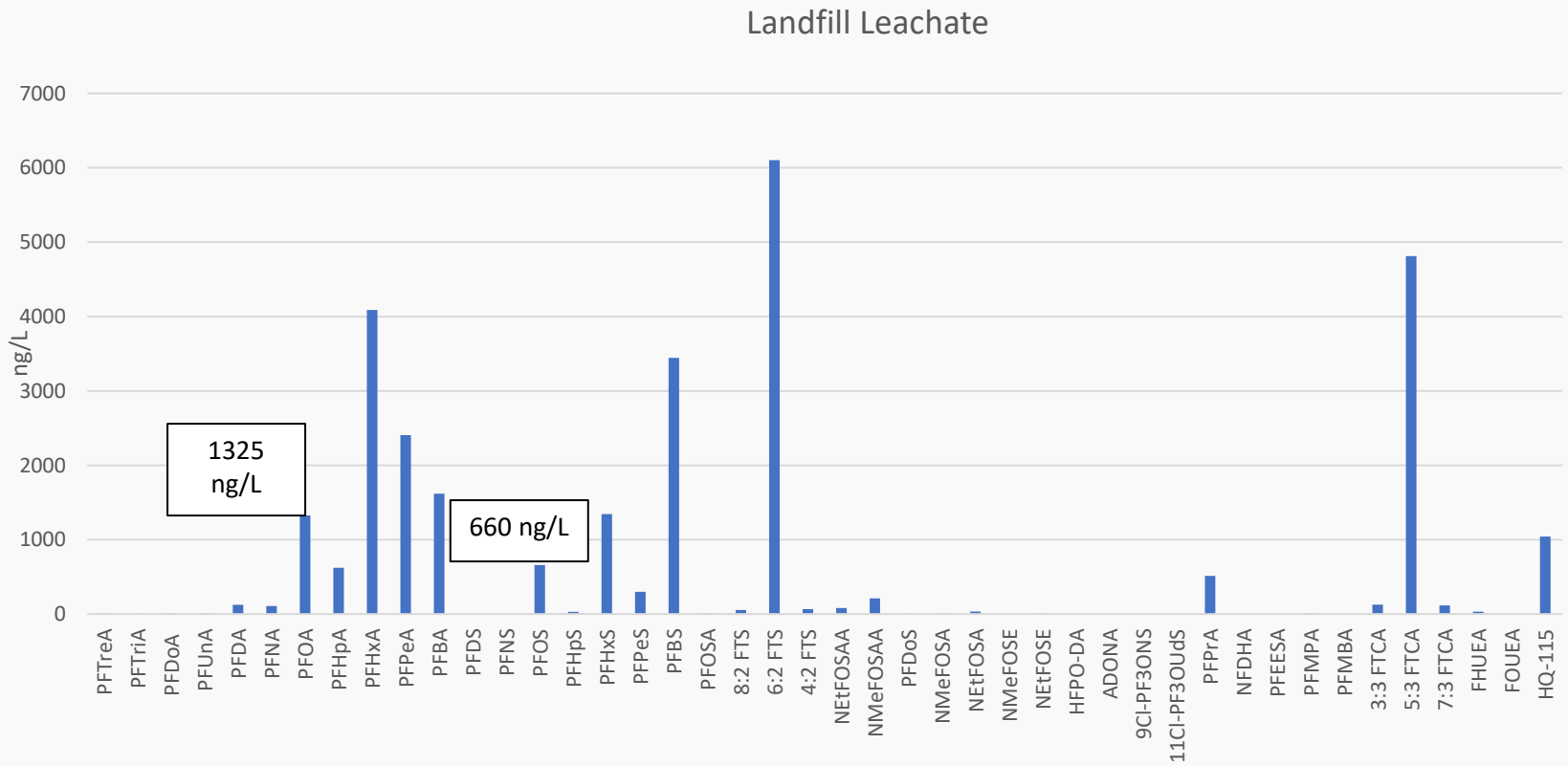
(Accounting for PFAS already present in Matrix)



PFAS-Unspiked Landfill Leachate

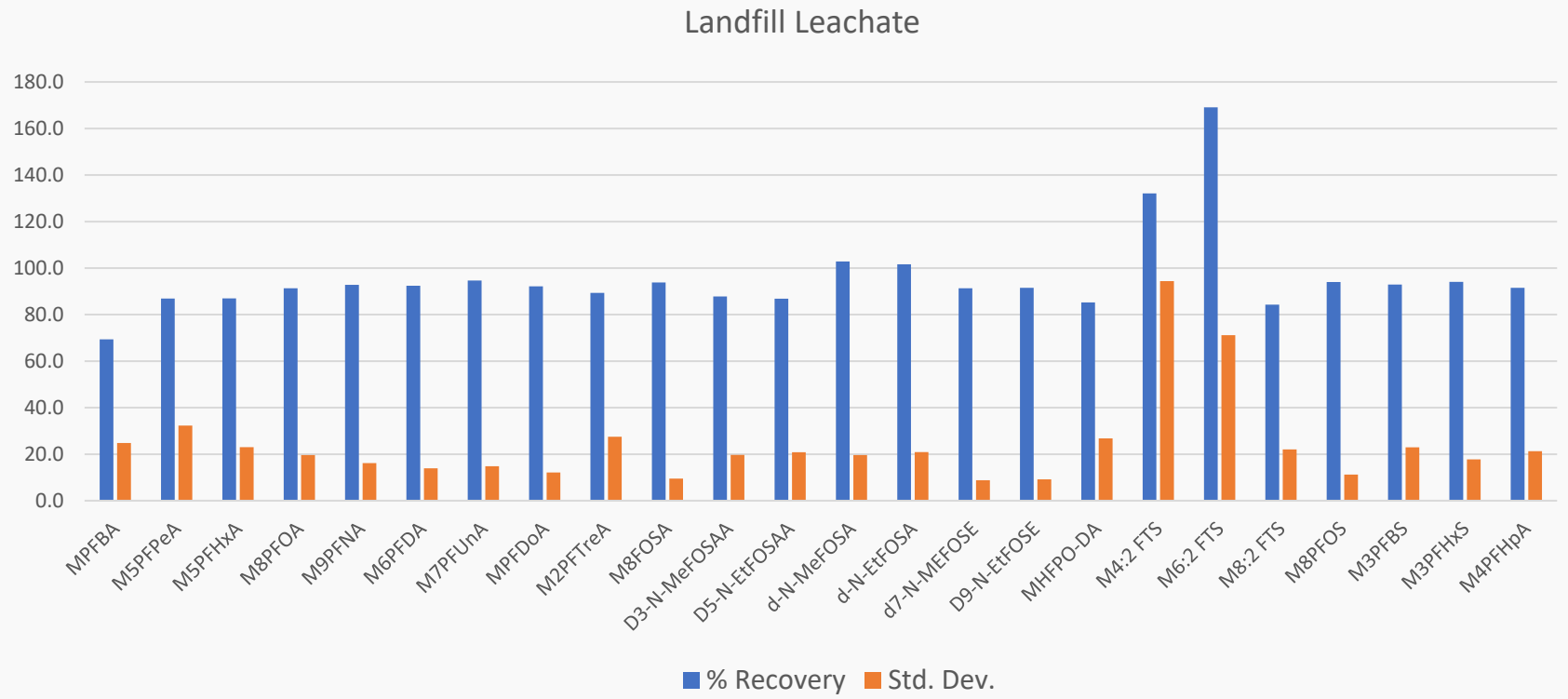
DW Proposed Maximum Contaminant Levels (MCL) (enforceable levels): 4 ng/L PFOA and PFOS

non-enforceable Maximum Contaminant Level Goals: Zero



Surrogate Recoveries (%)

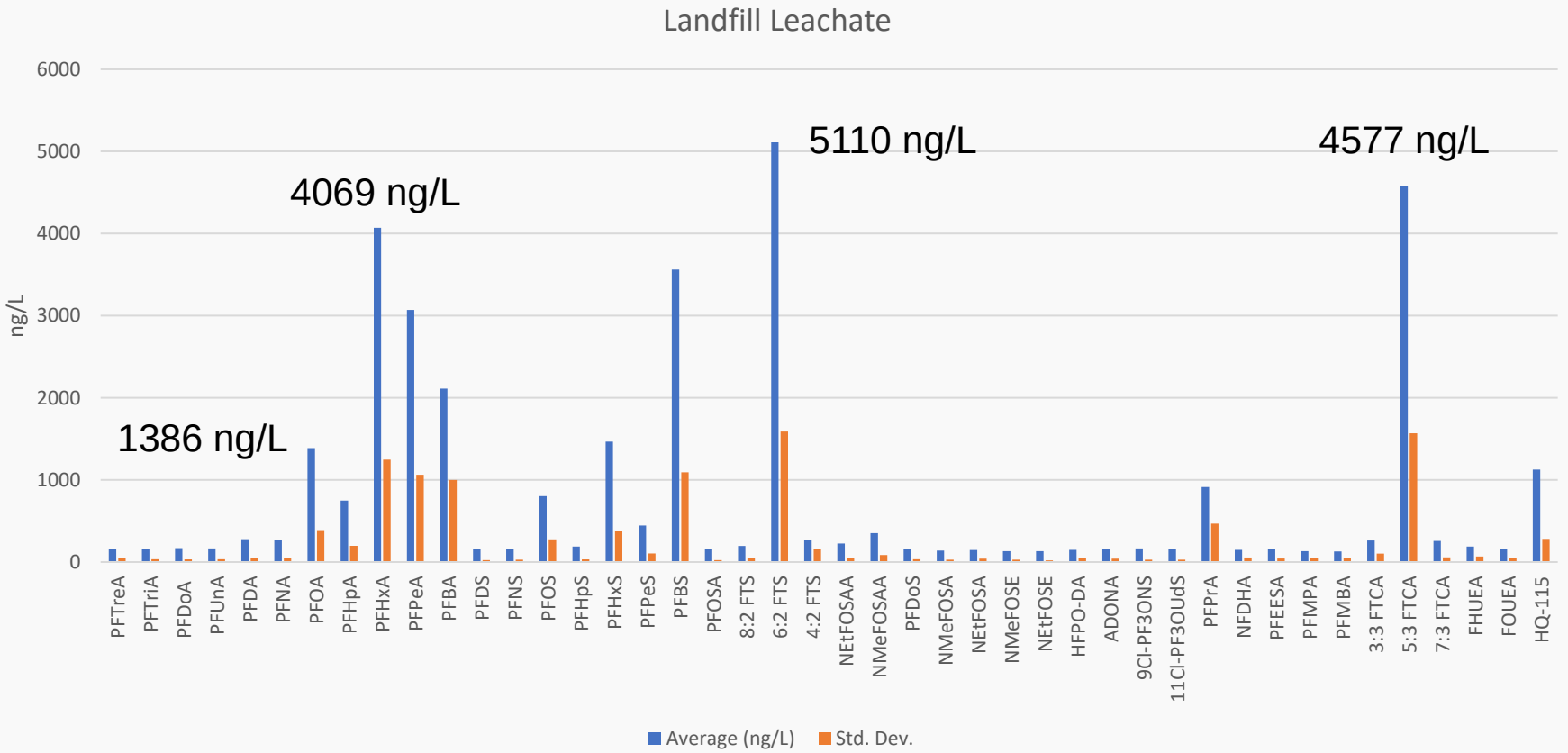
8 Labs, Leachate Spike Samples



Landfill Leachate

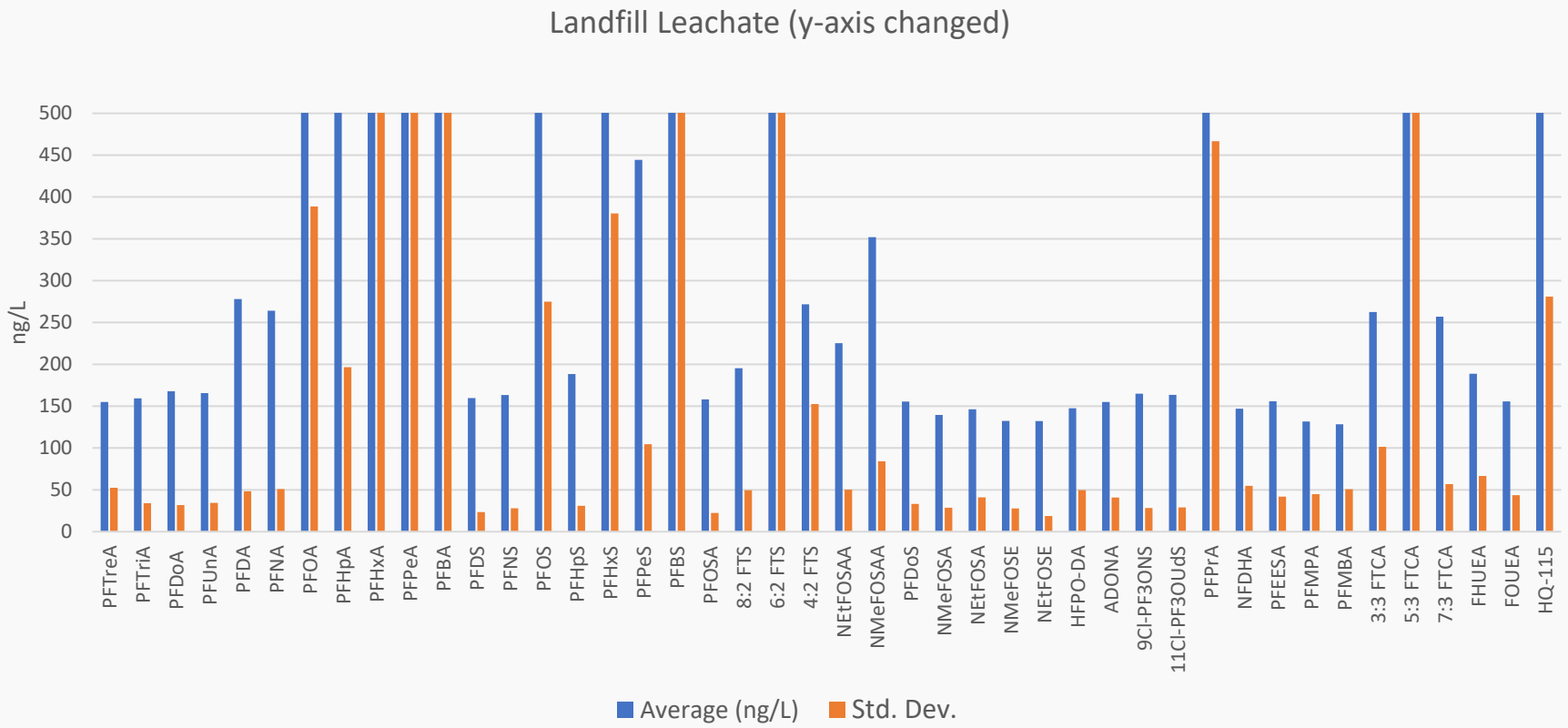
8 Labs, Leachate Spike Samples

Graph- Concentration in Sample and Std. Dev.

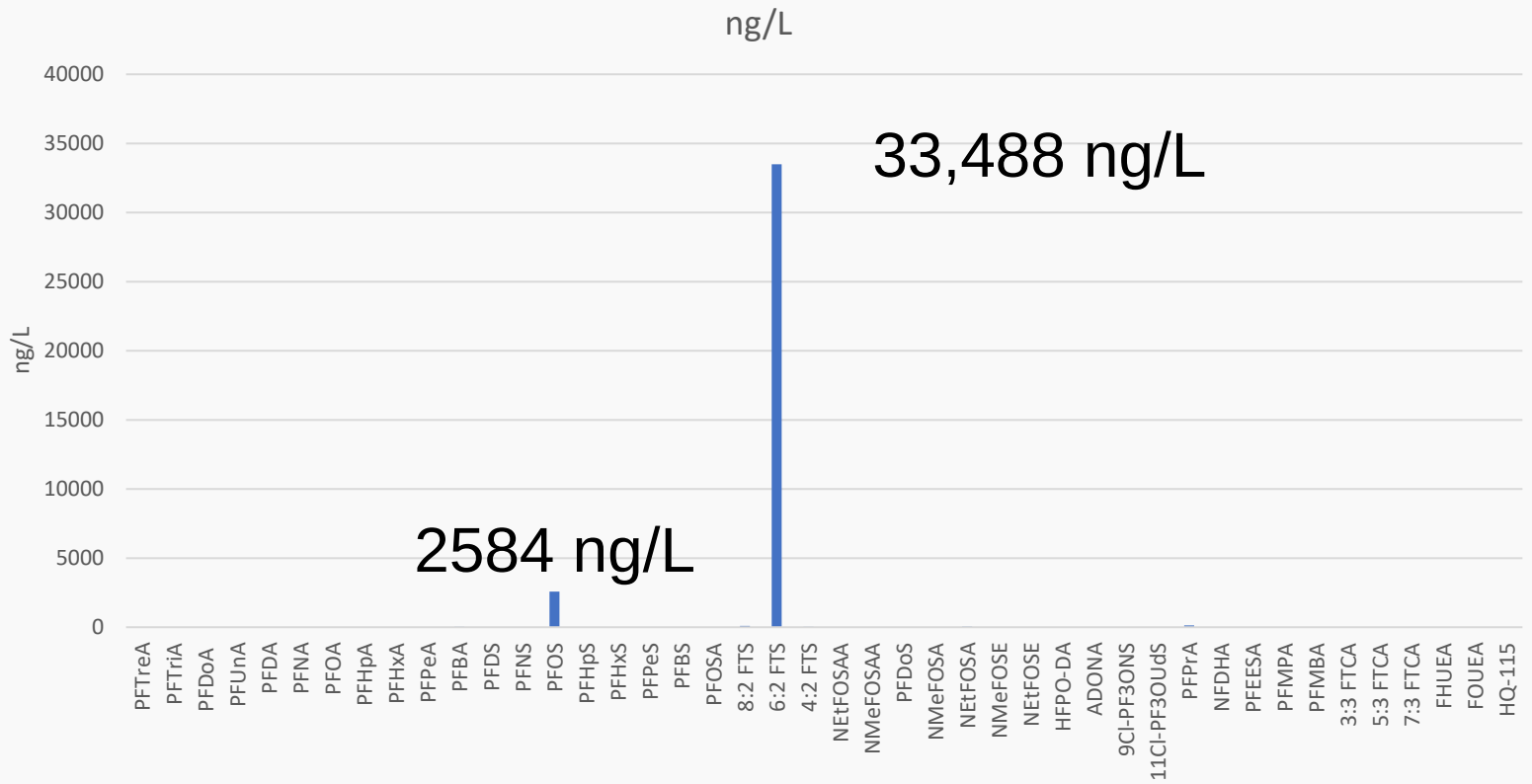


Graph- Concentration in Sample and Std. Dev.

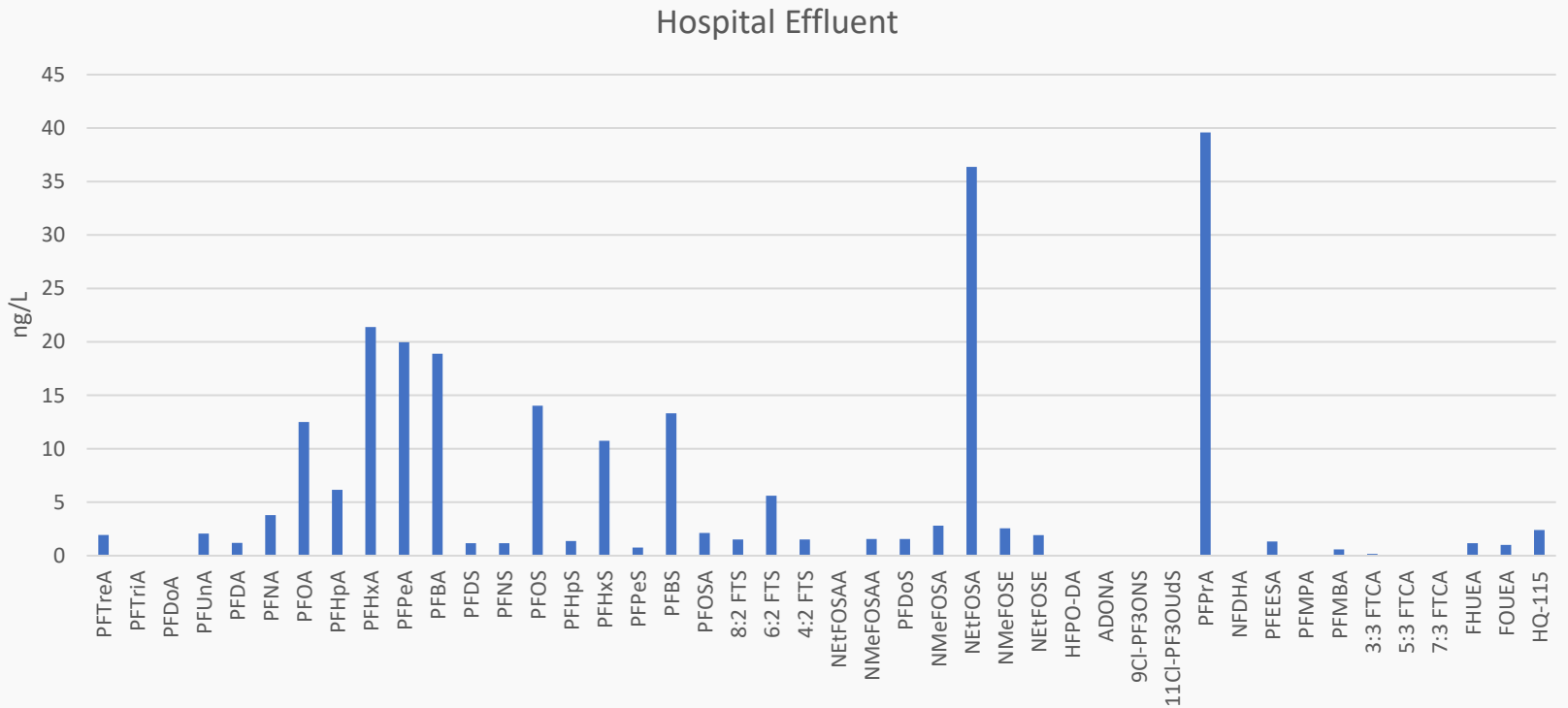
Not subtracting native in sample. 160 ng/L spike, 800 ng/L PFBA, PFPeA, PFPrA



PFAS-Unspiked Metal Finisher



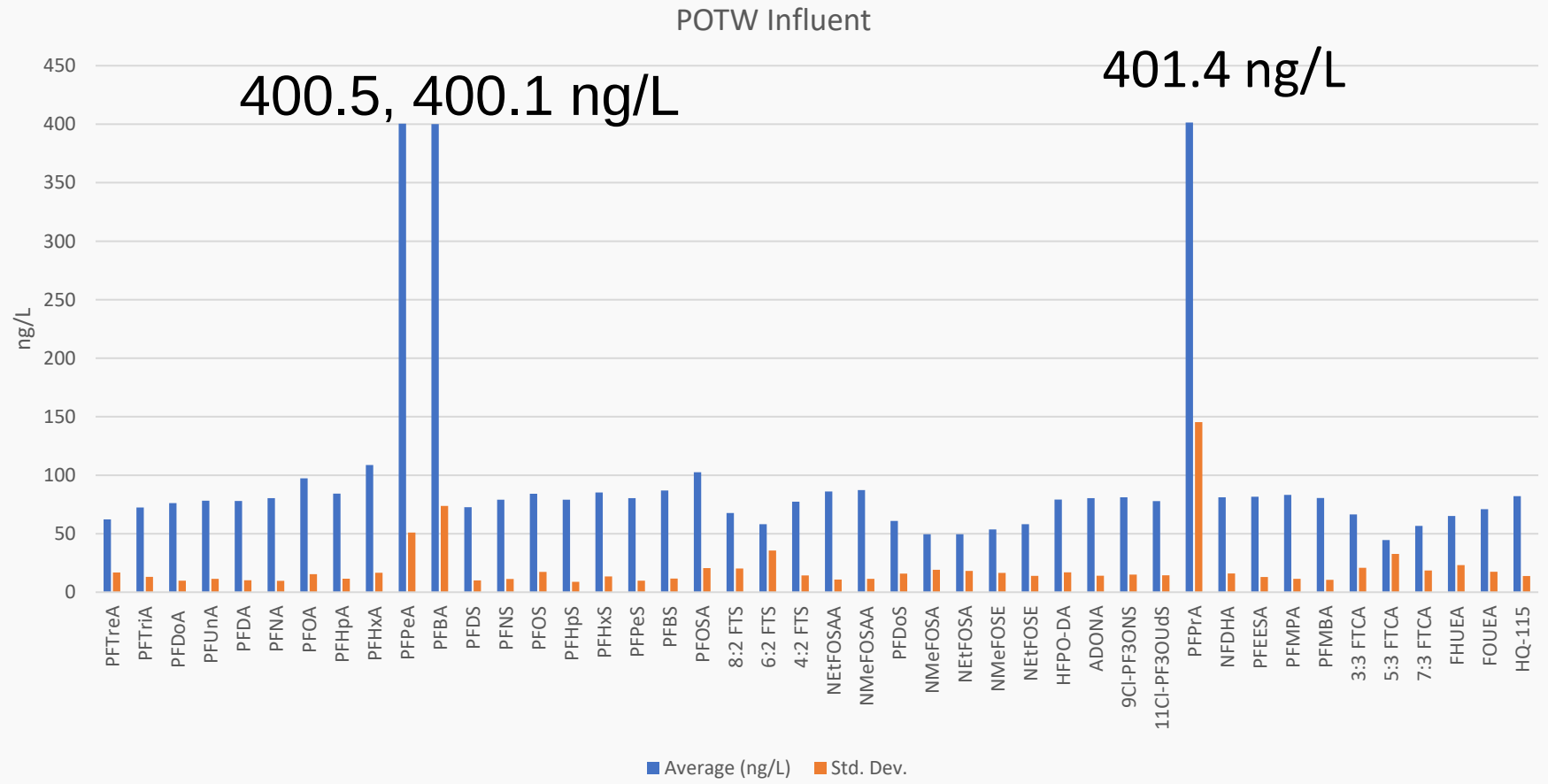
PFAS-Unspiked Hospital Effluent



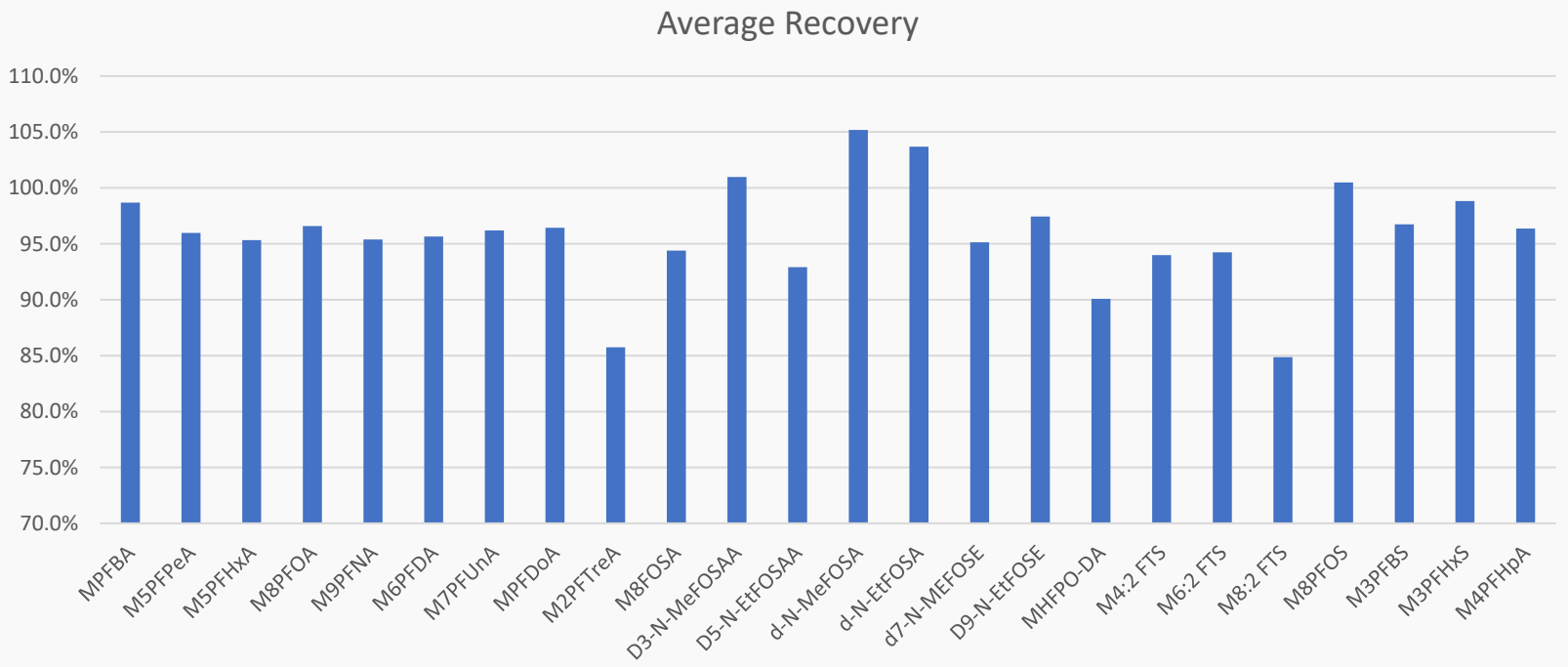
POTW Influent 8 Labs

Graph- Concentration in Sample and Std. Dev.

Not subtracting native in sample. 80 ng/L spike, 400 ng/L PFBA, PFPeA, PFPrA



Average Surrogate Recovery
All Eleven Matrices Combined Amongst Eight Labs



ASTM D8421

- Water Analysis
- Collaborative Study Statistics Final Fall/Winter 2023
- Study Report with complete statistics and evaluation will be available.
- Hopefully proposed into 40CFR Part 136 Soon After

Challenging Matrices

- More challenging soil/biosolids matrices.
- How about Precision and Accuracy with Soils/Biosolids?
- Robust?
- Easy to implement?
- Tomorrow- Tuesday 8/1/23- 2:00 pm. Crafting Consensus Methods for Environmental Sampling and Measurement.

What do you need?

- Evaluate what methods meet your needs.
- Lower cost of analysis.
- Simpler Sample preparation
- Sporadic contamination at these low levels, all samples in duplicate to identify false positives.
- EPA Region 5 Laboratory analyzes all PFAS samples by ASTM D7979, D7968 and D8421.
- This presentation was very brief, if you require more information, please contact us!

R5 Lab Contact Info if you have any questions or in need of a more in-depth analysis and conversation about what we briefly touched on in this brief overview presentation

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