



**Validation of ASTM D7968, Standard Test Method for  
Determination of Per- and Polyfluoroalkyl Substances  
(PFAS) in Soil, for the Complete Analyte List in ASTM D8421.**

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## Disclaimer

- Data shown are Draft, under review and will be corrected for any errors discovered.
- Method will be written as an ASTM Standard and balloted in committee ASTM D34 on Waste Management.

# Proposed ASTM Standard

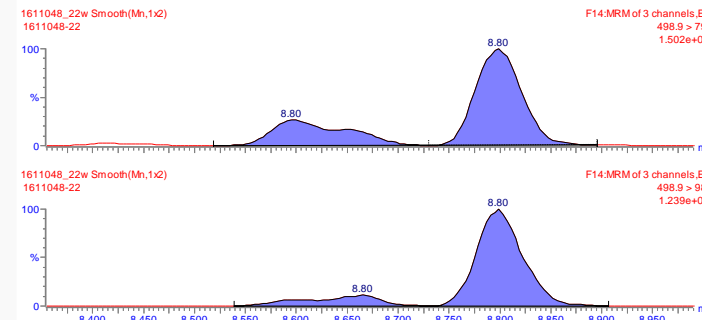


- Standard Test Method for Determination of Polyfluorinated Compounds in Soil and Biosolids by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)
  - Developed at EPA R5 lab
  - Single-lab validated according to ASTM validation protocol (sand, lean clay, fat clay, silt, Biosolids (Idaho, Missouri, California, Georgia))
- External standard method
  - Previous Version ASTM D7968: 31 Target Analytes, 19 Surrogates
  - Proposed updated Standard: 44 Target Analytes, 24 Surrogates (Some don't work well in all matrices).
  - All the analytes in EPA 1633 plus PFPrA, HQ-115, FOUEA and FHUEA were evaluated.

# 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
- ◆ 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
  - Spiked blanks
- ◆ Laboratory Contamination – Method/Reagent blanks – 2/batch





# 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.
- Since PFAS contamination has become an issue with PFAS analysis all field samples are taken in duplicate.
- The complete data package and replicates need to be evaluated by the user in order to make sound conclusions and identify false positives.
- **NO DATA SHOULD BE USED BELOW YOUR REPORTING LIMIT**, this method was only evaluated or tested to the reporting limit.

# 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]	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	

[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

## MBI-Method Blank Interference

U.S. Environmental Protection Agency





## Proposed ASTM Standard (Soil/Biosolids)

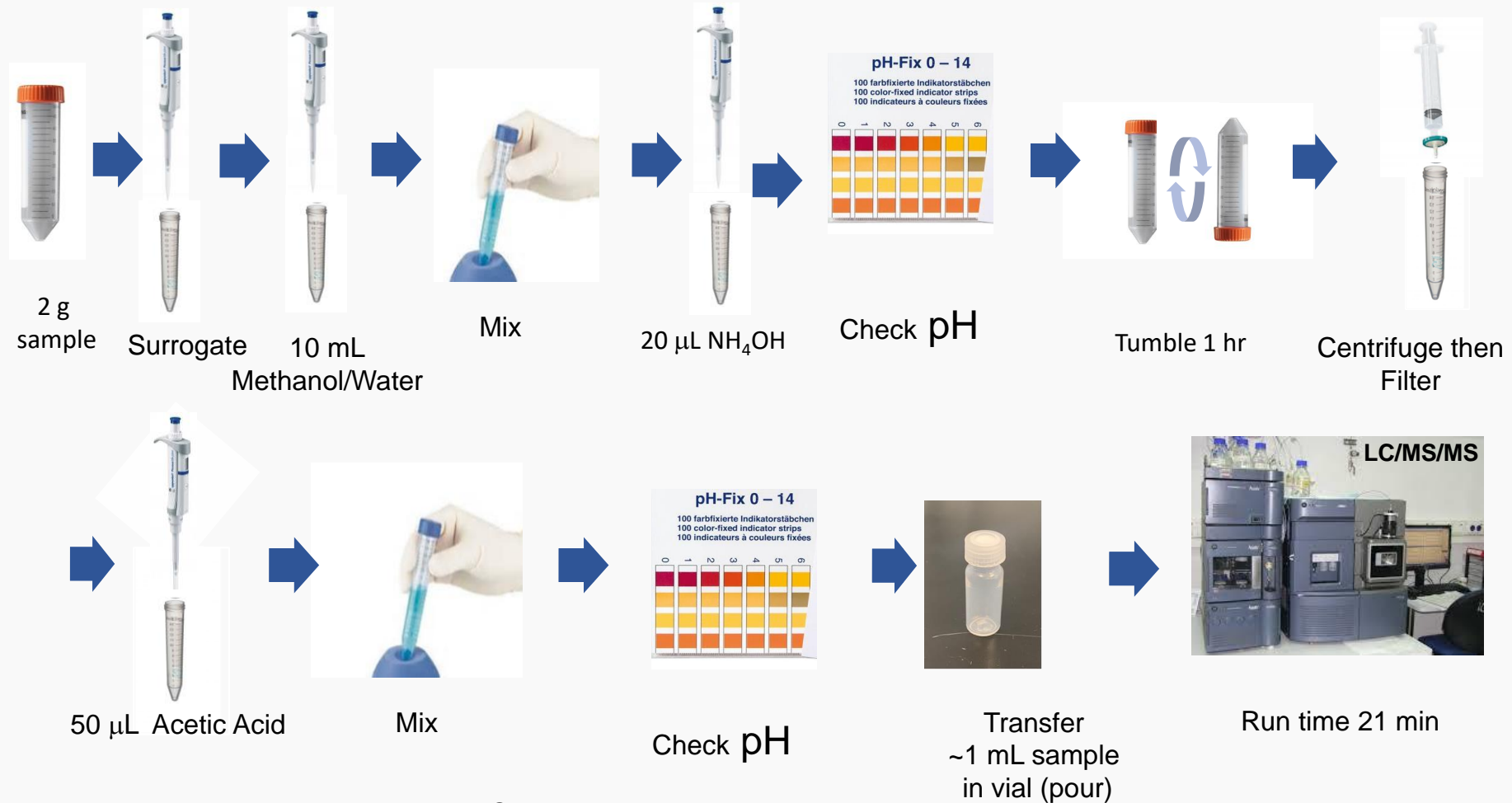
- Evaluated all analytes in EPA Method 1633 (A few do not work well)
- 25 ng/Kg RL for all except for PFBA and PFPeA (125 ng/Kg)
- Simple Extraction LCMSMS method
  - Minimal sample manipulation reduces prep time
  - Minimizes risk of contamination
- Labelled surrogates for many target analytes
  - Used to evaluate method performance
- Confirmatory transitions for almost all target analytes
  - Ion ratios calculated to support qualitative IDs



## Proposed ASTM Standard (Soil/Biosolids)

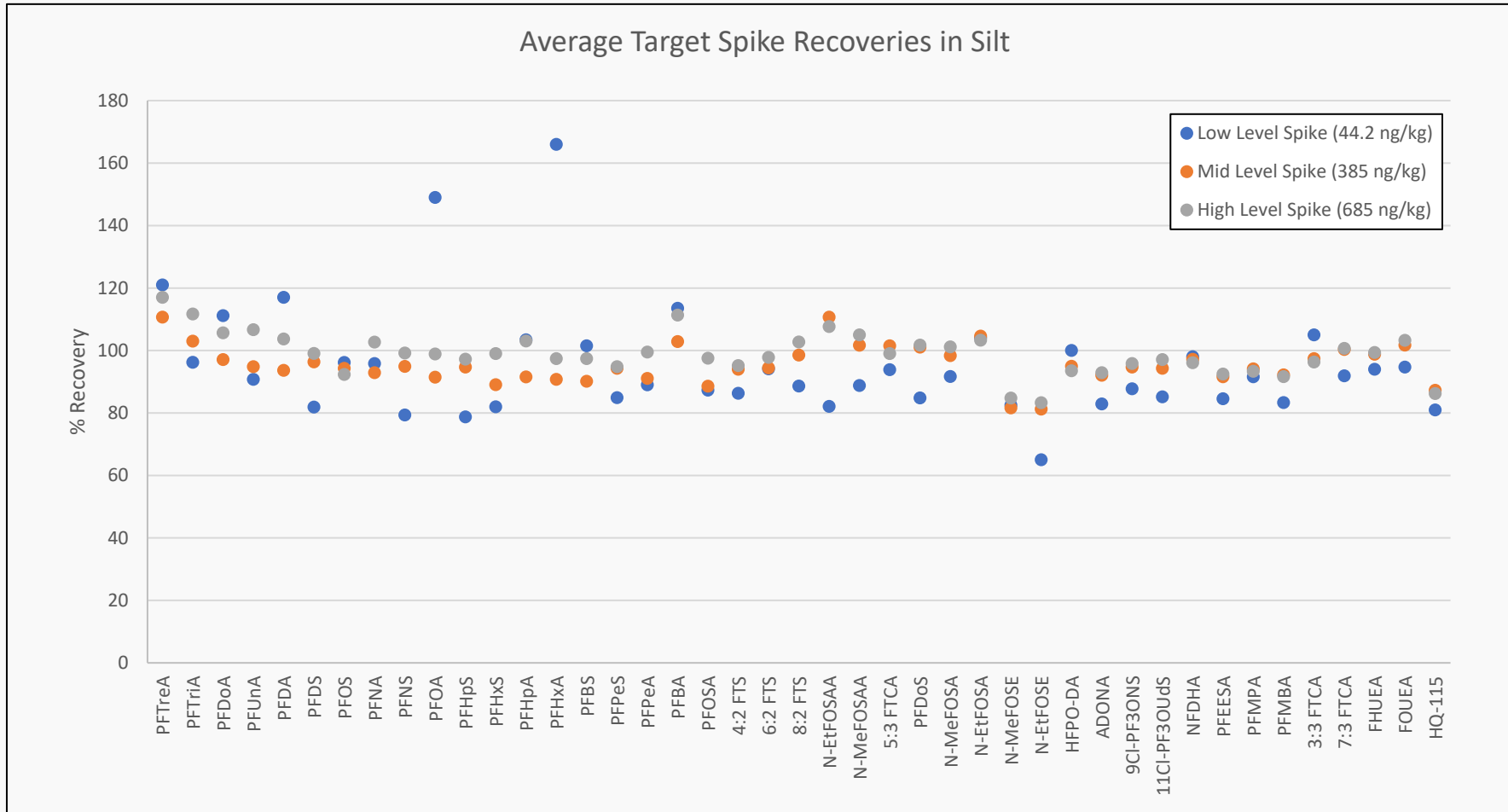
- Preparation:
  - 2 gram sub-sample
  - Spike with surrogates, extract via tumbling with 10 mL 1:1 methanol/water at pH 9 – 10 (adjusted w/ammonium hydroxide) for 1 hour
  - Centrifuge extract, filter through hydrophilic polypropylene membrane, acidify w/acetic acid (pH 3 – 4)
  - 10 mL final volume
- Analysis by UPLC/MS/MS
  - 21 minute run time
  - LC gradient (95:5 water/ACN, ACN, 5% constant- 400 mM ammonium acetate solution in 95:5 water/ACN)

# LC/MS/MS Analytical Method – Sample Preparation



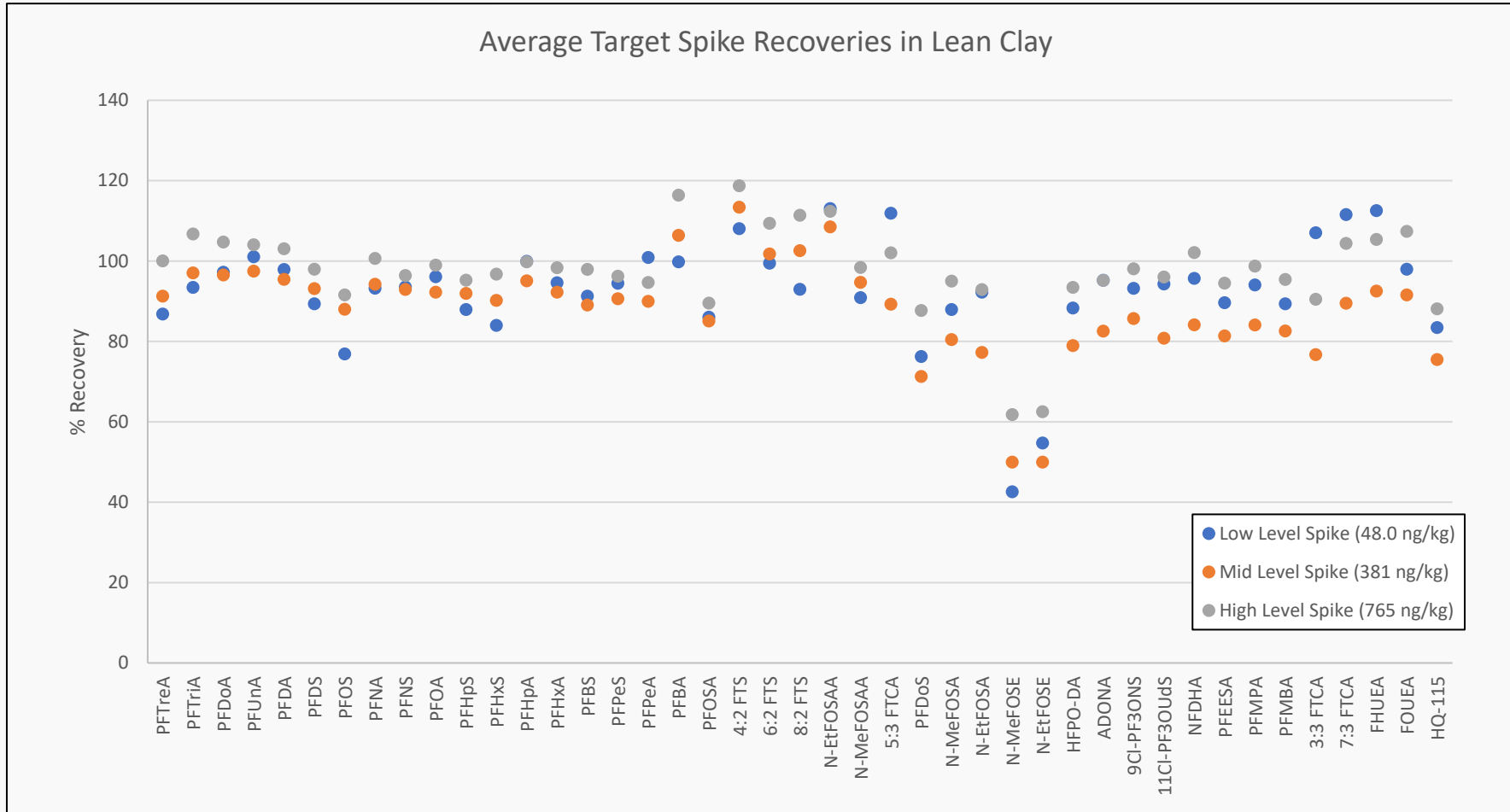
Based on schematic by William Lipps, Shimadzu

# ASTM Soils Recoveries



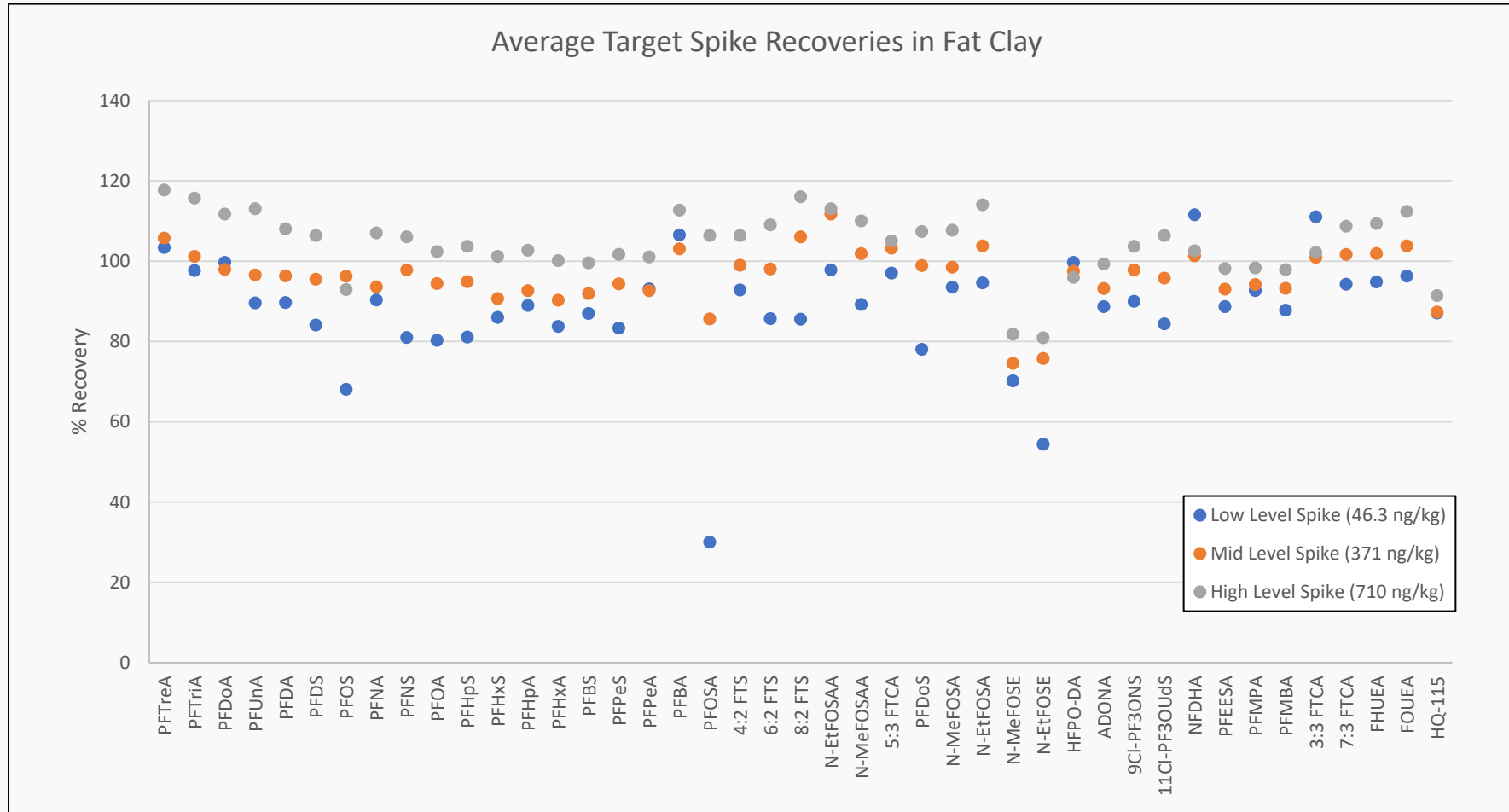
**NOTE:** Spike levels of PFBA and PFPeA 5x the spike levels shown.

# ASTM Soils Recoveries



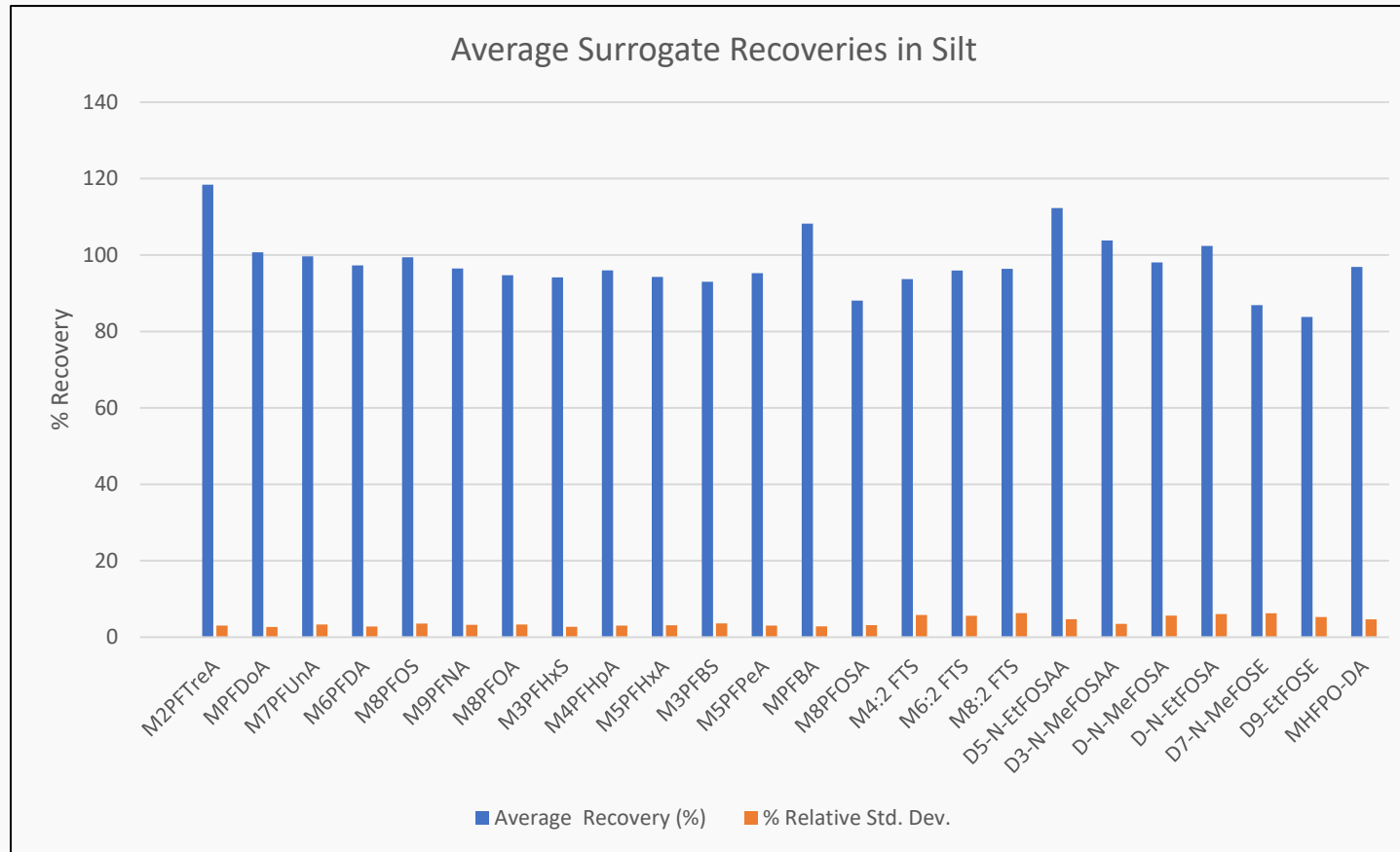
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# ASTM Soils Recoveries

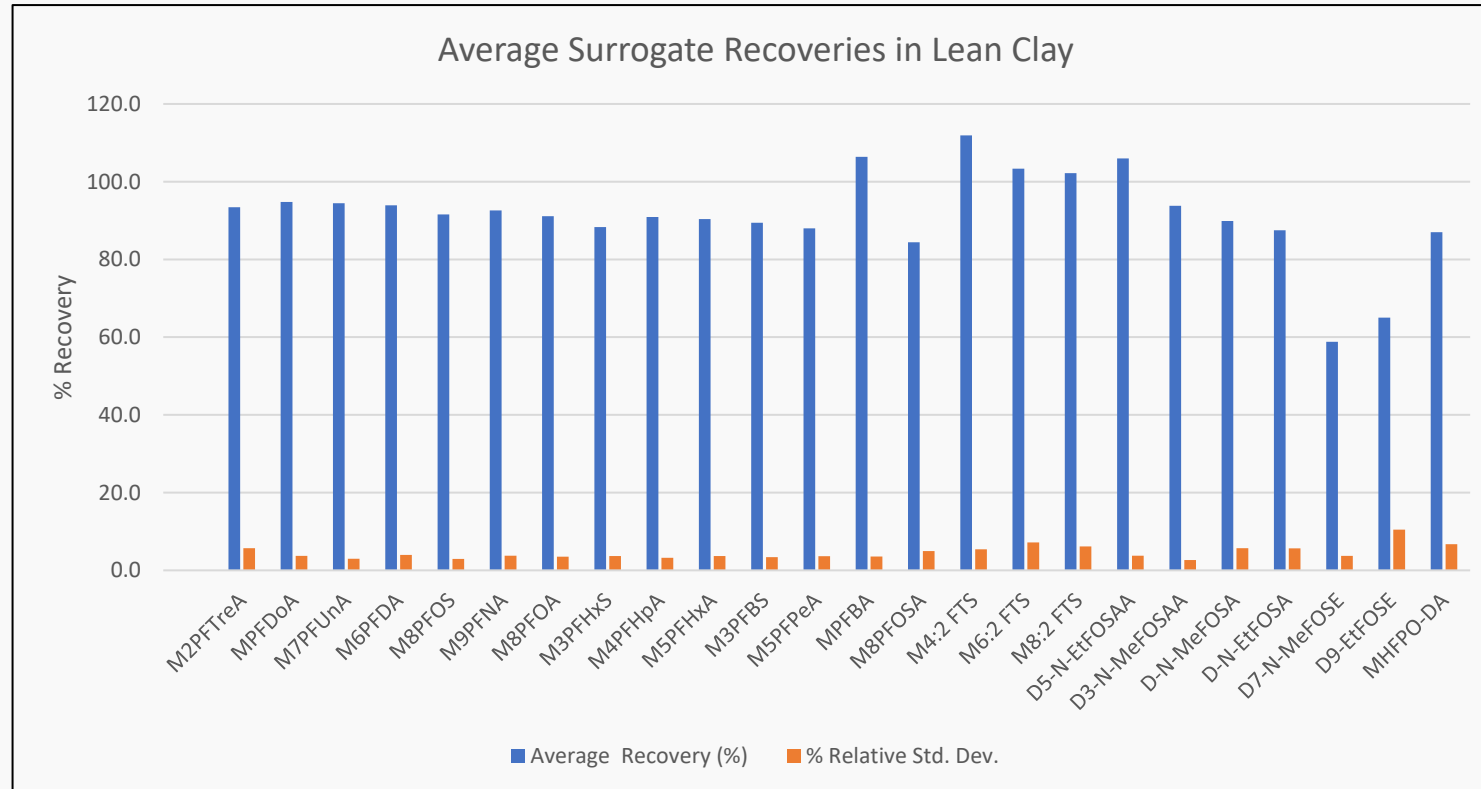


**NOTE:** Spike levels of PFBA and PFPeA 5x the spike levels shown.

# SILT (Surrogate Recoveries)



# Lean Clay (Surrogate Recoveries)

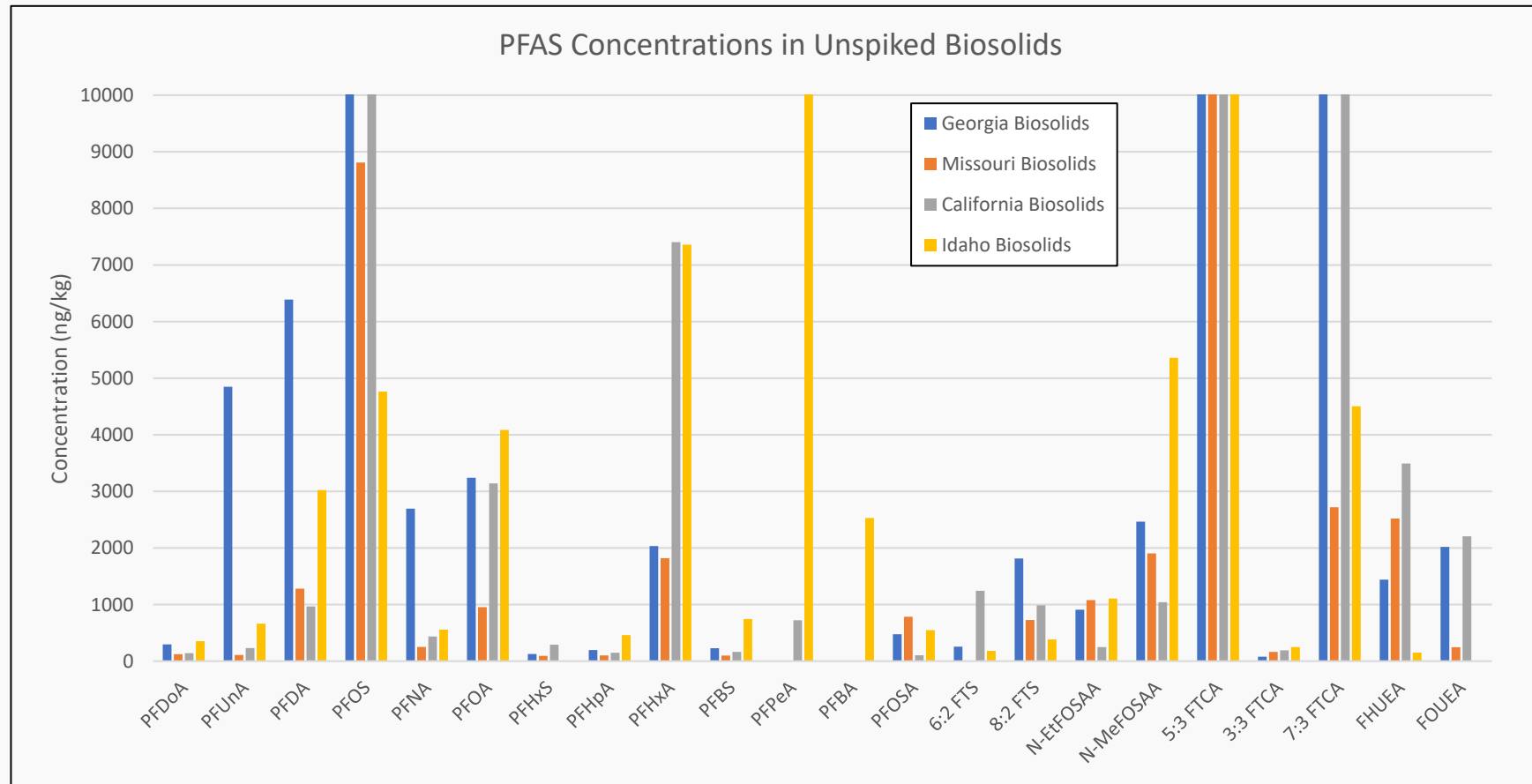




# “Natural” PFAS in Biosolids Utilized

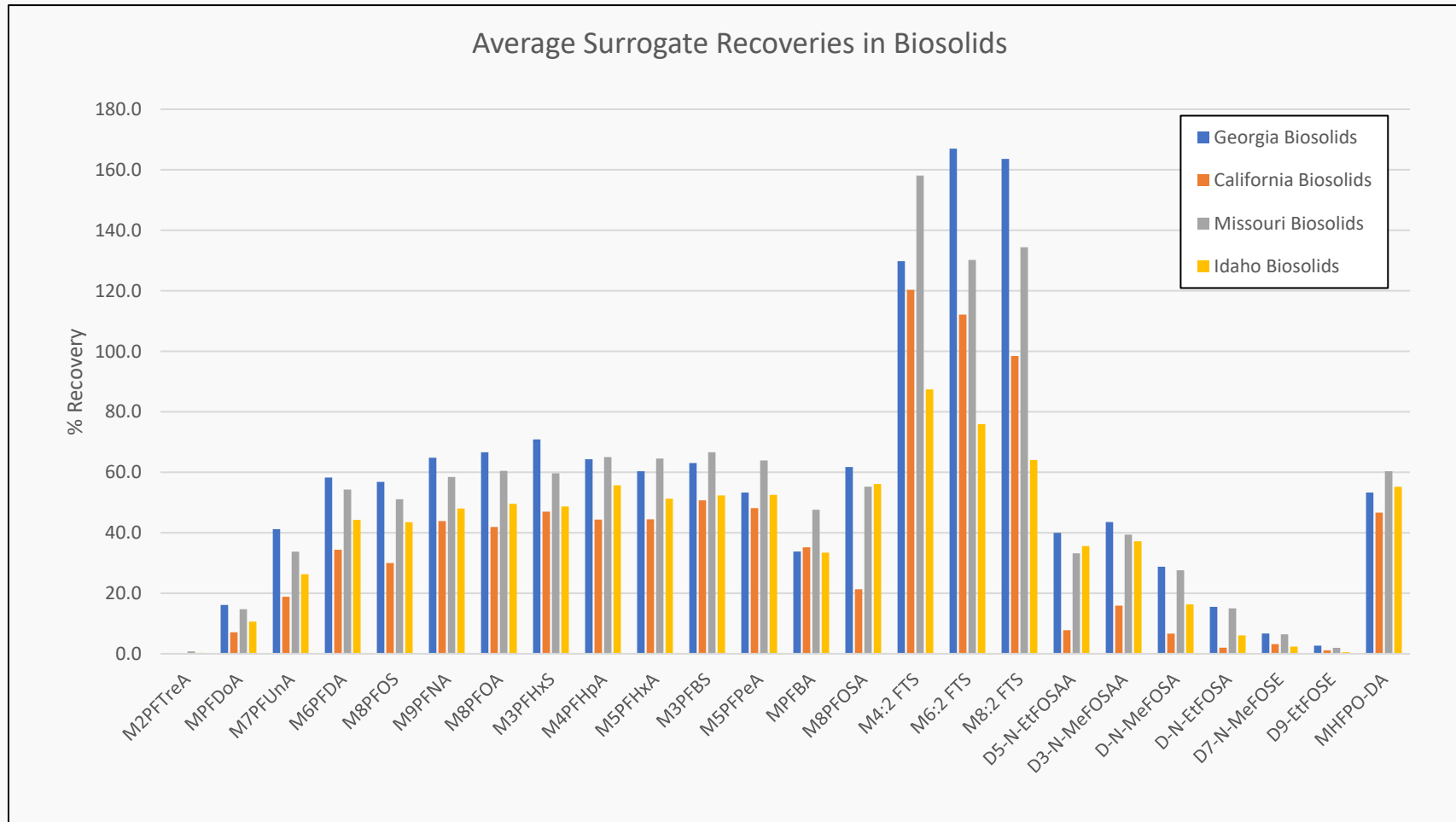


## 26/44 PFAS Found

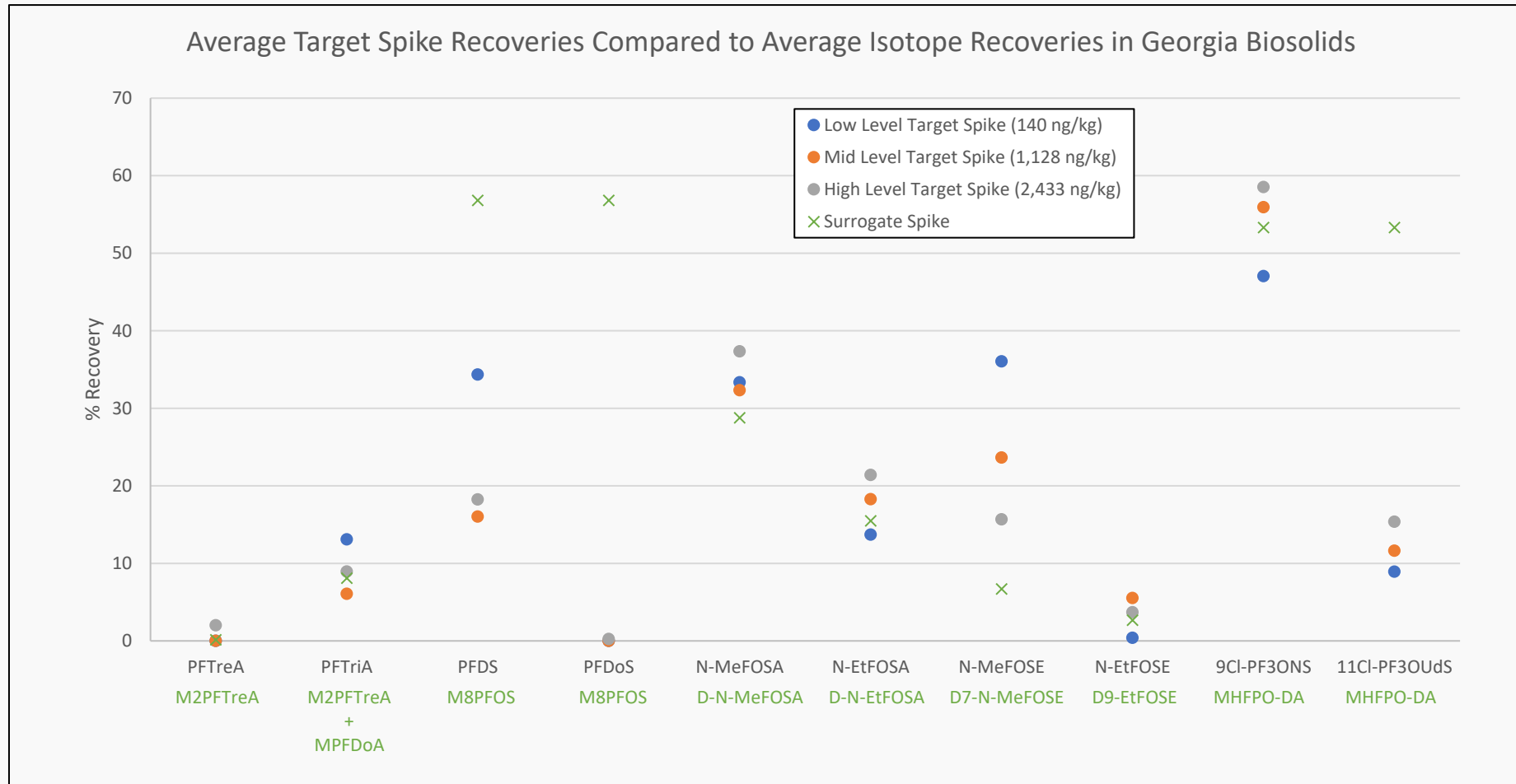


**NOTE:** PFOS, PFPeA, 5:3 FTCA, 7:3 FTCA above y-axis concentration range.

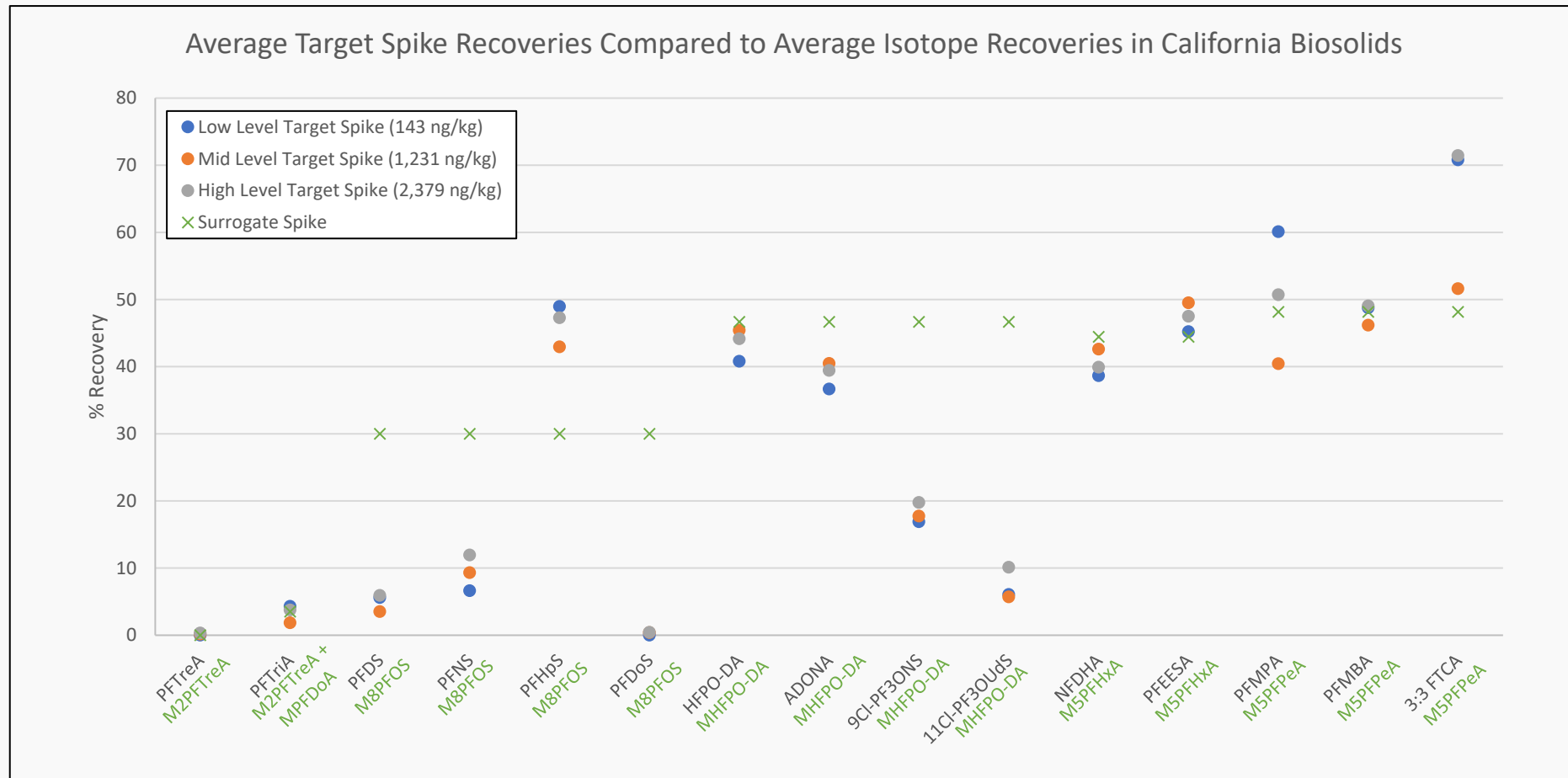
# Surrogate Recoveries



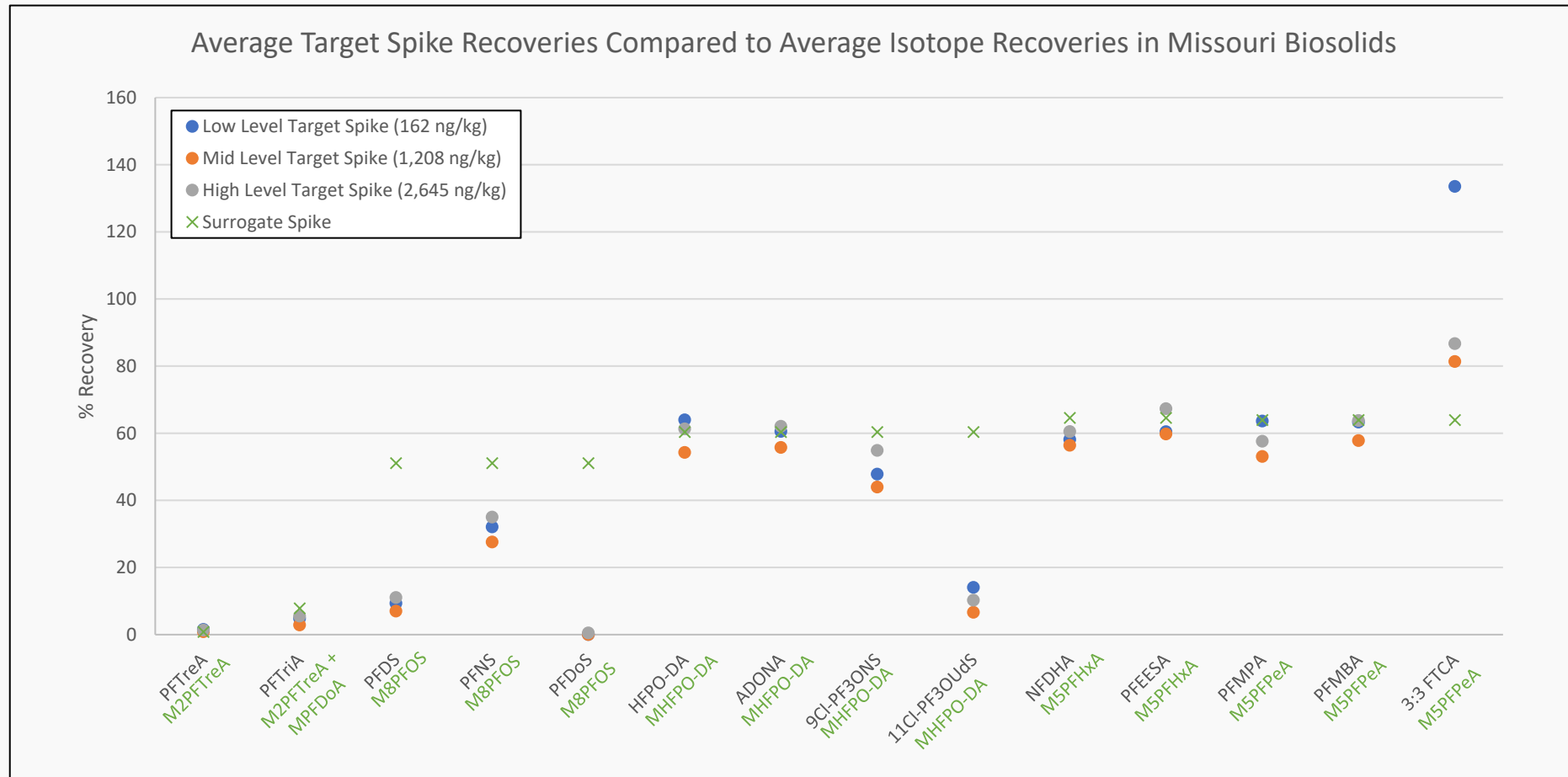
# Native Recoveries vs. Isotope (Some not identical) (Georgia)



# Native Recoveries vs. Isotope (Some not identical) (California)



# Native Recoveries vs. Isotope (Some not identical) (Missouri)





## Analyte Issues

- All Forty analytes and 24 isotopes from EPA 1633 were evaluated.
- PFTreA, PFTriA, PFDoA, PFDS, PFDoS, NMeFOSA, N-EtFOSA, N-MeFOSE, N-EtFOSE and 11Cl-PF3OUdS don't work well.
- Isotope dilution is acceptable in the ASTM Standards but only an exact isotope can be used, some "similar" isotopes may not mimic the native.
- PFTreA, PFDoA, N-MeFOSE, N-EtFOSE, N-MeFOSA and N-EtFOSA do have isotopes but they have low recoveries in biosolids.
- Analytes with and only one MRM may prove Difficult in biosolid matrices (Forget about PFPrA).



## What's next?

- Finalize all Data
- Evaluate
- Write as ASTM Standard
- ASTM Subcommittee Ballot and then Main
- Detailed performance of the Standard is in the Standard itself or in the Study Report for all Standards.
- Collaborative Study...Is ASTM/EPA interested?



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