Precision and Accuracy Data of Per- and Polyfluoroalkyl Substances (PFAS) in Multiple Soil Matrices Using ASTM Standard D7968

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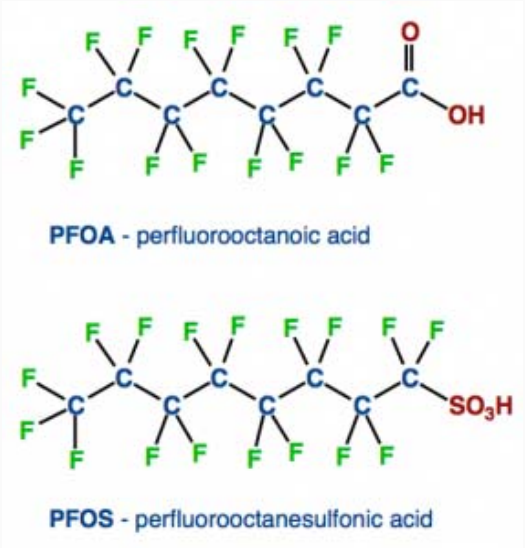
PFAS Background

- Compounds manufactured to make products more resistant to stains, grease, and water
- Found in many products:
  - Foams used for fire suppression
  - Non-stick cookware
  - Waterproof and stain-resistant textiles
  - Water and oil resistant papers
  - Metal plating and etching fluids
- Most studied PFAS:
  - Perfluorooctanoate (PFOA)
  - Perfluorooctyl sulfonate (PFOS)



PFAS Background

- PFAS are commonly observed, persistent, and appear to be resistant to many treatment processes
- EPA has issued Health Advisories for PFOA and PFOS
- EPA has a PFAS Action Plan
- EPA methods for PFAS:
  - 537/537.1 (drinking water)
  - 8327 (surface/ground water, wastewater, etc.)

- <u>No EPA method exists for PFAS in soil matrices</u>

ASTM Standard D7968

- Standard Test Method for Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)
  - Developed at R5 lab
  - Single-lab validated according to ASTM validation protocol (sand, lean clay, fat clay, silt)
- External standard method
  - Published in D7968: 31 target analytes, 14 surrogates
  - Current R5 lab list: 23 target analytes, 18 surrogates

ASTM Standard D7968

- 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
  - Ternary LC gradient (95:5 water/ACN, ACN, 400 mM ammonium acetate solution in 95:5 water/ACN)

ASTM Standard D7968

- "Direct injection" method
  - Minimal sample manipulation reduces prep time
  - Minimizes risk of blank 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

Target Analyte	Reporting Limit (ng/kg)	Labelled Surrogate
PFBA, PFPeA	125	x
PFBS	25	x
PFPeS	25	
PFHxA	50	x
PFHxS, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTreA	25	x
PFHpS, PFNS, PFDS	25	
PFOS	30	x
PFTriA	25	
FOSA, 4:2 FTS, 8:2 FTS, N-EtFOSAA, N-MeFOSAA	25	x

Common Contamination Sources in the Lab

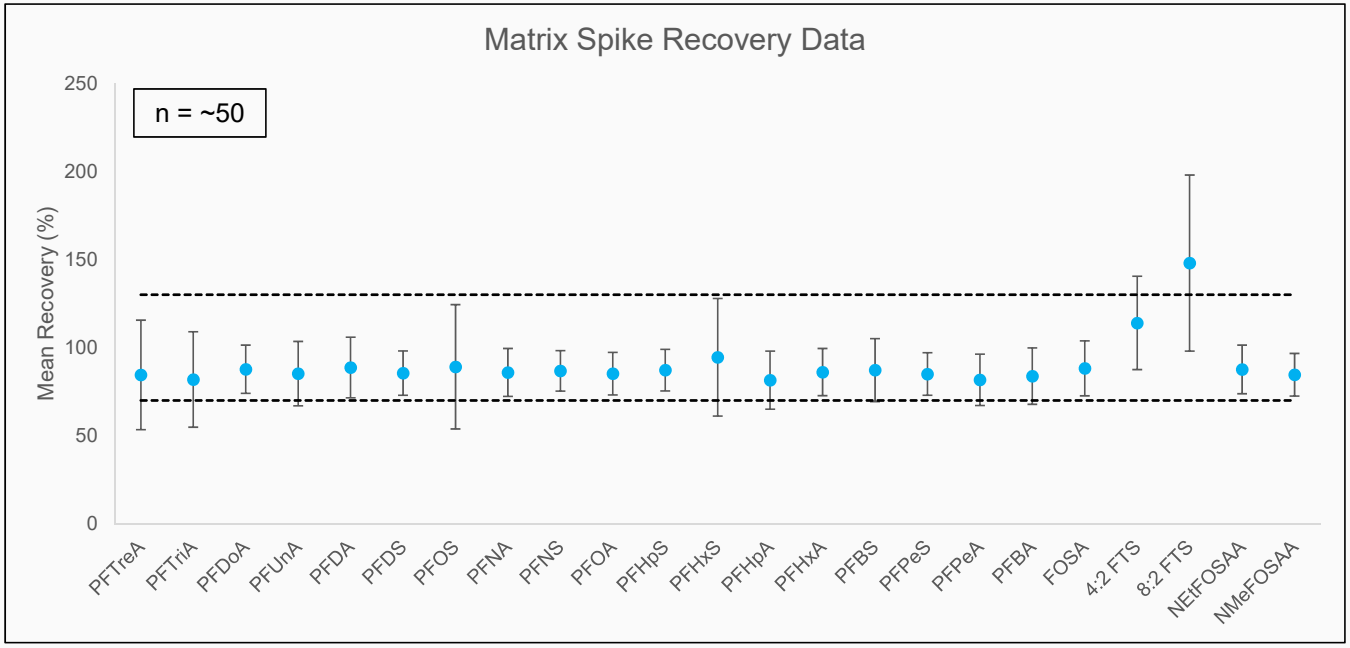
- Teflon® (or PTFE)-containing products
- Waterproof, water-resistant, or stain-resistant clothing/products (lab coats)
- Plastic clipboards, binders, or spiral hardcover books
- Post-it notes
- Chemical (blue) ice packs
- Disposable glass pipettes
- Aluminum foil
- Kim wipes

Contamination Solutions

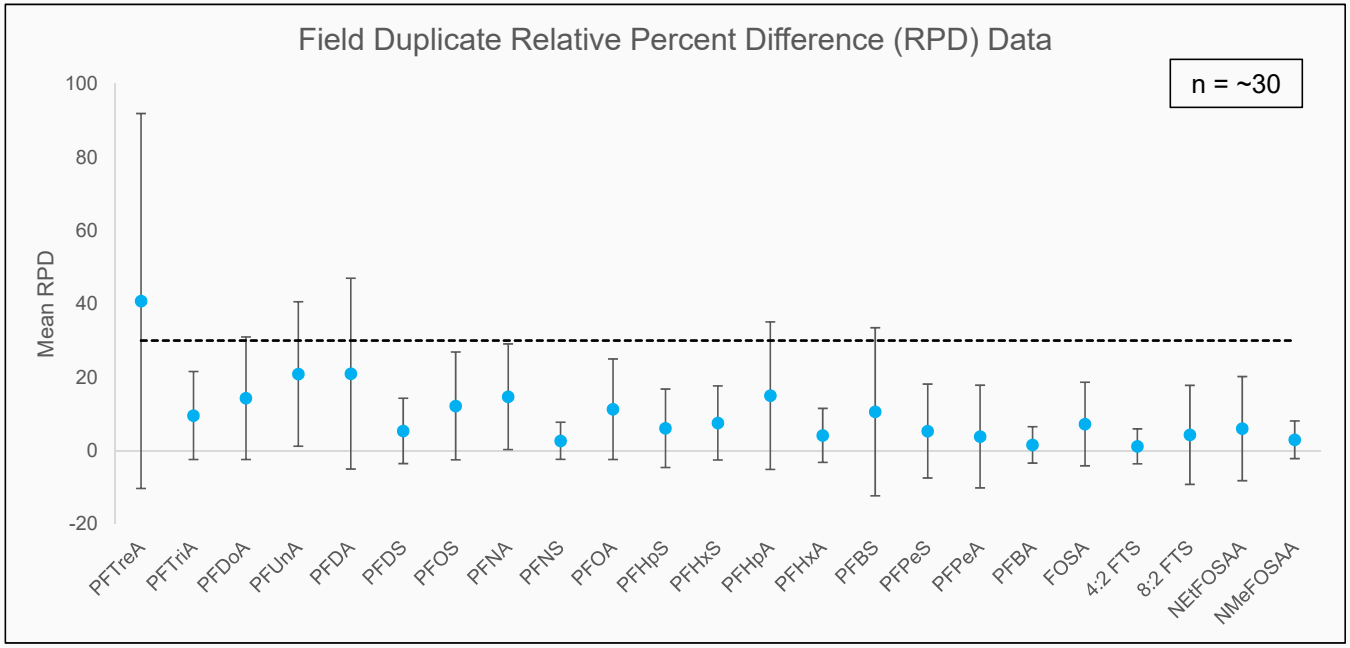
- Replace all PTFE tubing in your LC
  - Install an isolator column between the degasser and the sample injection valve to isolate any low-level PFAS that may still be in your system from samples
- Thoroughly rinse filter syringes and polypropylene filter units before use with acetonitrile and methanol
- Use polyethylene LC vial caps (<u>not</u> PTFE)
  - Polyethylene caps don't re-seal after they're punctured, so LC vials must be re-prepared for every analysis sequence

- <u>Blank check everything, all the time</u>

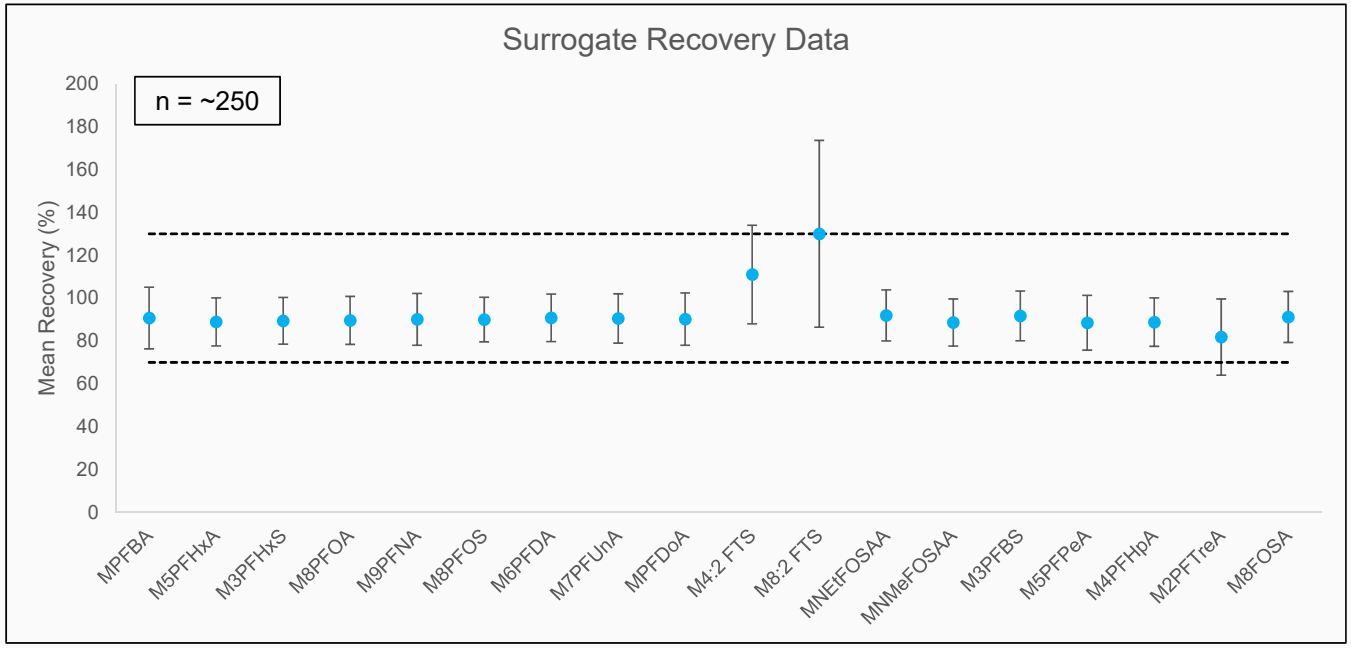
Method Accuracy



Method Precision



Surrogate Performance in Field Samples



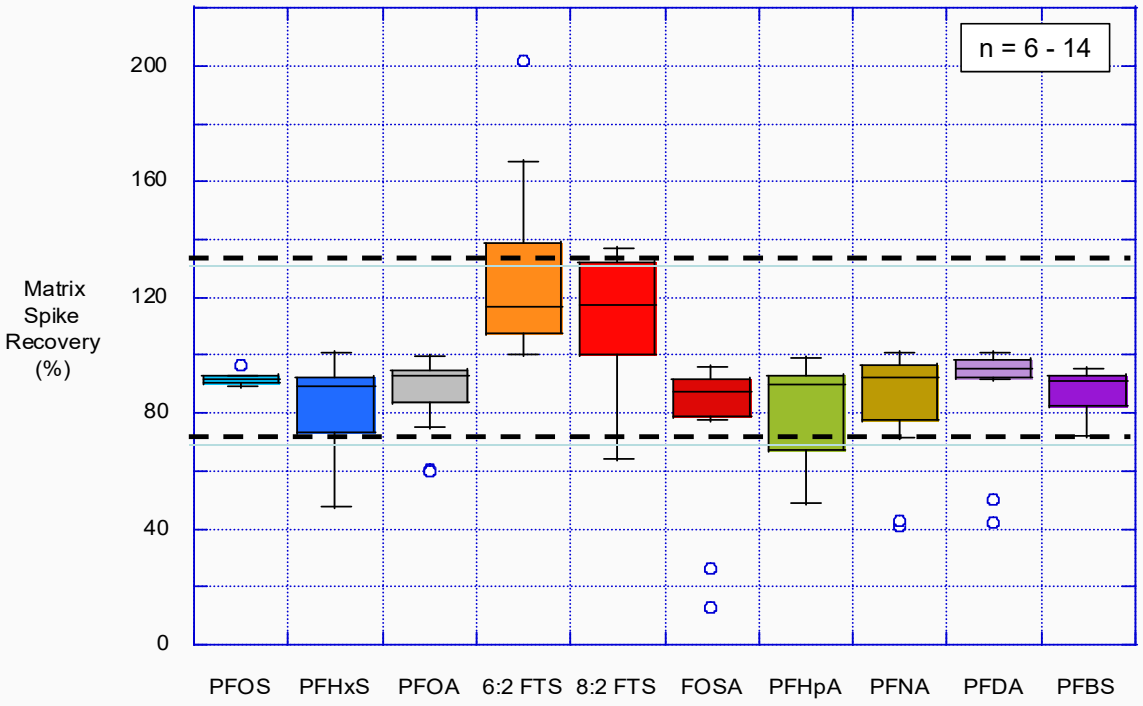
Site-Specific Data: AFFF

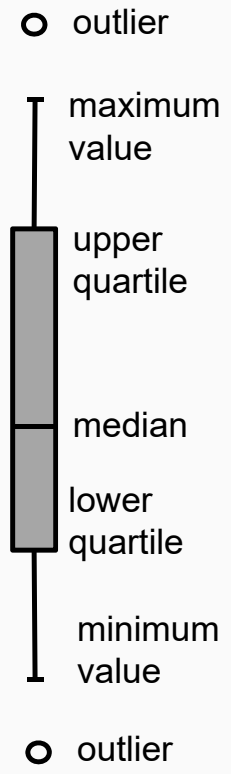
- Large amounts of aqueous film-forming foam (AFFF) administered on site
- Sediment and soil sampled from site for analysis by R5 lab (D7968)

Analyte	Site Conc. Range (ng/kg)
PFOA	33 – 14,300
PFOS	116 – 281,000
PFBS	25 – 2,160

Site-Specific Data: AFFF

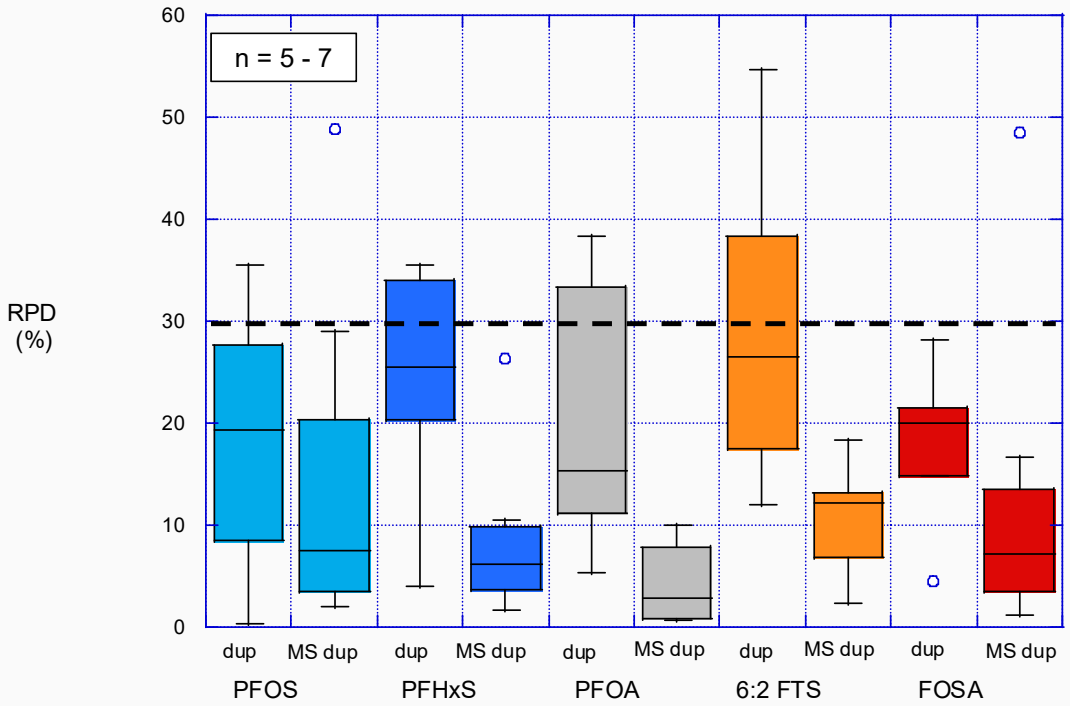
Matrix Spike Recovery Data





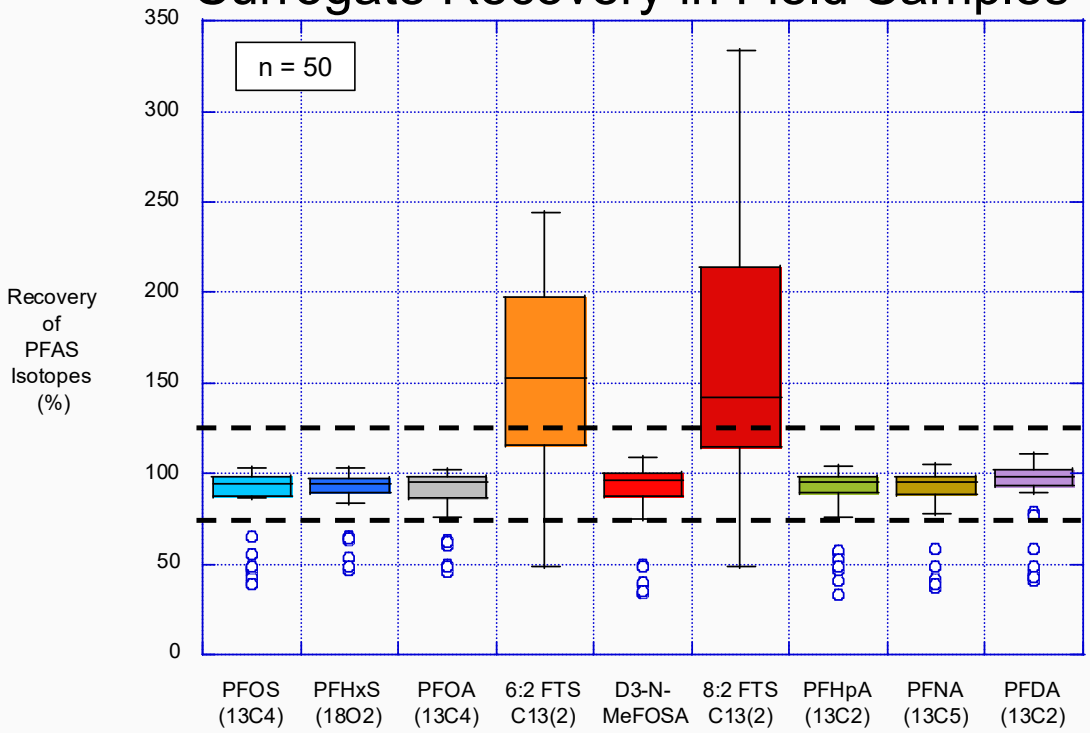
Site-Specific Data: AFFF

Field and Matrix Spike Duplicate Data



Site-Specific Data: AFFF

Surrogate Recovery in Field Samples



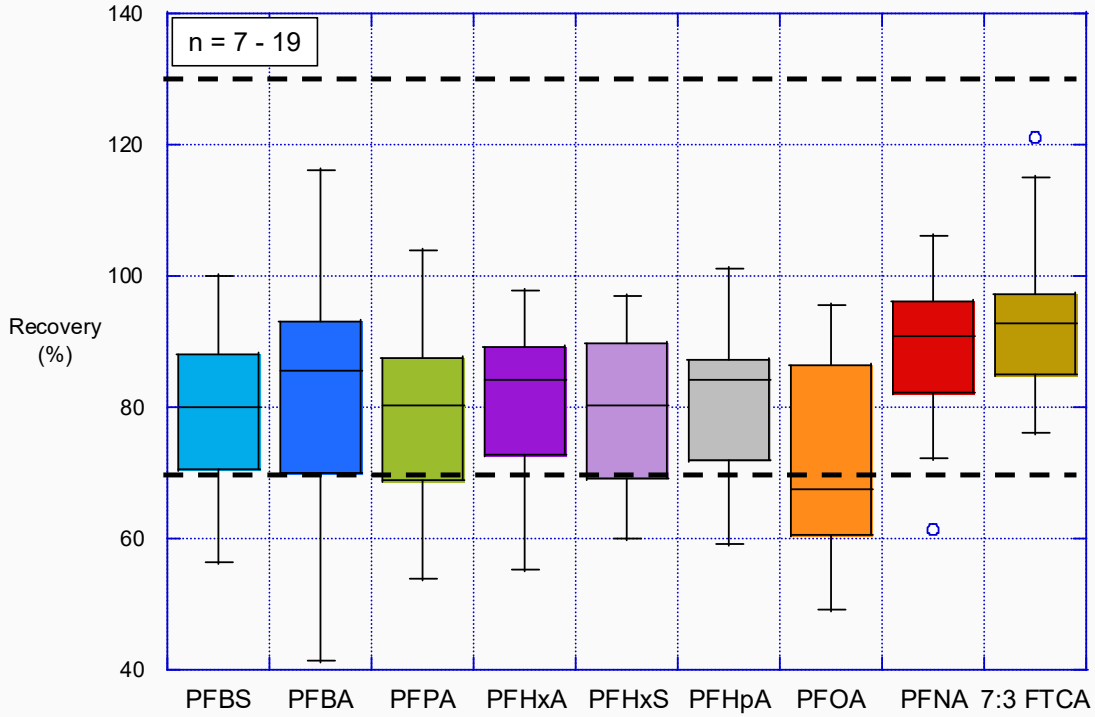
Site-Specific Data: Biosolids

- Class B biosolids from WWTP applied on field study site
- Soil sampled from site over 13 month period for analysis by R5 lab (D7968)

Analyte	Site Conc. Range (ng/kg)
PFOA	291 – 19,700
PFOS	6,220 – 27,100
PFHxA	81 – 36,000

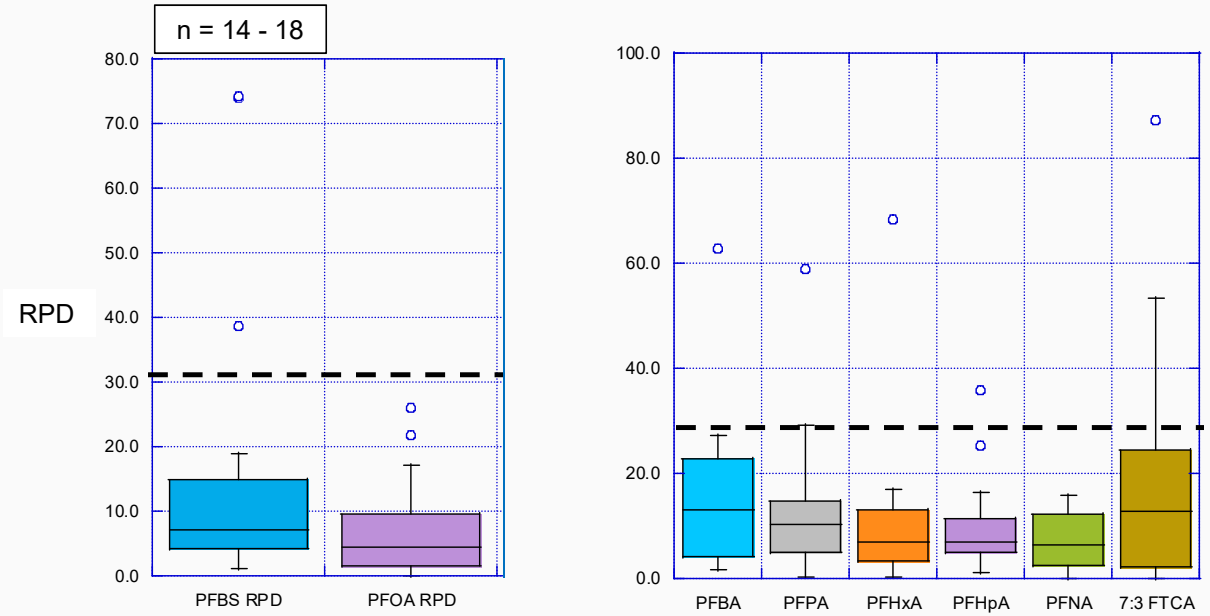
Site-Specific Data: Biosolids

Matrix Spike Recovery Data



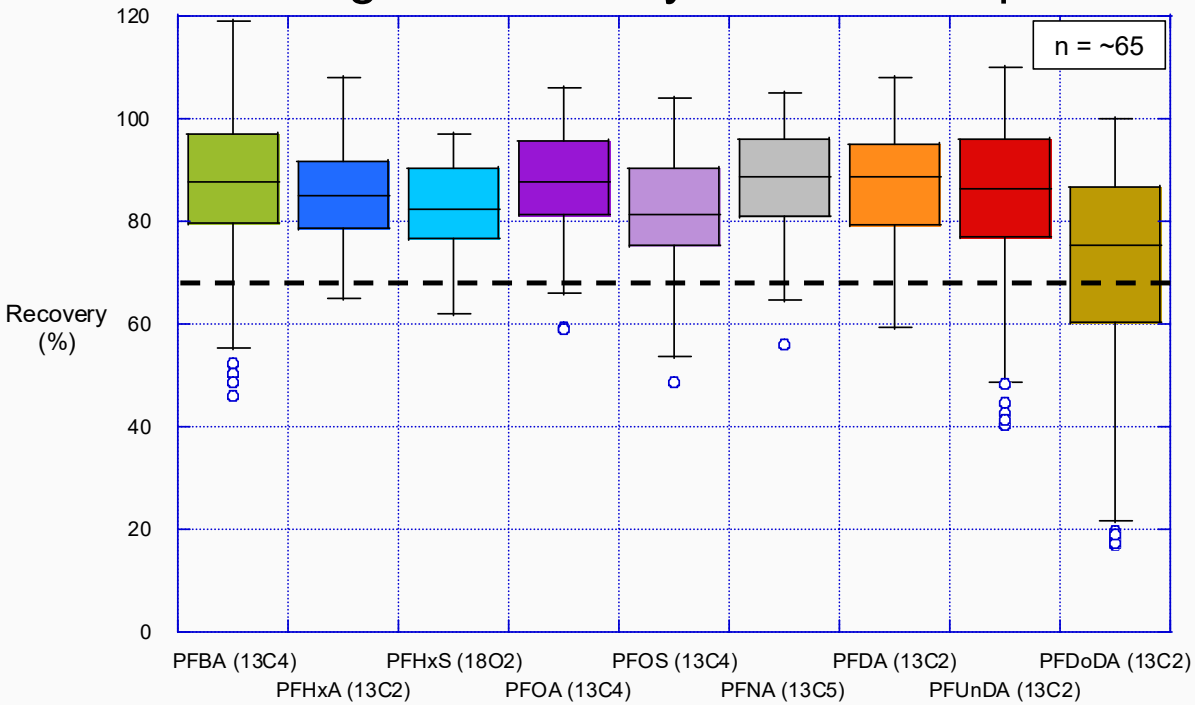
Site-Specific Data: Biosolids

Field Duplicate Data



Site-Specific Data: Biosolids

Surrogate Recovery in Field Samples



Acknowledgements

Sandra Halstead
US EPA – Region 10

Katrin Friesen
University of Alabama

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