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Observations at a PFAS Contaminated Site: Variability and Precursor Occurrence

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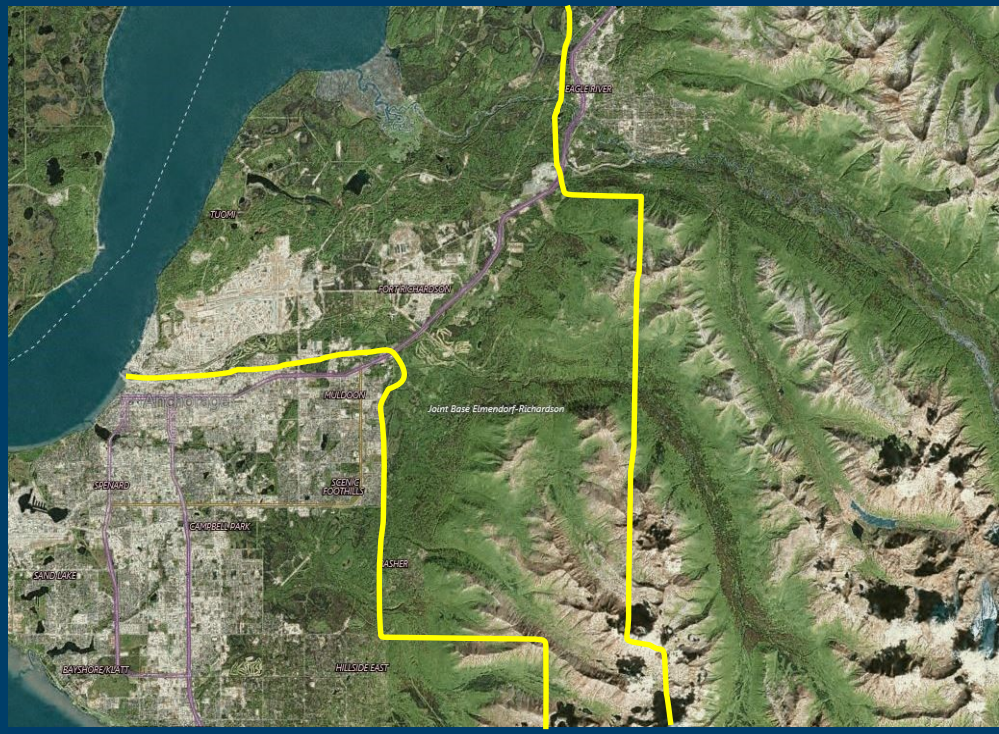
The views expressed in this presentation are those of the authors and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.

Joint Base Elmendorf Richardson

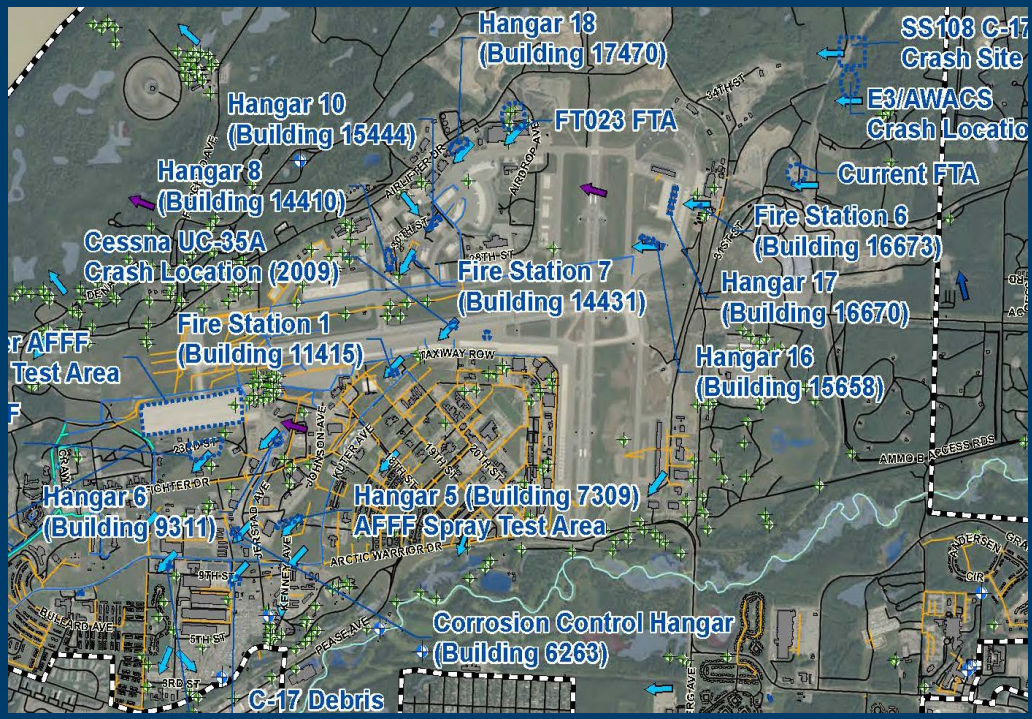
- Located in Anchorage, AK
- Active from early 1940's
- Listed on NPL
- 14 OUs+ combined
  - Size - 86,000 acres
  - Geology - coastal, glacial, forested, mountainous
  - Contaminants - solvents, landfills, munitions
- Air Force (AF) lead in 2010
- Anchorage drinks surface water



2016 JBER Sampling Effort

- 26 Areas of Concern investigated
  - Flightline, hangars, fire stations, fire training pits, crash sites
  - Media included ground water and soils
  - Later ground water seeps and surface water collected

- EPA
  - EPA collected samples immediately after AF collected samples
  - 17 ground water locations
  - 4 auxiliary locations not sampled by AF
  - 6 seeps sampled later



EPA objectives for JBER sampling

- Evaluate EPA analytical method on new matrices
  - Accuracy
  - Precision
- Evaluate sample variability in replicate samples
  - 3 field replicates for many locations
- Analyze samples for a larger suite of PFAS including precursors and transformation products
  - 12 PFCAs: C4 - C14
  - 7 PFSAs: C4 - C10
  - 12 precursors

EPA used ASTM Method D7979

- Environmental Waters (non-potable)
- Direct Injection, analysis by LC/MS/MS
- Single laboratory validated
- Target Analytes:
  - 12 PFCAs – C4 - C14
  - 7 PFSAs – C4 - C10
  - 12 precursors
- Isotopically labeled surrogates:
  - 7 PFCAs, 2 PFSAs, 3 precursors
  - Used to monitor analytical method performance/quality
  - Not used to “correct” the data
- Uses confirmation ion ratios to identify compounds and minimize matrix issues
- ASTM D7979 updated since this study was conducted

ASTM D7979 method

EPA United States Environmental Protection Agency

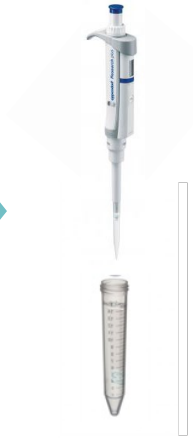
5 ml sample

Surrogate

5 mL MeOH

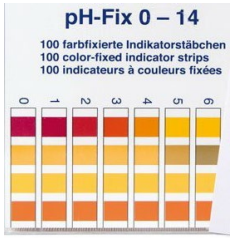
Mix

Filter



10 µL Acetic Acid

Mix



Check pH

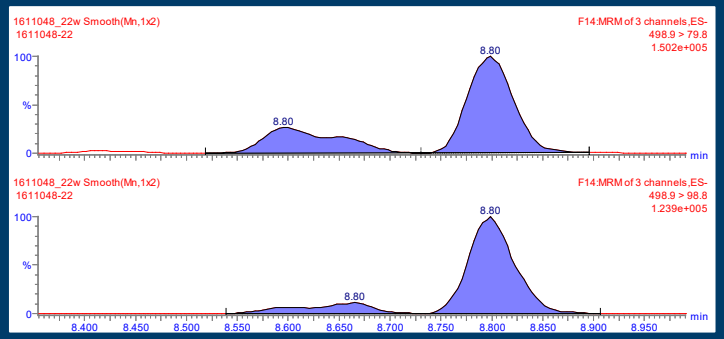
Transfer 1mL sample in vial (pour)

Run time 21 min

Based on schematic by William Lipps, Shimadzu

Analytical Method Quality Controls

- Analyte Identification
  - Each batch: Initial calibration, Calibration check, and Second source check
  - Each analyte: Retention time, Primary and Confirmation ion masses, and Ion ratio
- Accuracy – 2 of each/batch unless specified
  - Surrogate spiking - All samples and blanks
    - Used to assess method performance
    - Not used to alter reported concentrations
  - Matrix spike samples – MS and MS duplicates
  - Spiked blanks
  - Method reporting limit checks
- Precision - 2 of each/batch
  - Duplicate samples
  - Matrix spike duplicates
  - Spiked blanks
- Laboratory Contamination – method blanks – 2/batch



Deviations from ASTM D7979 in JBER sampling and analysis

- 50 mL sample collected - required sample processing changes (purple arrows)
- Sample coolers arrived above 6 C in some cases
- Sample holding time exceeded


50 ml sample


Add to HDPE bottle


50 mL MeOH rinse


Add to HDPE bottle


Mix (shake)


10 mL subsample

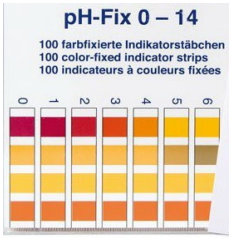

Surrogate


Mix


Filter


10 µL Acetic Acid


Mix



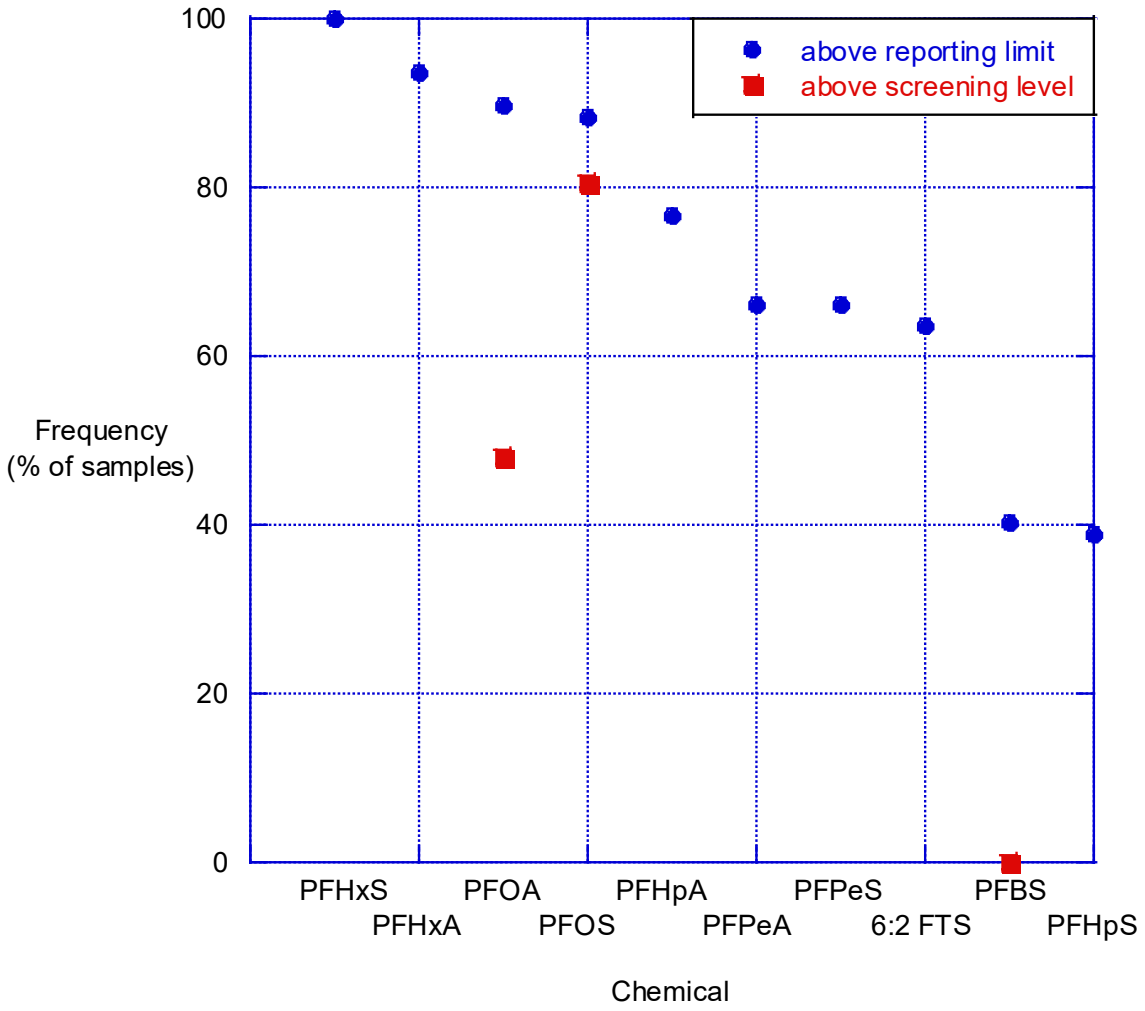
Check pH


Transfer 1mL sample in vial (pour)

Run time 21 min

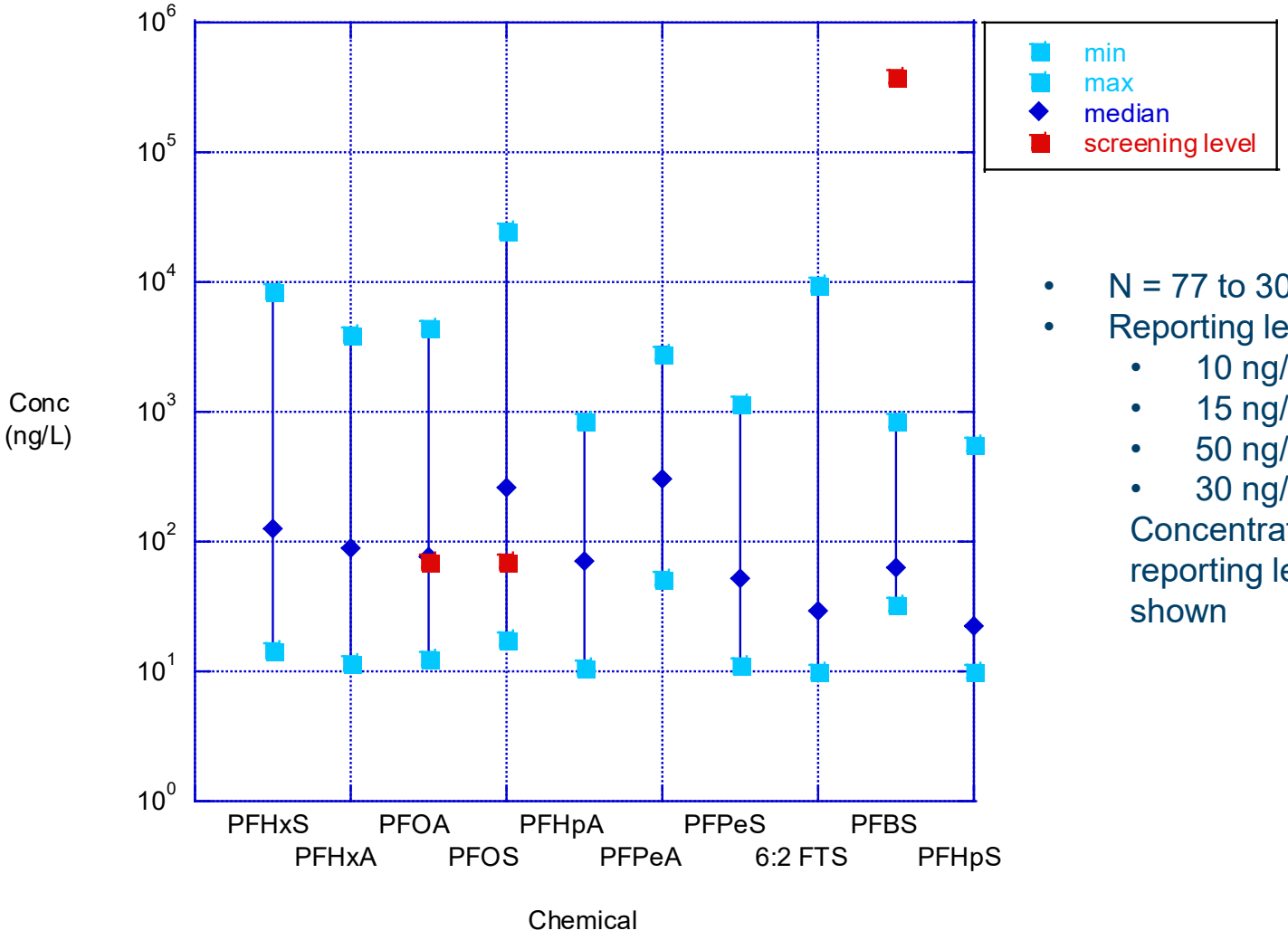
Based on schematic by William Lipps, Shimadzu

Most commonly observed PFAS in JBER samples



- N= 77 samples
- Reporting level
  - 10 ng/L – most
  - 15 ng/L PFOS
  - 50 ng/L PFPeA
  - 30 ng/L PFBS
- Screening level
  - PFOA 70 ng/L
  - PFOS 70 ng/L
  - PFBS 380 µg/L

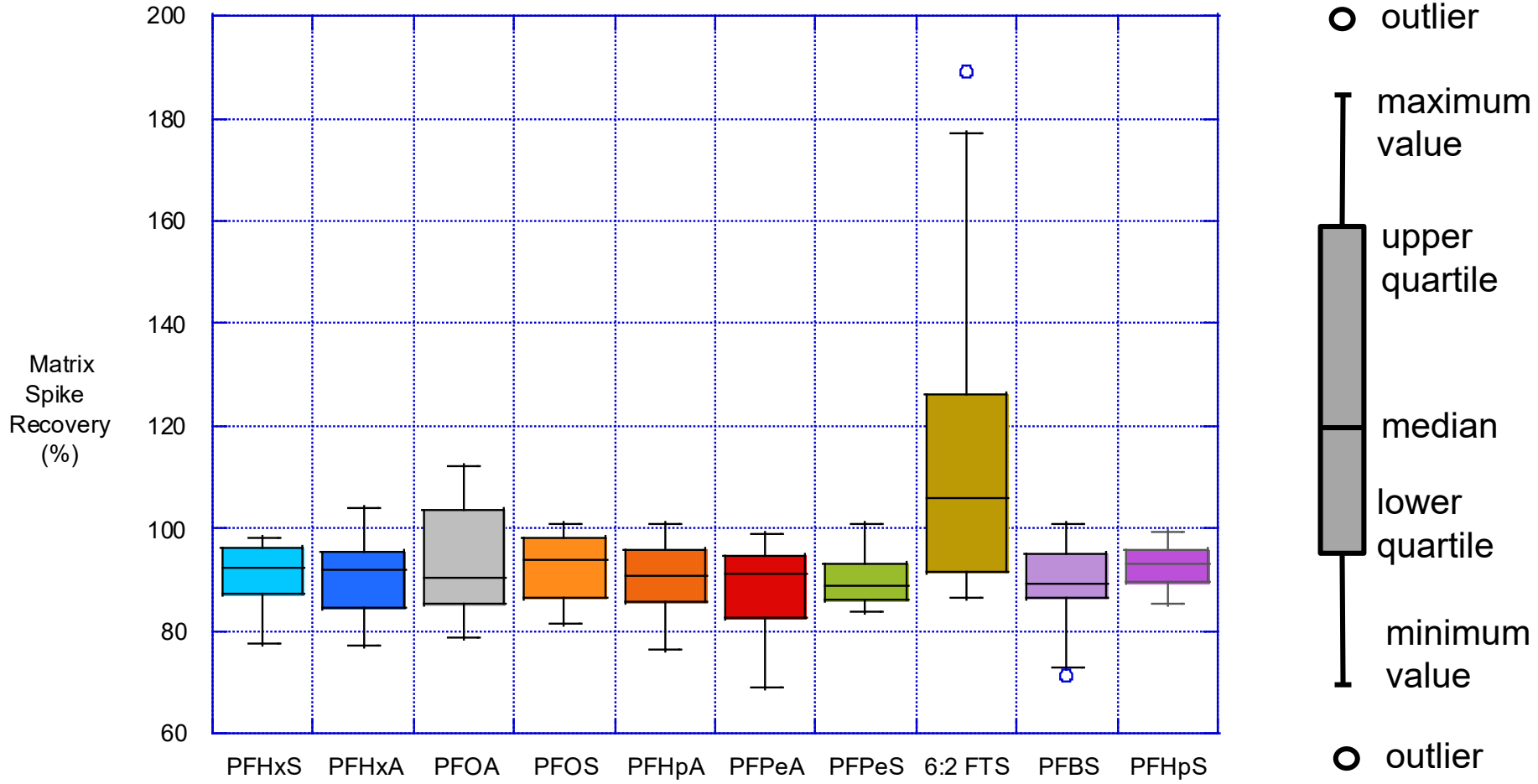
Concentration ranges observed



- N = 77 to 30
- Reporting level
  - 10 ng/L – most
  - 15 ng/L PFOS
  - 50 ng/L PFPeA
  - 30 ng/L PFBS

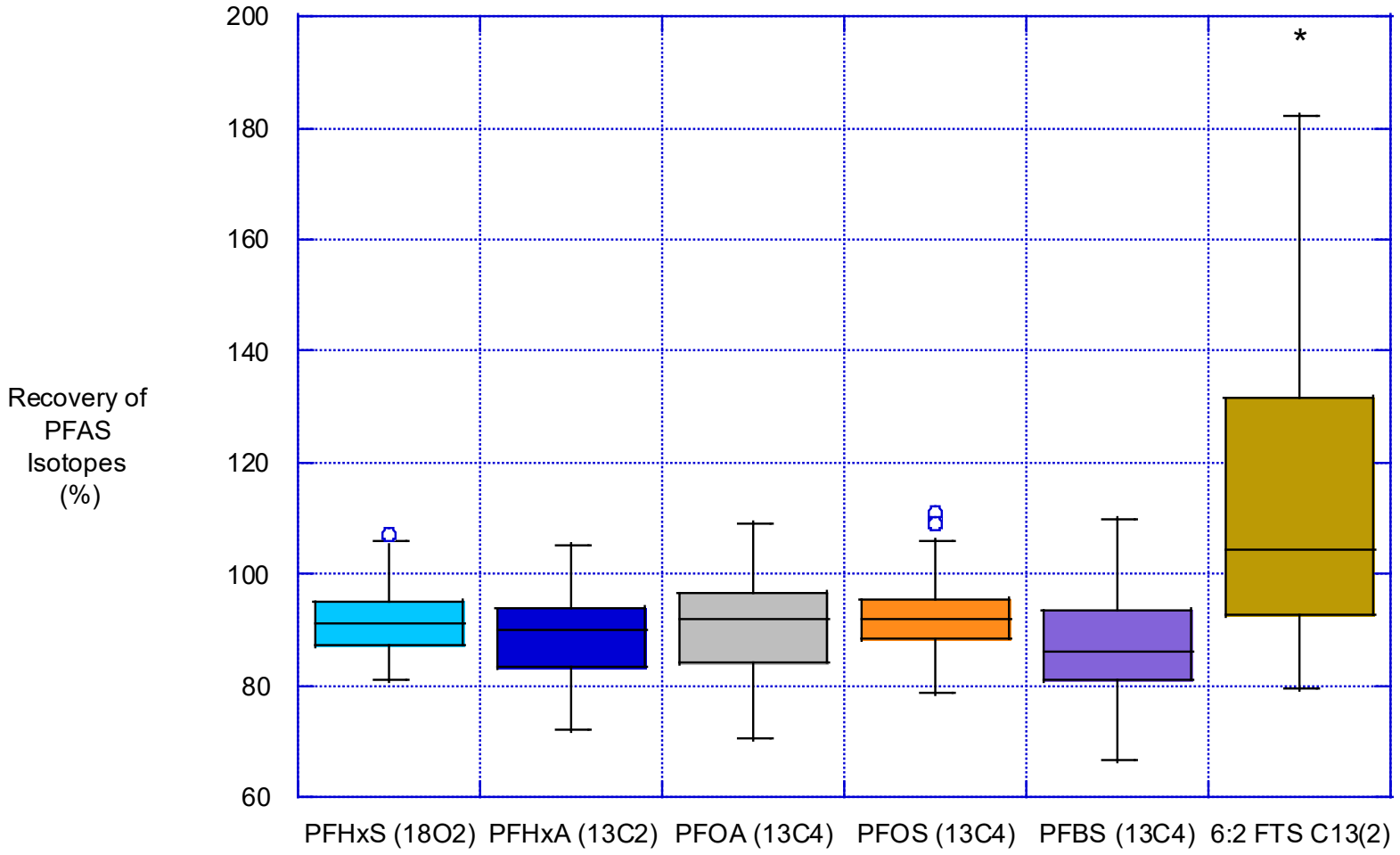
  Concentrations below reporting level not shown

Method Performance Accuracy - Matrix Spike Data



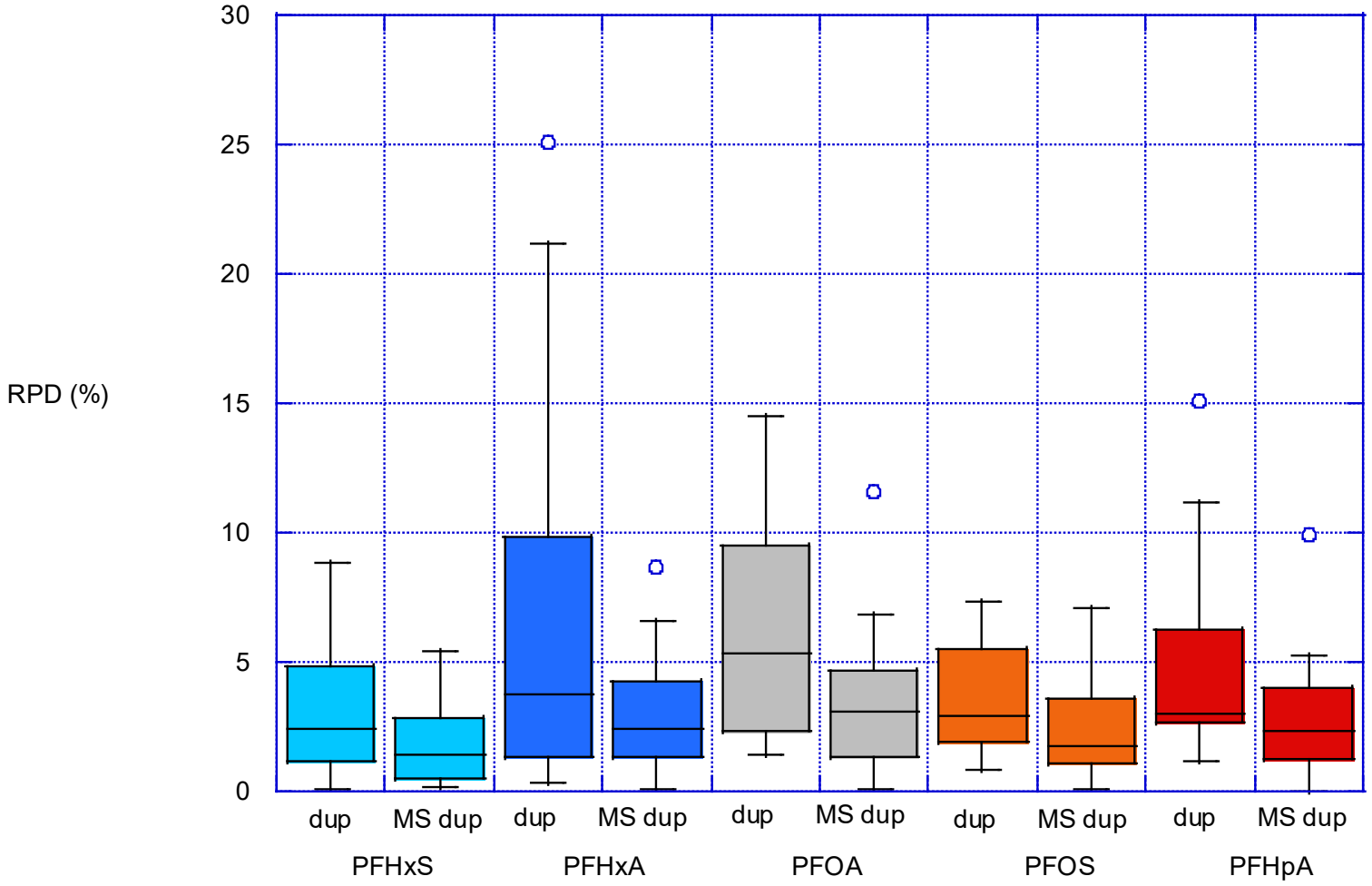
N= 25 to 29

Method Performance Accuracy - Surrogate Recovery



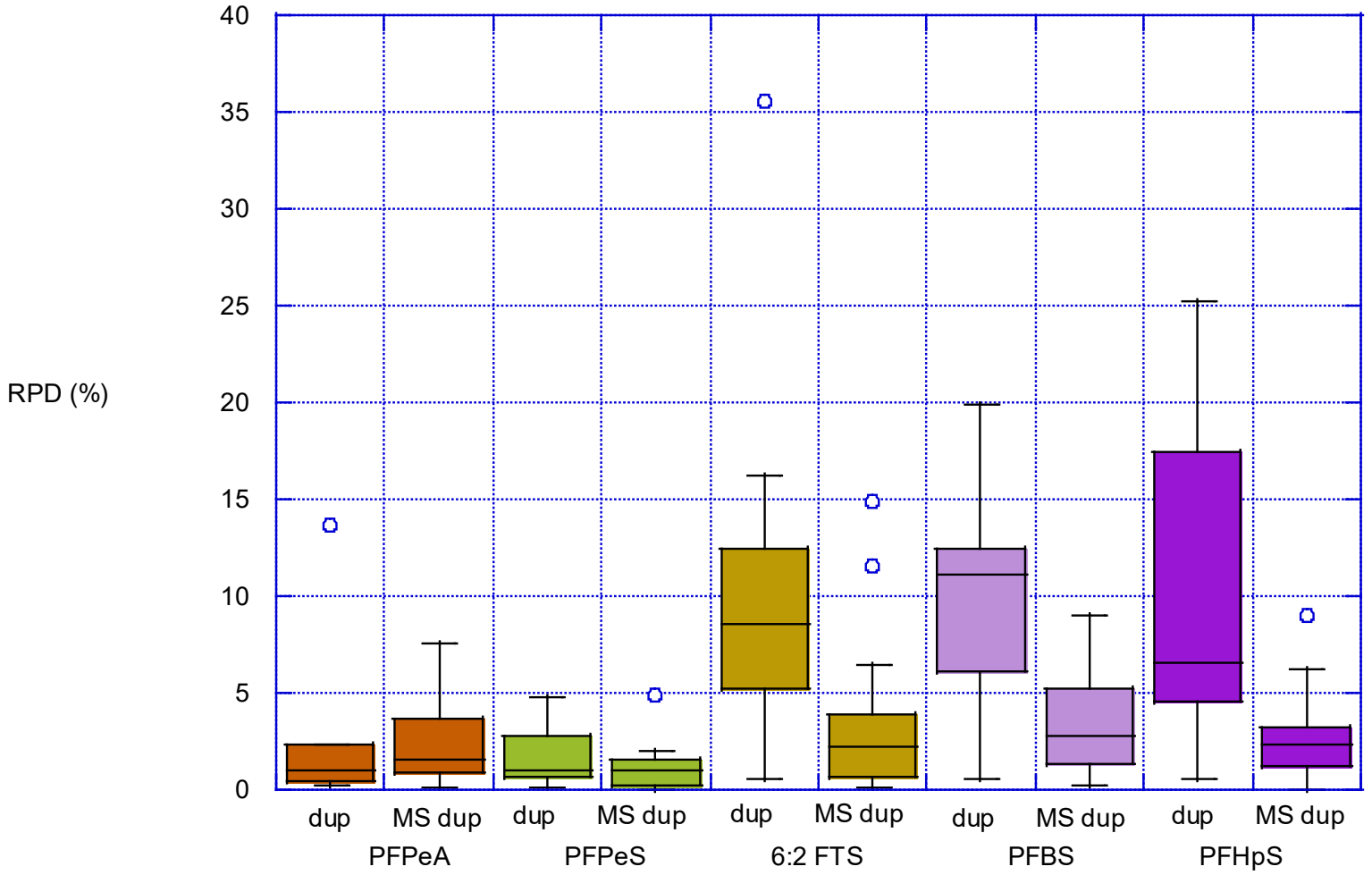
* 4 outliers between 280 and 370 % not shown
N = 108

Method Performance - Precision Matrix Spike and Lab Duplicates



N dup = 9 to 12
N MS Dup = 16

Method Performance - Precision Matrix Spike and Lab Duplicates



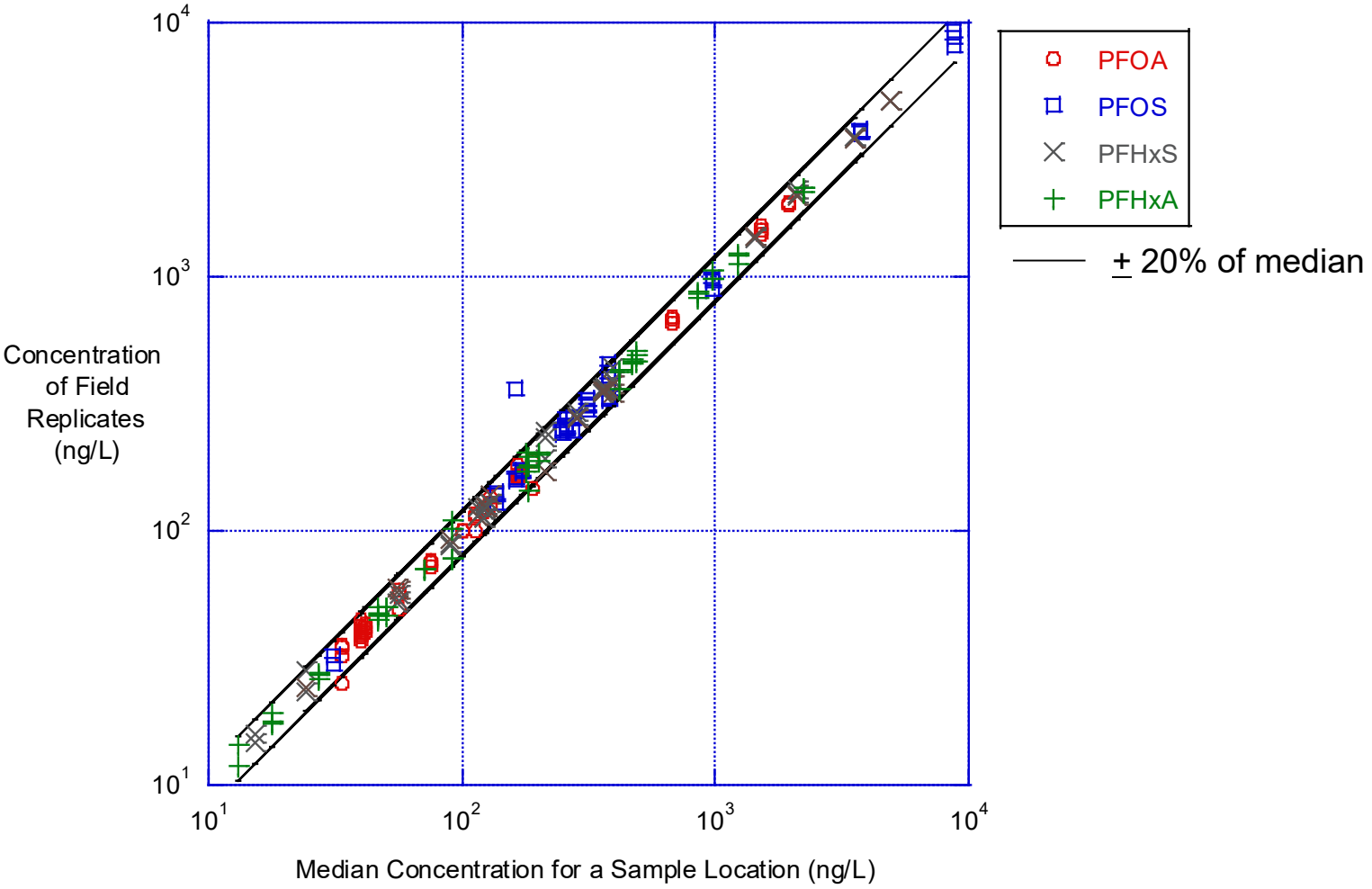
N dup = 6 to 10
N MS Dup = 16

Additional Analytical Results

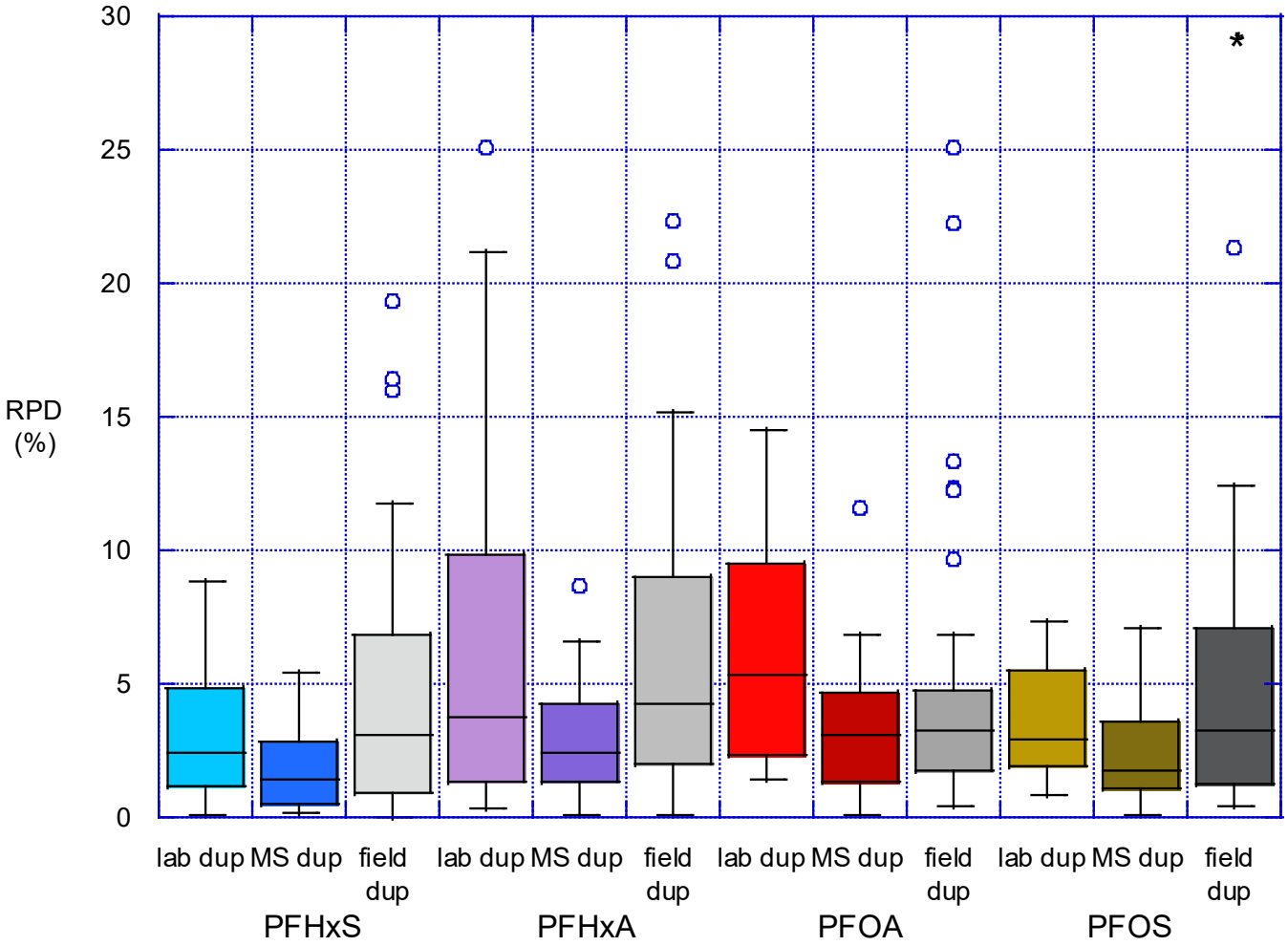
- Field and Equipment Blanks – no analytes observed above reporting levels
- Performance Evaluation Sample
  - Double Blind sample
  - Results – within duplicate data acceptance criteria

Chemical	Measured Conc (ng/L)	Spiked Conc (ng/L)	RPD (%)
PFOA	115	100	15
Surrogate recovery	99.6 %		
PFOS	210	200	5.0
Surrogate recovery	101 %		

Variability in Field Replicates



Variability in Field Replicates compared to Lab Replicates



RPD for field dup based on median

Field dup data not meeting DQOs are not shown

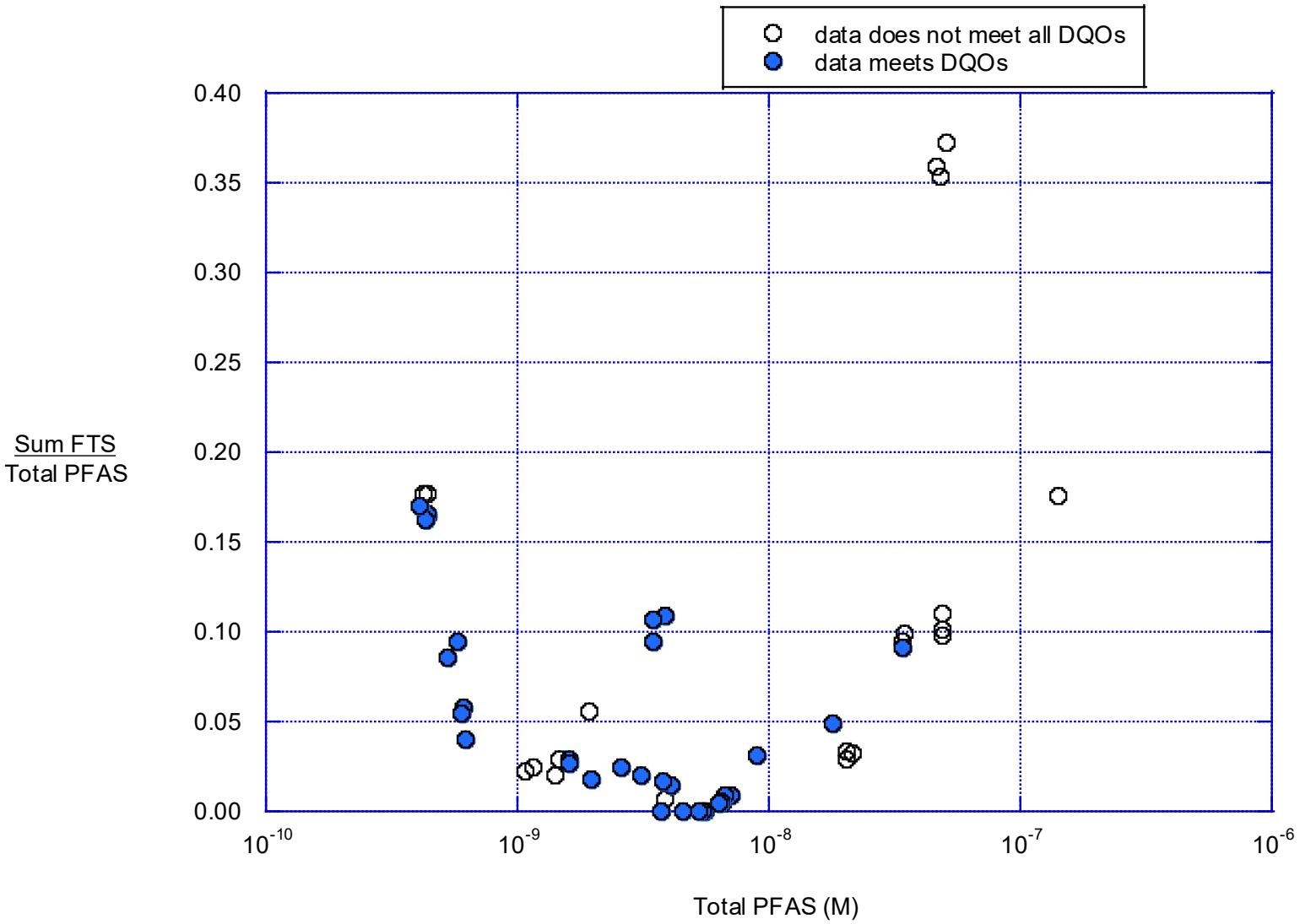
*1 outlier at 125% not shown

Field dups
N= 37 to 42

Precursor observations

- Observed in 70 % of sample locations
- Analytes observed
  - 6:2 FTS - 49 samples
  - 4:2 and 8:2 FTS - 9 samples
  - 6:2 FTUCA and FOSA - 1 sample
  - Not observed – 6:2 FTCA, 8:2 FTCA, 8:2 FTUCA, 7:3 FTCA, 10:2 FTCA, N-EtFOSAA, N-MeFOSAA

FTS Precursors compared to Total PFAS – Molar basis



JBER Conclusions

- Analytical method used by EPA
  - accurately and precisely measured concentrations for most analytes
  - 6:2 FTS analysis - further method development useful
- Sample variability
  - Variability in field replicates similar to lab precision data
  - $\pm$ 20% for many locations at this site
- Precursors
  - 6:2, 8:2 and 4:2 FTS most commonly observed precursors
  - Observed in 70 % of sample locations
  - Precursors relative to total measured PFAS molar basis
    - Common 10 %
    - Could be as high as 40 %

Next Steps

- Use exploratory data interpretation techniques such as:
  - Principal Component Analysis (PCA)
  - Hierarchical Cluster Analysis (HCA)
  - Bayesian Networks and machine learning

to evaluate the data such as identifying similarities in sample locations and PFAS patterns

Sample location clusters

- All PFAS and surrogate data analyzed using PCA and HCA
- Seven clusters were identified:

Cluster	Total PFAS Conc (M)	PFOS/PFOA ratio
Fire stn 7	1.4×10^{-7}	6
Hangar 18	4.7 to 5.1×10^{-8}	50
GW seep OU5SP-11 and seep WCSW-2	3.3 to 4.9×10^{-8}	2
FSFS and Fire stn 1	1.8 to 2.1×10^{-8}	2
GW seep OU5SP1 and 2, and pump stn OU5CP	5.3 to 7.1×10^{-9}	1
CHD3, Hangar 10, Hangar 8, and Hangar 6	3.1 to 9.0×10^{-9}	1 to 4
All other sample locations	$< 3.3 \times 10^{-9}$	

PCA/HCA Clusters

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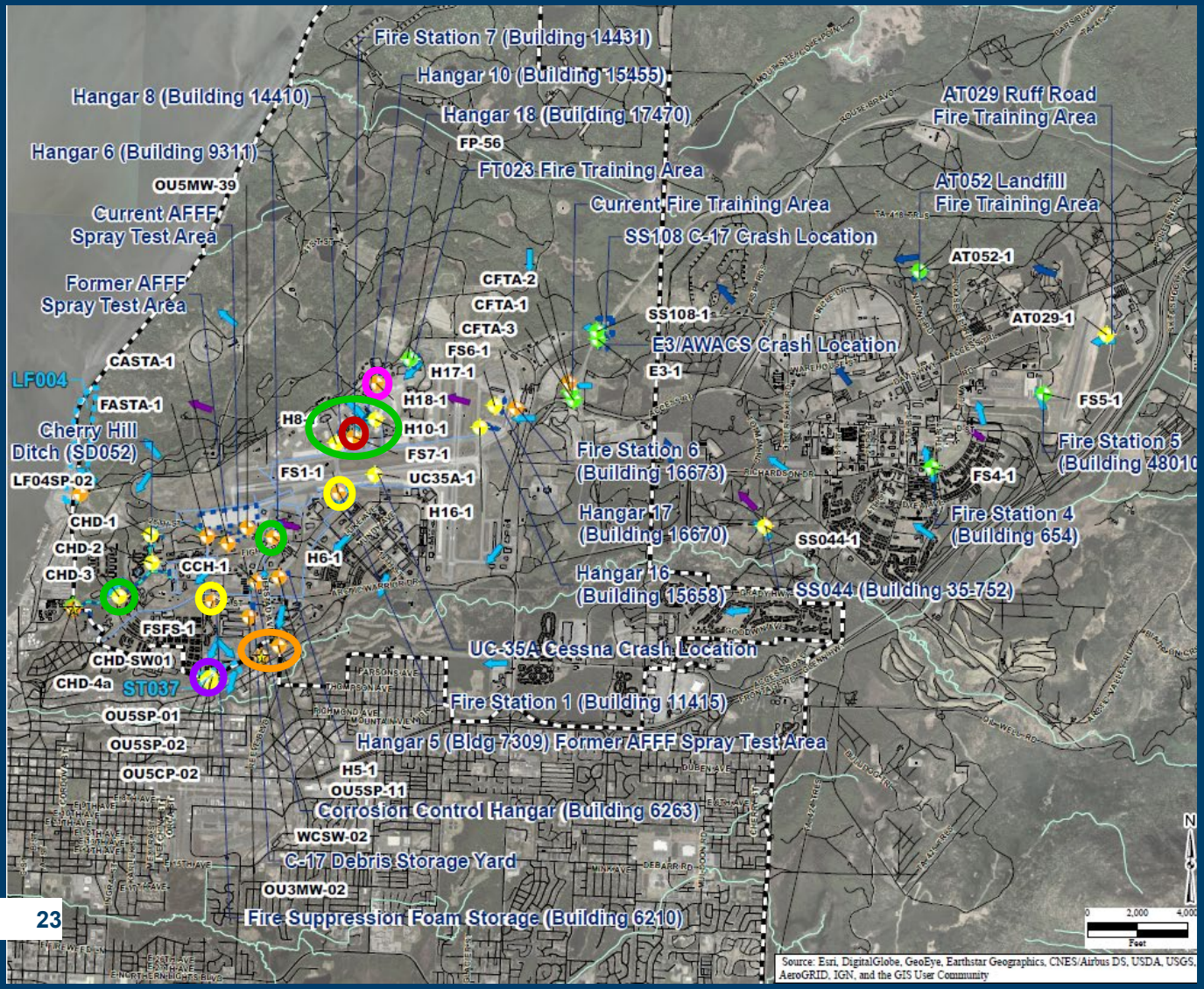


Fire stn 7

Hangar 18

Seep OU5SP-11
Seep WCW-02

FSFS
Fire stn 1

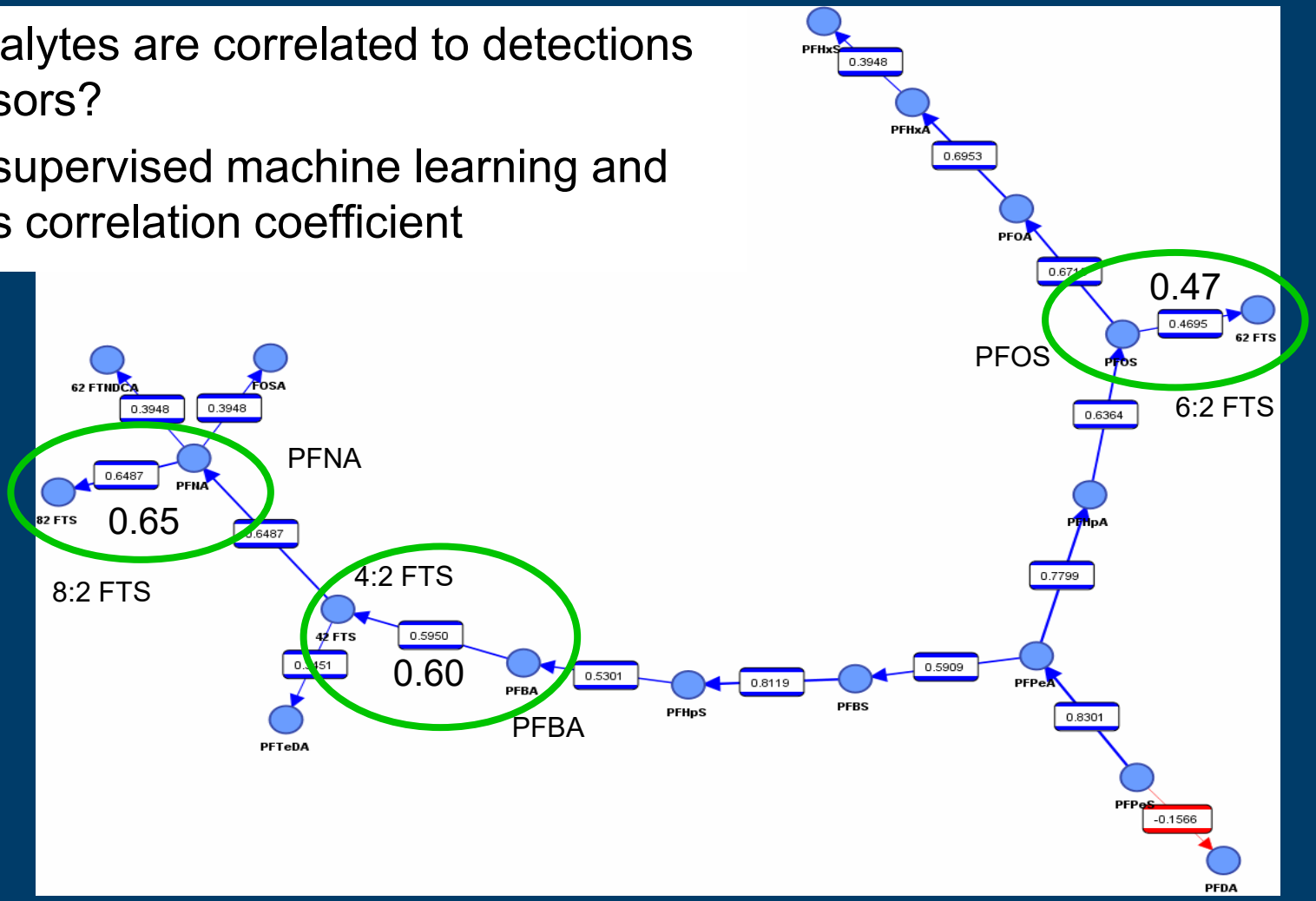
Seep OU5SP-01
Seep OU5SP-02
Seep OU5CP-02

CHD3
Hangar 10
Hangar 8
Hangar 6

Bayesian Networks

Which analytes are correlated to detections of precursors?

Using unsupervised machine learning and Pearson‘s correlation coefficient



Acknowledgements

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