Per- and Polyfluoroalkyl Substances (PFAS) Contamination in Materials Used to Collect, Prepare, and Analyze for PFAS in the Environment

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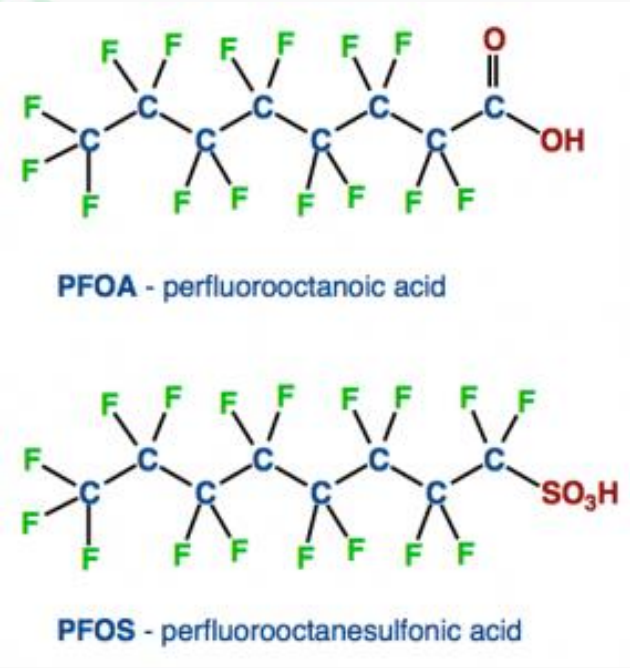
Background

- PFAS are commonly observed, persistent, and appear to be resistant to many treatment processes (“forever chemicals”)
- 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



Historically Common Contamination Sources in the Field or Lab

- PTFE- or FEP-containing products (e.g. Teflon®)
- PVDF- or ETFE-containing products (e.g. certain kinds of tubing)
- Waterproof, water-resistant, or stain-resistant clothing/products (e.g. outdoor wear, lab coats, fast food wrappers)
- Certain personal care products (e.g. cosmetics, lotions)
- Certain insect repellants and sunscreens
- Plastic clipboards, binders, or hardcover spiral books
- Post-it® notes
- Recycled paper products (e.g. paper towels, notebook paper)
- Chemical (blue) ice packs
- Disposable glass pipettes
- Aluminum foil
- Kim® wipes
- Latex gloves

ASTM Standards D7979 and D7968

- Developed at Region 5 lab for non-drinking water and solid matrices
  - ~3,000 field samples analyzed since 2012 (+ ~2,800 QC samples)
- Direct injection methods (i.e. “dilute and shoot”)
  - Minimal sample manipulation reduces prep time, minimizes risk of blank contamination
- External standard methods
  - Labelled surrogates for most target analytes, used strictly to evaluate method performance
- Analysis by LC/MS/MS
  - Confirmatory transitions for most target analytes
  - Ion ratios calculated to support qualitative IDs

Current Region 5 Lab PFAS Analyte List

Target Analyte	Reporting Limit in Water (ng/L)	Reporting Limit In Soil (ng/kg)	Labelled Surrogate
PFBA, PFPeA	50	125	x
PFBS	10	25	x
PFPeS	10	25	
PFHxA	10	50	x
PFHxS, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTreA	10	25	x
PFHpS, PFNS, PFDS	10	25	
PFOS	10	30	x
PFTriA	10	25	
FOSA, 4:2 FTS, 6:2 FTS, 8:2 FTS, N-EtFOSAA, N-MeFOSAA	10	25	x

ASTM Standards – Sample Preparation

D7979 (PFAS in Water Method)

- 5 mL sample (no sub-sampling!)
- Spike with surrogates, dilute 1:1 with 5 mL methanol, shake for 2 minutes
- Filter through pre-rinsed hydrophilic polypropylene membrane, acidify with acetic acid (pH 3 – 4)
- 10 mL final volume

D7968 (PFAS in Soil Method)

- 2 gram sub-sample
- Spike with surrogates, extract via tumbling with 10 mL 1:1 methanol/water at pH 9 – 10 (adjusted with ammonium hydroxide) for 1 hour
- Centrifuge extract, filter through pre-rinsed hydrophilic polypropylene membrane, acidify with acetic acid (pH 3 – 4)
- 10 mL final volume

ASTM Standards – Analysis

- Parts-per-trillion (ppt) analyte calibration range
- 21-minute run time
- Ternary LC gradient

		% Solvent Line A	% Solvent Line B	% Solvent Line C
Time (min)	Flow (mL/min)	95% Water : 5% Acetonitrile	Acetonitrile	400mM Ammonium Acetate (95% Water : 5% Acetonitrile)
0	0.3	95	0	5
1	0.3	75	20	5
6	0.3	50	45	5
13	0.3	15	80	5
14	0.4	0	95	5
17	0.4	0	95	5
18	0.4	95	0	5
21	0.4	95	0	5

Lab Consumables

- Lab consumable = lab supply that is considered one-time use, disposable, and inexpensive
- Lab consumables in Region 5 lab PFAS methods:
  - Polypropylene sampling containers (15 mL and 50 mL conical centrifuge tubes)
    - Used also for reagent storage and standard preparation/storage
  - 2 mL amber glass instrument vials (i.e. autosampler vials)
  - Polyethylene screw caps for 2 mL instrument vials
  - Polypropylene pipette tips (200 µL, 1 mL, 10 mL)
  - Polypropylene filtration disks (with 0.2 µm GHP membrane)

Erratic Lab Consumables Contamination

- In July 2020, erratic PFAS contamination was discovered while processing a data set
  - Contamination varied in frequency, concentration, and affected PFAS target analytes
  - Such contamination caused the data set to be of unknown quality
  - All PFAS preparation/analysis ceased in the lab until the root cause of the contamination could be determined and corrected
  - After 4 months of investigation, the following lab consumables used for PFAS were found to erratically contain PFAS:
    - 2 mL amber glass instrument vials (i.e. autosampler vials)
    - 15 mL and 50 mL polypropylene conical centrifuge tubes (used for field sampling, reagent storage, and standard preparation/storage)
    - 10 mL polypropylene pipette tips

Erratic Lab Consumables Contamination

- Several brands, part numbers, and lots of affected consumables were extensively tested
  - Other brands and part numbers contained erratic PFAS contamination as well
  - Determined in-house self-certification of lots not feasible with limited staff/resources
- Short-term solution: all PFAS field samples required to be collected, prepared, analyzed, and reported in triplicate
  - Allows for easy identification of false positives or biased-high results
    - "T" flag created to notify data users of potential false positives/biased-high results in data reports
  - Provides needed assurance to data users that the reported PFAS results are both precise and accurate

PFAS Contamination Data

- 98 aqueous field samples (236 in triplicate) have been prepared/analyzed since triplicate requirement enacted in November 2020
- Method blanks, reporting limit checks, blank spikes, and triplicate field data all monitored for erratic contamination
  - 2 method blanks, 2 reporting limit checks, and 2 blank spikes required for each batch of 20 (including triplicates) field samples
  - 7,776 data points collected and evaluated
- Contamination is determined using percent difference between the 3 replicates
  - ± 30% difference is limit used to determine if result is a false positive or biased high

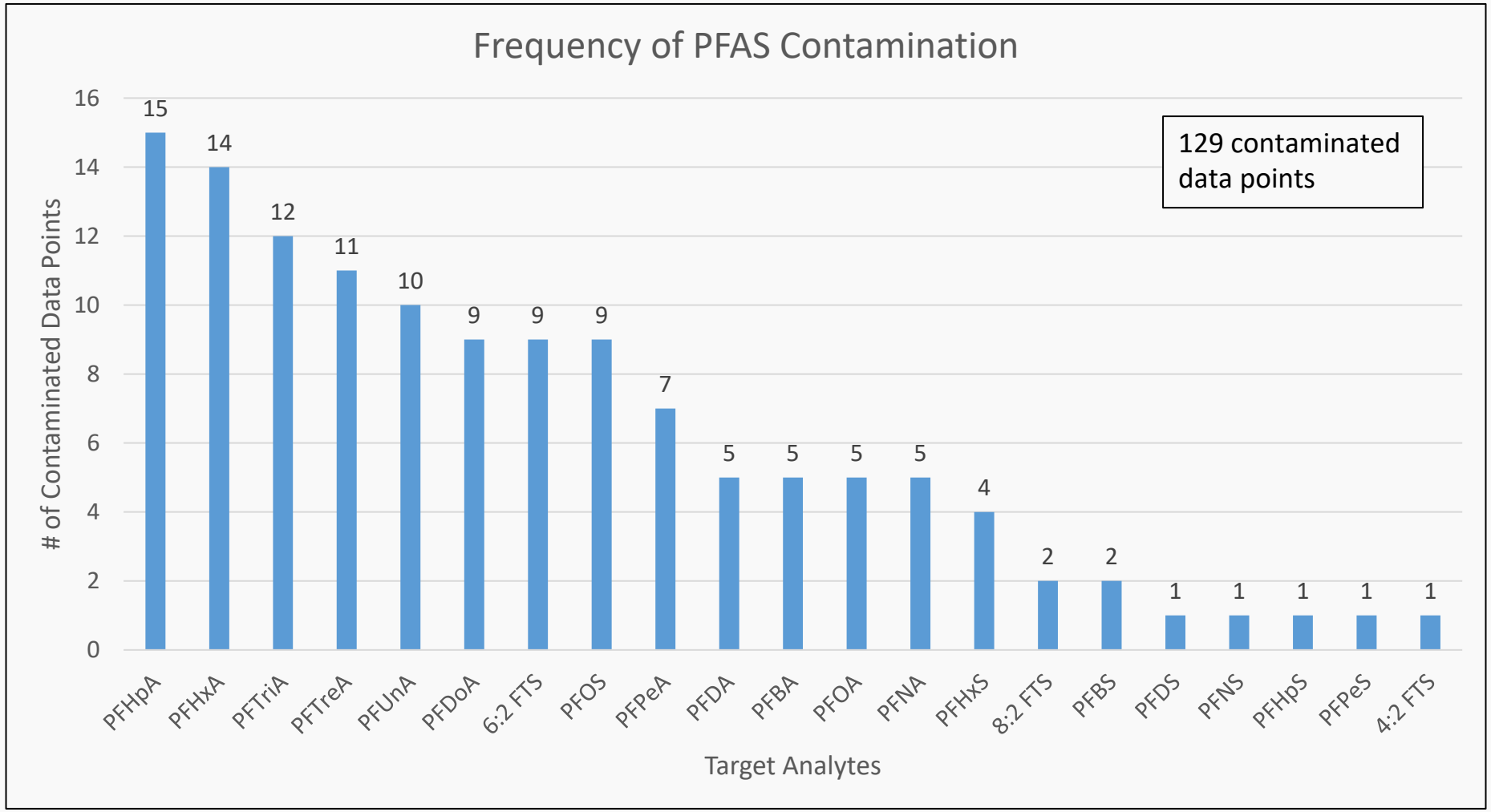
PFAS Contamination Data

Example of False Positive Result

- PFOS in field sample 2102012-02 was flagged “T” in the data report to notify the client that the data point is likely a false positive

		≥ Reported RL		*> ± 30% Difference (D) Limit*		
Sample ID	**Analyte**	**Reported Result (ppt)**	**Reported RL (ppt)**	**%D -02 vs. -02RE1**	**%D -02 vs. -02RE2**	**%D -02RE1 vs. -02RE2**
2102012-02	PFOS	28.9	11.1	826	820	-0.64
2102012-02RE1	PFOS	3.12	10.3			
2102012-02RE2	PFOS	3.14	10.1			

PFAS Contamination Data



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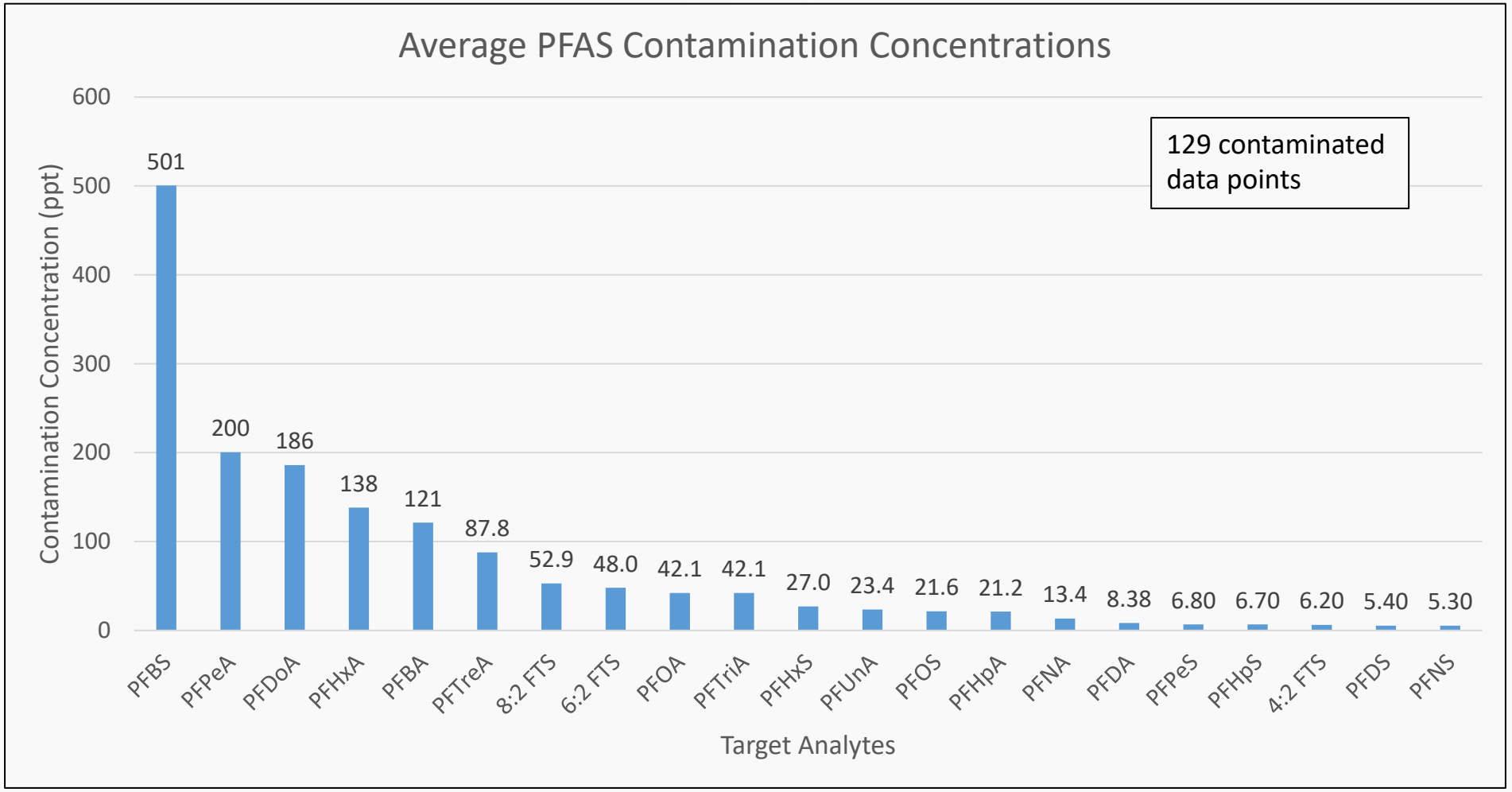

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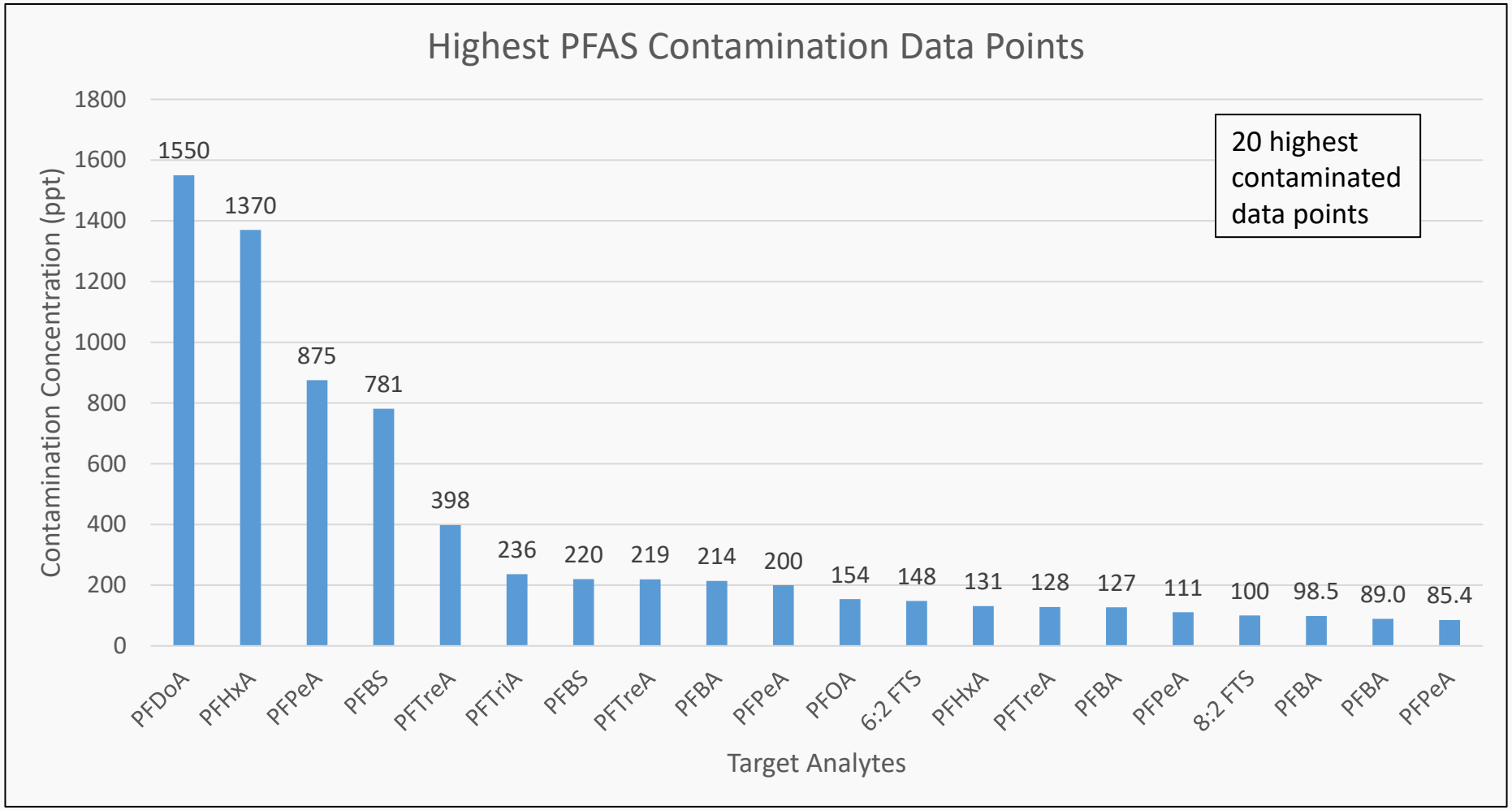

PFAS Contamination Data – Summary

- Additional statistics:
  - 88% of Region 5 lab PFAS method target analytes affected by continued erratic contamination
  - 67% of contaminated data points at or near method reporting limits
  - On average, 2% of data points from each data set impacted by contamination
- Caution should still be taken by data users when evaluating data variability in low-level results in terms of project decision making as replicate PFAS samples are co-located
- Long-term solution: consumable vendors provide certified, trace-level (low ppt) PFAS-free products

Considerations When Requesting PFAS Analysis

- What analytical method does the lab run?

	EPA Method 533	EPA Method 537.1	ASTM Standard D7979	EPA Method 8327
Lowest Target Analyte Calibration Range:	0.5 - 25 ppb (on-column)	0.5 - 25 ppb* (on-column)	5 - 200 ppt (on-column)	5 - 200 ppt (on-column)
Lowest Demonstrated Reporting Limit:	10 ppt	16 ppt	10 ppt	10 ppt
Initial Sample Volume:	250 mL	250 mL	5 mL	5 mL
Final Sample Volume (for Analysis):	1 mL	1 mL	10 mL	10 mL

**not published, assumed*

Considerations When Requesting PFAS Analysis

- What analytical method does the lab run?
  - If the method calibrates PFAS analytes in the ppt-range (on-column), it is strongly recommended to request triplicate sampling, preparation, analysis, and reporting for each sampling location
    - E.g. ASTM Standards D7979 and EPA Method 8327
  - If the method calibrates PFAS analytes in the ppb-range (on-column), the presented data suggests that the currently observed contamination in lab consumables may not impact these methods
    - E.g. EPA Methods 533 and 537.1 (providing the analyte calibration range or method RLs are not modified to be lower)
    - Also note that consumables used for these methods may differ from those used in D7979 or 8327

Considerations When Requesting PFAS Analysis

- Why not just always use EPA Methods 533 or 537.1?
  - These are drinking water methods that were only validated by the EPA to be used for drinking water matrices
  - ASTM Standard D7979 and EPA Method 8327 were validated to be used for several aqueous matrices including surface water, groundwater, and wastewater (influent and effluent)
    - These direct injection methods also have significantly higher sample throughput rates, even when preparing samples in triplicate, than the labor-intensive drinking water methods

Once consumable vendors begin providing certified, trace-level (low ppt) PFAS-free products, triplicate analysis will no longer be necessary

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