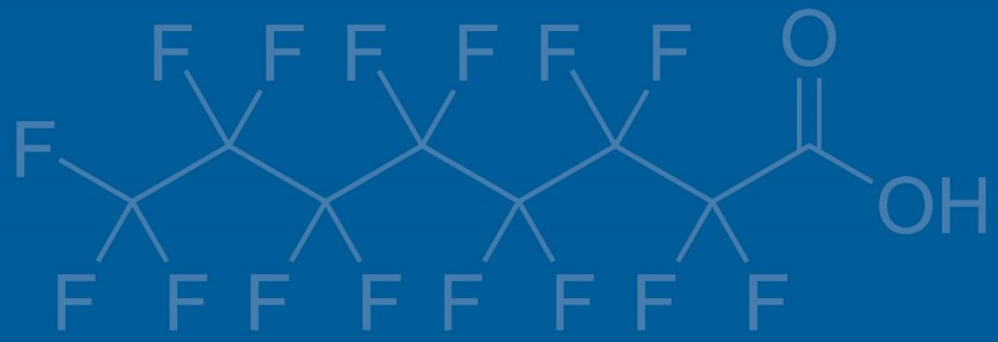


Understanding Usability of PFAS Data

NEWMOA Webinar Series – May 4, 2021

Nancy C. Rothman, Ph.D., NEH, Inc. & Elizabeth Denly, ASQ CMQ/OE, TRC

Today's Learning Objectives

- Sampling Precautions
- Holding Times, Containers, and Preservation
- Analytical Methods
- Data Review for Usability

Why Do We Need to Evaluate the Lab's Data?

- Data may be used to make costly decisions
- Data may have potential to impact human health
- Need to confirm quality data available and appropriate to support decisions
- Need to determine potential low or high biases, potential uncertainties, potential false positive or false negative results

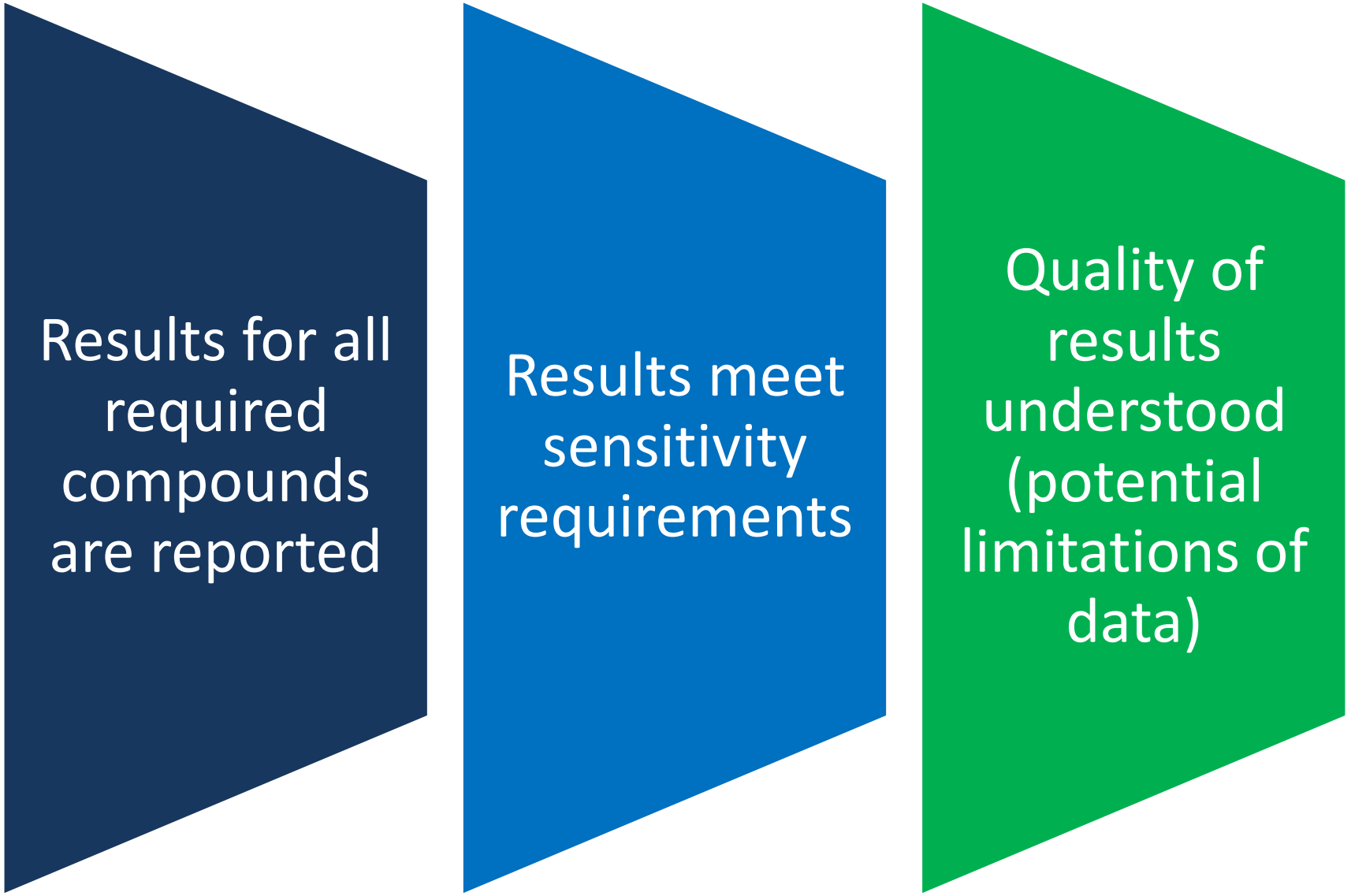
Even if the lab follows all method-required procedures, there can still be data quality/usability issues.

Data Validation vs. Data Usability Assessment

- Data Validation
  - Formal, systematic process
  - Follow specific guidelines created by EPA
  - Look at effects of lab performance and matrix on results
  - Apply qualifiers to data (e.g., J, UJ, R, J-, J+, NJ)
  - Limited or full validation

- Data Usability Assessment
  - Also look at effects of lab performance and matrix on results
  - No qualifiers typically applied
  - Spends more time looking at the effect of the lab and matrix issues on the achievement of the project objectives
  - Can we use the data for decision-making?

How is Usability Determined?



What Questions Do I Need to Answer While Preparing Lab Scope of Work?

Sampling Event Preparation

Consider the overarching objectives of the project and conceptual site model will influence the fundamentals of any sampling and analysis program

- Site History (e.g., potential sources, quantities used)
- Project Action Levels

Develop a project-specific Sampling and Analysis Plan (SAP) which addresses the increased risk of contamination and project-specific considerations

Why Am I Collecting This Sample?

- Is it a permit requirement?
- Is it for waste characterization?
- Will a human health or ecological risk assessment be performed?
- Are you evaluating nature & extent of contamination?
- Source Identification?
- Are you measuring effectiveness of remediation system?

Field Quality Control: What are the Options?

QC Sample	Why Should I Collect?	How Often Should I Collect?
Field Blank	To evaluate presence of contaminants in ambient air at the site	1 per day per parameter
Equipment Blank	To evaluate presence of contaminants on equipment after decontamination	1 per day per matrix and parameter
Field Duplicate*	To evaluate sampling and analytical precision	1 per 20 samples per matrix and parameter
MS/MSDs**	To evaluate matrix-specific bias	1 per 20 samples per matrix and parameter
Cooler Temperature Blank	To ensure proper preservation of samples maintained during shipment	1 per each cooler

*Collect from location with moderate to heavy contamination
**Collect from location with lower level of contamination

Evaluation Categories

- Laboratory Performance
- Field Performance

Laboratory Performance	Field Performance	Matrix Interferences
Method Blanks	Equipment Blanks	Extracted Internal Standards
Lab Control Samples	Sample Preservation	Injection Internal Standards*
Holding Times	Field Duplicates	Matrix Spikes
Calibrations*		Laboratory Duplicates
Tunes*		

**Not typically included in Level 2 deliverables*

What is Affected by Each Parameter?

Sample-Specific	Batch-Specific
Holding Time	Method Blanks
Sample Preservation	Lab Control Samples
Field Duplicates	Calibrations*
Extracted Internal Standards	Tunes*
Injection Internal Standards*	Equipment Blanks
Matrix Spikes	
Laboratory Duplicates	

**Not typically included in Level 2 deliverables*

PFAS

Why is a PFAS Sampling Event Different From Other Sampling Events?

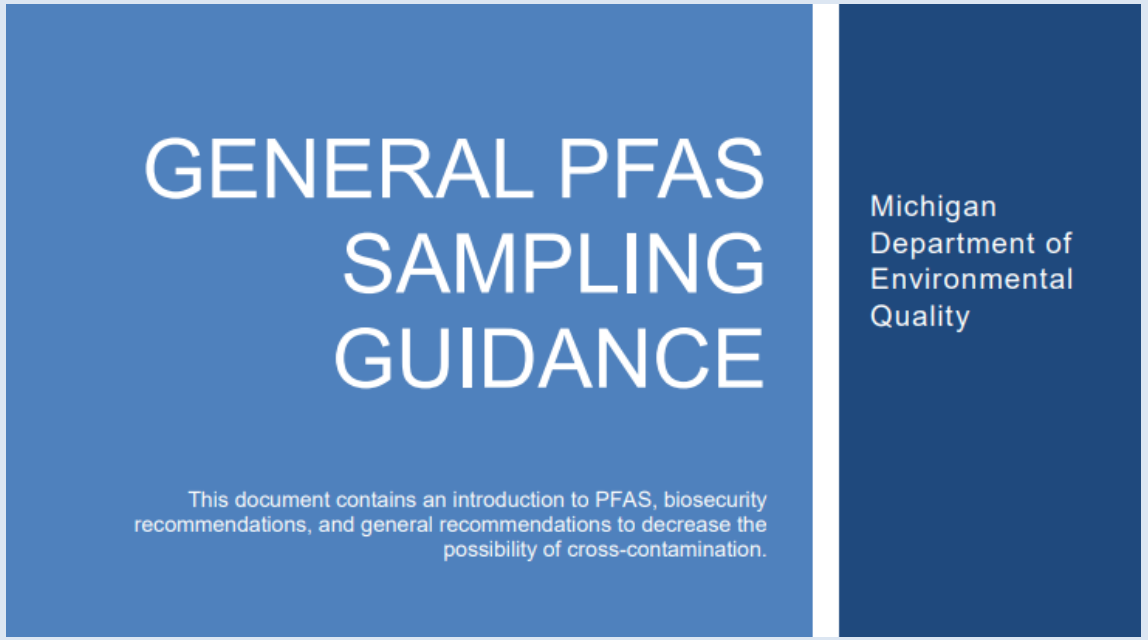
- Unusually low screening/regulatory criteria for PFAS
- Increased cross-contamination potential
- Sampling equipment and materials typically used for sampling contain or may contain PFAS



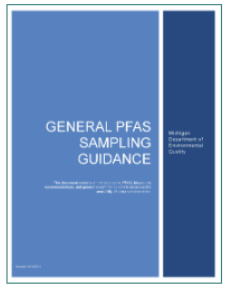


How Do We Sample PFAS?

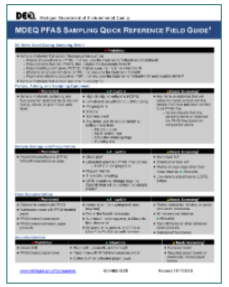
- Similar to conventional sampling (e.g., low-flow techniques, direct push, etc.)
- Special care required to prevent cross contamination
- Use of and exclusion of specific sampling equipment and materials



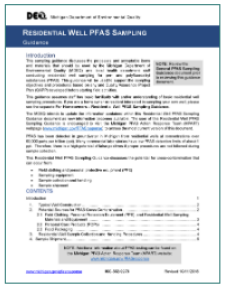
Technical Guidance Documents



General PFAS Sampling Guidance
Revised October 16, 2018



PFAS Sampling Quick Reference Field Guide
Revised October 17, 2018



Residential Well PFAS Sampling Guidance
Revised October 11, 2018

Groundwater PFAS Sampling Guidance
Uploaded October 2018

Wastewater PFAS Sampling Guidance
Revised October 11, 2018

Surface Water PFAS Sampling Guidance
Revised November 28, 2018

Soil PFAS Sampling Guidance
Revised November 28, 2018

Fish Tissue PFAS Sampling Guidance
Uploaded January 2019

PFAS Sampling Dos and Don'ts

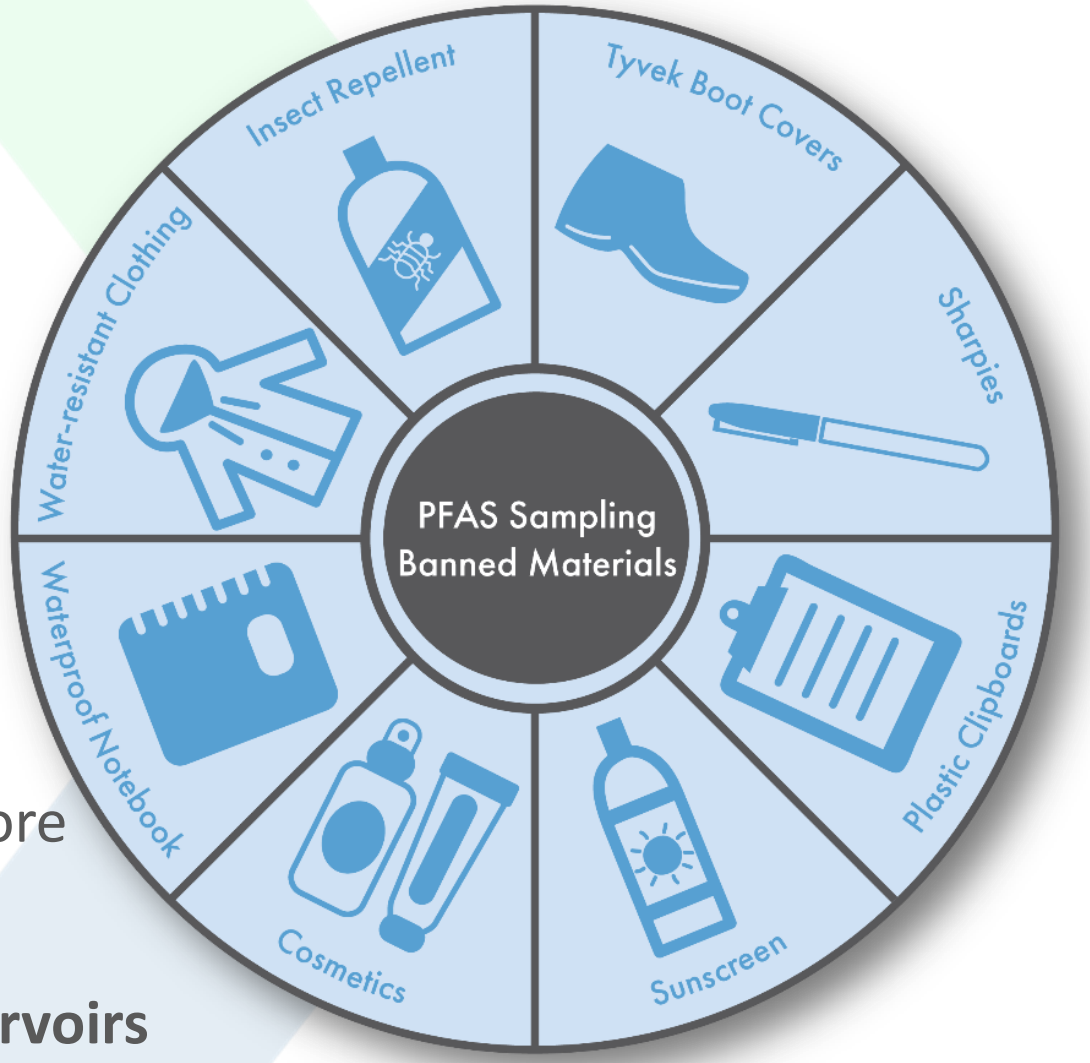
WHAT SHOULD I AVOID?	USE INSTEAD
Passive diffusion bags (PDBs)	
LDPE Hydrasleeves	✓ HDPE Hydrasleeves
Post-It notes during sample handling	
Blue Ice® (chemical ice packs)	✓ Regular ice in Ziploc® bags
Waterproof field books, plastic clipboards and spiral bound notebooks	✓ Field notes recorded on loose paper ✓ Field forms maintained in aluminum or Masonite clipboards
Unnecessary handling of items with nitrile gloves	✓ Personnel collecting and handling samples should wear nitrile gloves at all times while collecting and handling samples or sampling equipment

PFAS Sampling Dos and Don'ts

WHAT SHOULD I AVOID?	USE INSTEAD
Equipment with **Teflon®** (e.g., bailers, tubing, parts in pump) during sample handling or mobilization/demobilization	✓ High density polyethylene (HDPE) or silicone tubing/materials in lieu of Teflon®
Low-density polyethylene (LDPE) or glass sample containers or containers with Teflon-lined lids	✓ HDPE or polypropylene containers for sample storage ✓ HDPE or polypropylene caps
Tyvek® suits and waterproof boots	✓ Clothing made of cotton preferred ✓ Boots made with polyurethane and polyvinyl chloride (PVC)
Waterproof labels for sample bottles	✓ Paper labels with clear tape
Sunscreens, insect repellants	✓ Products that are 100% natural, DEET
Sharpies	✓ Ballpoint pens
Aluminum foil	✓ Thin HDPE sheeting

Other Special Considerations

- Field QC
- Decontamination of sampling equipment
- No pre-wrapped food or snacks
- Avoid cosmetics, moisturizers, hand creams on day of sampling.
- Visitors to site must remain at least 30 feet from sampling area.
- Wash hands with water after leaving vehicle before setting up on a well.
- **Partitioning of PFAS to surface in wells and reservoirs**

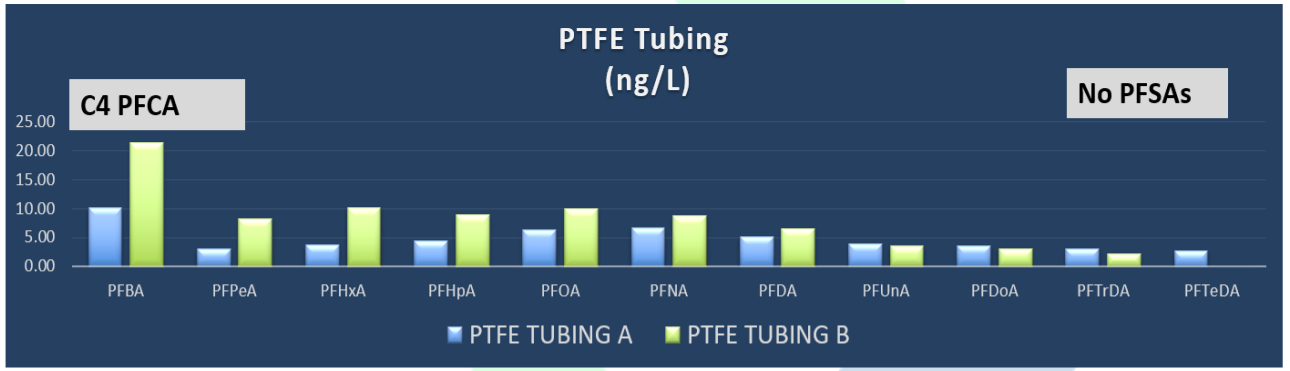


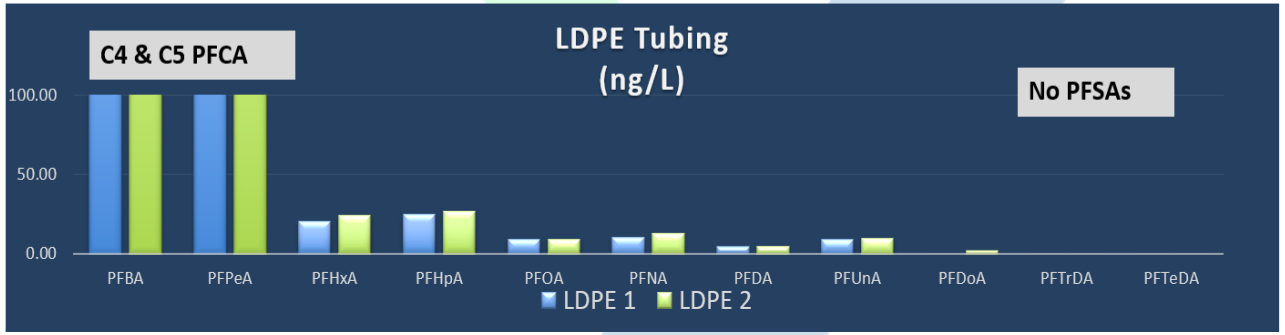
What Should I Wear?

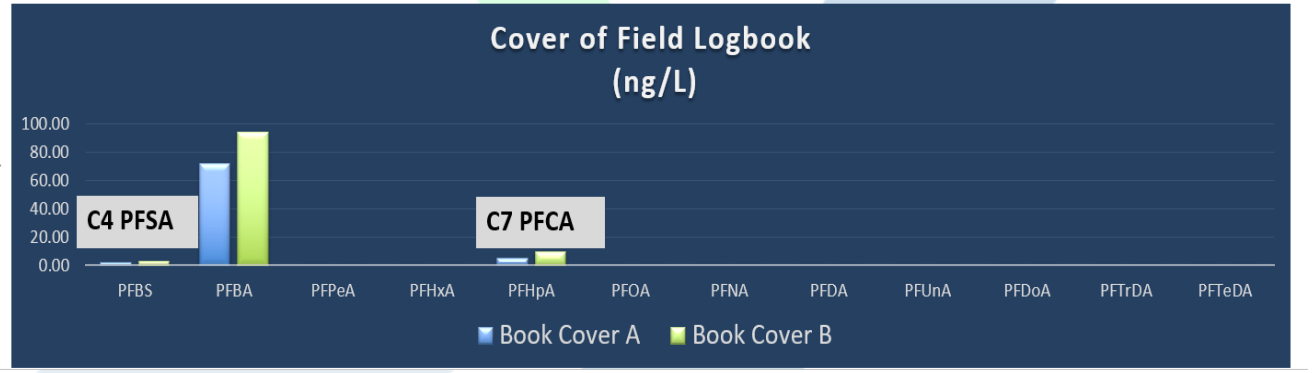
- No clothing with fabric softeners
- No new clothing
- Avoid boots and other field clothing containing waterproof/resistant material
- Cotton is best

Equipment Study:
PFCAs vs PFSAs vs Polyfluoroalkyl Substances

PFCAs	PFSAs	Polyfluoroalkyl Substances
PTFE Tubing	Bailer Line	PTFE-lined Tubing
PTFE-lined Tubing	Sample Labels	Bailer Line
LDPE Tubing	Nitrile Gloves	
Bailer Line	Field Book Cover	
Sample Labels		
Pizza Box		
Water Level Tapes		
Silastic Tubing		
Nitrile Gloves		
Field Book Pages		
Field Book Cover		
PTFE Bladder		

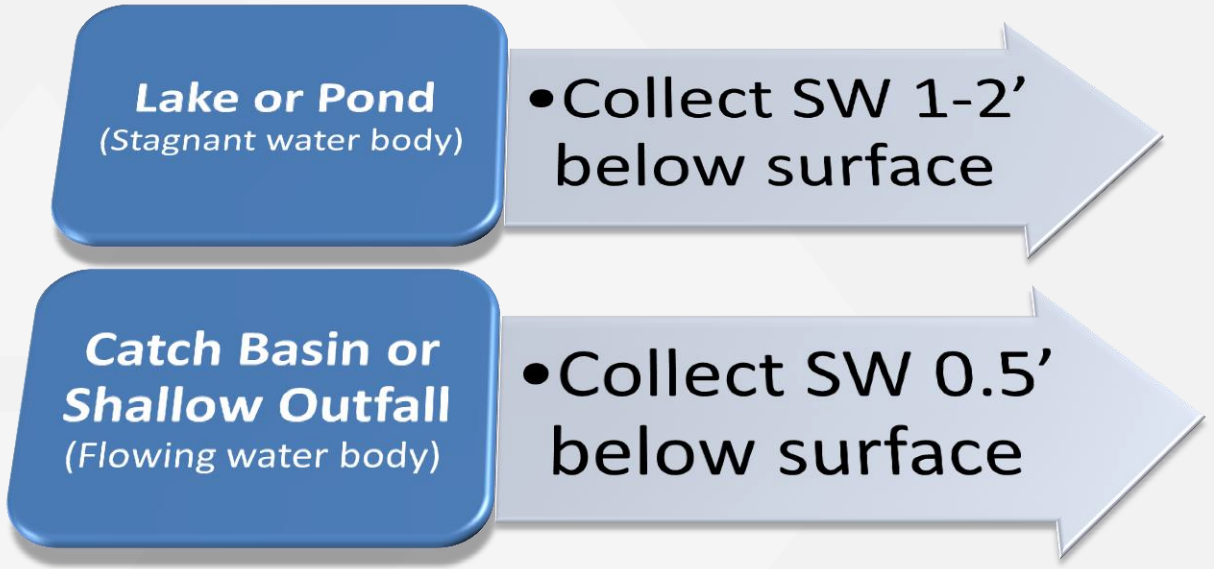






Other Potential Sampling Concerns Which May Affect Data Interpretation

- How should the sampler deal with surface soil during the installation of soil borings or monitoring wells?
- What method should be used for the collection of groundwater samples?
- What depth is recommended for surface water samples?
  - Is the surface water body stagnant or flowing?

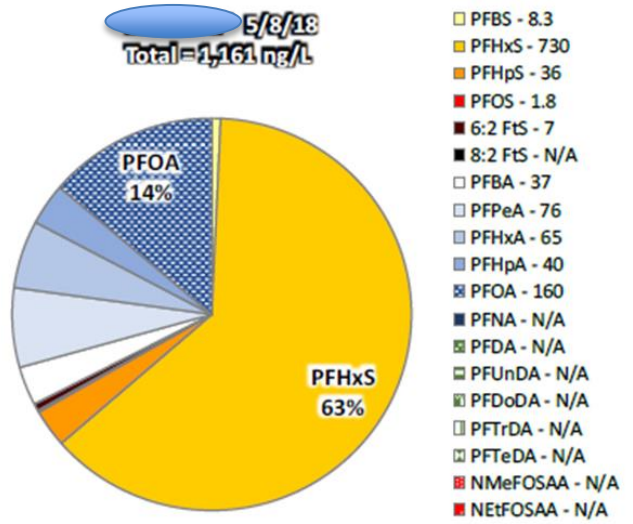


- Is homogenization of soil and sediment samples being performed properly in the field?
- Are there suspended solids in the surface water, groundwater, or wastewater samples?

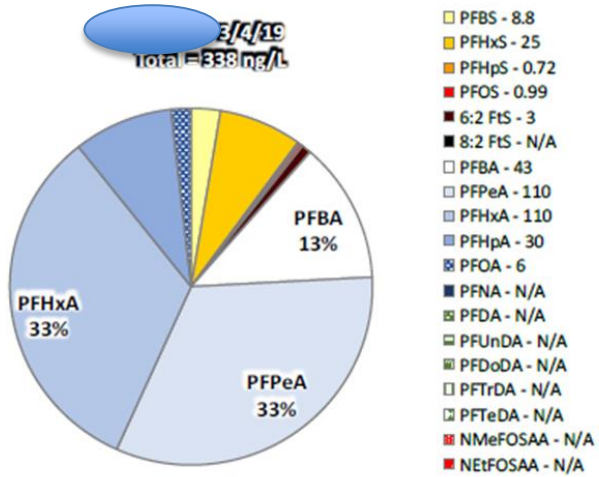
How Do Labs Deal With Solids in Aqueous Samples?

- The following samples *contain* non-settleable particulate matter which plugged the solid-phase extraction column.
- The following samples *were decanted* prior to preparation due to excessive sediment in bottle.
- The following sample *was decanted* prior to preparation due to having floating sediment particles and also some wood material.
- The following sample *was centrifuged* prior to spiking and the extraction due to the color being a dark yellow with floating material instead, which we cannot decant.
- Samples have fine sediment at the bottom of the bottle *and mixed in with the sample water.*
- *Due to residual amounts of sediment in the sample, the sample container was placed in the oven and dried after extraction, and the weight was then recorded. The container was then extracted per the SOP.*

Sample from 1" temporary well turbid

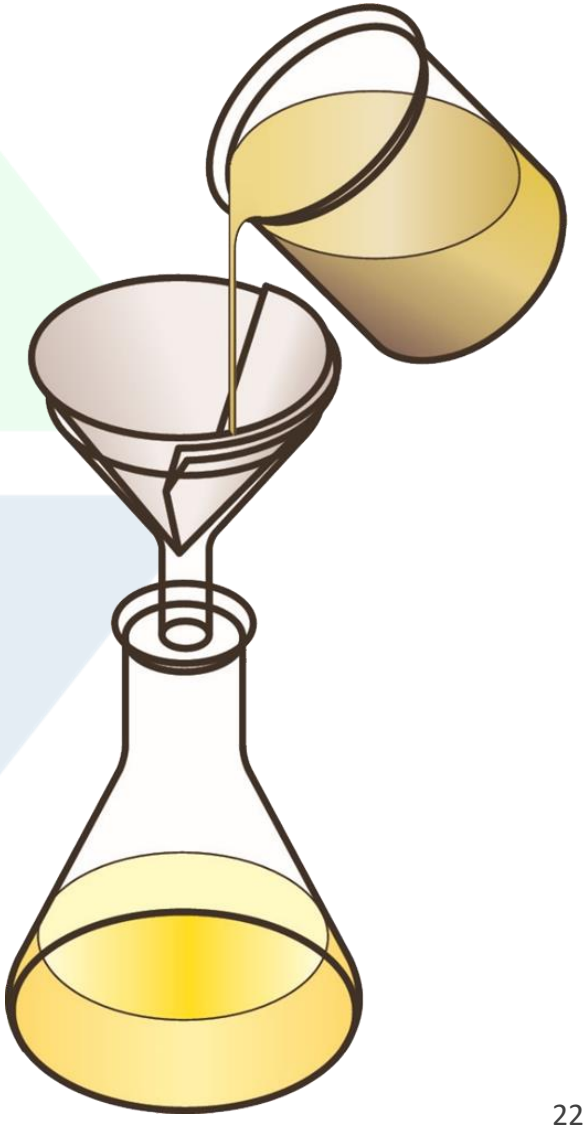


Sample from 2" developed MW clear



Filtering of Water Samples

- PFAS may sorb onto glass fiber filters; therefore do not use these filters.
- Filtered/unfiltered data:
  - Is PFAS sorbed to soil or sediment in the water sample?
  - Is PFAS sorbed onto the glass fiber filter?
- Preferred method of dealing with particulates: low flow sampling or use of a centrifuge in the lab
- Consider Centrifugation and Decanting (spike isotopes prior to this)



Keep in Mind

PFAS Methods

Method	Year	Applicable Matrices	# PFAS Analytes
EPA 537 v 1.1	2009	Drinking Water	14 analytes
EPA 537.1	2020	Drinking Water	18 analytes
EPA 533	2019	Drinking Water	25 analytes
ASTM D7979-17	2017	Water, Wastewater	21 analytes
ASTM D7968-17	2017	Soil	21 analytes
ISO 25101	2009	Aqueous	PFOA/PFOS
DoD QSM 5.1	2017	Solid & Aqueous	24+ analytes
DoD QSM 5.2	2018	Solid & Aqueous	24+ analytes
DoD QSM 5.3	2019	Solid & Aqueous	24+ analytes
EPA 537 “Modified”	Current	All	24+ analytes

Current PFAS Reportable by Analytical Laboratories

Analyte	CAS No.	UCMR3 (6)	537.1 (18)	NYSDEC (21)	ISO 25101 (2)	MDEQ IPP (28)
Perfluorobutanoic acid (PFBA)	375-22-4			X		X
Perfluoropentanoic acid (PFPeA)	2706-90-3			X		X
Perfluorohexanoic acid (PFHxA)	307-24-4		X	X		X
Perfluoroheptanoic acid (PFHpA)	375-85-9	X	X	X		X
Perfluorooctanoic acid (PFOA)	335-67-1	X	X	X	X	X
Perfluorononanoic acid (PFNA)	375-95-1	X	X	X		X
Perfluorodecanoic acid (PFDA)	335-76-2		X	X		X
Perfluoroundecanoic acid (PFUnA)	2058-94-8		X	X		X
Perfluorododecanoic acid (PFDoA)	307-55-1		X	X		X
Perfluorotridecanoic Acid (PFTrA)	72629-94-8		X	X		X
Perfluorotetradecanoic acid (PFTeA)	376-06-7		X	X		X
Perfluorohexadecanoic acid (PFHxDA)	67905-19-5					
Perfluorooctadecanoic acid (PFODA)	16517-11-6					
Perfluorobutanesulfonic acid (PFBS)	375-73-5	X	X	X		X
Perfluoropentanesulfonic acid (PFPeS)	2706-91-4					X
Perfluorohexanesulfonic acid (PFHxS)	355-46-4	X	X	X		X
Perfluoroheptanesulfonic Acid (PFHpS)	375-92-8			X		X
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	X	X	X	X	X
Perfluorononanesulfonic acid (PFNS)	474511-07-4					X
Perfluorodecanesulfonic acid (PFDS)	335-77-3			X		X
Perfluorooctane Sulfonamide (FOSA)	754-91-6			X		X
N-methyl perfluorooctane sulfonamidoacetic acid (NMeFOSAA)	2355-31-9		X	X		X
N-ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)	2991-50-6		X	X		X
6:2 Fluorotelomer sulfonic acid (6:2 FTSA)	27619-97-2			X		X
8:2 Fluorotelomer sulfonic acid (8:2 FTSA)	39108-34-4			X		X
4:2 Fluorotelomer sulfonic acid (4:2 FTSA)	757124-72-4					X
10:2 Fluorotelomer sulfonic acid (10:2 FTSA)	120226-60-0					
N-Methyl perfluorooctane sulfonamidoethanol (N-MeFOSE)	24448-09-7					
N-Ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE)	1691-99-2					
N-Methyl perfluorooctane sulfonamide (MeFOSA)	31506-32-8					
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	4151-50-2					
HFPO-DA (Gen-X)	62037-80-3		X			
ADONA			X			
F-53B-9Cl			X			
F-53B-11Cl			X			

TRC

NEH new environmental horizons, inc

Analyte lists vary by method, laboratory, and regulatory agency; so…

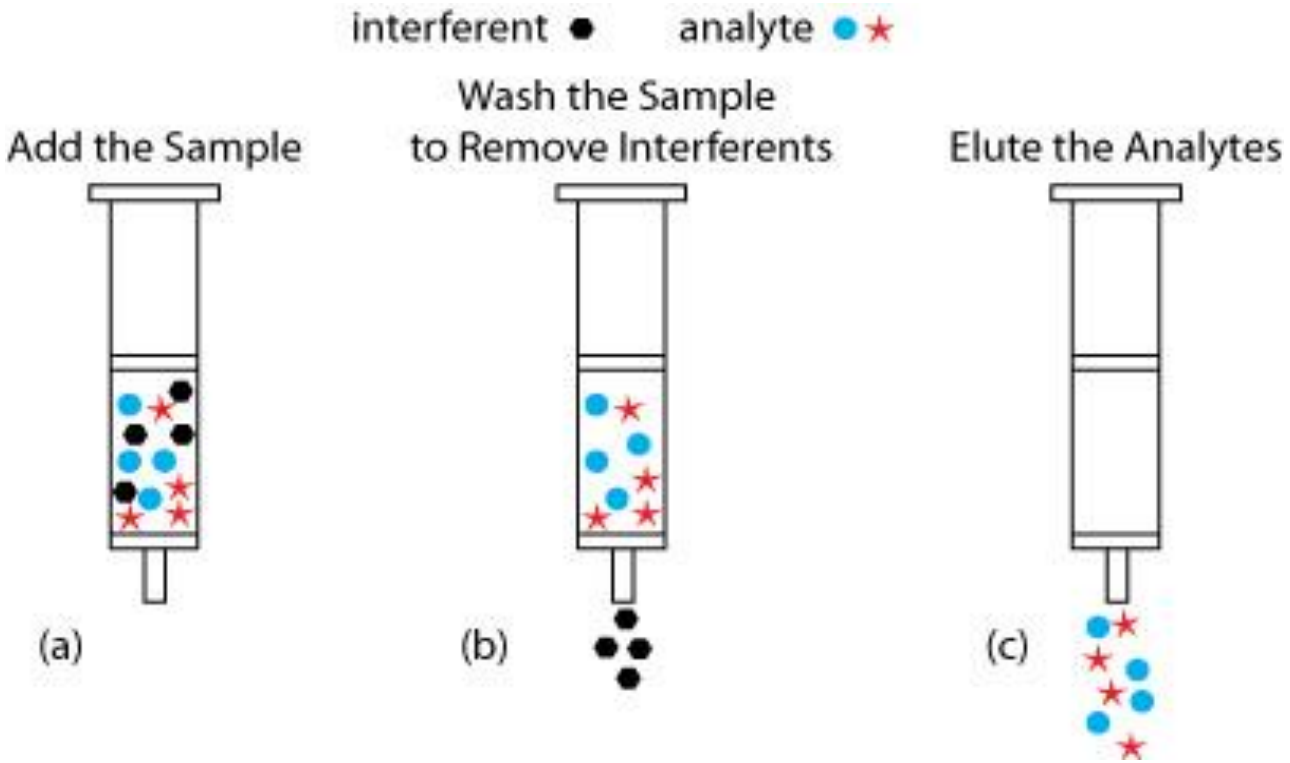
Project-specific list of PFAS compounds needs to be communicated to the laboratory!

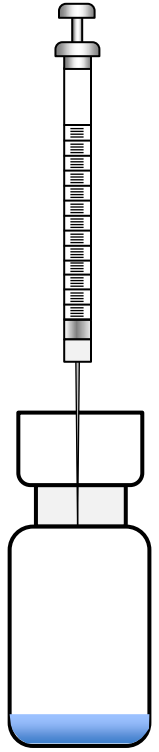
Solid Phase Extraction

- Is the lab extracting the entire sample and rinsing the sample bottle?
- What cartridge is the lab using?
  - *Styrenedivinylbenzene (SDVB) sorbent phase*
  - *Reverse phase copolymer characterized by a weak anion exchange (WAX) sorbent phase*
- Is the lab doing washes to remove interferences on the SPE cartridge?

PFBA, PFPeA poor recoveries

250 mL sample





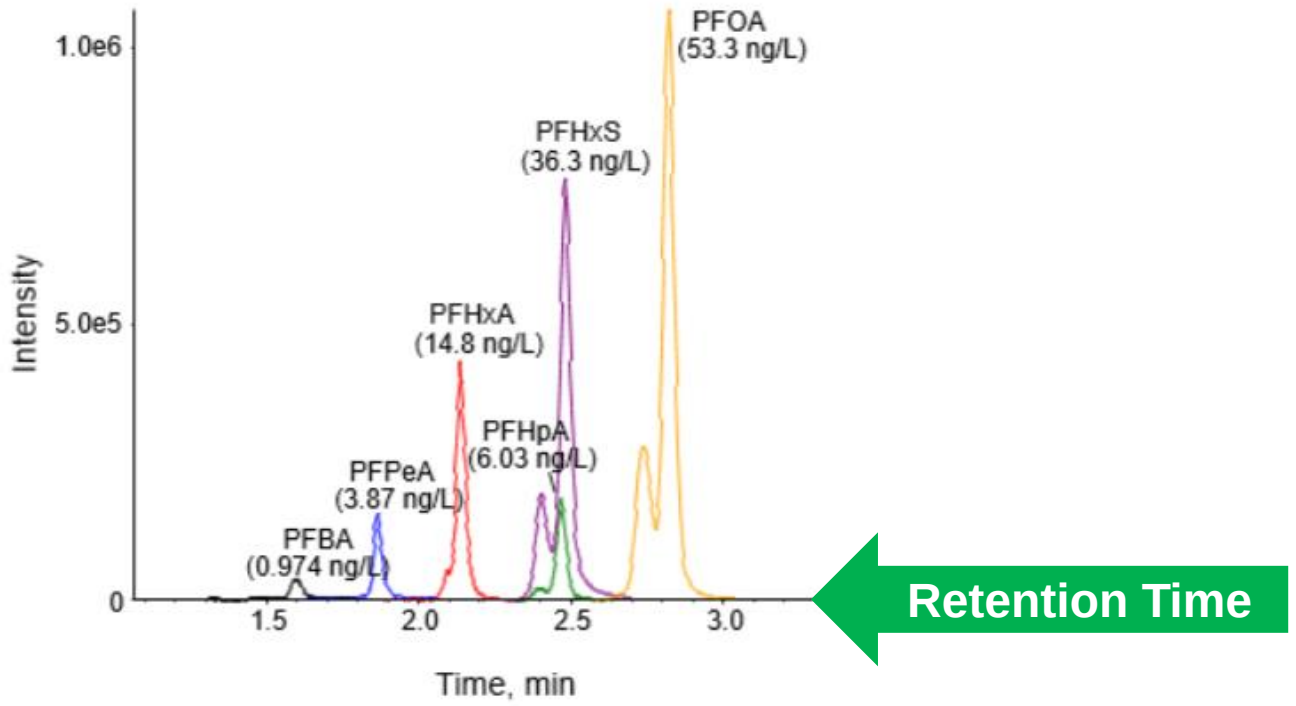
1 mL final extract

Sample Analysis: HPLC Separation *(Part 1)*

Separates compound mixtures on column. Column has high affinity for PFAS. The affinity of each compound to the column is different based on its solubility.

- Characteristic **retention times**
- **Step 1 in compound identification**: time the compound comes off the column

Retention time increases with carbon number

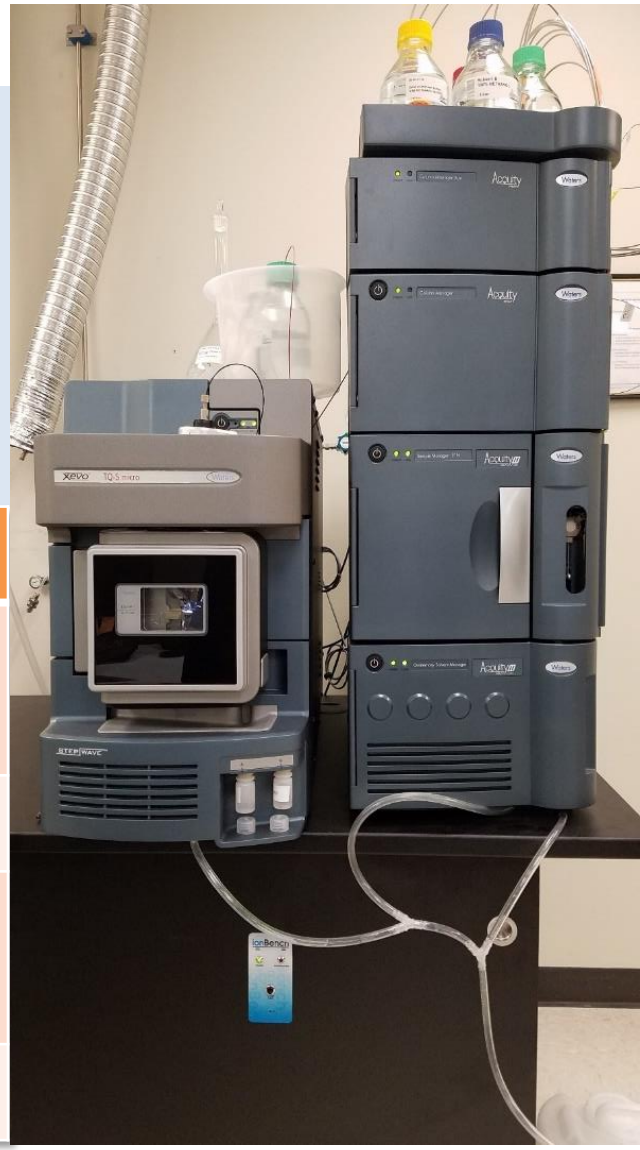


Analyte	Retention Time (min)
PFBA	1.527
$^{13}C_4$PFBA	1.525
PFOS	3.028
$^{13}C_4$PFOS	3.026

Sample Analysis: MS/MS *(Part 2)*

- Unique fragmentation patterns **(Step 2 of compound identification)**
- Parent/daughter combinations = definitive ID, more sensitive analysis

Analyte	Retention Time (min)	Parent/Daughter Ions
PFBS	1.754	299/80 299/99
$^{13}C_3$PFBS	1.752	302/83
PFOS	3.028	499/80 499/99
$^{13}C_4$PFOS	3.026	503/80

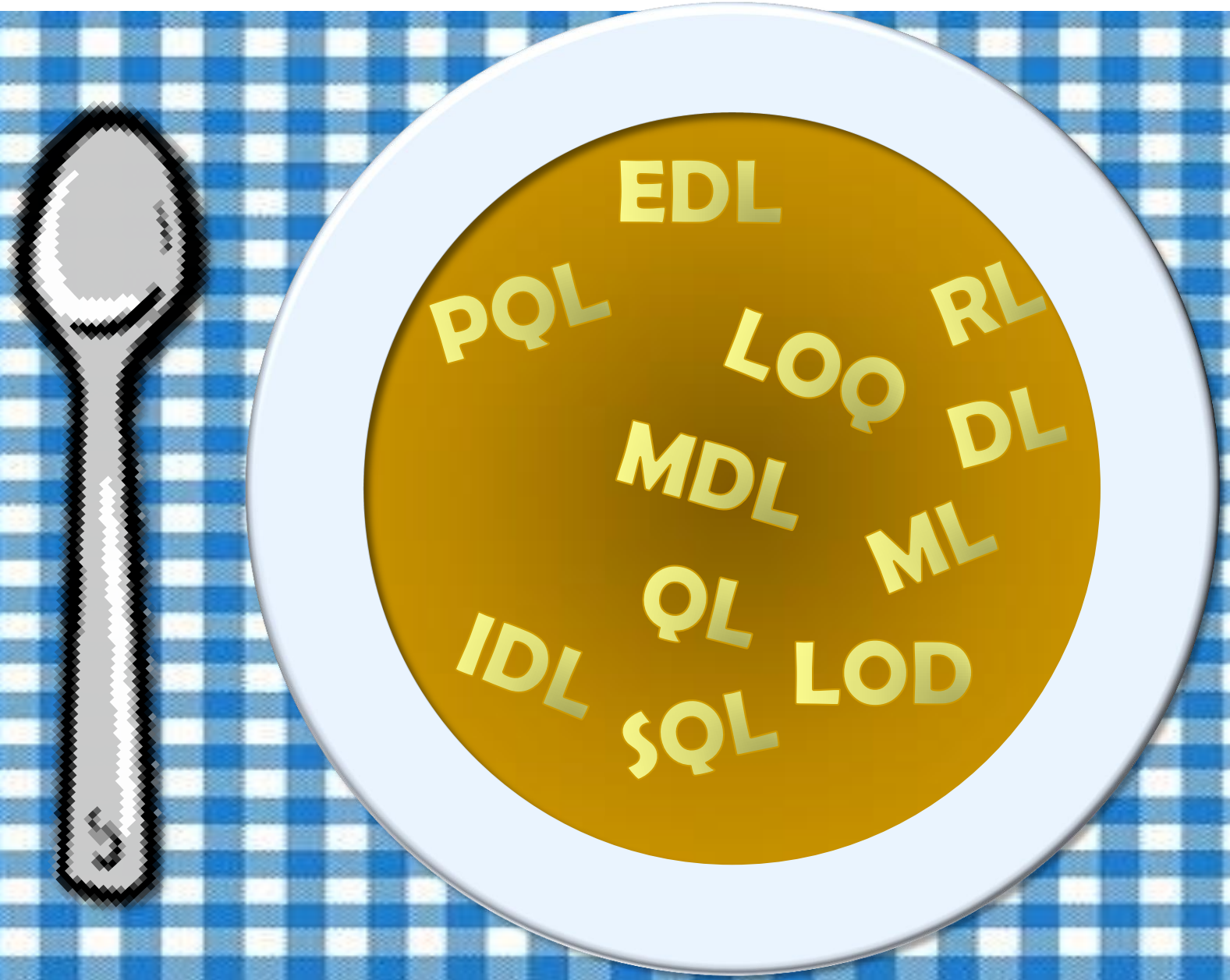


Transition Ions (Parent/Daughter Ions)

- **Definitive Identification of Compounds**
  - Retention time from HPLC separation
  - Transition to characteristic daughter ions
  - Ion ratios
- **What happens when the ion ratios are outside limits?**
  - What are the limits?
- **What if there is no confirmation ion?**
  - PFBA
  - PFPeA
  - NMeFOSAA
  - NEtFOSAA

Analyte	Retention Time (min)	Parent/ Daughter Ions	Ion Ratio	Ion Ratio Limit
PFBS	1.754	299/80 299/99	2.91	1.35-4.05
$^{13}C_3$PFBS	1.752	302/83	NA	NA
PFOS	3.028	499/80 499/99	4.19	2.04-6.12
$^{13}C_4$PFOS	3.026	503/80	NA	NA

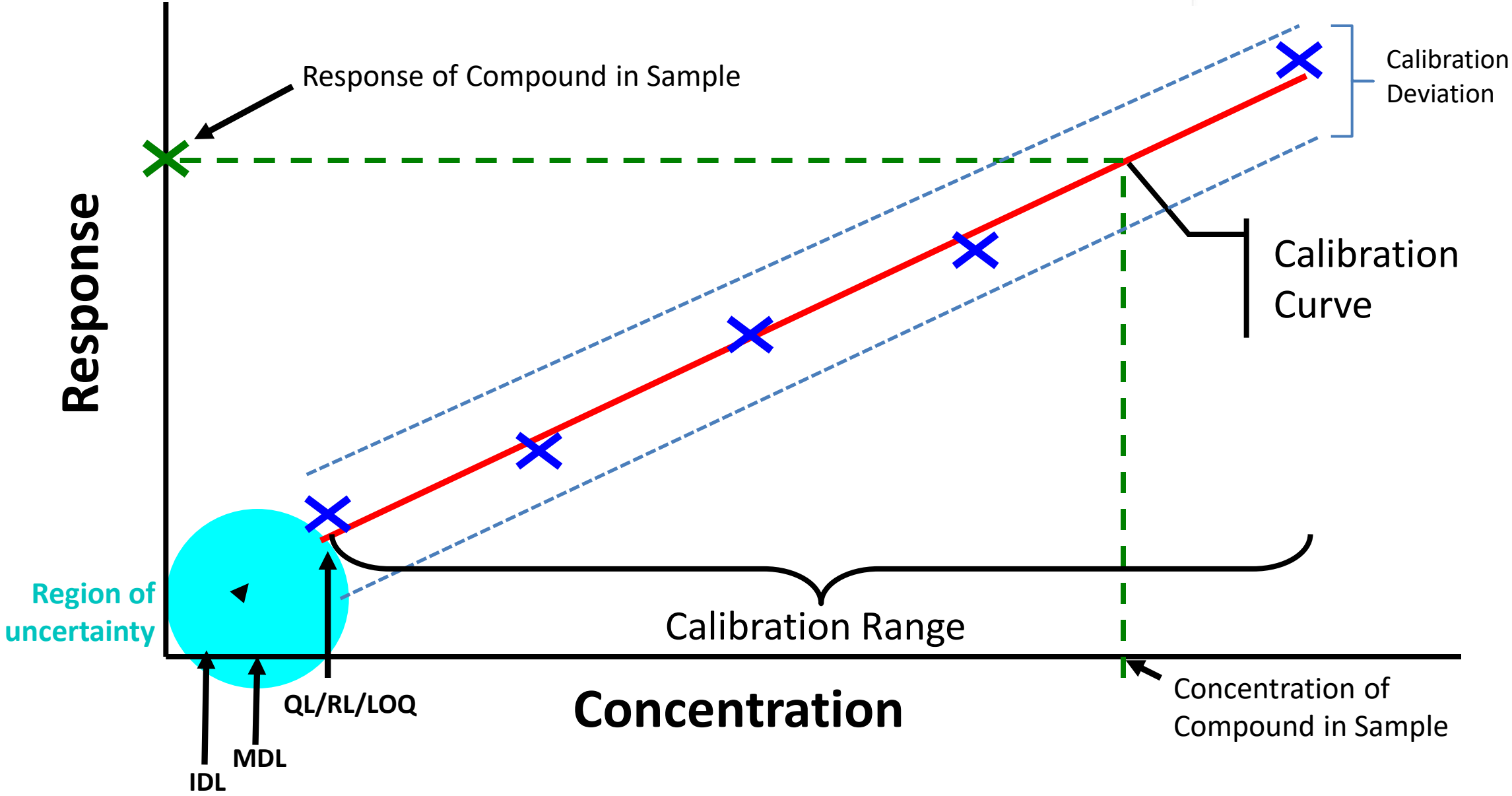
Detection Limits



Detection Limit Terminology

Acronym	Definition
IDL	Instrument Detection Limit
EDL	Estimated Detection Limit
DL	Detection Limit
MDL	Method Detection Limit
PQL	Practical Quantitation Limit
RL	Reporting Limit
QL	Quantitation Limit
LOD	Limit of Detection
LOQ	Limit of Quantitation

Calibration



Different Detection Limits

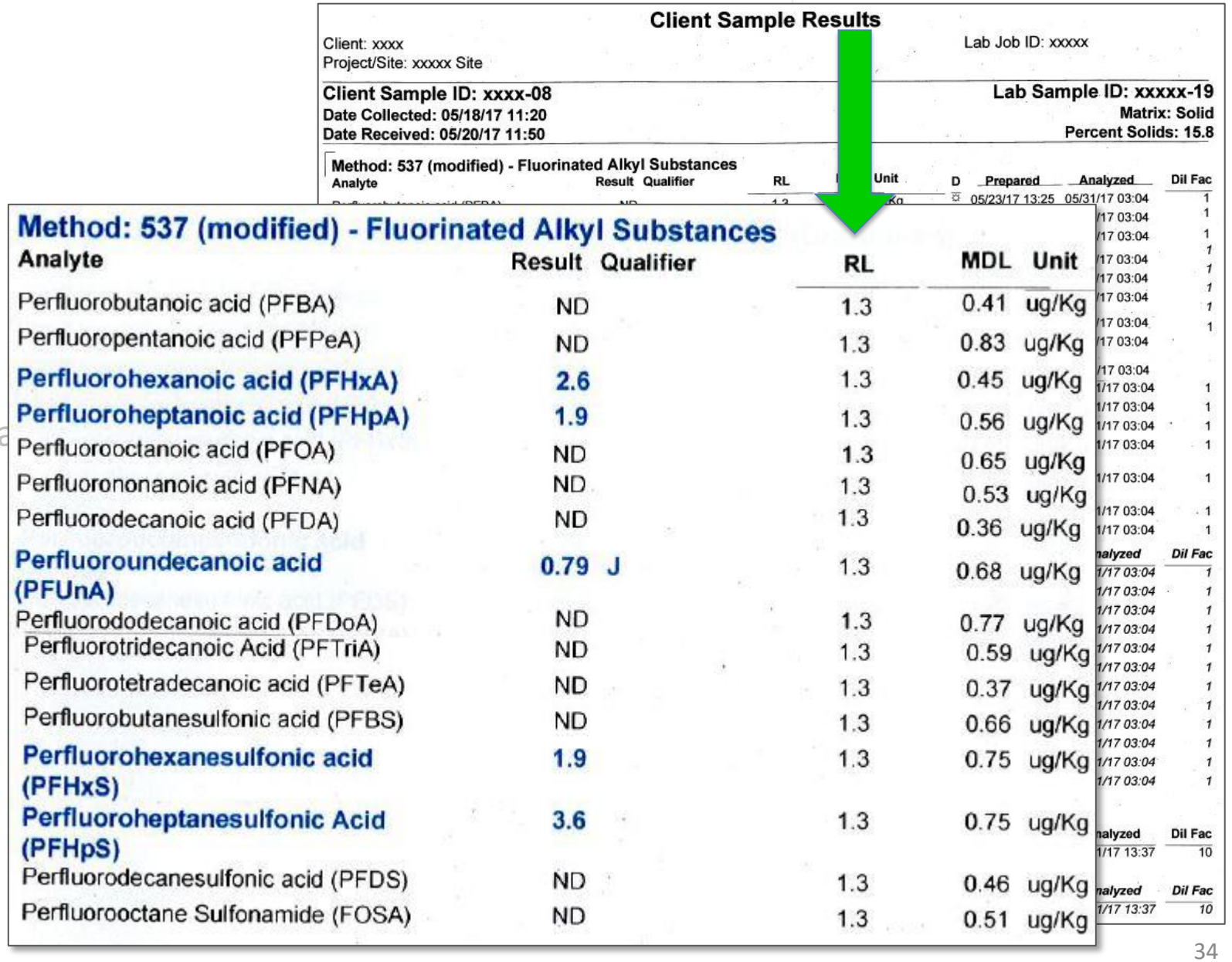
Detection Limit	Accurate?	Precise?	Use to Demonstrate Below Cleanup Standards?	Use Values in Risk Assessment?
IDL	No	Yes	No	No
EDL[1]	No	Yes	Yes	Yes
MDL / DL	No	Yes	No	Maybe
LOD	No	Yes	Yes[2]	Yes[2]
RL / QL / LOQ	Yes	Yes	Yes	Yes

[1]Specific to Dioxins/furans and PCB Congeners
[2]Specific to DOD projects

PFAS Analytical Reports

Typical sample result summary form

- Number of PFAS reported
- Results, RLs, units
- Dilution results
- Collection date, prepared date, ana
- Percent solids (dry weight)
- Isotope Dilution recoveries



Client Sample Results

Client: xxxx
Project/Site: xxxxx Site

Lab Job ID: xxxxx

Client Sample ID: xxxx-08
Date Collected: 05/18/17 11:20
Date Received: 05/20/17 11:50

Lab Sample ID: xxxxx-19
Matrix: Solid
Percent Solids: 15.8

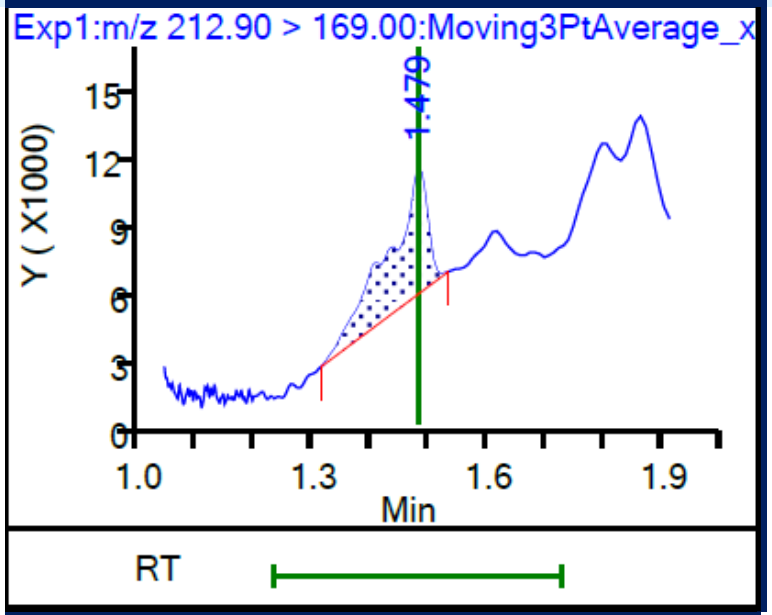
Method: 537 (modified) - Fluorinated Alkyl Substances

Analyte	Result	Qualifier	RL	MDL	Unit
Perfluorobutanoic acid (PFBA)	ND		1.3	0.41	ug/Kg
Perfluoropentanoic acid (PFPeA)	ND		1.3	0.83	ug/Kg
Perfluorohexanoic acid (PFHxA)	**2.6**		1.3	0.45	ug/Kg
Perfluoroheptanoic acid (PFHpA)	**1.9**		1.3	0.56	ug/Kg
Perfluorooctanoic acid (PFOA)	ND		1.3	0.65	ug/Kg
Perfluorononanoic acid (PFNA)	ND		1.3	0.53	ug/Kg
Perfluorodecanoic acid (PFDA)	ND		1.3	0.36	ug/Kg
Perfluoroundecanoic acid (PFUnA)	**0.79**	**J**	1.3	0.68	ug/Kg
Perfluorododecanoic acid (PFDoA)	ND		1.3	0.77	ug/Kg
Perfluorotridecanoic Acid (PFTriA)	ND		1.3	0.59	ug/Kg
Perfluorotetradecanoic acid (PFTeA)	ND		1.3	0.37	ug/Kg
Perfluorobutanesulfonic acid (PFBS)	ND		1.3	0.66	ug/Kg
Perfluorohexanesulfonic acid (PFHxS)	**1.9**		1.3	0.75	ug/Kg
Perfluoroheptanesulfonic Acid (PFHpS)	**3.6**		1.3	0.75	ug/Kg
Perfluorodecanesulfonic acid (PFDS)	ND		1.3	0.46	ug/Kg
Perfluorooctane Sulfonamide (FOSA)	ND		1.3	0.51	ug/Kg

What To Use for PFAS?

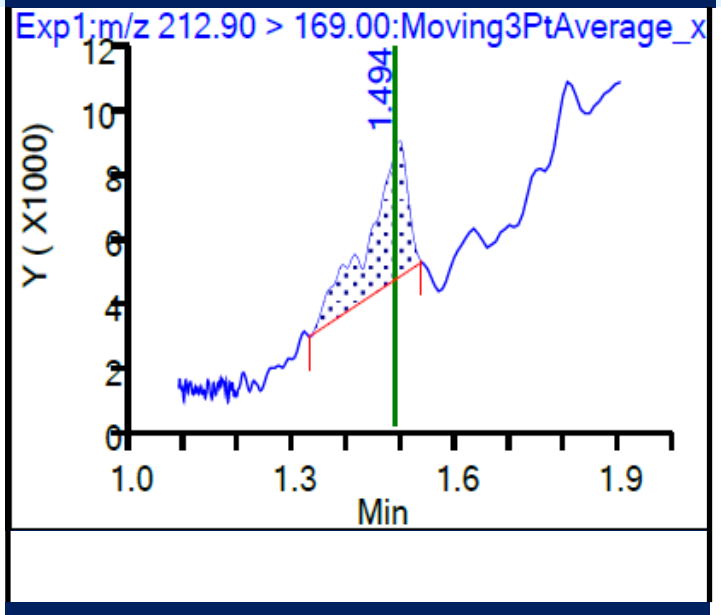
- RLs most reliable value (aka LOQ or QL) – define sensitivity
- Most labs RLs 2-10 ng/L or 1-5 ug/kg, depending on PFAS – must meet regulatory requirement
- DO NOT use MDLs as nondetect values
- Be careful of “J” values

2 Perfluorobutyric acid (M)



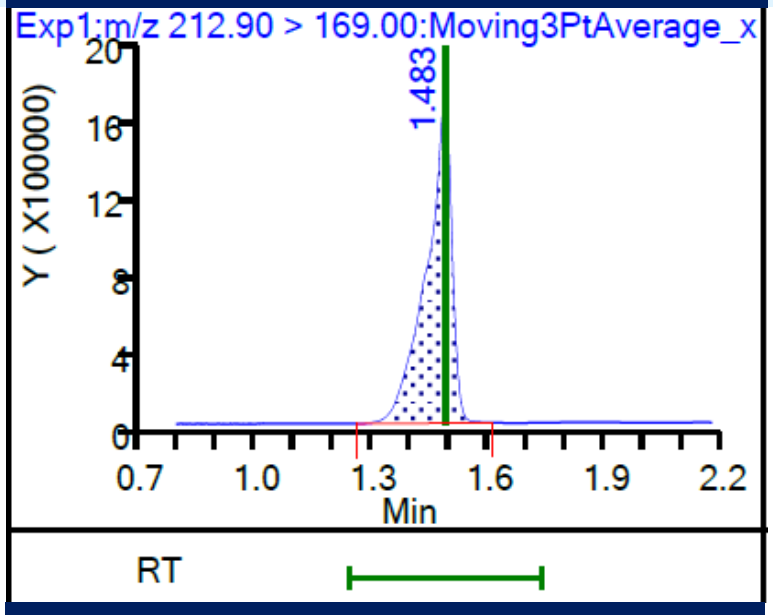
PFBA: 0.35 J ng/L

2 Perfluorobutyric acid (M)



PFBA: <2.0 ng/L

2 Perfluorobutyric acid



PFBA: 2.5 ng/L

Specific Laboratory QA/QC

- Sample preservation & handling
- Sample Holding Times / Analytical Batches (≤ 20 samples)
- QC Samples required for each Analytical Batch:
  - Method Blank (MB)
  - Laboratory Control Sample (LCS)
  - Matrix Spike (MS)
  - Matrix Sample Duplicate (MSD)
- Extracted Internal Standard (Labeled Surrogates) added to all samples & QC prior to extraction
- Injection Internal Standards added to all extracts prior to analysis

Assessing Quality

- Overall Quality depends on cumulative Quality from sampling through analysis
- Specifically for PFAS – Field Collection & Analytical Method differences can introduce uncertainty
- Guidelines for Evaluating Quality
  - *National Functional Guidelines for High Resolution Superfund Methods Data Review,* EPA-542-B-16-001 (April 2016)
  - *Data Review and Validation Guidelines for Perfluoroalkyl Substances (PFASs) Analyzed by Method 537*, EPA 910-R-18-001 (November 2018)
  - Table B-15 of *QSM 5.3 Consolidated Quality Systems Manual (QSM) for Environmental Laboratories*, Version 5.3 (DOD/DOE, 2019) http://www.denix.osd.mil/edqw/documents/documents/manuals/qsm-version-5-3-final-updated/
  - NYSDEC, *Guidelines for Sampling and Analysis of PFAS, Under NYSDEC's Part 375 Remedial Programs* (January 2021)

Evaluate Holding Times

537: 14 days to extraction; 28 days from extraction to analysis
533: 28 days to extraction; 28 days from extraction to analysis

Typical sample result summary form

- Number of PFAS reported
- Results, RLs, units
- Dilution results
- Collection date, prepared date, analysis date
- Percent solids (dry weight)
- Isotope Dilution recoveries

Client Sample Results

Client: xxxx
Project/Site: xxxxx Site
Lab Job ID: xxxxx

Client Sample ID: xxxx-08
Date Collected: 05/18/17 11:20
Date Received: 05/20/17 11:50

Lab Sample ID: xxxxx-19
Matrix: Solid
Percent Solids: 15.8

Method: 537 (modified) - Fluorinated Alkyl Substances

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Perfluorobutanoic acid (PFBA)	ND		1.3	0.41	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluoropentanoic acid (PFPeA)	ND		1.3	0.83	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorohexanoic acid (PFHxA)	**2.6**		1.3	0.45	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluoroheptanoic acid (PFHpA)	**1.9**		1.3	0.56	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorooctanoic acid (PFOA)	ND		1.3	0.65	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorononanoic acid (PFNA)	ND		1.3	0.53	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorodecanoic acid (PFDA)	ND		1.3	0.36	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluoroundecanoic acid (PFUnA)	**0.79**	**J**	1.3	0.68	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	
Perfluorododecanoic acid (PFDoA)	ND		1.3	0.77	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	
Perfluorotridecanoic Acid (PFTriA)	ND		1.3	0.59	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorotetradecanoic acid (PFTeA)	ND		1.3	0.37	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorobutanesulfonic acid (PFBS)	ND		1.3	0.66	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorohexanesulfonic acid (PFHxS)	**1.9**		1.3	0.75	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluoroheptanesulfonic Acid (PFHpS)	**3.6**		1.3	0.75	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorodecanesulfonic acid (PFDS)	ND		1.3	0.46	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorooctane Sulfonamide (FOSA)	ND		1.3	0.51	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1

Isotope Dilution	*%Recovery*	*Qualifier*	*Limits*	*Prepared*	*Analyzed*	*Dil Fac*
13C8 FOSA	*9*	*	*25 - 150*	*05/23/17 13:25*	*05/31/17 03:04*	*1*
13C4 PFOS	*76*		*25 - 150*	*05/23/17 13:25*	*05/31/17 13:37*	*10*

Client Sample ID: xxxx-08
Date Collected: 05/18/17 11:20
Date Received: 05/20/17 11:50

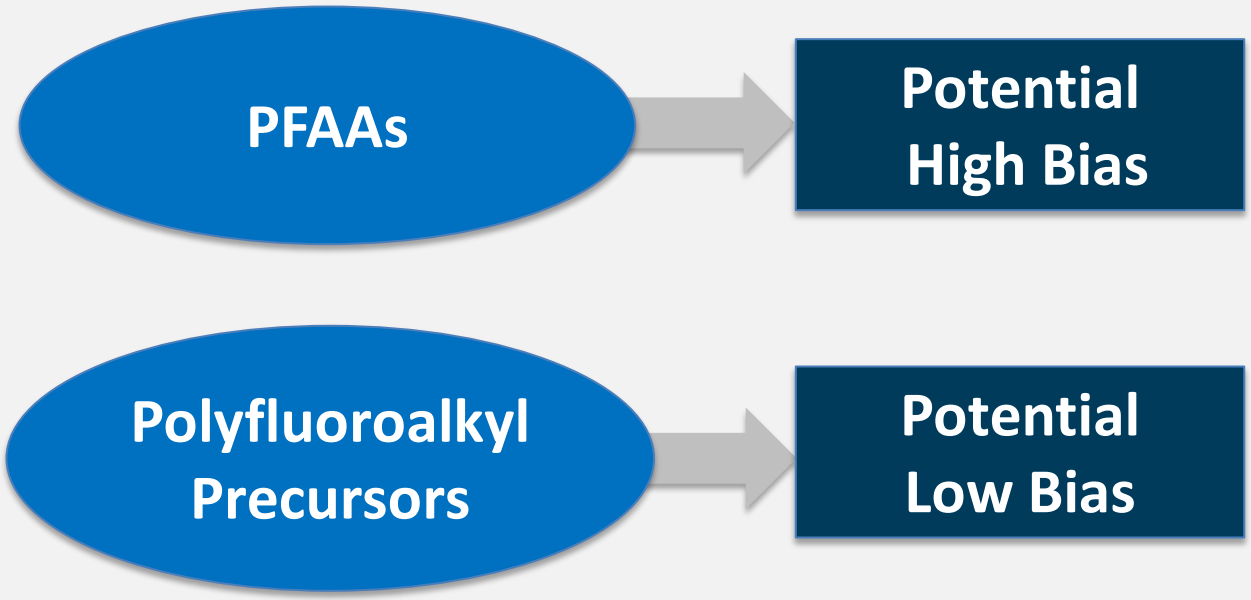
Lab Sample ID: xxxxx-19
Matrix: Solid
Percent Solids: 15.8

Method: 537 (modified) - Fluorinated Alkyl Substances

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Perfluorobutanoic acid (PFBA)	ND		1.3	0.41	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluoropentanoic acid (PFPeA)	ND		1.3	0.83	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1

Missed Holding Times: Low and High Biases

537: 14 days to extraction; 28 days from extraction to analysis
533: 28 days to extraction; 28 days from extraction to analysis



Example PFAAs:

- Perfluorobutanoic acid (PFBA)
- Perfluoropentanoic acid (PFPeA)
- Perfluorohexanoic acid (PFHxA)
- Perfluoroheptanoic acid (PFHpA)
- Perfluorooctanoic acid (PFOA)
- Perfluorononanoic acid (PFNA)
- Perfluorodecanoic acid (PFDA)
- Perfluoroundecanoic acid (PFUnA)
- Perfluorododecanoic acid (PFDoA)
- Perfluorotridecanoic Acid (PFTrA)
- Perfluorotetradecanoic acid (PFTeA)
- Perfluorohexadecanoic acid (PFHxDA)
- Perfluorooctadecanoic acid (PFODA)
- Perfluorobutanesulfonic acid (PFBS)
- Perfluoropentanesulfonic acid (PFPeS)
- Perfluorohexanesulfonic acid (PFHxS)
- Perfluoroheptanesulfonic Acid (PFHpS)
- Perfluorooctanesulfonic acid (PFOS)
- Perfluorononanesulfonic acid (PFNS)
- Perfluorodecanesulfonic acid (PFDS)

Example Polyfluoroalkyl Precursors:

- N-methyl perfluorooctane sulfonamidoacetic acid (NMeFOSAA)
- N-ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)
- 6:2 Fluorotelomer sulfonic acid (6:2 FTSA)
- 8:2 Fluorotelomer sulfonic acid (8:2 FTSA)
- 4:2 Fluorotelomer sulfonic acid (4:2 FTSA)
- 10:2 Fluorotelomer sulfonic acid (10:2 FTSA)
- N-Methyl perfluorooctane sulfonamidoethanol (N-MeFOSE)
- N-Ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE)
- N-Methyl perfluorooctane sulfonamide (MeFOSA)
- N-Ethyl perfluorooctane sulfonamide (EtFOSA)

Blanks: Method Blanks, Field Blanks, & Equipment Blanks

- Purposes:

  Method Blank:
  To check for potential lab contamination in the sample preparation and analysis step

  Field/Equipment Blanks:
  To check for potential contamination from ambient field conditions or equipment

- Does each prep batch have its own method blank?

Blank Evaluation

- **Any PFAS detected in blanks?**
- Are there any potential false positive results in samples?
- **General Rule of Thumb: If concentration in sample <10x the blank concentration, the result is potentially a false positive**
- **Applies to lab method blanks as well as equipment blanks**

Results will be in analytical data package

Lab Sample ID: MB 320-400500/1-A
Matrix: Water
Analysis Batch: 400716

Client Sample ID: Method Blank
Prep Type: Total/NA
Prep Batch: 400500

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
	0.858	J	2.0	0.35	ng/L		08/03/20 04:46	08/03/20 14:47	1
	ND		2.0	0.49	ng/L		08/03/20 04:46	08/03/20 14:47	1
	ND		2.0	0.58	ng/L		08/03/20 04:46	08/03/20 14:47	1
	ND		2.0	0.25	ng/L		08/03/20 04:46	08/03/20 14:47	1
	ND		2.0	0.85	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluorononanoic acid (PFNA)	ND		2.0	0.27	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluorodecanoic acid (PFDA)	ND		2.0	0.31	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluoroundecanoic acid (PFUnA)	ND		2.0	1.1	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluorododecanoic acid (PFDoA)	ND		2.0	0.55	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluorotridecanoic acid (PFTriA)	ND		2.0	1.3	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluorotetradecanoic acid (PFTeA)	ND		2.0	0.29	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluorobutanesulfonic acid (PFBS)	ND		2.0	0.20	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluorohexanesulfonic acid (PFHxS)	0.270	J	2.0	0.17	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluoroheptanesulfonic Acid (PFHpS)	ND		2.0	0.19	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluorooctanesulfonic acid (PFOS)	ND		2.0	0.54	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluorodecanesulfonic acid (PFDS)	ND		2.0	0.32	ng/L		08/03/20 04:46	08/03/20 14:47	1
Perfluorooctanesulfonamide (FOSA)	ND		2.0	0.35	ng/L		08/03/20 04:46	08/03/20 14:47	1
N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	ND		20	3.1	ng/L		08/03/20 04:46	08/03/20 14:47	1
N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	ND		20	1.9	ng/L		08/03/20 04:46	08/03/20 14:47	1
6:2 FTS	ND		20	2.0	ng/L		08/03/20 04:46	08/03/20 14:47	1
8:2 FTS	ND		20	2.0	ng/L		08/03/20 04:46	08/03/20 14:47	1

PFOS in Blank = 2 ng/L

10x Blank = 20 ng/L

Sample conc = 120 ng/L

Real Hit

10x Blank = 20 ng/L

Sample conc = 8 ng/L

False Positive

Isotope Dilution: What is It?

- Sample spiked with KNOWN amount of extracted internal standards (EIS) (aka labeled surrogates)
- EIS match target analytes
  - $^{13}C_4$PFBA is EIS associated with PFBA
  - $^{13}C_4$PFOS is EIS associated with PFOS
  - etc. for each PFAS analyte
- Target PFAS result corrected by proportional amount based on isotope
- **BENEFITS**:
  - Corrects for analytical error associated with matrix
  - Corrects for matrix interferences

EPA 537 and ASTM Method do NOT utilize isotope dilution

DoD QSM requires isotope dilution

Concentration Target PFAS = $\frac{\text{Target PFAS Area} * \text{True Concentration Isotope}}{\text{Area EIS} * \text{Calibration Factor}}$

PFAS Analytical Reports

Typical sample result summary form

- Number of PFAS reported
- Results, R
- Dilution r
- Collectio
- Percent solids (dry weight)
- Isotope Dilution recoveries

Results will be in analytical data package

Isotope Dilution	%Recovery	Qualifier	Limits
13C8 FOSA	9	*	25 - 150
13C4 PFBA	27		25 - 150
13C2 PFHxA	49		25 - 150
13C4 PFOA	48		25 - 150

Client Sample Results

Client: xxxx
Project/Site: xxxxx Site

Lab Job ID: xxxxx

Client Sample ID: xxxx-08
Date Collected: 05/18/17 11:20
Date Received: 05/20/17 11:50

Lab Sample ID: xxxxx-19
Matrix: Solid
Percent Solids: 15.8

Method: 537 (modified) - Fluorinated Alkyl Substances

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Perfluorobutanoic acid (PFBA)	ND		1.3	0.41	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.83	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.45	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.56	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.65	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.53	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.36	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			.3	0.68	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	
			.3	0.77	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	
			3	0.59	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			3	0.37	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			3	0.66	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			3	0.75	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
			3	0.75	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
(PFHpS)									
Perfluorodecanesulfonic acid (PFDS)	ND		1.3	0.46	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1
Perfluorooctane Sulfonamide (FOSA)	ND		1.3	0.51	ug/Kg	☼	05/23/17 13:25	05/31/17 03:04	1

Isotope Dilution	*%Recovery*	*Qualifier*	*Limits*	*Prepared*	*Analyzed*	*Dil Fac*
C8 FOSA	9	*	25 - 150	05/23/17 13:25	05/31/17 03:04	1
C4 PFBA	27		25 - 150	05/23/17 13:25	05/31/17 03:04	1
C2 PFHxA	49		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C4 PFOA	48		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C5 PFNA	43		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C2 PFDA	63		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C2 PFUnA	64		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C2 PFDoA	57		25 - 150	05/23/17 13:25	05/31/17 03:04	1
18O2 PFHxS	65		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C4 PFOS	49		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C4-PFHpA	47		25 - 150	05/23/17 13:25	05/31/17 03:04	1
13C5 PFPeA	41		25 - 150	05/23/17 13:25	05/31/17 03:04	1

Method: 537 (modified) - Fluorinated Alkyl Substances - DL

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Perfluorooctanesulfonic acid (PFOS)	930		13	8.0	ug/Kg	☼	05/23/17 13:25	05/31/17 13:37	10

Isotope Dilution	*%Recovery*	*Qualifier*	*Limits*	*Prepared*	*Analyzed*	*Dil Fac*
13C4 PFOS	76		25 - 150	05/23/17 13:25	05/31/17 13:37	10

How Can Isotope Dilution Vary Between Labs?

EIS	Lab 1 (%)	Lab 2 (%)	Lab 3 (%)	Lab 4 (%)	DoD (%)
13C3-PFBS	25-150	50-150	26-148	31-159	50-150
13C3-PFHxS	25-150	50-150	34-126	47-153	50-150
13C4-PFHpA	25-150	50-150	35-126	30-139	50-150
13C8-PFOA	25-150	50-150	43-112	36-149	50-150
13C8-PFOS	25-150	50-150	43-115	42-146	50-150
13C9-PFNA	25-150	50-150	32-134	34-146	50-150

- If ≥10% recovery, results most likely not significantly affected.
- If <10% recovery, higher probability that results may be affected
  - Some data validation guidelines recommend rejecting nondetect results if <10%
  - Detected results: potential low bias or indeterminate bias
  - Only associated target PFAS affected

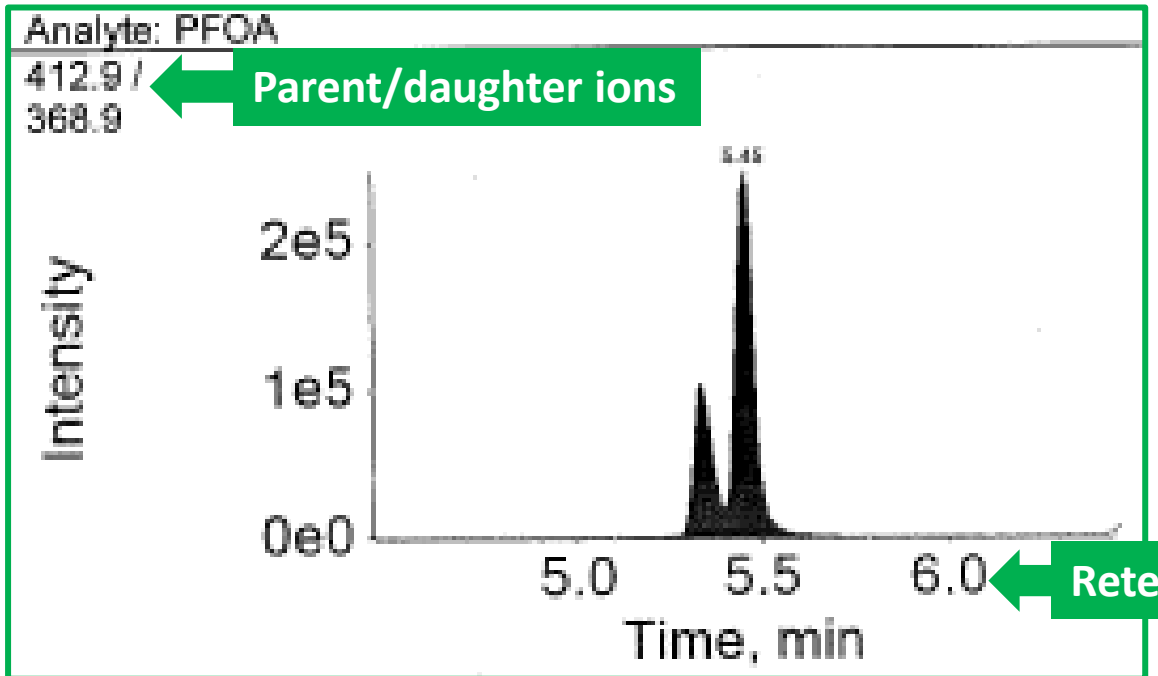
Example:
If 13C3-PFBS exhibits low %R, only affects PFBS.

Linear & Branched Isomers

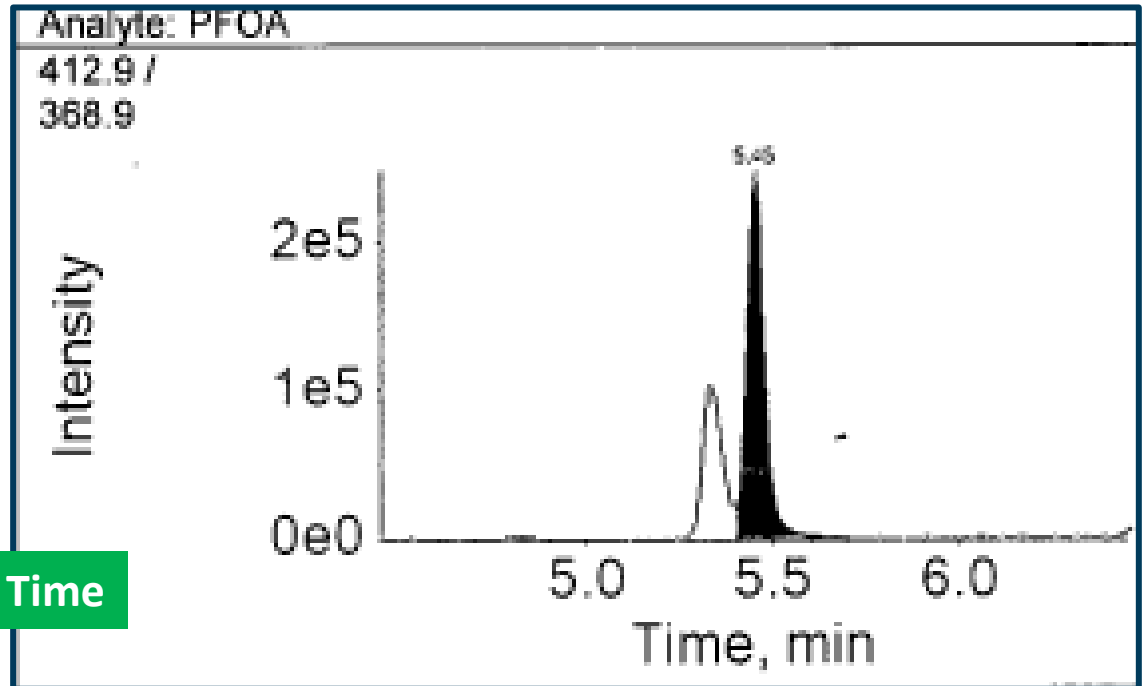
- Before September 2016, some inconsistency in how this performed
- PFHxS, PFOS, PFOA, NMeFOSAA, NEtFOSAA
- If branched isomers not included, result is biased low.

EPA United States Environmental Protection Agency

Technical Advisory- Laboratory Analysis of Drinking Water Samples for Perfluorooctanoic Acid (PFOA) Using EPA Method 537 Rev. 1.1



Correct integration of PFOA



Incorrect integration of PFOA

Only obvious in Level 4 analytical data package

TISSUE LC MS/MS INTERFERENCES

Compound	Parent	Ion 1	Ion 2	Ion 3
Taurochendeoxycholate	498.2	79.8	106.8	123.8
Taurodeoxycholate	498.2	79.8	106.8	123.8
Tauroursodeoxycholate	498.2	79.8	106.8	123.8
PFOS	498.9	79.9	98.9	N/A

- PFOS reported as false positives of up to 120 ng/g in eggs since Bile Acids have common transition
- **PFOS measured using 499→99 allowing Interference to be eliminated**

Laboratory Control Samples (LCS)

- **Purposes:** To check the accuracy of the method in the absence of any matrix effects
- What are LCSs?
- Does each analytical or prep batch have its own LCS?

LCS Evaluation

✓ Were **all** target analytes reported?

✓ Were all recoveries within the acceptance limits? → **ACCURACY**

If LCS recoveries are outside limits:

- **POTENTIAL LOW BIAS (affects non-detects and detects)**
- **POTENTIAL HIGH BIAS (affects only detects)**

UNLESS

Percent Recovery < 10%, potentially unusable data

Affects all samples in the analytical batch for the compound(s) out in LCS

Matrix Spikes/Matrix Spike Duplicates (MS/MSDs)

- What are these?
- Were these analyses performed on a project sample?

MS/MSD

- ✓ Were **all** target analytes reported?
- ✓ Were all recoveries within the acceptance limits? → **ACCURACY**
- ✓ Were all RPDs within the acceptance limits? → **PRECISION**

If MS recoveries are outside limits:

- **POTENTIAL LOW BIAS (affects non-detects and detects)**
- **POTENTIAL HIGH BIAS (affects only detects)**

UNLESS

Percent Recovery < 10%, potentially unusable data

Affects only the unspiked sample for the compound(s) out in MS/MSD

Let's Summarize Potential Biases

Blanks	• ***Detected results***	**HIGH BIAS**	All Associated Samples in Batch
Holding Times	• ***Missed holding times***	**LOW BIAS** **HIGH BIAS**	Sample-Specific
LCS	• ***Low recoveries*** • ***High recoveries***	**LOW BIAS** **HIGH BIAS**	All Associated Samples in Batch
EIS, Matrix Spikes	• ***Low recoveries*** • ***High recoveries***	**LOW BIAS** **HIGH BIAS**	Sample-Specific Compound-Specific
Subsampling Water Sample		**LOW BIAS** >C8 PFSAs & >C10 PFCAs:	Sample-Specific
No Methanol Rinse on Bottle		**LOW BIAS** Long chain PFAAs	Sample-Specific

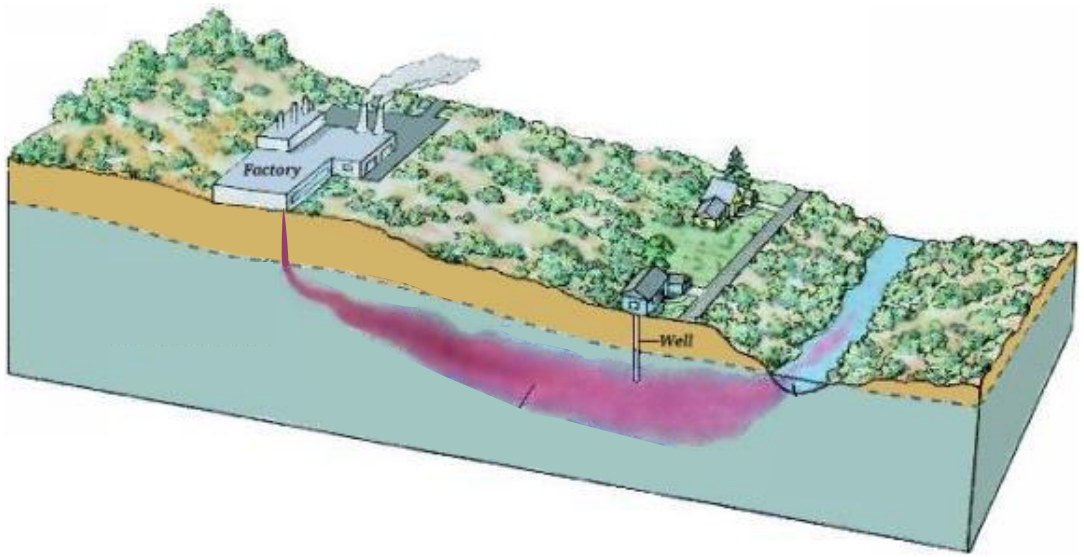
Factors Affecting Data Comparability - PFAS

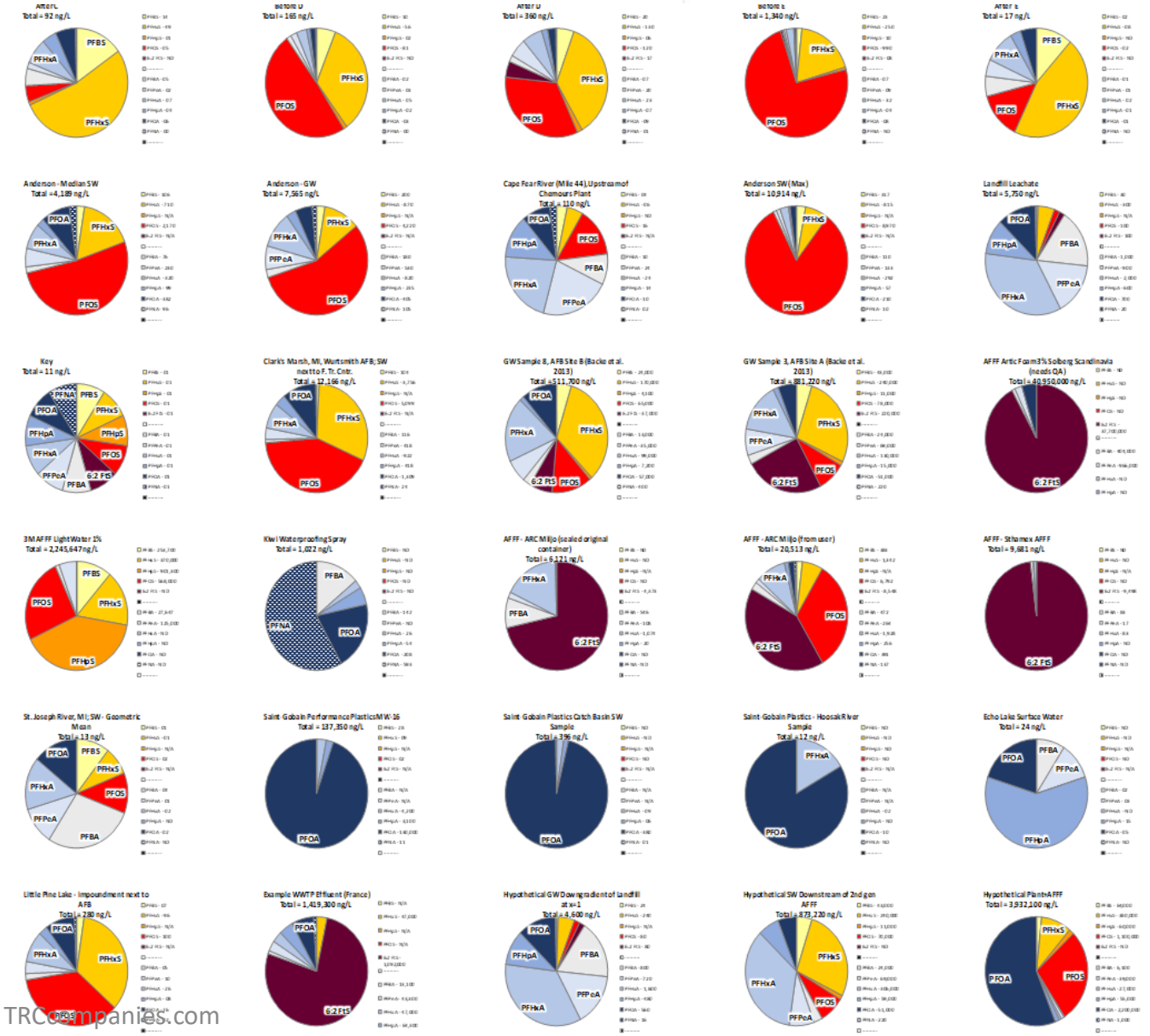
- Field Collection Techniques
- Sample Handling in the Laboratory (e.g., SPE, solids)
- Field / Method Blank issues
- Not using Isotope Dilution for Recovery Correction
- Degradation of Precursors
- Not including Branched Isomers
- Calibration differences (e.g., isotope dilution vs internal standard)
- Sensitivity differences (RLs not the same)
- Compound name differences

Forensics

Chemical Signatures

Signatures reflect various source and fate/transport scenarios





We Understand Signatures

Paper & Food Packaging

- **Side-chain fluoropolymers**
- PAPs/diPAPs
- **NEtFOSE**, **NEtFOSAA**, PFBS, PFOA, PFHxA

Textile & Leather

- Polymers
- Polymer raw materials
- PFOA, FTOHs

AFFF

- PFOA, PFOS, PFHxS
- C8 fluorotelomers (8:2 FTS)
- C6 fluorotelomers, PFOA

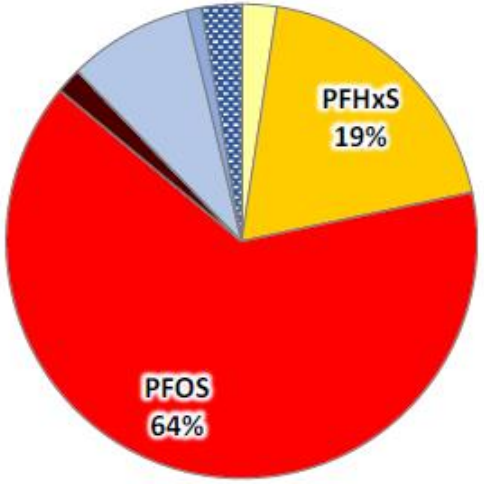
WWTPs & Landfills

- n:2 FTUCA
- n:3 FTCA **(5:3FTCA)**
- n:2 FTSA
- EtFOSA

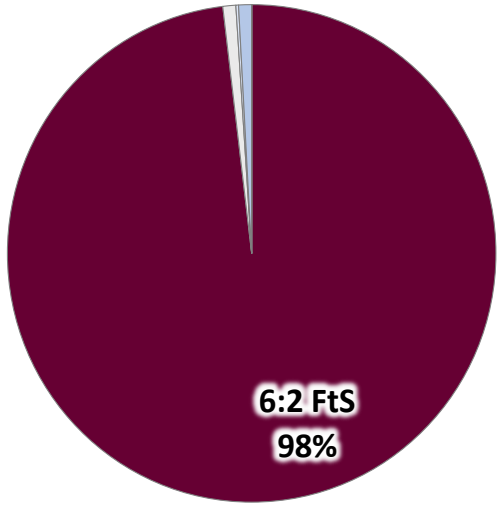
Metal Plating

- PFOS
- 6:2 FTS, 8:2 FTS
- F53B

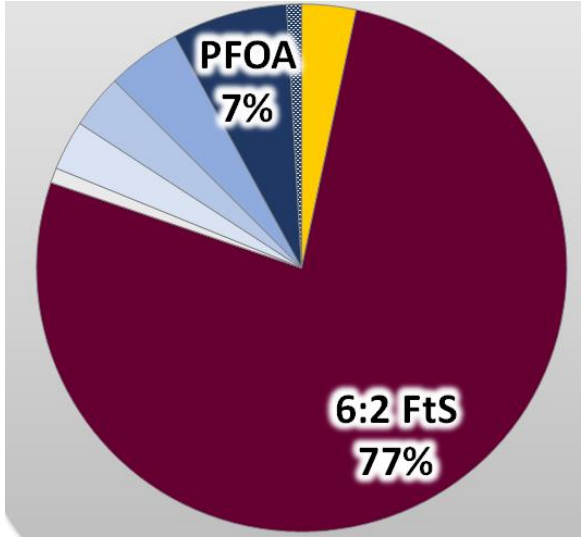
PFAS Source Signature Differentiation



1st Generation AFFF (PFOS-Based)

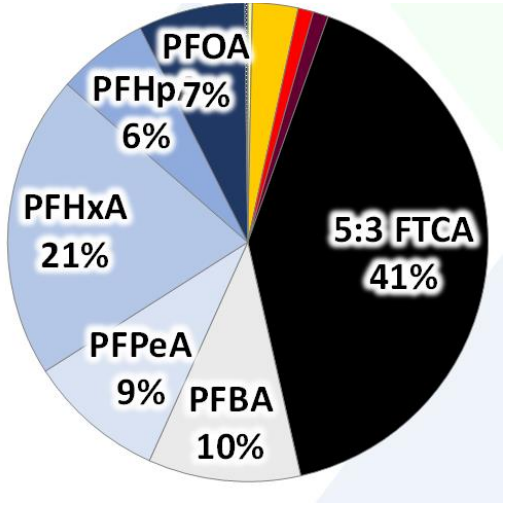


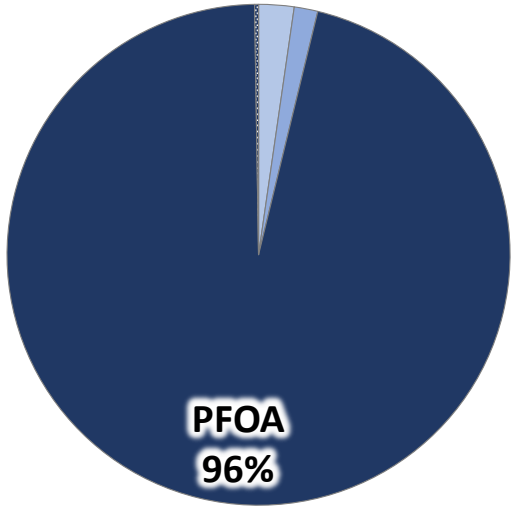
Modern Fluorotelomer AFFF



WWTP Effluent from Chrome Plater

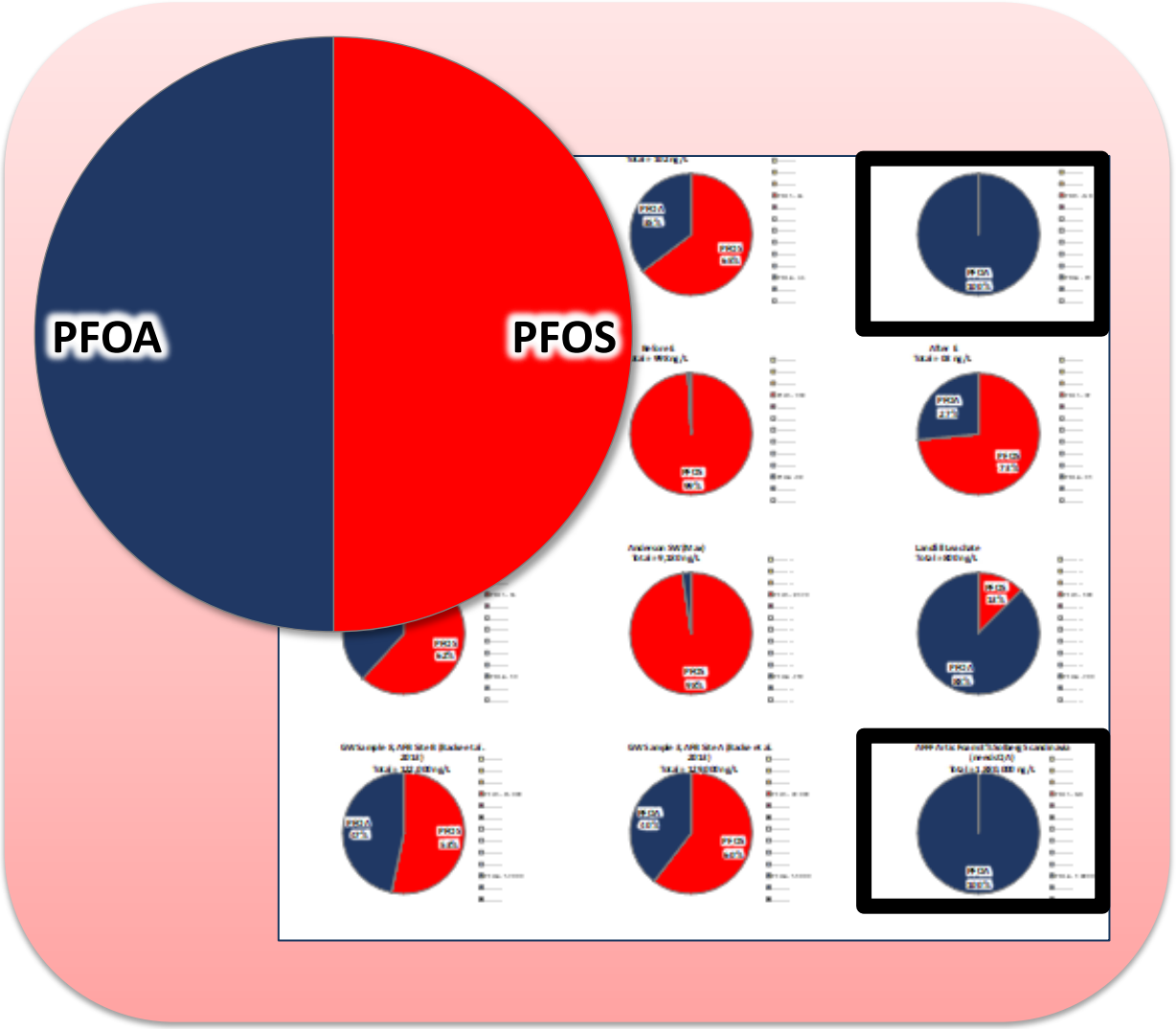
Landfill Leachate

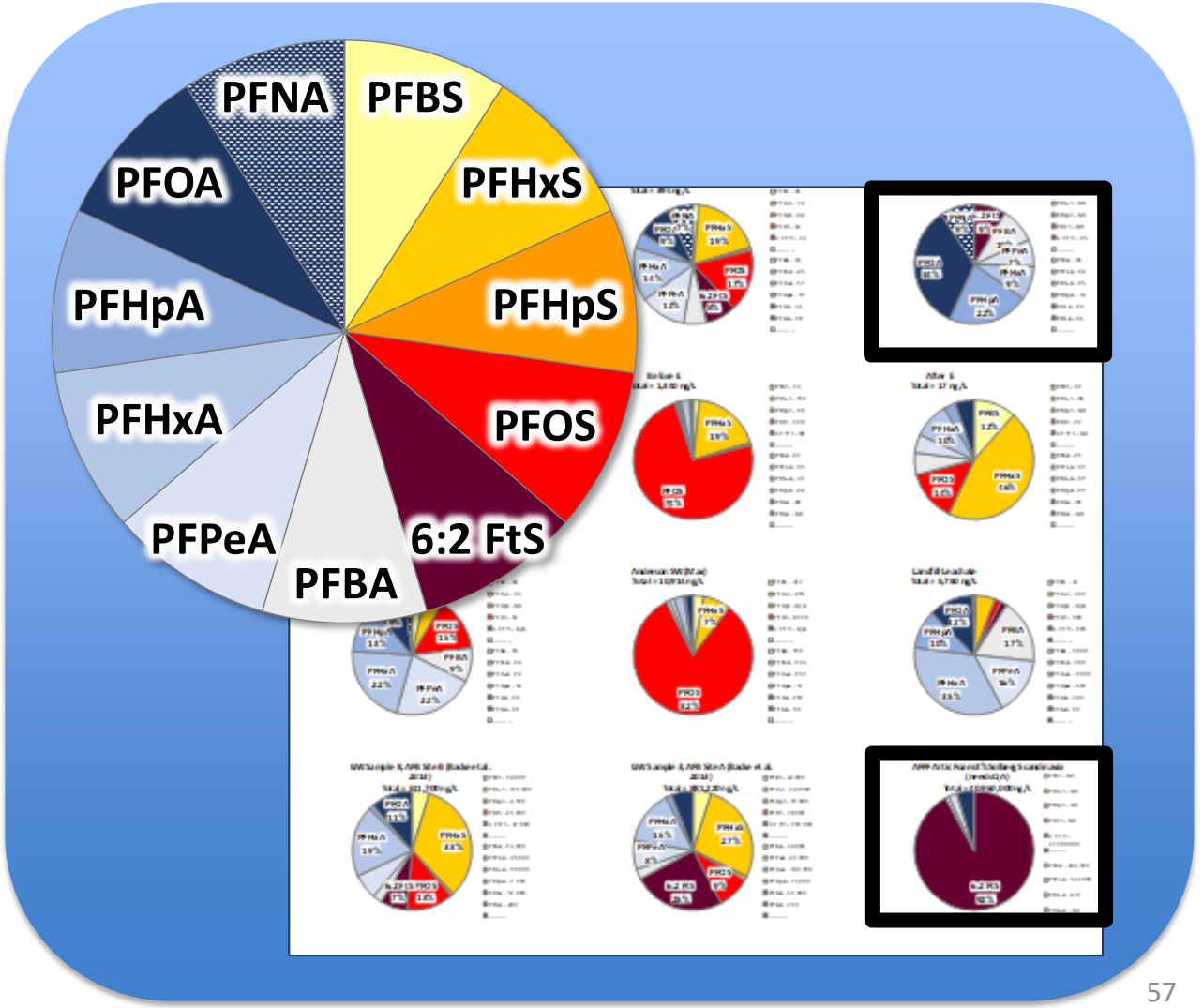




Plastics Manufacturing

Example Difference Based on Analytes Selected for Signature Evaluation





Thank you

Questions?

Nancy C. Rothman, Ph.D.

P: (908) 874-5686 | **E:** NRothman_neh@comcast.net

www.neh-inc.com

Elizabeth Denly, ASQ CMQ/OE, PFAS Group Program Director

P: (978) 656-3577 | **E:** EDenly@TRCCompanies.com

www.TRCcompanies.com