

Understanding Usability of PFAS Data NEWMOA Conference – April 6, 2022

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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? **WEH** New Norizons, include the second seco

- 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 **NEH New environmental TRC**

- Data Validation
 - Formal, systematic process
 - Follow specific guidelines created by EPA
 - Look at effects of lab performance and matrix <u>on results</u>
 - 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 <u>on the</u> <u>achievement of the project objectives</u>
 - Can we use the data for decision-making?

How is Usability Determined?



Results for all required compounds are reported

Results meet sensitivity requirements Quality of results understood (potential limitations of data)





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?

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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	Field/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 Sample Collection

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

Technical Guidance Documents

• Use of and exclusion of specific sampling equipment and materials

GENERAL PFAS SAMPLING GUIDANCE

This document contains an introduction to PFAS, biosecurity recommendations, and general recommendations to decrease the possibility of cross-contamination.

Michigan Department of Environmental Quality



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General PFAS Sampling

Guidance

Wastewater PFAS Sampling Guidance Revised October 11, 2018

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PFAS Sampling Quick Reference Field Guide Revised October 17, 2018



Surface Water PFAS Sampling Guidance Revised November 28, 2018

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<u>Fish Tissue PFAS Sampling</u> <u>Guidance</u> 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

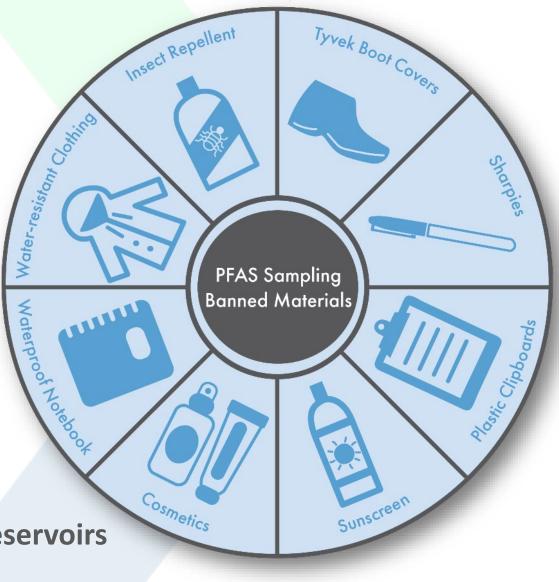


WHAT SHOULD I AVOID?	USE INSTEAD
Equipment with Teflon [®] (e.g., bailers, tubing, parts in pump) during sample handling or mobilization/demobilization	 High density polyethylene (HDPE) or silicone tubing/materials in lieu of Teflon[®]
Low-density polyethylene (LDPE) or glass sample containers or containers 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 16

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

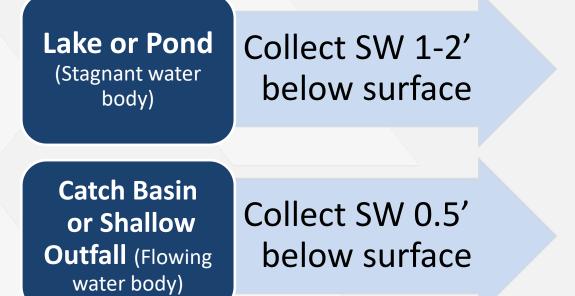
Equipment Study: PFCAs vs PFSAs vs Polyfluoroalkyl Substances



PFCAs	PFSAs	Polyfluoroalkyl Substances		25.00	C4 P	FCA				P.	TFE Tub (ng/L)				No Pl	SAs	
PTFE Tubing	Bailer Line	PTFE-lined Tubing	ng/L	20.00 15.00 10.00				_				_					
PTFE-lined Tubing	Sample Labels	Bailer Line		5.00 0.00		A	PFPeA	PFHxA	PFHp4	PFOA PTFE TUBI	PFNA NG A	PFD PTFE TUB		PFDoA	PFTrDA	PFTeDA	
LDPE Tubing	Nitrile Gloves				C4	& C5 F	FCA			LC	DPE Tub	ng					
Bailer Line	Field Book Cover		ng/L	100.00 50.00							(ng/L)				No PFSAs		
Sample Labels					0.00	PFB		PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	 PFDoA	PFTrDA	PFTeDA
Pizza Box										L[OPE 1 📕 L						
Water Level Tapes										Cover	of Field (ng/L)		k				
Silastic Tubing			ng/L	100.0 80.0	0		_				(87)						
Nitrile Gloves			0, -	60.0 40.0 20.0	⁰ C4 P	FSA				C7 PFCA							
Field Book Pages				0.0	0 — — PFI	BS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA		JnA PF	DoA PFTrD	A PFTeDA	
Field Book Cover			-							■ Book Co	iver A 📕	BOOK COV	ег в 				
PTFE Bladder																19	

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?



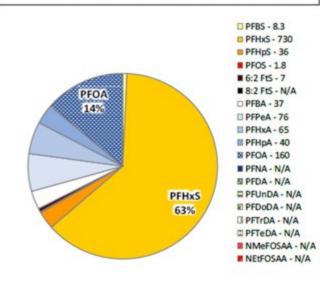
- Is homogenization of soil and sediment samples being performed properly in the field?
- Are there suspended solids in the surface water, groundwater, or wastewater samples?



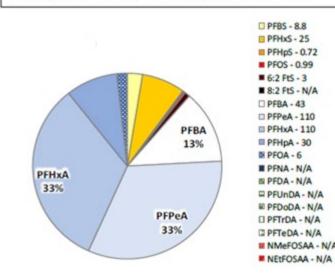
Fate & Transport: Sorption to Solids







Sample from 2" developed MW clear



Issue: Chemical sorption of PFAS to particulates or solids. Longer-chain PFAS and PFSAs tend to absorb more to solids.

- Particulates in aqueous samples can interfere with extraction procedure.
- Labs have variable procedures for dealing with this; can vary from lab to lab and within a lab.
- 1. Floating particulates versus sediment which has settled at the bottom of the container
- 2. Centrifuge and decant
- 3. Just decant
- *4. Rinse the remaining particulates or sediment with methanol and include the methanol rinse in the extraction*
- *5. Perform an extraction of the particulate or sediment portion of the sample*
- 6. Dealing with particulates that clog extraction cartridges
- 7. Documentation of issues with particulates by laboratory
- 8. Cut-off value for total suspended solids (TSS) causing extraction issues





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	2019	Aqueous	PFOA/PFOS
DoD QSM 5.3	2019	Solid & Aqueous	24+ analytes
OTM-45	2021	Air	50 analytes
SW-846 8327	2019	All	24 analytes
EPA 1633 Draft	2021	All	40 analytes
EPA 537 "Modified"(user-defined)	Current	All	Up to 70 analytes



	Ambient Air EPA is considering both sampling and analysis methods, targeted	Ambient/Near-Source (coming soon)	Field deployable Time of Flight/Chemical Ionization Mass Spectrometer for real time detection and measurement.
/hat's ming?	and non-targeted for PFAS ambient air measurements. Applications will include fenceline monitoring for fugitive emissions, deposition, and receptor exposure. Total These types of methods aim to quantify large groups of PFAS in environmental samples.	Semivolatile PFAS (coming soon)	A performance-based method guide by EPA TO-13a.
		Volatile PFAS (coming soon)	Uses SUMMA canisters and sorbent traps for GC/MS targeted and non-targeted analysis.
		Total Organic Fluorine (TOF) <i>(coming soon)</i>	EPA is developing a potential rapid screening tool to identify total PFAS presence and absence. This eventual standard operating procedure will be used to quantify TOF. Note: <i>EPA is working to develop this method in 2021.</i>
		Total Organic Precursors (TOP) <i>(coming soon)</i>	EPA is considering the development of a method, based on existing protocols, to identify PFAS precursors that may transform to more persistent PFAS. Note: TOP methods are commercially available. EPA will consider the need for a thorough multi-laboratory validation study in 2021.

https://www.epa.gov/water-research/pfas-analytical-methods-development-and-sampling-research

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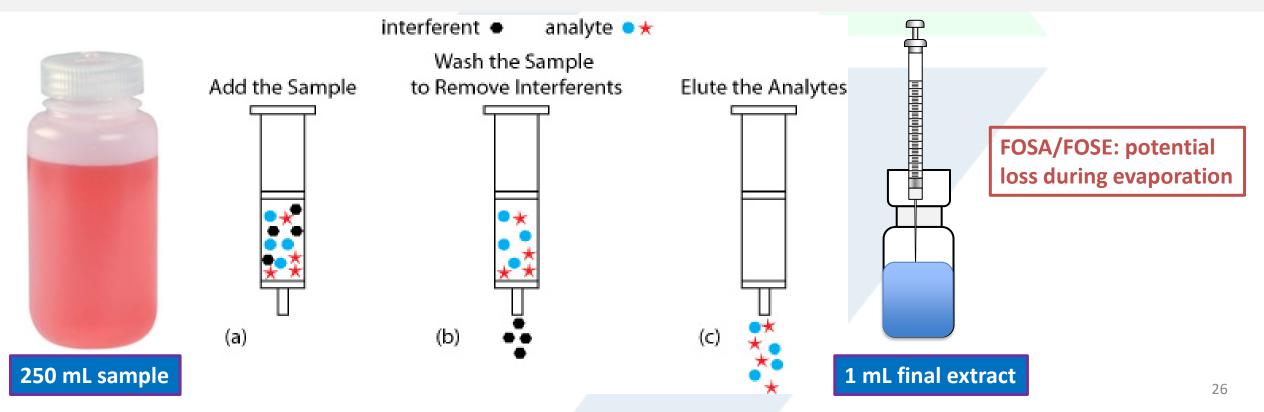
Analyte	CAS No.	UCMR3	537.1	NYSDEC	ISO 25101	MDEQ IPP	I I I I I I I I I I I I I I I I I I I
		(6)	(18)	(21)	(2)	(28)	
Perfluorobutanoic acid (PFBA)	375-22-4			Х	i i	Х	
Perfluoropentanoic acid (PFPeA)	2706-90-3			Х		Х	
Perfluorohexanoic acid (PFHxA)	307-24-4		Х	Х		Х	new
Perfluoroheptanoic acid (PFHpA)	375-85-9	Х	Х	Х		Х	NEH new environmen horizons, inc
Perfluorooctanoic acid (PFOA)	335-67-1	Х	Х	Х	Х	Х	norizons, inc
Perfluorononanoic acid (PFNA)	375-95-1	Х	Х	Х		Х	
Perfluorodecanoic acid (PFDA)	335-76-2		Х	Х		Х	
Perfluoroundecanoic acid (PFUnA)	2058-94-8		Х	Х		Х	
Perfluorododecanoic acid (PFDoA)	307-55-1		Х	Х		Х	
Perfluorotridecanoic Acid (PFTrA)	72629-94-8		Х	Х		Х	
Perfluorotetradecanoic acid (PFTeA)	376-06-7		Х	Х		Х	
Perfluorohexadecanoic acid (PFHxDA)	67905-19-5						
Perfluorooctadecanoic acid (PFODA)	16517-11-6						Analyte lists
Perfluorobutanesulfonic acid (PFBS)	375-73-5	Х	Х	Х		Х	
Perfluoropentanesulfonic acid (PFPeS)	2706-91-4					Х	vary by metho
Perfluorohexanesulfonic acid (PFHxS)	355-46-4	Х	Х	Х		Х	laboratory, and
Perfluoroheptanesulfonic Acid (PFHpS)	375-92-8			Х		Х	
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	Х	Х	Х	Х	Х	regulatory
Perfluorononanesulfonic acid (PFNS)	474511-07-4					Х	
Perfluorodecanesulfonic acid (PFDS)	335-77-3			Х		Х	agency; so
Perfluorooctane Sulfonamide (FOSA)	754-91-6			Х		Х	
N-methyl perfluorooctane sulfonamidoacetic acid (NMeFOSAA)	2355-31-9		Х	Х		Х	Project-specific
N-ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)	2991-50-6		Х	Х		Х	
3:2 Fluorotelomer sulfonic acid (6:2 FTSA)	27619-97-2			Х		Х	list of PFAS
2:2 Fluorotelomer sulfonic acid (8:2 FTSA)	39108-34-4			Х		Х	compounds
I:2 Fluorotelomer sulfonic acid (4:2 FTSA)	757124-72-4					Х	
0:2 Fluorotelomer sulfonic acid (10:2 FTSA)	120226-60-0						needs to be
N-Methyl perfluorooctane sulfonamidoethanol (N-MeFOSE)	24448-09-7						
I-Ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE)	1691-99-2					I	communicated
I-Methyl perfluorooctane sulfonamide (MeFOSA)	31506-32-8						to the
I-Ethyl perfluorooctane sulfonamide (EtFOSA)	4151-50-2						
IFPO-DA (Gen-X)	62037-80-3		Х				laboratory!
DONA			X				
-53B-9CI			X				-
53B-501			X			I	2

Solid Phase Extraction

- Is the lab extracting the <u>entire</u> sample and <u>rinsing</u> the sample bottle?
- What cartridge is the lab using?
 - <u>Styrenedivinylbenzene</u> (SDVB) sorbent phase

PFBA, PFPeA poor recoveries

- Reverse phase copolymer characterized by a weak anion exchange (WAX) sorbent phase
- Is the lab doing washes to remove interferences on the SPE cartridge?





Sample Analysis: HPLC Separation (Part 1) 1.0e6

Intensity

5.0e5

1.5

Analyte

PFBA

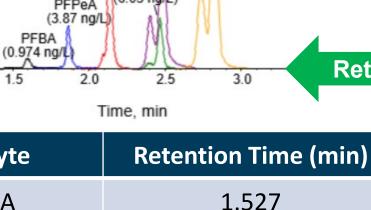
¹³C₄PFBA

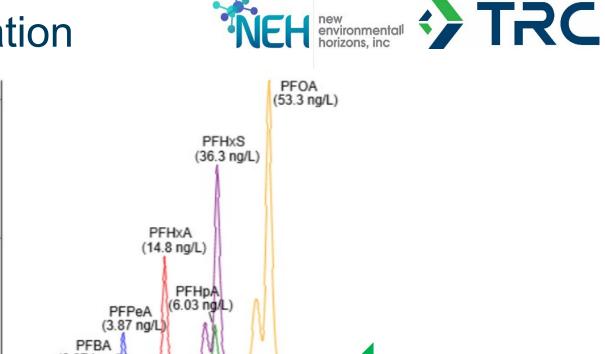
PFOS

¹³C₄PFOS

- 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





1.525

3.028

3.026

Retention Time

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 lons
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 lons (Parent/Daughter lons)



Definitive Identification of Compounds

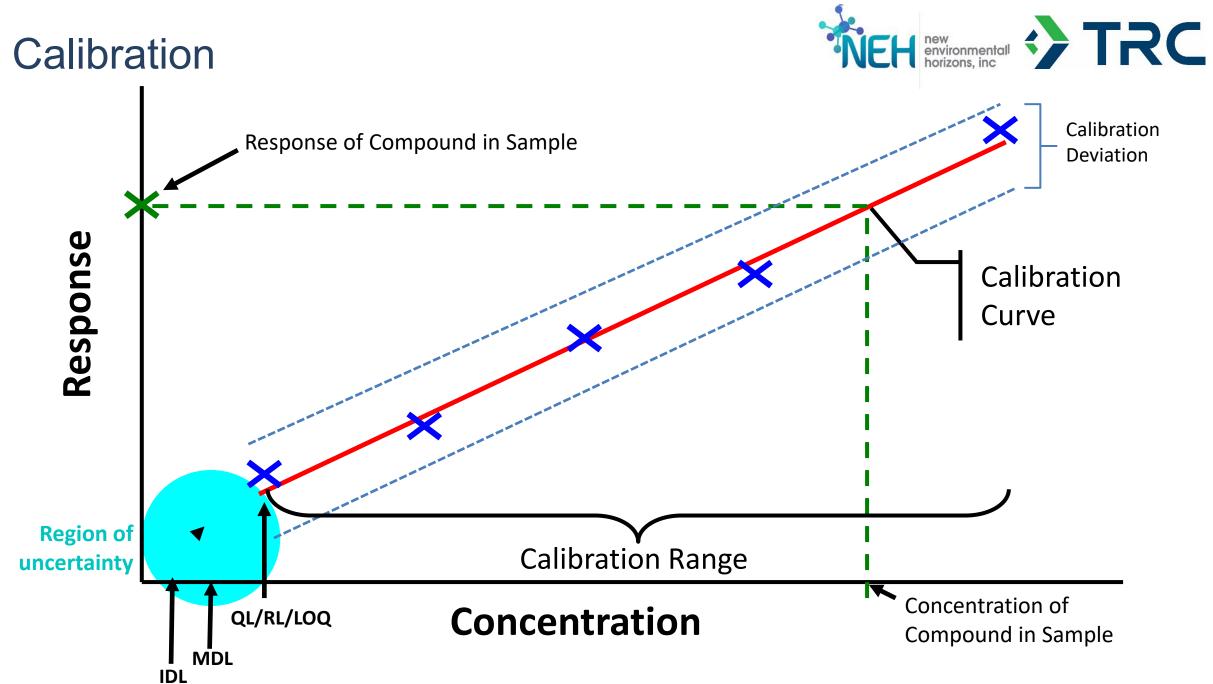
- Retention time from HPLC separation
- Transition to characteristic daughter ions
- Ion ratios
- What happens when the ion ratios are outside limits?
 - What are the limits?
- What if there is no confirmation ion?
 - PFBA
 - PFPeA
 - NMeFOSAA
 - NEtFOSAA

Analyte	Retention Time (min)	Parent/ Daughter Ions	lon 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 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				



PFAS Analytical Reports



Lab Job ID: xxxxx

Lab Sample ID: xxxxx-19

Client Sample Results

Typical sample result summary form

- Number of PFAS reported
- Results, RLs, units
- Dilution results
- Collection date, prepared date, anal

- Percent solids (dry weight)
- Isotope Dilution recoveries

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	Date Collected: 05/18/17 11:20 Date Received: 05/20/17 11:50					Ma	Matrix: Solid Percent Solids: 15.8	
	Method: 537 (mod Analyte		d Alkyl Substances Result Qualifier	RL I	Unit D_Prep	ared Analyzed		
Method: 537 (modifie	d) - Fluorin	ated Alky	I Substanc	es		/17 03:0 /17 03:0)4 1	
Analyte		Result	Qualifier	RL	MDL	Unit (17 03:0	4	
Perfluorobutanoic acid (PFB	A)	ND		1.3	0.41	ug/Kg /17 03:0	14	
Perfluoropentanoic acid (PFI	PeA)	ND		1.3	0.83	ug/Kg (17 03:0-		
Perfluorohexanoic acid (I	PFHxA)	2.6		1.3	0.45	ug/Kg /17 03:0		
Perfluoroheptanoic acid	(PFHpA)	1.9		1.3	0.56	ug/Kg 1/17 03:0		
Perfluorooctanoic acid (PFO,	A)	ND		1.3	0.65	ua/Ka		
Perfluorononanoic acid (PFN	IA)	ND.		1.3		1/17 03:	04	
Perfluorodecanoic acid (PFD	A)	ND	*	1.3	0.36	ug/Kg 1/17 03:		
Perfluoroundecanoic acid (PFUnA)	Ŀ	0.79	J	1.3	0.68	ug/Kg 1/17 03: 1/17 03:	04	
Perfluorododecanoic acid (Pl	FDoA)	ND		1.3	0.77	ug/Kg 1/17 03:		
Perfluorotridecanoic Acid (P	PFTriA)	ND		1.3	0.59	ug/Kg 1/17 03:		
Perfluorotetradecanoic acid	(PFTeA)	ND		- 1.3	0.37	ug/Kg 1/17 03:	04 1	
Perfluorobutanesulfonic acid	d (PFBS)	ND		1.3	0.66	1/1/ 03:		
Perfluorohexanesulfonic (PFHxS)	acid	1.9		1.3	0.75	1/17 03:	:04 :04	
Perfluoroheptanesulfonie (PFHpS)	c Acid	3.6		1.3	0.75	ug/Kg		
Perfluorodecanesulfonic aci	d (PFDS)	ŃD		1.3	0.46			
Perfluorooctane Sulfonamid	e (FOSA)	ND		1.3	0.51	1/17 12	1.	

Client: xxxx

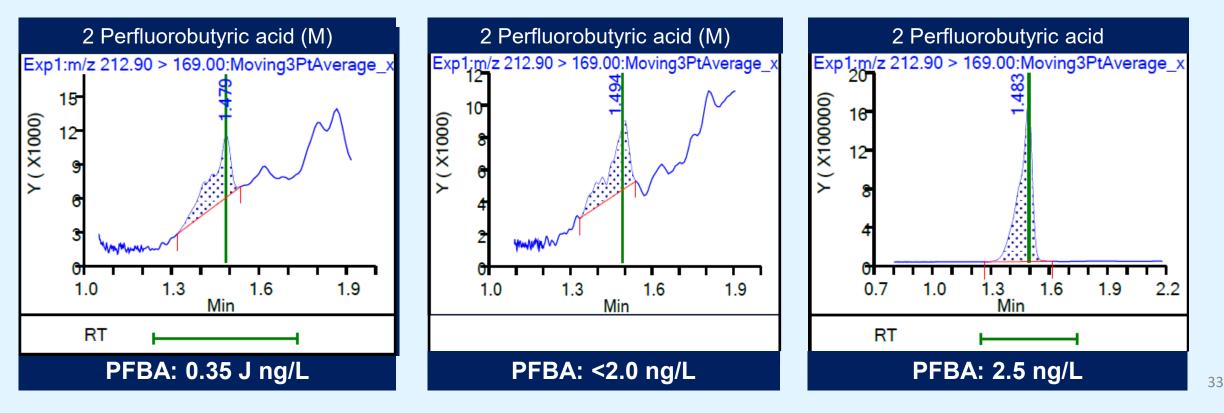
Project/Site: xxxxx Site

Client Sample ID: xxxx-08

A Few More Items



- 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
- <u>DO NOT</u> use MDLs as nondetect values
- Be careful of "J" values



Specific Laboratory QA/QC

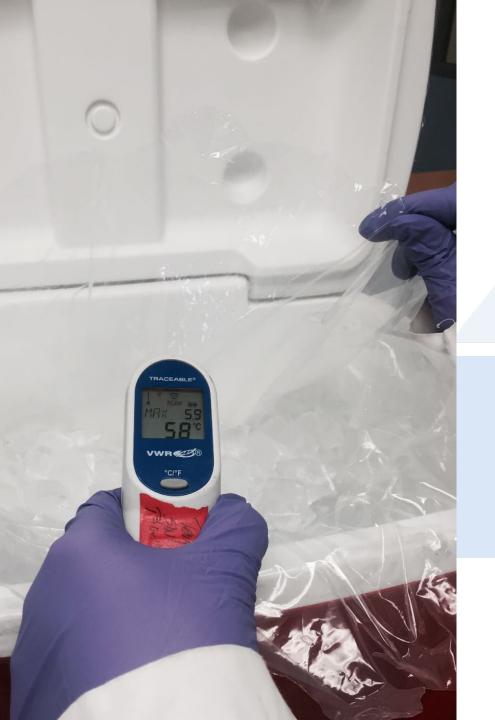


- Sample preservation & handling
- Sample Holding Times / Analytical Batches (≤ 20 samples)
- QC Samples required for each Analytical Batch:
 - Method Blank (MB)
 - Laboratory Control Sample (LCS)
 - Matrix Spike (MS)
 - Matrix Sample Duplicate (MSD)
- Extracted Internal Standard (Labeled Surrogates) 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
- Field Collection & Analytical Method differences can introduce uncertainty
- Guidelines for Evaluating Quality
 - National Functional Guidelines for Data Review (for Organics, High Resolution Organics, and Inorganics)
 - 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) <u>http://www.denix.osd.mil/edqw/documents/documents/manuals/qsm-version-5-3-final-updated/</u>
 - NYSDEC, Guidelines for Sampling and Analysis of PFAS, Under NYSDEC's Part 375 Remedial Programs (January 2021)
 - MCP Representativeness Evaluations And Data Usability Assessments, Policy # WSC-07-350 (September 2007)





Sample Preservation & Integrity Was the Cooler Temperature $\leq 10^{\circ}$ C?

Typically noted on COC or separate cooler receipt form.

What if samples are delivered to the laboratory on the same day of collection and temperatures are outside of the acceptance criteria but samples are on ice?

Temperature too low: likely okay as long as waters not frozen Temperature too high: use professional judgment

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
1633: ASAP to 7 days to 28 days to 90 days, depending on storage and analyte

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

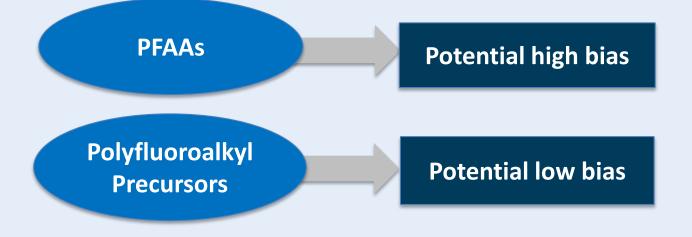
		Client	Sam	ple	Result	S				
Client: xxxx Project/Site: xxxxx Site				ι,		2. 2		Lab Job ID: x	XXXX	
Client Sample ID: xxxx-08 Date Collected: 05/18/17 11:20 Date Received: 05/20/17 11:50							с + 1	Lab Sar	nple ID: xxx Matrix Percent Solid	c: Solid
Method: 537 (modified) - Fluor Analyte	inated Alky Result	l Substan Qualifier	ces	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Perfluorobutanoic acid (PFBA)	ND			1.3	0.41	ug/Kg	ā	05/23/17 13:25		1
Perfluoropentanoic acid (PFPeA)	ND			1.3	0.83	ug/Kg	· 🛱	05/23/17 13:25		
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	
Perfluorooctanoic acid (PFOA)	ND			1.3	0.65	ug/Kg	æ	05/23/17 13:25	05/31/17 03:04	10 A
Perfluorononanoic acid (PFNA)	ND			1.3		ug/Kg	₽	05/23/17 13:25	05/31/17 03:04	
Perfluorodecanoic acid (PFDA)	ND	4		1.3		ug/Kg	· 🛱	05/23/17 13:25	05/31/17 03:04	
Perfluoroundecanoic acid (PFUnA)	0.79	J		1.3	0.68	ug/Kg	¢	05/23/17 13:25	05/31/17 03:04	2
Perfluorododecanoic acid (PFDoA)	ND		12	1.3		ug/Kg	₽	05/23/17 13:25		
Perfluorotridecanoic Acid (PFTriA)	ND	÷ .		1.3		ug/Kg	ø		05/31/17 03:04	
Perfluorotetradecanoic acid (PFTeA)	ND			1.3		ug/Kg	\$		05/31/17 03:04	
Perfluorobutanesulfonic acid (PFBS)	ND			1.3		ug/Kg	*		05/31/17 03:04	a 18
Perfluorohexanesulfonic acid (PFHxS)	1.9			1.3	0.75	ug/Kg	, ¤		05/31/17 03:04	
Perfluoroheptanesulfonic Acid (PFHpS)	3.6			1.3		ug/Kg	¢		05/31/17 03:04	
Perfluorodecanesulfonic acid (PFDS)	ND			1.3		ug/Kg	¢		05/31/17 03:04	- ¹ 43
Perfluorooctane Sulfonamide (FOSA)	ND			1.3	0.51	ug/Kg	Ċ.	05/23/17 13:25	05/31/17 03:04	15
Isotope Dilution	%Recovery	Qualifier	Limit	ts	(注)こ (丸)			Prepared	Analyzed	Dil Fa
13C8 FOSA	9	•	25-1	50					05/31/17 03:04	
13C4 PFBA	27		25 - 1	50					05/31/17 03:04	
13C2 PFHxA	49		25-1	50					05/31/17 03:04	3
13C4 PFOA	48		25-1	50					05/31/17 03:04	
13C5 PFNA	43		25 - 1	50					05/31/17 03:04	
13C2 PFDA	63	÷ 12	25-1	50				05/23/17 13:25	05/31/17 03:04	36 B

Client Comple Deculte

	Client Sample ID: xxxx-08 Date Collected: 05/18/17 11:20 Date Received: 05/20/17 11:50	llected: 05/18/17 11:20					Lab Sa		xxx-19 ix: Solid ids: 15.8
	Method: 537 (modified) - Fluor Analyte	rinated Alkyl Substances Result Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
trcsolutions.com	Perfluorobutanoic acid (PFBA)	ND	1.3	0.41	ug/Kg	ā	05/23/17 13:25	05/31/17 03:04	1
	Perfluoropentanoic acid (PFPeA)	ND	1.3	0.83	ua/Ka	Ω.	05/23/17 13:25	05/31/17 03:04	37 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 **1633:** ASAP to 7 days to 28 days to 90 days, depending on storage and analyte





	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)
Example	Perfluorotridecanoic Acid (PFTrA)
	Perfluorotetradecanoic acid (PFTeA)
PFAAs:	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

NEH new environmental horizons, inc

- 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

	Lab Sample ID: MB 320-400500/ Matrix: Water Analysis Batch: 400716	Client Sample ID: Method Blank Prep Type: Total/NA Prep Batch: 400500					
	Analysis Baten. 400110	MB MB				Trop Duten.	400500
	Analyte	Result Qualifier	RL	MDL Unit	D Prepared	Analyzed	Dil Fac
		0.858 J ND	2.0	0.35 ng/L	08/03/20 04:46	08/03/20 14:47	′ 1
متعاد المعالينا ويترو منا وما الأبير وتاريه	ill be in analytical data package		2.0	0.49 ng/L	08/03/20 04:46		
suits will be in analytical data			2.0	0.58 ng/L	08/03/20 04:46		
		ND	2.0	0.25 ng/L	08/03/20 04:46		
	Ferridorooctanoic acid (FFOA)	ND	2.0	0.85 ng/L	08/03/20 04:46		
	Perfluorononanoic acid (PFNA)	ND	2.0	0.27 ng/L	08/03/20 04:46		
	Perfluorodecanoic acid (PFDA)	ND	2.0	0.31 ng/L	08/03/20 04:46		
	Perfluoroundecanoic acid (PFUnA)	ND	2.0	1.1 ng/L	08/03/20 04:46		
	Perfluorododecanoic acid (PFDoA)	ND	2.0	0.55 ng/L	08/03/20 04:46		
	Perfluorotridecanoic acid (PFTriA)	ND	2.0	1.3 ng/L	08/03/20 04:46		
	Perfluorotetradecanoic acid (PFTeA)	ND	2.0	0.29 ng/L	08/03/20 04:46		
	Perfluorobutanesulfonic acid (PFBS)	ND 0.270 J	2.0 2.0	0.20 ng/L	08/03/20 04:46		
	Perfluorohexanesulfonic acid (PFHxS)			0.17 ng/L	08/03/20 04:46		
	Perfluoroheptanesulfonic Acid (PFHpS)	ND	2.0	0.19 ng/L	08/03/20 04:46	00/03/20 14.4/	
	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-methylperfluorooctanesulfonamidoa	ND	20	3.1 ng/L	08/03/20 04:46		
	cetic acid (NMeFOSAA) N-ethylperfluorooctanesulfonamidoac	ND	20	1.9 ng/L	08/03/20 04:46	08/03/20 14:47	1
	etic acid (NEtFOSAA) 6:2 FTS	ND	20	2.0 ng/L	08/03/20 04:46	08/02/20 14-47	· 1
	8:2 FTS	ND	20	2.0 ng/L	08/03/20 04:46		
I '	0.2113	NB	20	2.0 Hg/L	0000720 04.40	00100/20 14:47	
	PFOS in	Blank :	= 2	ng/L			
10x Blank = 20 ng/L		10v		nk -	20 n	σ/I	
10X Dialik – 20 lig/L	•	TOX	Dic	-	2011	8/ L	
0,						0.	

Sample conc = 120 ng/L

Real Hit

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
 - ¹³C₄PFBA is EIS associated with PFBA
 - ¹³C₄PFOS 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

Concentration Target PFAS = <u>Target PFAS Area * True Concentration Isotope</u> Area EIS * Calibration Factor EPA 537 and ASTM Method do NOT utilize isotope dilution

DoD QSM requires isotope dilution





PFAS Analytical Reports



	12	lient: xxx			Client S	ample F	Results	Lab Jo	b ID: xxx	oox .	
Tructual converte manuference de forme		Client Sa Date Colle	e: xxxxx Site ample ID: xxxx-08 cted: 05/18/17 11:20		0 100			La			rix: Soli
Typical sample result summary form	-		ived: 05/20/17 11:50 537 (modified) - Fluor	rinated Alkyl	Substance	5		+ 10 		Percent Soli	ds: 15
		Analyte		Result Q	Qualifier	RL	MDL Unit			Analyzed	
Number of PFAS reported		Perfluorobut	tanoic acid (PFBA)	ND	8	1.3	0.41 ug/Kg 0.83 ug/Kg)5/31/17 03:04	
	S15320032-0-0-0-0					.3	0.45 ug/Kg			5/31/17 03:04	
Isotope Dilution	%Recove	erv	Qualifier	1	imits	.3	0.56 ug/Kg	☆ 05/23/1	7 13:25 0	5/31/17 03:04	
		/	second		- 1111163	.3	0.65 ug/Kg			5/31/17 03:04	
13C8 FOSA		9	*	5	25 - 15	3	0.53 ug/Kg	☆ 05/23/1	7 13:25 0	5/31/17 03:04	
					0-10		0.36 ug/Kg			5/31/17 03:04	
Dilution re 13C4 PFBA		27		0	DE 16	o 3	0.68 ug/Kg	© 05/23/1	7 13:25 0	5/31/17 03:04	
Dilution refer		21		4	25 - 15	U .3	0.77 ug/Kg			05/31/17 03:04	
13C2 PFHxA		10				3	0.59 ug/Kg			05/31/17 03:04 05/31/17 03:04	
Collection		49		2	25 - 15	U g	0.37 ug/Kg 0.66 ug/Kg			05/31/17 03:04	
Collection dated area						3	0.75 ug/Kg			05/31/17 03:04	
13C4 PFOA		48		2	25 - 15	0	0.75 ug/Kg	© 05/23/	17 13:25	05/31/17 03:04	4
Percent solids (dry weight)		(PFHpS)	canesulfonic acid (PFDS)	ND		1.3	0.46 ug/Kg			05/31/17 03:04	
			tane Sulfonamide (FOSA)	ND		1.3	0.51 ug/Kg			05/31/17 03:04	
		Isotope Dil	lution	%Recovery (Qualifier	Limits		Pre	pared	Analyzed	Dil
Isotope Dilution recoveries		C8 FOSA			• • •	25 - 150		05/23/	17 13:25	05/31/17 03:04	i —
isotope Dilution recoveries		C4 PFBA		27		25 - 150				05/31/17 03:04	
		C2 PFHx		49		25-150				05/31/17 03:04	
		13C4 PFO/ 13C5 PFN/		48 43	2.10	25 - 150 25 - 150				05/31/17 03:04 05/31/17 03:04	
		13C2 PFDA		63		25-150				05/31/17 03:04	
		13C2 PFUr		64		25 - 150		05/23/	17 13:25	05/31/17 03:04	1
		13C2 PFDc	A	57		25 - 150				05/31/17 03:04	
		1802 PFH>		65		25 - 150	2 83 A			05/31/17 03:04	
Results will be in analytical data package		13C4 PFOS 13C4-PFH		49 47		25 - 150 25 - 150				05/31/17 03:04 05/31/17 03:04	
		13C5 PFPe		41		25-150				05/31/17 03:04	
		Mothod	537 (modified) - Fluor	ringtod Alley	Substance	e - DI		5 B			
		Analyte	537 (modified) - Fluor	Result C		RL	MDL Unit	D Pre	pared	Analyzed	Dil
			octanesulfonic acid	930		13	8.0 ug/Kg	₩ 05/23/	17 13:25	05/31/17 13:37	1
		Isotope Dil	lution	%Recovery (Qualifier	Limits			pared	Analyzed	Dil
ompanies.com		13C4 PFO3	S	76		25-150	100 C	05/23/	17 13:25	05/31/17 13:37	/

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.

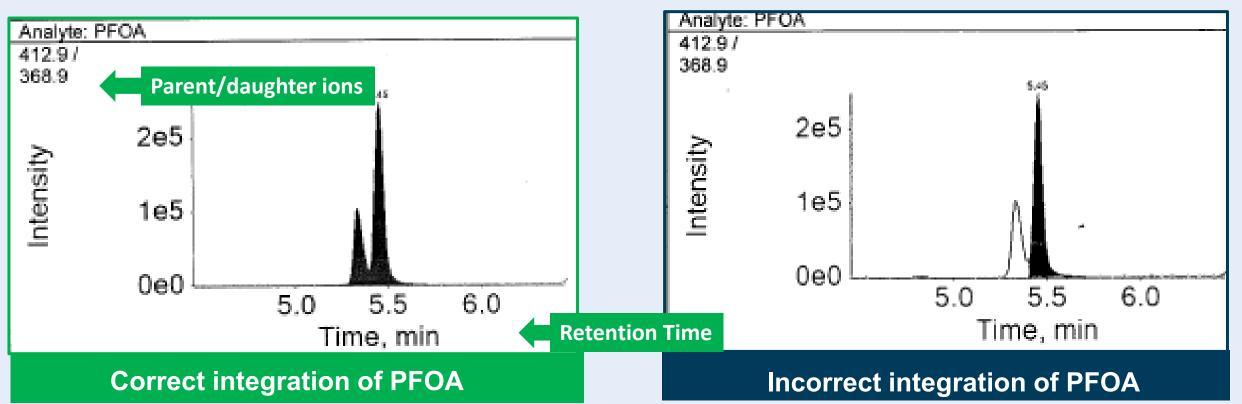
Linear & Branched Isomers





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

Only obvious in Level 4 analytical data package



Currently labs reporting L&B consistently for: PFHxS, PFOS, PFOA, NMeFOSAA, NEtFOSAA **New draft EPA 1633**: will also include L&B for PFNA, PFOSA, NMeFOSA, NEtFOSA, NEtFOSE, NMeFOSE





TISSUE LC MS/MS INTERFERENCES

Compound	Parent	lon 1	lon 2	lon 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 positive in eggs since Bile Acids have common transition
- PFOS measured using 499→99 allowing Interference to be eliminated

LCS & MS/MSD

- Laboratory Control Sample (LCS)
 - Blank Matrix spiked with all target compounds
 - Required for each Analytical Batch
- Matrix Spike/Matrix Spike Duplicate (MS/MSD)
 - Site sample spiked with all target compounds
 - Only performed if extra sample is collected and if analysis requested on Chain-of-Custody





LCS & MS/MSD Evaluation

✓ Were all recoveries within the acceptance limits? → ACCURACY

✓ Were all RPDs within the acceptance limits?

If 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

LCS affects all samples in Extraction Batch but MS/MSD affects only the unspiked sample for the compound(s) outside criteria





Lab QA/QC 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
Extraction IS, Matrix Spikes	 Low recoveries High recoveries 	LOW BIAS HIGH BIAS } Sample-Specific Compound-Specific

Summary of Potential PFAS-Specific Biases **NEH** Revented **TRC**



PFAS	Bias	Reason for Bias
Long-chain PFAS (≥ C8)	Low bias	Not using entire aqueous sample for extraction
Long-chain PFAS (≥ C8)	Low bias	No methanol rinse on aqueous sample bottle
Short-chain PFAS	Low bias	SPE cartridge goes dry
FOSAs/FOSEs	Low bias	Extract goes to dryness
Long-chain PFAS and PFSAs	Low bias	Particulates not included in extraction of aqueous samples
PFBA, NMeFOSE, NEtFOSE, PFMPA, PFMBA	High bias (J values)	No confirmation ions available
PFOA data prior to 2016	Low bias	May not include branched isomers
PFOS in fish tissue	Potential false positives	Interference from TCDA

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



Thank you

ппапк уоц

Questions?

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