PFAS: Assessing Laboratory Data Quality

NEWMOA Webinar
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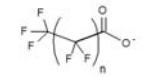
SGS AXYS

PER AND POLYFLUORINATED COMPOUNDS (PFAS/PFC)

PFCAs incl. PFOA

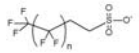


n=2, PFBA; n=3, PFPeA;
n=4, PFHxA; n=5, PFHpA;
n=6, PFOA; n=7, PFNA;
n=8, PFDA; n=9, PFUnDA;
n=10, PFDoDA;

PFSA incl. PFOS

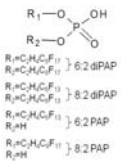
n=3, PFBS
n=5, PFHxS
n=7, PFOS

FTS

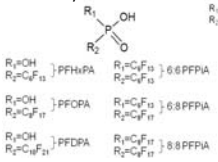


n=3, 4:2 FTS
n=5, 6:2 FTS
n=7, 8:2 FTS

PAP, DiPAP



PFPA/PFPiA



FTOH

Poly- or perfluorinated alkyl substances (PFAS) or Perfluorocarbons (PFC) – General term for all chemicals formed from carbon chains with fluorine substituting some/all of the hydrogens on the chain

- **C-F bond** very strong
- **Unique properties** – repel water and oil, surfactant, stable
- **Diverse and complex** chemistries based on product use
- **Precursors** FTS (Fluorotelomer Sulfonate) , PAP (Polyfluorinated Alkyl Phosphate Esters), PFPA (Polyfluorinated phosphonic acid), FTOH (Fluorotelomer alcohol) can all degrade to Carboxylates and Sulfonates

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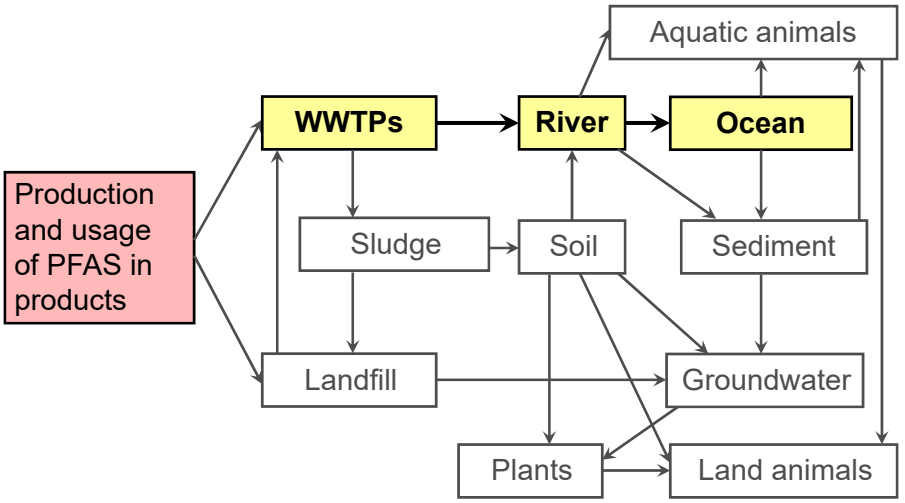
Environmental Fate of PFAS



Ahrens et al. *J. Environ. Monitor.* 2011, 13, 20-31

Analysis of PFAS

USEPA Method 537.1 (version 1.0, 2018)

- Only applicable to Drinking Water samples
- No Recovery Correction
- Analyte list limited - 18 PFAS (14 PFAS required by Method 537 + 4 added compounds)
- New DW method (**Summer 2019**) - 25 PFAS includes 11 "short chain" compounds

ASTM D7979-17 & **ASTM D7968 - 17a** (2017)

- Non-Drinking water Aqueous & Soils
- No Recovery Correction
- 25 PFAS

Analysis of PFAS

SW-846 Method 8327 (Summer 2019)

- Direct Injection
- Non-Drinking Water Aqueous
- 24 PFAS
- No Recovery Correction

SW-846 Method 8328 (late 2019)

- Solid Phase Extraction/Isotope Dilution (SPE-ID)
- Non-Drinking Water Aqueous & Solids
- 24+ PFAS
- Recovery Correction

Lab-Specific Methods

- Modifications to the above methods
- Vary lab-to-lab

Analysis of PFAS

Total Oxidizable Precursors (TOP)

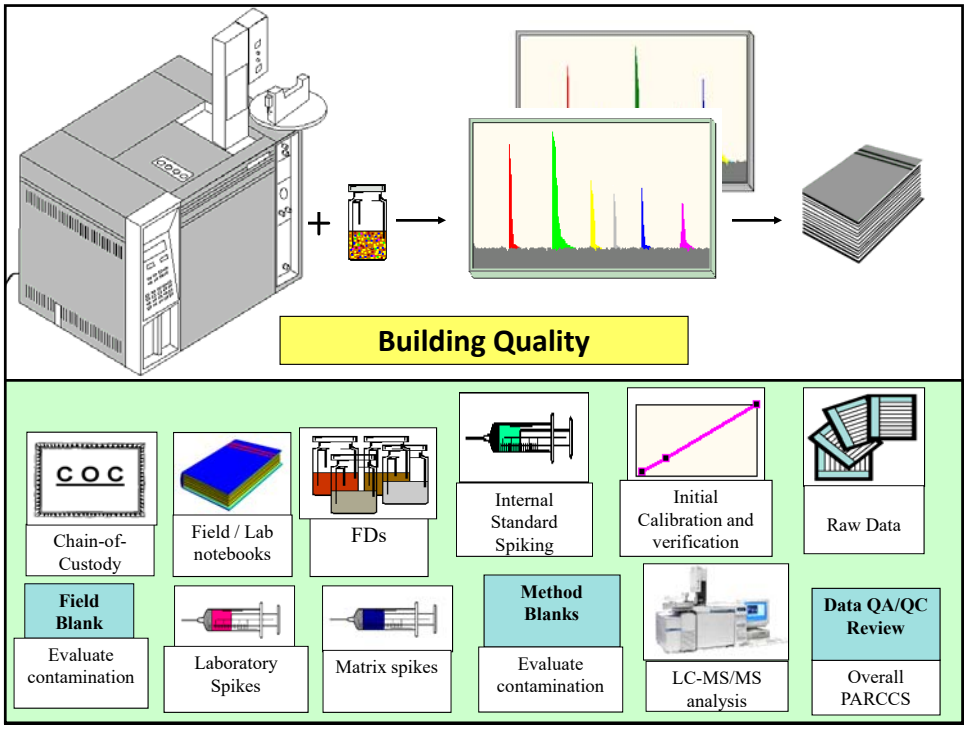
- Comparison of LCS-MS/MS results for sample pre- and post-oxidation
- Useful for evaluating Precursor potential – may be biased low

Proton Induced Gamma-ray Emission (PIGE)

- Non-destructive technique for Total Fluorine

Adsorbable Organic Fluorine /Combustible Ion Chromatography (AOF/CIC)

- Destructive technique for Total Fluorine

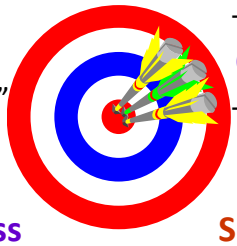


Data Quality Using PARCCS

Precision
- Variability, reproducibility
- QC = replicates

Accuracy
- bias from "true"
- QC = blanks, spikes, calibration

Representativeness
- Data point *vs.* population
- QC = field duplicates, sample locations



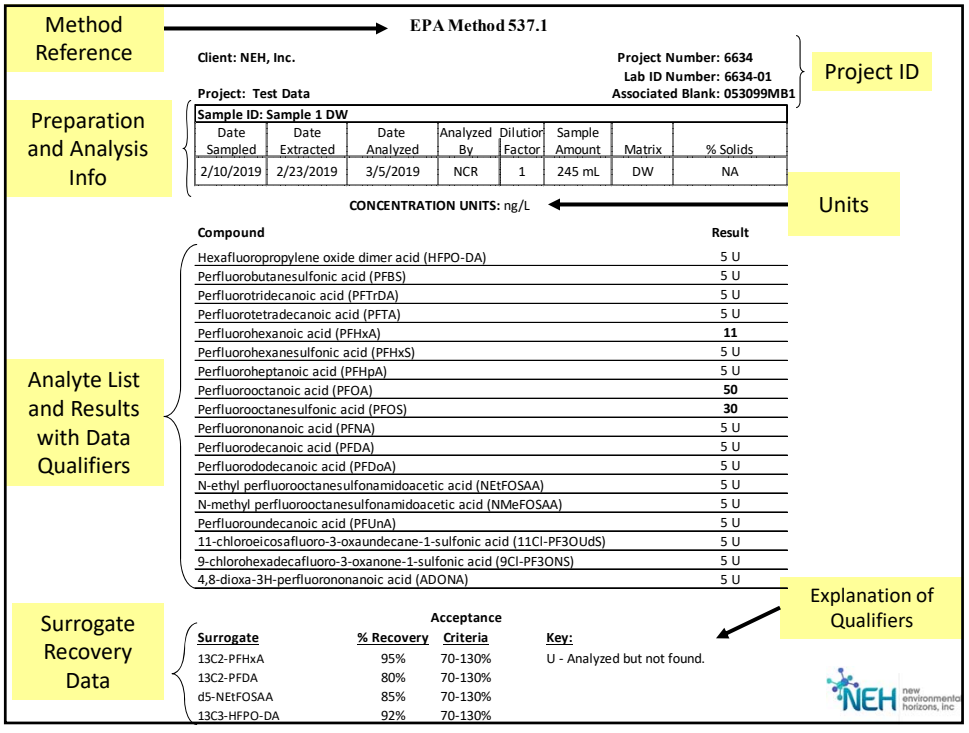
Comparability
- Temporal and methodological consistency
- field *vs.* lab data

Completeness
- amount of data planned *vs.* usable data collected

Sensitivity
- Quantitation Limits
- Regulatory Standards

Types of Data Reports

1. Summary Data Package - ***Recommended***
   - Narrative explaining Method of Analysis and any issues with sample receipt and analysis
   - Sample Results (including FB and FD) + Surrogate recoveries
   - QC results (MB, LCS, MS, & MSD or FD)
   - Executed Chain-of-Custody
2. Full Deliverable – all of above + raw data
3. Result Forms/Tables only – ***Not Recommended***



Specific Laboratory QA/QC For PFAS

- Sample preservation
- Sample Holding Times / Analytical Batches (≤ 20 samples)
- QC Samples required for each Analytical Batch:
  - Laboratory Reagent Blank (LRB) / Method Blank (MB)
  - Laboratory Fortified Blank (LFB) / Laboratory Control Sample (LCS)
  - Laboratory Fortified Sample Matrix (LFSM) / Matrix Spike (MS)
  - Laboratory Fortified Matrix Sample Duplicate (LFSMD) or Field Duplicate (FD)
- Surrogates added to all samples & QC prior to extraction
- Internal Standards added to all extracts prior to analysis

Holding Time

- Check sample data sheet for HT acceptance

Date Sampled	Date Extracted	Date Analyzed
2/20/19	2/23/19	3/5/19

Date extracted - Date sampled ≤ Preparation Holding Time
Method 537.1 preparation HT = 14 days; 2/23/19 - 2/20/19 = 3 days: HT OK

Date analyzed - Date extracted ≤ Analytical Holding Time
Method 537.1 analytical HT = 28 days; 3/5/19 - 2/23/19 = 11 days: HT OK

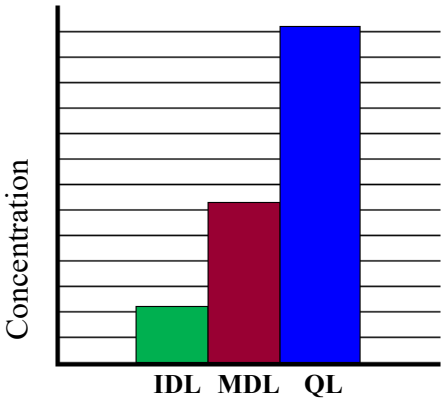
Preservation & Holding Time

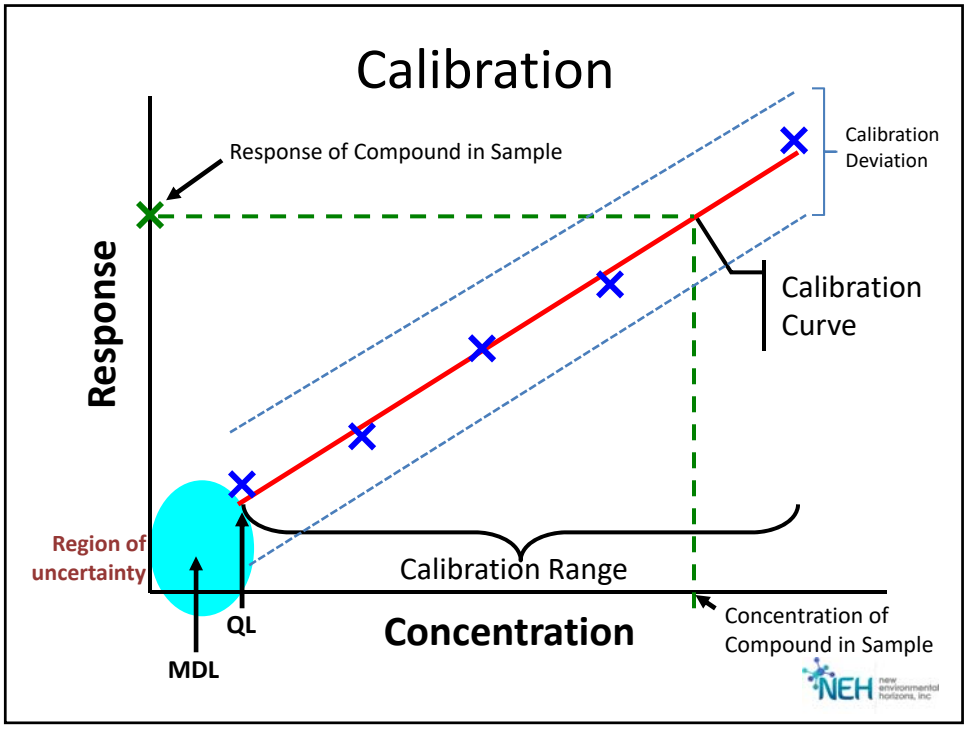
- Method 537.1 requires addition of Trizma
  - Acts as a buffer and removes free-chlorine from Drinking Water samples
- Samples shipped cold (< 10 ^{o}C) to lab
- If Preservation not correct or Holding Time (HT) exceeded – potential for loss of PFAS content and false negative results

If Preservation and/or HT a problem, all results are considered uncertain with possible low bias

Detection and Reporting Limits

- **Instrument Detection Limit** (IDL) is the "Best" the instrument can detect
- **Method Detection Limit** (MDL or LOD) is the "Best" the instrument can detect by the method - statistically
- **Quantitation Limit** (QL/RL/LOQ) is the "Practical" level of accurate quantitation – **Must be supported by calibration curve and should be < Project Level of Concern**





Recovery Surrogates *vs.* Isotope Dilution Surrogates

Similarities:

Added directly to the sample prior to preparation and analysis

Differences:

Recovery Surrogates

- Surrogates used to *infer* accuracy of preparation and analysis
- Internal Standards spiked prior to analysis to quantitate surrogates and target compounds

Isotope Dilution Surrogates

- Labeled Isotopes of most target compound (e.g., 13C4-PFOA, 13C4-PFOS) used for quantitation
- Loss in Isotope mirrors loss of Unlabeled compound = data are **Recovery-Corrected**

Recovery Surrogates *vs.* Isotope Dilution Surrogates

Non- Isotope Dilution Methods

$$\text{Compound Concentration} \equiv \frac{\text{Compound Response}}{\text{Internal Standard Response}} \qquad \text{Recovery Surrogate Concentration} \equiv \frac{\text{Rec. Surrogate Response}}{\text{Internal Standard Response}}$$

Compound = Target PFAS

Rec. Surrogate = Recovery Surrogate

Isotope Dilution Methods

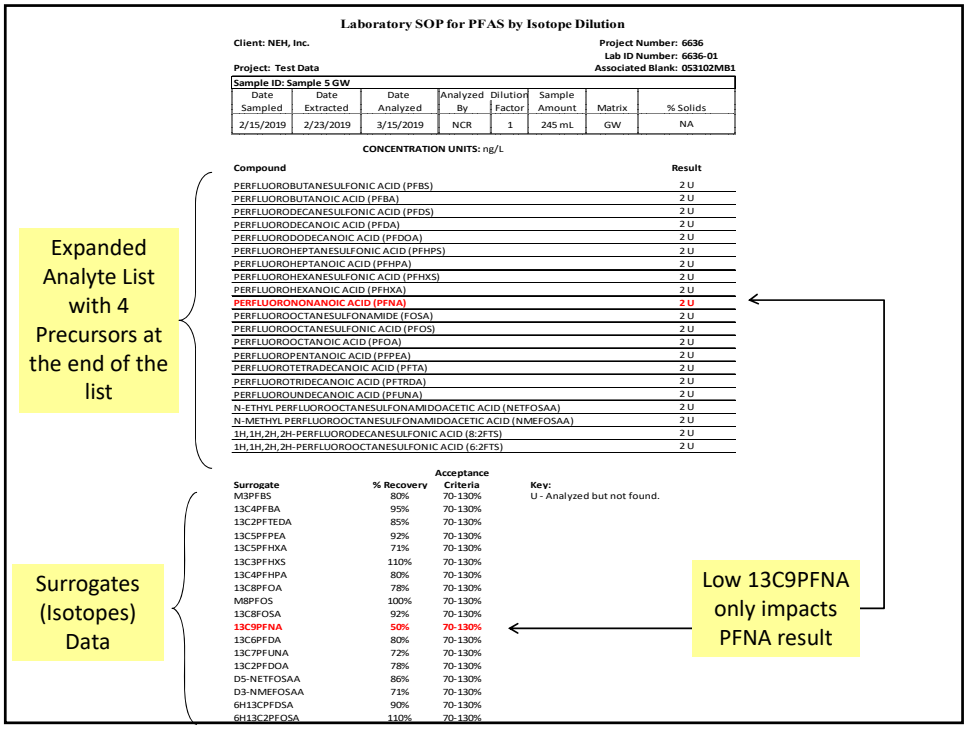
$$\text{Compound Concentration} \equiv \frac{\text{Compound Response}}{\text{ID Surrogate Response}} \qquad \text{ID Surrogate Concentration} \equiv \frac{\text{ID Surrogate Response}}{\text{Internal Standard Response}}$$

Compound = Target PFAS

ID Surrogate = Isotope Dilution

Surrogate Recovery Problems

- Surrogate recovery below criteria: potential low bias in data
  - Due to lab error or matrix effects
- Surrogate recovery above criteria: potential high bias
  - Due to interferences or instrument issues
- **Non-Isotope Dilution Analysis** = Detected and non-detected results may be uncertain
- **Isotope Dilution Analysis** = Only compound(s) associated with Isotope affected. Uncertain whether data are biased at all since results are recovery corrected



Laboratory SOP for PFAS by Isotope Dilution

Client: NEH, Inc.
Project: Test Data
Project Number: 6636
Lab ID Number: 6636-01
Associated Blank: 053102MB1

Sample ID: Sample 5 GW

Date Sampled	Date Extracted	Date Analyzed	Analyzed By	Dilution Factor	Sample Amount	Matrix	% Solids
2/15/2019	2/23/2019	3/15/2019	NCR	1	245 mL	GW	NA

CONCENTRATION UNITS: ng/L

Compound	Result
PERFLUOROBUTANESULFONIC ACID (PFBS)	2 U
PERFLUOROBUTANOIC ACID (PFBA)	2 U
PERFLUORODECANESULFONIC ACID (PFDS)	2 U
PERFLUORODECANOIC ACID (PFDA)	2 U
PERFLUORODODECANOIC ACID (PFDOA)	2 U
PERFLUOROHEPTANESULFONIC ACID (PFHPS)	2 U
PERFLUOROHEPTANOIC ACID (PFHPA)	2 U
PERFLUOROHEXANESULFONIC ACID (PFHXS)	2 U
PERFLUOROHEXANOIC ACID (PFHXA)	2 U
PERFLUORONONANOIC ACID (PFNA)	2 U
PERFLUOROOCTANESULFONAMIDE (FOSA)	2 U
PERFLUOROOCTANESULFONIC ACID (PFOS)	2 U
PERFLUOROOCTANOIC ACID (PFOA)	2 U
PERFLUOROPENTANOIC ACID (PFPEA)	2 U
PERFLUOROTETRADECANOIC ACID (PFTA)	2 U
PERFLUOROTRIDECANOIC ACID (PFTRDA)	2 U
PERFLUOROUNDECANOIC ACID (PFUNA)	2 U
N-ETHYL PERFLUOROOCTANESULFONAMIDOACETIC ACID (NETFOSAA)	2 U
N-METHYL PERFLUOROOCTANESULFONAMIDOACETIC ACID (NMEFOSAA)	2 U
1H,1H,2H,2H-PERFLUORODECANESULFONIC ACID (8:2FTS)	2 U
1H,1H,2H,2H-PERFLUOROOCTANESULFONIC ACID (6:2FTS)	2 U

Surrogate	% Recovery	Acceptance Criteria
M3PFBS	80%	70-130%
13C4PFBA	95%	70-130%
13C2PFTEDA	85%	70-130%
13C5PFPEA	92%	70-130%
13C5PFHXA	71%	70-130%
13C3PFHXS	110%	70-130%
13C4PFHPA	80%	70-130%
13C8PFOA	78%	70-130%
M8PFOS	100%	70-130%
13C8FOSA	92%	70-130%
13C9PFNA	50%	70-130%
13C6PFDA	80%	70-130%
13C7PFUNA	72%	70-130%
13C2PFDOA	78%	70-130%
D5-NETFOSAA	86%	70-130%
D3-NMEFOSAA	71%	70-130%
6H13CPFDSA	90%	70-130%
6H13C2PFOSA	110%	70-130%

Key:
U - Analyzed but not found.

Expanded Analyte List with 4 Precursors at the end of the list

Surrogates (Isotopes) Data

Low 13C9PFNA only impacts PFNA result

Blank Samples

- Method Blank (MB) – lab-generated
  - Evaluates whether contamination may have been introduced by the laboratory
  - Associated with all samples in the Analytical Batch
- Field Blank (FB) / Equipment Blank (EB)
  - Evaluates whether contamination may have been introduced during sample collection and transport
  - Associated with specific field sample results

Compare Blank results to Sample results to evaluate potential lab/field contamination that may cause high bias or false positives in field sample data

Laboratory Control Sample (LCS)

- LCS = Method Blank that is spiked with all the PFAS compounds of interest
- LCS Recoveries = within acceptance criteria as specified in Method or project QAPP
- LCS recovery outside criteria = impact for affected compound for all samples in the Analytical Batch

Compare LCS results to Method / QAPP acceptance criteria to evaluate potential accuracy / bias in associated Sample data; may qualify results

Example LCS Evaluation

Compound	%Recovery	Acceptance Criteria	Issue?
PFOA	75%	70-130%	No
PFOS	80%	70-130%	No
PFNA	**60%**	70-130%	PFNA in all associated samples may be biased low
FOSA	**145%**	70-130%	Non-detects acceptable but detected results may be biased high

Matrix Spike Samples (MS/MSD)

- MS/MSD = Sample aliquots spiked with all PFAS compounds of interest
- MS/MSD Recoveries = within acceptance criteria as specified in Method or project QAPP
- If MS/MSD recovery outside criteria = impact for affected compound in the **unspiked sample**
- If MS/MSD RPD outside criteria = results for **unspiked sample** uncertain

Compare MS/MSD results to Unspiked Sample to evaluate potential accuracy / bias and precision issues in Unspiked Sample data; may qualify results

Example MS/MSD Evaluation

Cpd	Unspiked Sample (ng/L)	MS %Rec	MSD %Rec	RPD	Acceptance Criteria Recovery/RPD	Issue?
PFOA	5 U	75%	80%	6.4%	70-130% / 30%	No
PFOS	5 U	71%	128%	**57.3%**	70-130% / 30%	Imprecision may indicate result is non-representative and uncertain
PFNA	8	**60%**	**57%**	5.1%	70-130% / 30%	PFNA in unspiked sample may be biased low
FOSA	5 U	**145%**	**145%**	0%	70-130% / 30%	No Issue – Non-detect for Unspiked sample accurate as reported

Data Comparability

Precision = variability and reproducibility of results

- Assessed by evaluating the Relative Percent Difference (RPD) between duplicate results or Percent Relative Standard Deviation (RSD) between more than 2 results

$$RPD = \frac{|(Result\ 1 - Result\ 2)|}{\frac{(Result\ 1 + Result\ 2)}{2}}$$

Compare RPD to Method / QAPP criteria and possibly qualify results due to imprecision

Data Comparability

Factors Affecting Comparability

- Changes in Field Collection Techniques
  Elimination or introduction of PFAS during Sampling
- Not using Isotope Dilution for Recovery Correction of data
  Sample data may vary by ±30% based on Surrogate recovery acceptance limits of 70-130%
- Degradation of Precursors
  Formation of compounds of concern over time
- Not including Branched Isomers in reporting of data
  Historic data may not have included branched isomers
- Sensitivity differences in data sets (QLs not the same)

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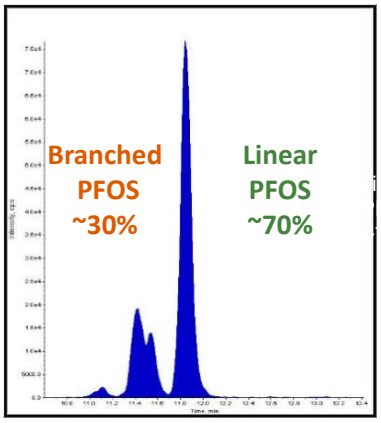
LINEAR VS. BRANCHED ISOMERS



- Eleven *known* isomers of PFOS
- 499>80 and 499>99 transitions have different relative response factors for the linear and the branched isomers.
- Quantitative biases possible depending on standard type and MRM transitions used for quantitation
- Distribution/half lives in tissue are different between linear and branched
- Speciation is more important in research applications. Contaminant analysis issues centered around accuracy of quantitation

Riddell, N. et. al, Environ Sci. Technol. 2009 (43) 7902-7908

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Sampling QA - Representativeness and Precision

- **Representativeness** of samples to site conditions acceptable?
  - Review MS/MSD and FD precision as quantitative measures of quality – Heterogeneity issues
  - Generally, results may be considered uncertain due to precision QC results but are not rejected

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Field Duplicate Comparison

Compound	QL (ng/L)	Sample Result (ng/L)	FD result (ng/L)	RPD	Issue?
PFOA	2	2 U	2 U	NC	No: Both results are non-detect
PFAS	2	11	8	32%	Yes: Both results > 2 x QL and RPD > 30%
PFNA	2	2.2	3.9	56%	Yes: Both results < 2 x QL and RPD > 50%
FOSA	2	9	10	11%	No: Both results > 2 x QL and RPD < 30%

Method 537.1 RPD acceptance: RPD ≤ 30% for values > 2x QL and RPD ≤ 50% for values < 2x QL

As a conservative approach, the highest of the two values should be associated with PFAS and PFNA for the sampling location

Usability Evaluation Example

Sample	Advisory Level (ng/L)	Result (ng/L)	Surrogate %R	LCS %R	MS/MSD %R/RPD	Issue?
A	70	5 U	High	High	OK	No: Non-detect accurate as reported
B	70	66	OK	OK	%R low	Yes: result may be biased low and really >70 ng/L
C	70	63	Low	High	OK	Maybe: conflicting bias
D	70	110	Low	OK	High	No: conflicting bias but 110 >70 ng/L

Must evaluate the cumulative effect of <u>all</u> Quality Control to determine Usability and whether an Action Level has been exceeded

Conclusion

- 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
  - *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 5.2 Consolidated Quality Systems Manual (QSM) for Environmental Laboratories*, Version 5.2 (DOD/DOE, 2018)
    http://www.denix.osd.mil/edqw/documents/documents/manuals/qsm-version-5-2-final-updated/

ITRC PFAS Resource

- **Seven Fact Sheets (available now) and Technical Guidance Document (late 2019)**
  - History and Use
  - Nomenclature Overview and Physicochemical Properties
  - Regulations, Guidance, and Advisories
  - Environmental Fate and Transport
  - Site Characterization Considerations, Sampling Techniques and Laboratory Analytical Methods
  - Remediation Technologies and Methods
  - Aqueous Film Forming Foam

https://pfas-1.itrcweb.org/