Limitation of PFAS Data and Recommendations to Obtain Appropriate Data for Environmental Decision Making

NJWEA

AAEES - Contaminants of Emerging Concern (CECs)

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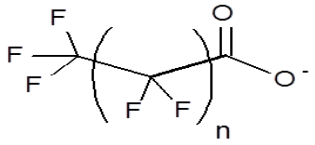
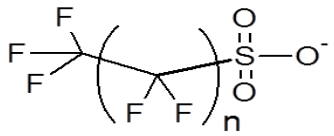
PER AND POLYFLUORINATED COMPOUNDS (PFAS/PFC)

PFCAs incl. PFOA



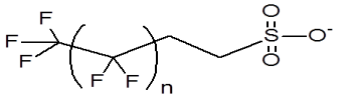
n=2, PFBA; n=3, PFPeA;
n=4, PFHxA; n=5, PFHpA;
n=6, PFOA; n=7, PFNA;
n=8, PFDA; n=9, PFUnDA;
n=10, PFDoDA;

PFSA incl. PFOS



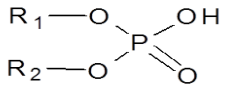
n=3, PFBS
n=5, PFHxS
n=7, PFOS

FTS



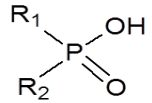
n=3, 4:2 FTS
n=5, 6:2 FTS
n=7, 8:2 FTS

PAP, DiPAP



R_1=$C_2H_4C_8F_{17}$, R_2=$C_2H_4C_8F_{17}$ } 6:2 diPAP
R_1=$C_2H_4C_6F_{13}$, R_2=$C_2H_4C_6F_{13}$ } 8:2 diPAP
R_1=$C_2H_4C_6F_{13}$, R_2=H } 6:2 PAP
R_1=$C_2H_4C_8F_{17}$, R_2=H } 8:2 PAP

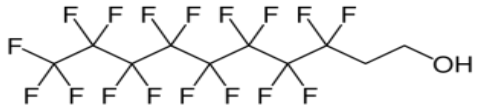
PFPA/PFPiA



R_1=OH, R_2=C_6F_{13} } PFHxPA
R_1=OH, R_2=C_8F_{17} } PFOPA
R_1=OH, R_2=$C_{10}F_{21}$ } PFDPA

R_1=C_6F_{13}, R_2=C_6F_{13} } 6:6 PFPiA
R_1=C_6F_{13}, R_2=C_8F_{17} } 6:8 PFPiA
R_1=C_8F_{17}, R_2=C_8F_{17} } 8:8 PFPiA

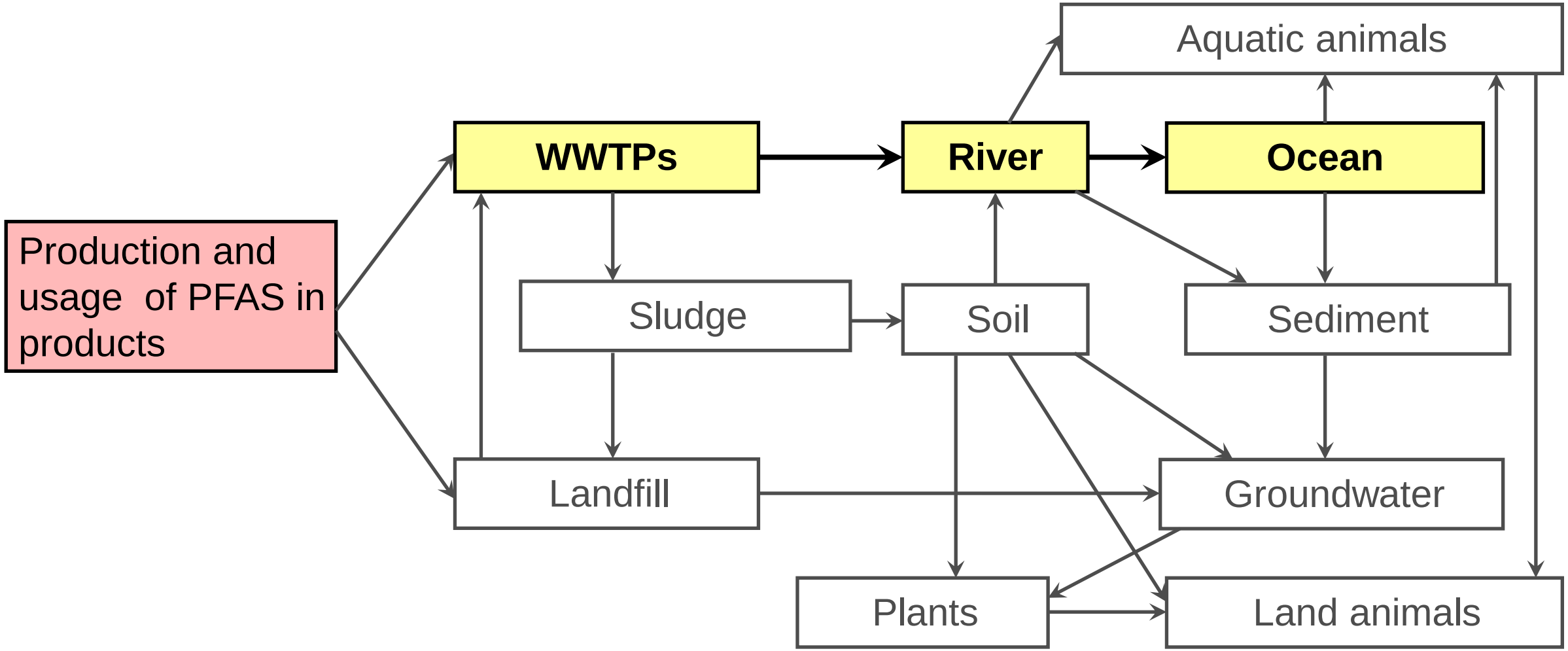
FTOH



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

Environmental Fate of PFCs



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

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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

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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

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Analytical Issues Begin With Collection of the Samples

DoD Requirements for Personnel Collecting Samples

- No Post-it Notes; No Notebooks; No Sharpies/Markers; No Gore-Tex or Tyvek material; No Cosmetics, insect repellants, sun block, lotions worn unless 100% natural; No Waterproof material; Nitrile Gloves MUST be worn at all times

All sources of possible cross-contamination need to be eliminated and/or Evaluated

- Use Disposable Equipment if Possible
- Decontaminate equipment, if necessary, with Alconox or Liquinox using Lab Certified "PFC-free" water
- Samples should be collected in High Density Polypropylene (HPDE) with Unlined HDPE screw Caps (Teflon-lined caps MUST NOT be used)
- Trip Blanks and Field Blanks should be collected

Field Sampling Protocols to Avoid Cross-Contamination During Water Sampling for Perfluorinated Compounds (PFCs); enclosure to Navy Drinking Water Sampling Policy for Perfluorochemicals Perfluorooctane Sulfonate and Perfluorooctanoic Acid, N45 Ser/15U132432, 14 SEP 15.

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***

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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

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

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

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

Compound = Target PFAS

Rec. Surrogate = Recovery Surrogate

Isotope Dilution Methods

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

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

Compound = Target PFAS

ID Surrogate = Isotope Dilution

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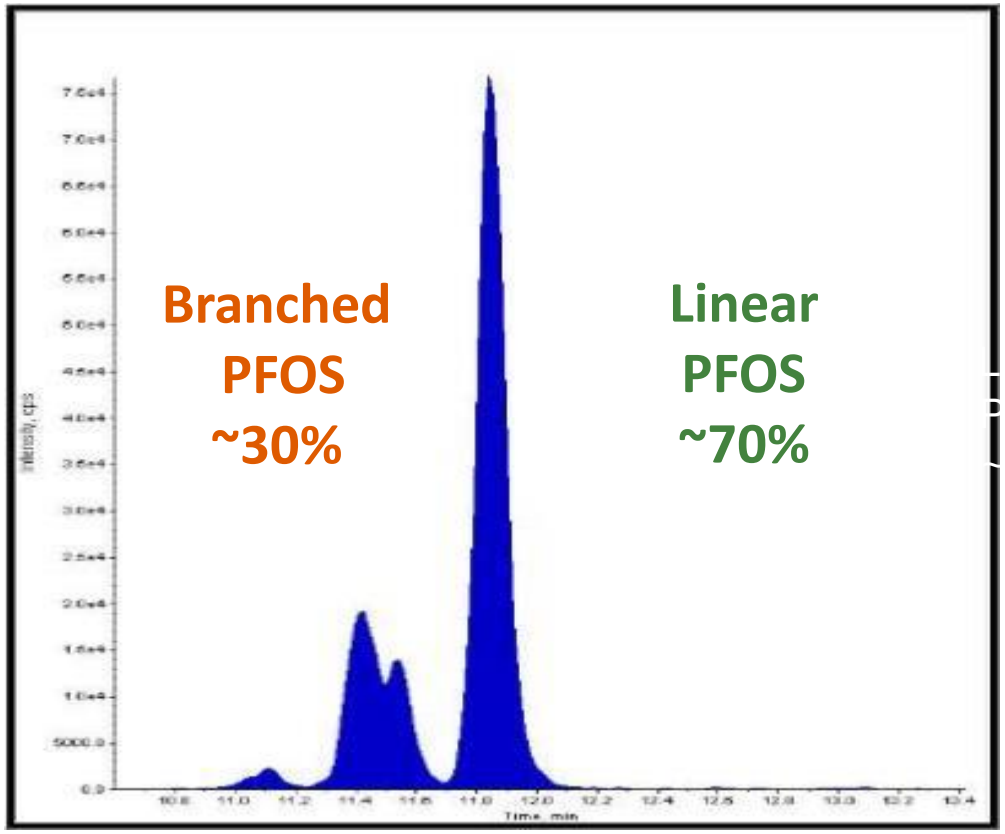
Surrogate Recovery Problems

- 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

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

Data Comparability - PFAS

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)
- Compound names being reported differently

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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

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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/

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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/

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