Down the Drain with PFAS: The Latest on Testing, Measuring, and Mitigating Community Water Contamination

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Collaborative on Health and the Environment (CHE) Webinar

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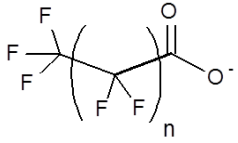
What Are Per- and Polyfluoroalkyl Substances (PFAS)?

- Large class of surfactants with unique chemical & physical properties that make many of them extremely persistent and mobile in the environment
- Used since 1940s in wide range of consumer and industrial applications

Source: open access images – bing.com

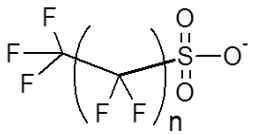
PER AND POLYFLUORINATED COMPOUNDS (PFAS/PFC)

PFCAs incl. PFOA



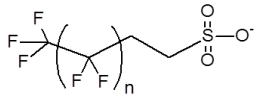
n=2, PFBA; n=3, PFPeA;
n=4, PFHxA; n=5, PFHpA;
n=6, PFOA; n=7, PFNA;
n=8, PFDA; n=9, PFUnDA;
n=10, PFDoDA;

PFSA incl. PFOS



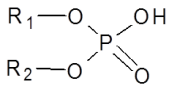
n=3, PFBS
n=5, PFHxS
n=7, PFOS

FTS



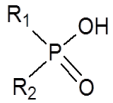
n=3, 4:2 FTS
n=5, 6:2 FTS
n=7, 8:2 FTS

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

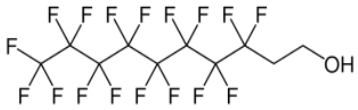
PFPA/PFPiA



$R_1=OH$, $R_2=C_6F_{13}$ } 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

Analysis of PFAS

- **USEPA Method 537** (version 1.1, 2009)
  - **Only applicable to Drinking Water samples**
  - **No recovery-correction**
  - **Analyte list limited - only 14 compounds**

- **ASTM D7979-17** & **ASTM D7968 - 17a** (2017)
  - **Applicable to non-Drinking water aqueous samples and soils**
  - **No recovery-correction**
  - **Analyte list expanded**

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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
- 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
- Lab-specific Methods
  - Modifications vary lab-to-lab

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ITRC PFAS Team

- Factsheets
  - History and Use (Nov. 2017, also Spanish ver.)
  - Naming Conventions & Physical and Chemical Properties (Nov. 2017)
  - Regulations, Guidance, and Advisories (Nov. 2017)*
  - Fate & Transport (Mar. 2018)
  - Site Characterization, Sampling Techniques, and Lab Analytical Methods (Mar. 2018)
  - Remediation Technologies (Mar. 2018)*
  - AFFF (to be published Aug. 2018)
- * Web-based, updated information tables
- Technical/Regulatory Document (to be published 2019)
- Internet Based Training (to go live in 2019)

DOD/DOE QSM 5.1

Table B-15 of QSM 5.1

- Focuses on PFAS analysis in Matrices other than Water
- **Establishes Quality Control (QC)**
  - Defines types of QC: Tune Check, Calibration Extracted Internal Standards, etc.
  - Minimum QC Frequency
  - QC Acceptance Criteria
  - QC Corrective Actions, Flagging Criteria, and Comments

***Consolidated Quality Systems Manual (QSM) for Environmental Laboratories*, Version 5.1 (DOD/DOE, 2017)**

http://www.denix.osd.mil/edqw/documents/documents/qsm-version-5-1-final/

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What Type of Data Do you Need?

- At a minimum: "Summary Data Package"
  - Cover Letter or Lab Narrative explaining the analyses performed and any deviations
  - Results for your Samples
  - Results for all Quality Control (recoveries for spiked compounds and results for Method Blanks & Laboratory Control Spike samples)
- **Critical Samples may require a "Full Deliverable"**

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Factors Affecting Analytical Results

- Background Contamination (field & lab)
  - Ubiquitous nature of PFAS
- Not quantitating Branched Isomers along with straight-chain Isomers
  - EPA Technical Advisory 815-B-16-021 (Office of Water, September 2016)
  - Quantitating Branched Isomers using Straight-chain isomer response factors
- Matrix Interferences causing Enhancement and/or Suppression of Analytical Signal

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Factors Affecting Analytical Results

- Not using Recovery-Correction through Isotope Dilution
  - EPA 537 & ASTM methods do not permit Isotope Dilution; but this is required by DOD/DOE
- Reporting Issues
  - Anions *vs.* Acids
- Temporal Issues for Sampling & Analysis
  - Conditions for Sample Collection
  - Partitioning of PFAS in extracts prior to analysis

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Surrogates *vs.* Isotope Dilution

Similarities:

- Added directly to the sample prior to preparation and analysis

Differences:

- **Surrogate Recovery**
  - Surrogates used to *infer* accuracy of preparation and analysis for all compounds reported
  - Internal Standards spiked just prior to analysis are used to quantitate surrogates and target compounds
- **Isotope Dilution Technique**
  - Labeled Isotopes of target compounds (e.g., 13C4-PFOA, 13C4-PFOS) used to quantitate the unlabeled compound in the sample
  - Loss in Isotope = loss of compound; data are **Recovery-Corrected** back to 100% for improved accuracy

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Analytical Recommendations

- Make sure lab has performed method of extraction and analysis on your matrix
- Use Isotope Dilution Technique & recovery-correction
- Extend List of Analytes to include C4- or C5-alkly acids & Precursors
- Modify sample extraction techniques and LC-MS/MS to eliminate PFAS to minimize background
- Include Branched Isomers
- Perform QC beyond method requirements *e.g.*, Field Blanks, Field Duplicates, SRMs, & MS/MSD

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Conclusions

- Field of Expertise expanding quickly
- Keep informed of changes to regulations & methods
  - ITRC Fact Sheets & Technical Guidance Documents
  - QSM 5.1 Table B-15
  - EPA Method Updates
- Use laboratories with experience in analysis & matrix
- Minimize Field and Lab contamination
- Perform data evaluation to ensure data are of acceptable quality

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