integral INSIGHT FOR AN EVOLVING WORLD

PFAS at Contaminated Sediment Sites

Evolving Technical, Regulatory, and Legal Priorities

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October 17, 2023

Topics

- PFAS 101: chemistry, uses, and properties (M. Henning)
- Investigation strategies for PFAS at sediment sites (J. Gasper)
- Regulatory/legal setting for PFAS at sediment sites (R. Fox)
- Q&A

PFAS 101

Defining PFAS

- Class of organofluorine chemicals manufactured and used for decades in applications such as firefighting foams, food packaging, textiles, etc.
- PFAS have carbon atoms linked to each other and bonded to fluorine atoms at most or all available carbon bonding sites.
- Often includes the manufactured substances + salts, degradants, impurities, metabolites, by-products, and other transformation products

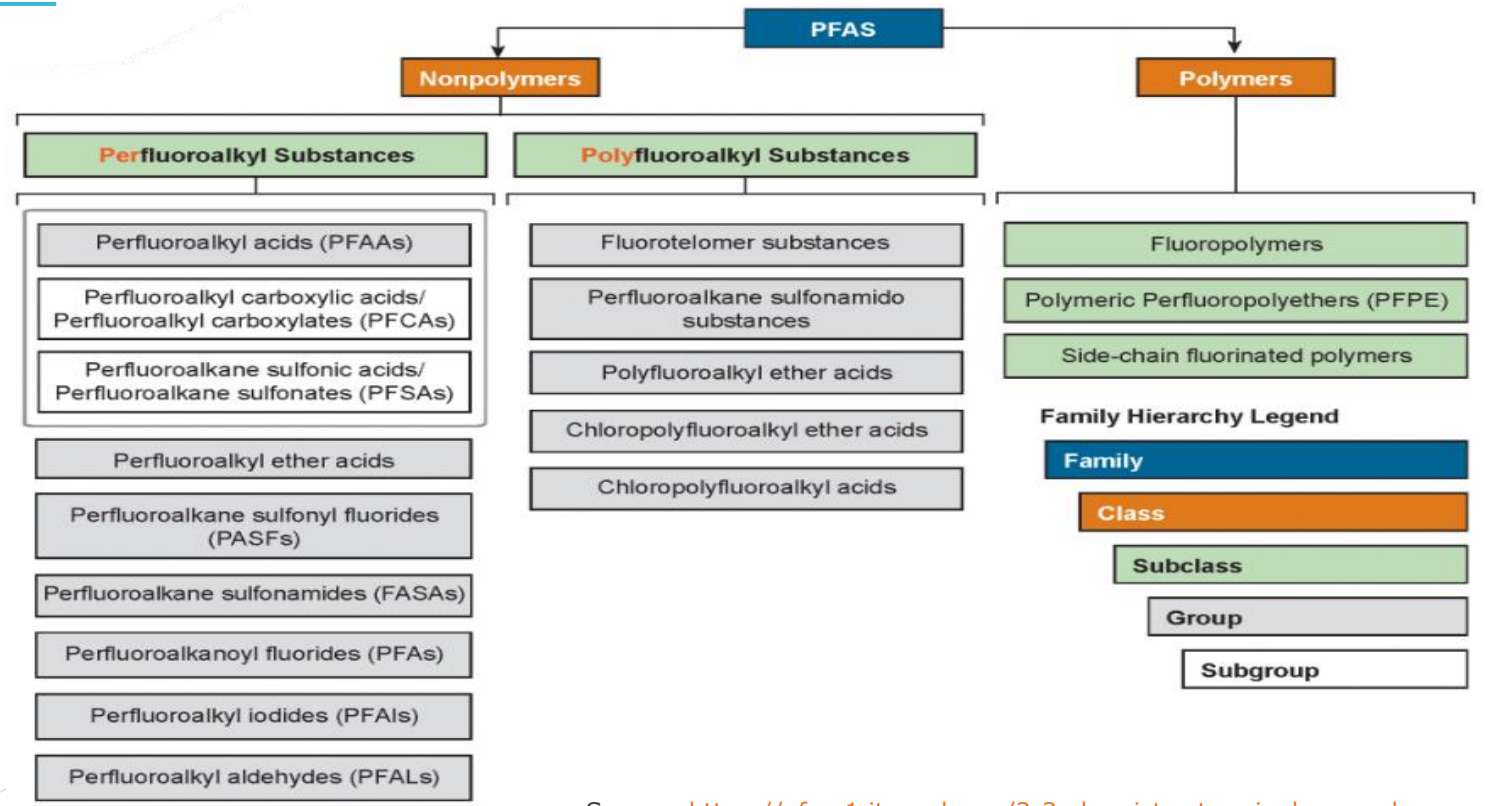
Some Ways to Define PFAS

Broadest Definition

Narrowest Definition

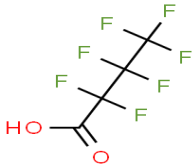
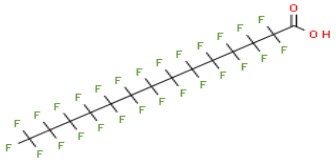
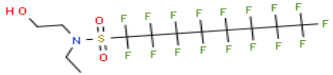
Source	Definition
NDAA for FY 2021	A man-made chemical in which all of the carbon atoms are fully fluorinated carbon atoms, and man-made chemicals containing a mix of fully fluorinated carbon atoms, partially fluorinated carbon atoms, and non-fluorinated carbon atoms.
Organisations for Economic Co-operation and Development 2021	Fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any hydrogen (H)/chlorine/bromine/iodine atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group (-CF3) or a perfluorinated methylene group (-CF_2-) is a PFAS.
Buck et al. 2011	Highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the H substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by fluorine (F) atoms, in such a manner that they contain the perfluoroalkyl moiety C_nF_{2n}.
EPA's Office of Pollution Prevention and Toxics	A structure that contains the unit R-CF,-CF(RP)(R"), where R, R', and R" do not equal H and the carbon-carbon bond is saturated (note: branching, heteroatoms, and cyclic structures are included).

The PFAS Family



Source: https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/

Dog Breeds Come in All Shapes and Sizes

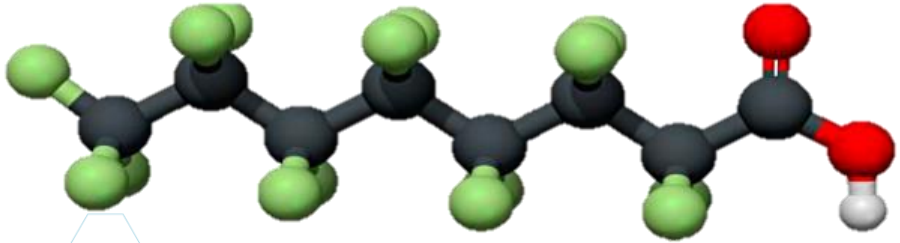
Is it a dog?	Is it a PFAS?
 Chihuahua—yes!	PFBA—yes! 
 Dachshund—yes!	PFTrDA—yes! 
 Komondor—yes!	NEtFOSE—yes! 

Diverse uses, diverse properties - same family

Deconstructing the Structure

PFOA = Perfluorooctanoic acid

1) Octanoic—eight carbons (black), "the backbone"
2) Perfluoro—carbons fully bonded to fluorine (green), "the tail"
3) Acid—carboxylic acid, "the head"



Example: 3d model of a PFOA (perfluorooctanoic acid), in its acid form.

Source: Manual Almagro Rivas (Own work using: Avogadro, Discovery Studio, GIMP) [CC By-SA 4.0

https://commons.wikimediaorg/wiki/File:PFOA-3D.png, via Wikimedia Commons.
https://commons.Wikimedia.org/wiki/File:PFOA-3D.png

History of Uses

PFAS[1]	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production		Protective Coatings				
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

Source: ITRC PFAS Fact Sheet, available from: https://pfas-1.itrcweb.org/fact-sheets/

Diverse Properties of PFAS

Wide-ranging structures and characteristics

- Solids, liquids and gases
- Inert to highly reactive
- Immobile to mobile and immobile
- Bioaccumulative and not

…which influence behavior in environment:

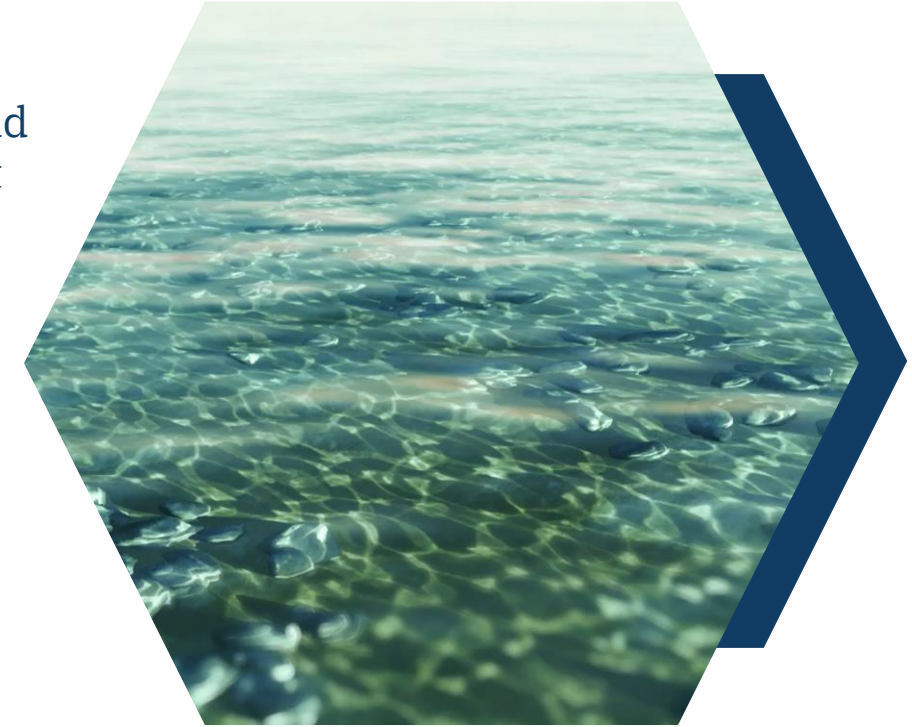
- Solubility & hydrophobicity
- Partitioning between air, water, sediment, and tissue
- Aggregation/surfactant properties

…leading to variability and uncertainty

- Chemical and physical properties → variability
- Varied quantity and quality of published data → uncertainty

Atypical Sediment Contaminant

- Many PFAS will leach from soil to GW and discharge to surface water, via sediment pore water
- Strong propensity to move to and stay at the air-water interface
- Bioaccumulation in fish via gill transfer of surface water
- Limited data on concentrations in sediment, water and biota that are safe for aquatic organisms and their consumers

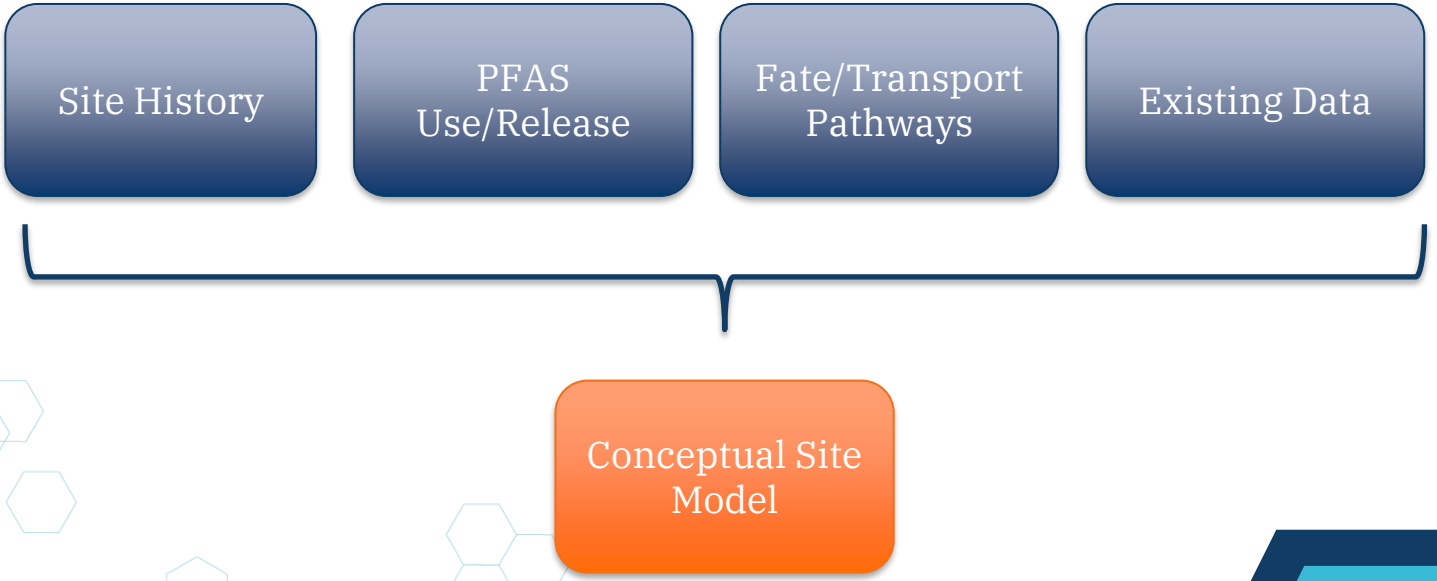


Investigation Strategies

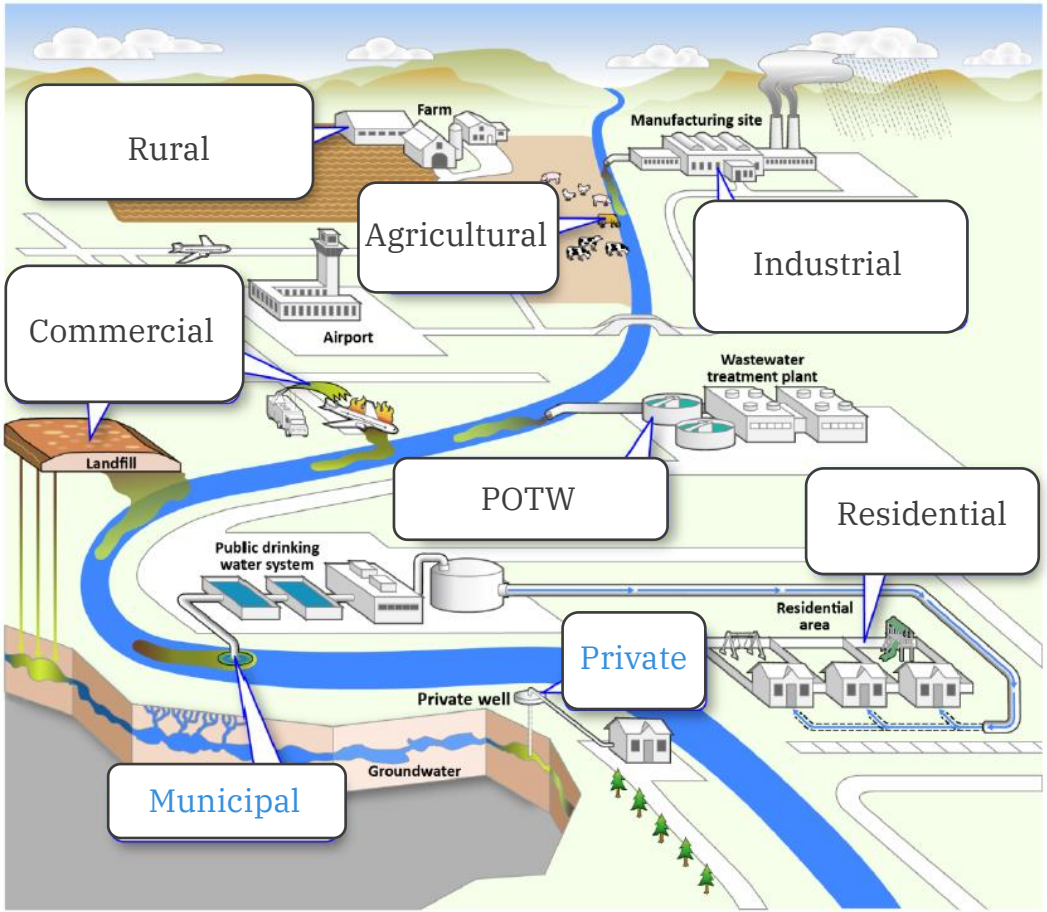
Topics

1. Site evaluation
2. Example CSMs
3. Source identification
4. Sediments

Site Evaluation

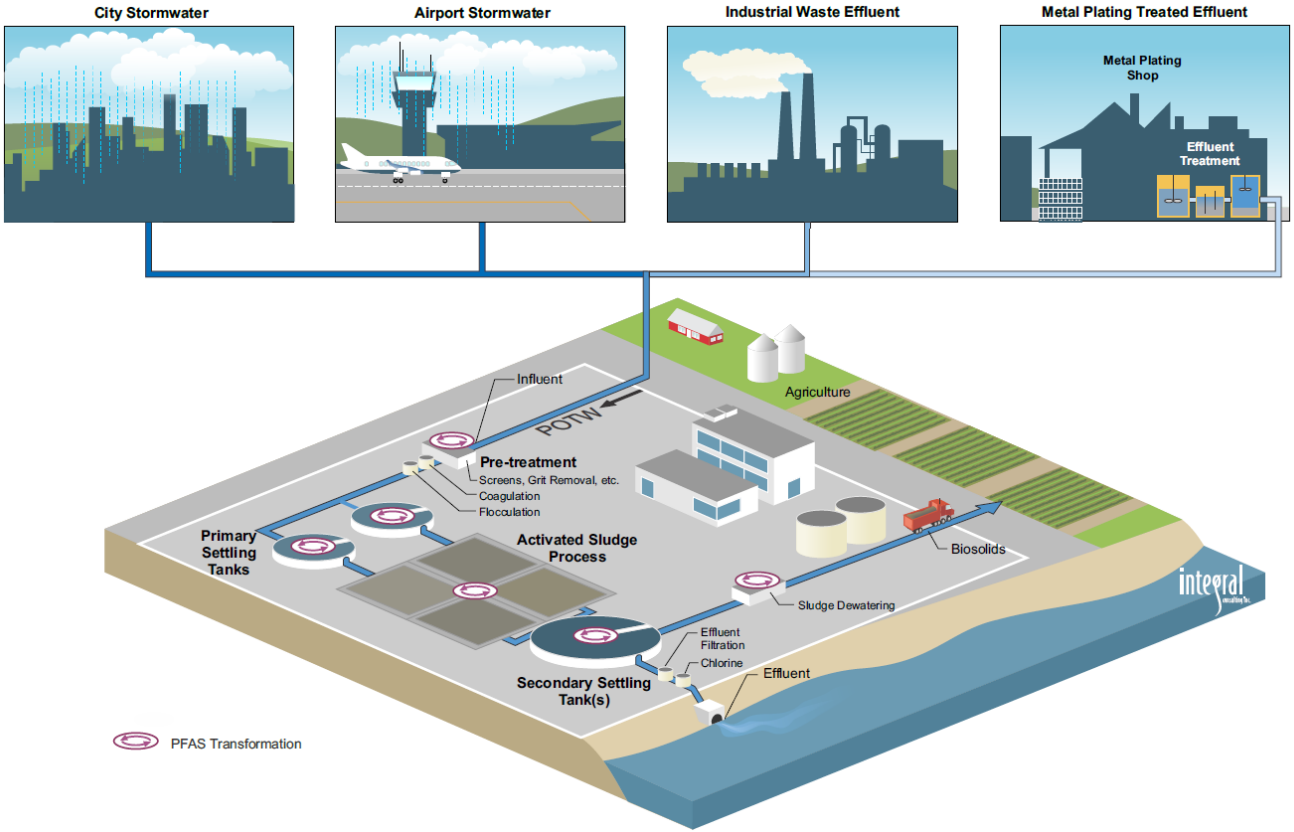


Watershed-scale CSM



Source: GAO. | GAO-22-105088

Publicly Owned Treatment Works CSM



Source Identification Challenges

- Not listed on packaging or Safety Data Sheet
- Proprietary and/or spec-based
- Technical mixtures are not pure compounds
- Formulations change over time
- Not previously defined as hazardous substances (no historical TRI or other reporting)

Source Identification—Sampling and Analysis

- What is the question you are asking?

- Screening or semi-quantitative methods
  - TOF (total organic fluorine)
- Quantitative methods
  - DRAFT EPA Method 1633
  - Custom/proprietary methods

- Precursor methods
  - TOP assay (total oxidizable precursor)

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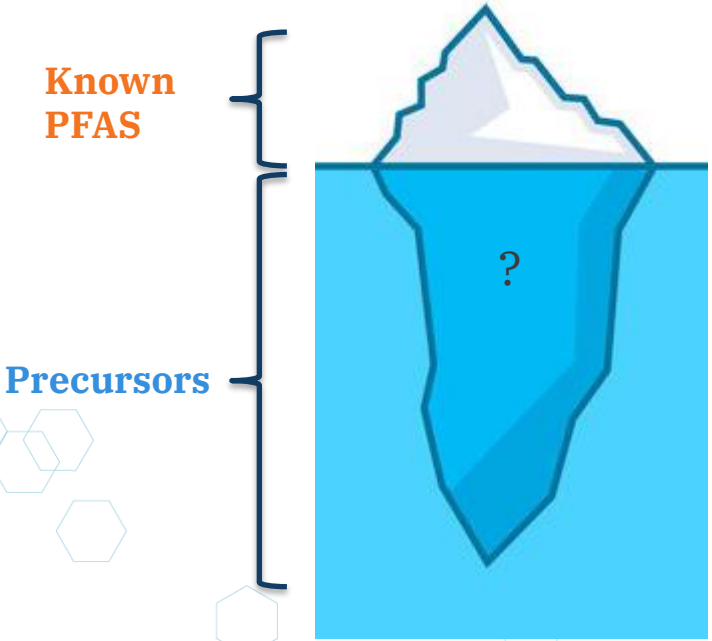
Source Identification--Transformation



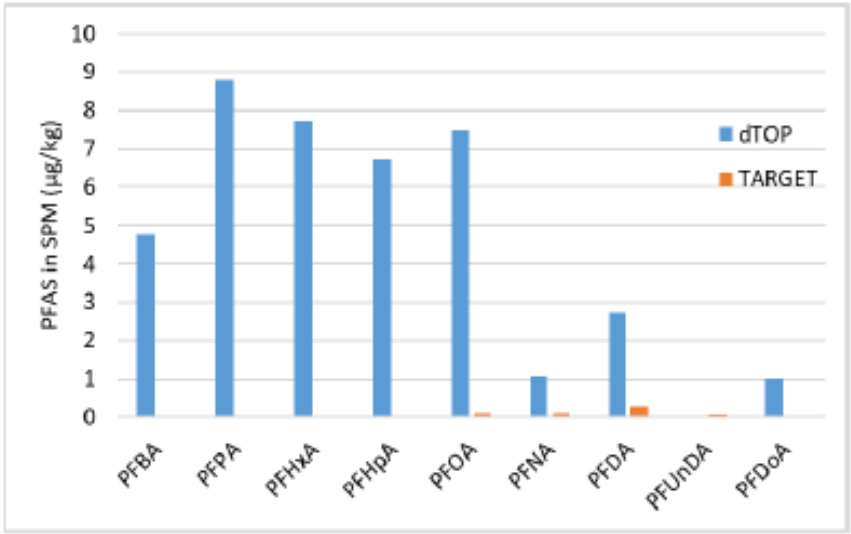


Figure 2.7: PFCAs after dTOP-analysis and target analysis in samples of 2017 (data Göckener et al., 2022).

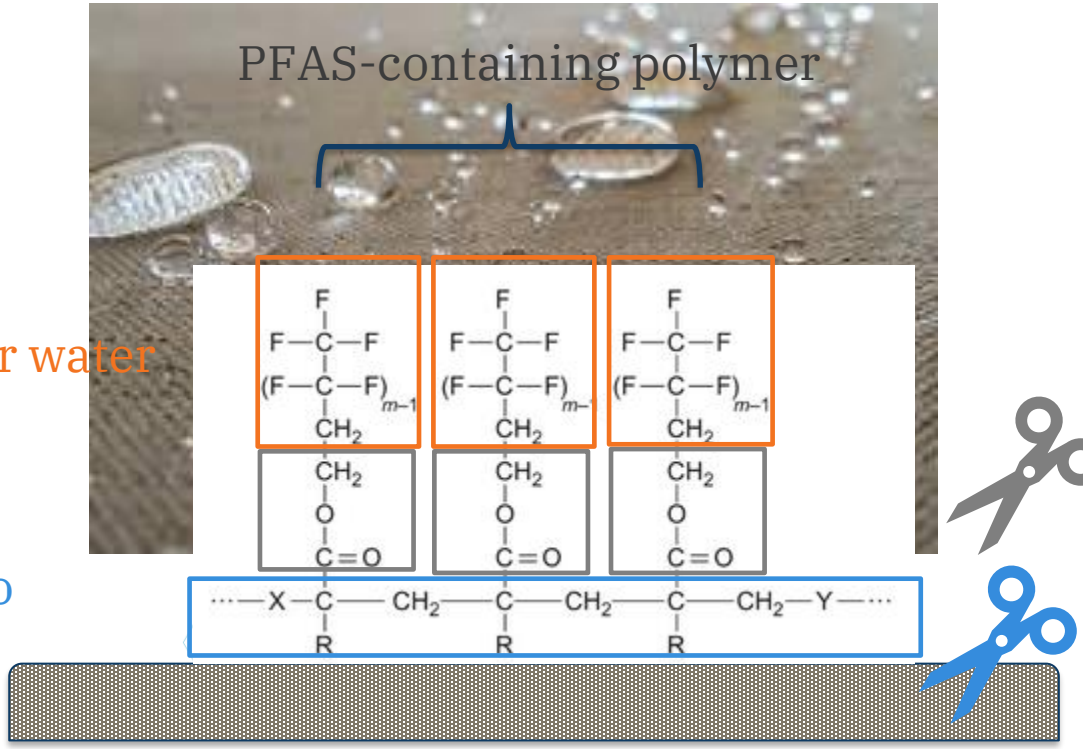
(Deltares, 2022)

Source Identification--Transformation

Stain and/or water resistance

Linkage

Adhesion to textile

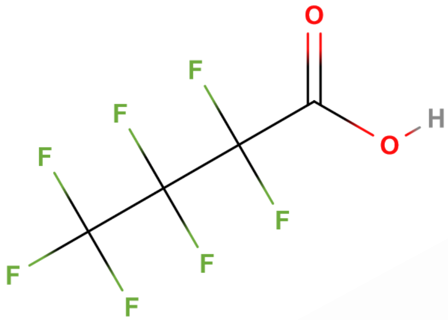


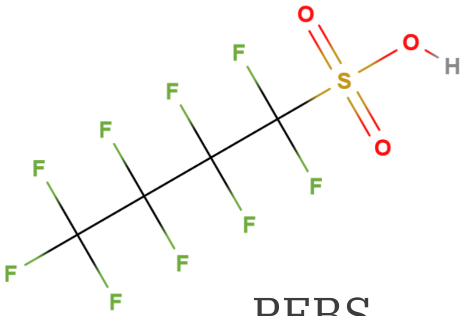
- Endpoint is ‘known’ PFAS
- Decreasing sorption
- Becomes ‘visible’

Source Identification

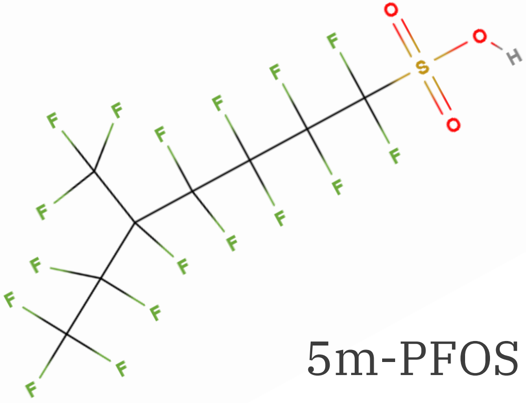
- Chain length
- Functional groups
- Linear vs branched

PFBA





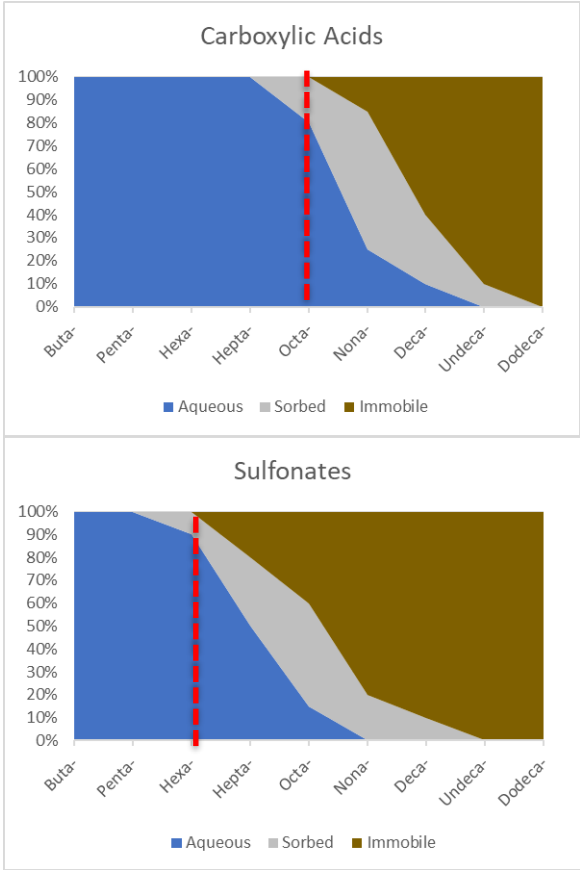
PFBS



5m-PFOS

Sediments — Fate and Transport

- Structure is destiny
- Not all compounds will accumulate/remain in sediments
  - Carboxylic acids with C8-C10 and above
  - Sulfonates with C6-C8 and above
- Precursors/other compounds more sorptive
- Shorter-chains
  - Predominately in aqueous phase
  - Will desorb from sediments



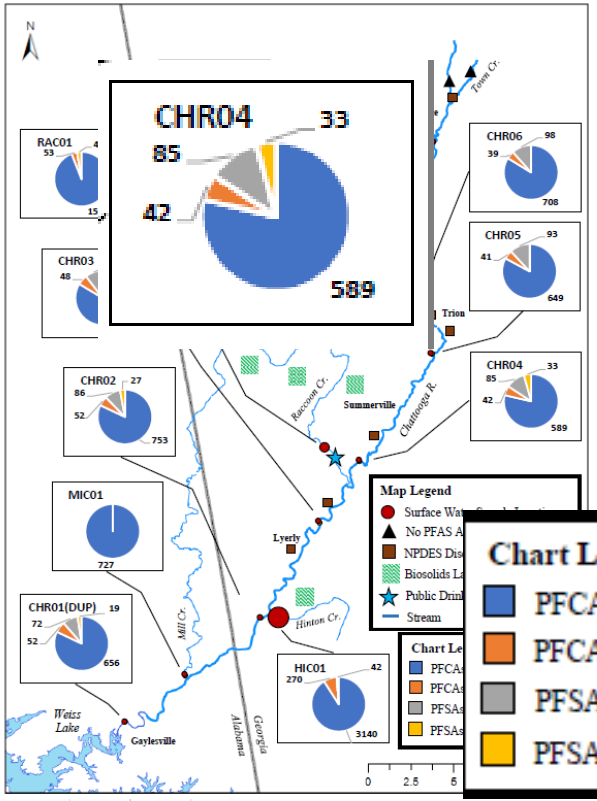
Based upon Chen, 2016

Case Study: Coosa River Basin, AL & GA

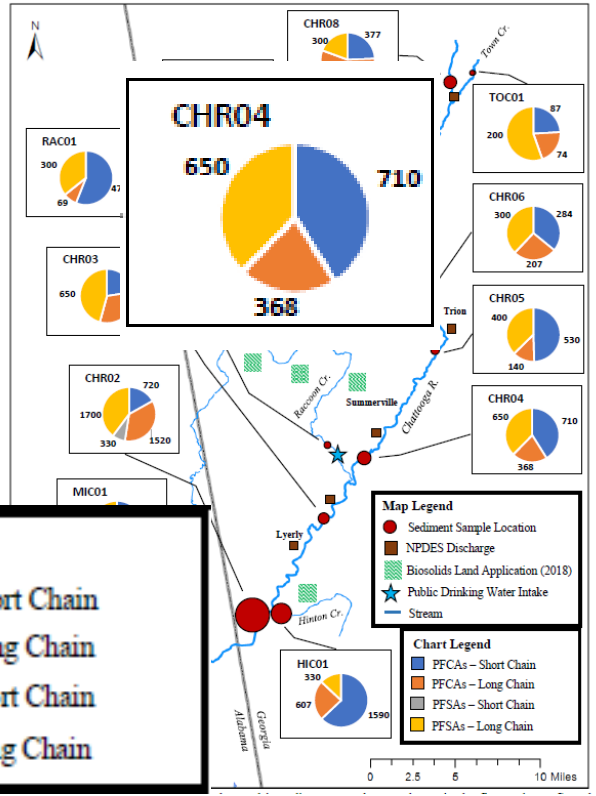
- Content excerpted from EPA studies
- Sources of diverse PFAS to the river
  - Textile mills
  - WWTP and runoff

Selective Sorption of PFAS

Surface Water



Sediments



USEPA, 2019, Characterization of Ambient PFAS in the Chattooga River Watershed

PFAS and Sediments—Key Points

- Characterize sources
- Fate and transport is linked to structure
- Transformation processes may be missing link
- Not all PFAS sorb to sediments
- Longer chains, complex molecules
- Sediment regulatory picture is unfolding

Legal and Regulatory Setting

Closing Thoughts

Key Points

- Understand the differences among definitions of PFAS and among individual substances
- Expect multiple sources, multiple substances, and transformation → complex CSM
- PFAS retained in sediment are longer-chain (or more complex molecules)
- Regulatory actions at State and Federal level are not coordinated

For More Information

Beginner

- White House PFAS Report (https://www.whitehouse.gov/wp-content/uploads/2023/03/OSTP-March-2023-PFAS-Report.pdf)
- Integral's PFAS page (https://integral-corp.com/our-services/PFAS/)

Intermediate

- ITRC Fact Sheets (https://pfas-1.itrcweb.org/fact-sheets/)
- USEPA PFAS Tool (https://awsedap.epa.gov/public/extensions/PFAS_Tools/PFAS_Tools.html)
- USEPA's CompTox Chemicals Dashboard for PFAS structures and predicted properties (https://comptox.epa.gov/dashboard/)

Advanced

- SERDP ESTCP (https://serdp-estcp.org/focusareas/e18ec5da-d0de-47da-99f9-a07328558149/pfas-afff)
- Integral's monthly PFAS Newsletter (https://www.integral-corp.com/pfas-monthly-newsletter/)

Q&A

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