

Housekeeping

- This event is being recorded; Event will be available On Demand after the event at the main training page: <https://www.clu-in.org/conf/itrc/PFASChem/>
- If you have technical difficulties, please use the Q&A Pod to request technical support
- Need confirmation of your participation today?
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Starting Soon: PFAS Chemistry Explained

- ITRC Resources:
<https://pfas-1.itrcweb.org/>
- CLU-IN Training Page (slides available):
<https://www.clu-in.org/conf/itrc/PFASChem/>



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Advancing
Environmental
Solutions



PFAS CHEMISTRY EXPLAINED

ITRC Technical Resources For Addressing Environmental
Releases Of Per- And Polyfluoroalkyl Substances



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Hosted by: US EPA Clean Up Information Network (www.clu-in.org)

Training Topics

PFAS Background

**PFAS Structure and
Naming Conventions**

**Chemical Properties
and Applications**



TRAINING PURPOSE

Today's PFAS Trainers



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PFAS BACKGROUND

MITCH OLSON

PFAS – per-and polyfluoroalkyl substances

- **Over 12,000** anthropogenic (man-made) chemicals (*PFAS-1, linked below: Section 2*)
- **Widely produced and used** in society since mid-1900s (*Section 2*)
- Unique **chemical/physical properties** – including water/oil repellency (*Section 4*)
- Unique **environmental transport properties** – surfactants (*Section 5*)
- **Globally present** in the environment at trace levels (*Section 6*)
- Identified with **health effects** (*Section 7*)
- Subject to **evolving regulations** (*Section 8*)
- PFAS in water **can be treated** via sorption, concentration, destruction (*Section 12*)

A Brief History of PFAS

PFAS Emergence Timeline

	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s	2010s	2020s
Production	Synthesis / Development									
			Manufacturing and Commercial Production							
			Electrochemical fluorination Fluorotelomerization							
								Phase-outs / Reductions / Alternatives		
Health & Environment					Health Concerns					
								Environmental Detection & Analytical Improvements		

PFAS Uses

- Aviation/automotive
- Chemical industries
- Cosmetics and personal care products
- Firefighting (Class B, flammable liquids)
- Fluoropolymers used in construction, wiring, mechanical components
- Food processing and storage
- Metal plating
- Paper and packaging
- PFAS production
- Plastics
- Textiles - upholstery, carpets, leather, and apparel

(see Section 2.5 and Table 2-6)



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PFAS Sources to the Environment

Aqueous Film Forming Foam (AFFF)

- **Class B (Flammable liquid) firefighting**
- Potentially associated with **storage, training, and response areas** at military installations, airports, fuel handling, & chemical facilities

Industrial Manufacturing & Uses

- Many industries (see Table 2-6)
- Production of **consumer goods** – non-stick surfaces, waterproofing, stainproofing



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Landfills

- Consumer products, industrial waste, biosolids from WWTP
- Potential release via leachate or landfill gas

Wastewater Treatment Plants

- PFAS in influent (from industrial & domestic sources) may not be treated and end up in effluent
- Potential release via liquid effluent or biosolids



[Iain Thompson](#) / Cathkin Landfill Site, [CC BY-SA 2.0](#), via Wikimedia Commons



Photo taken by [Watzmann \(c\) Günter Seggebäing](#). [CC BY-SA 3.0](#)
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Knowledge Check

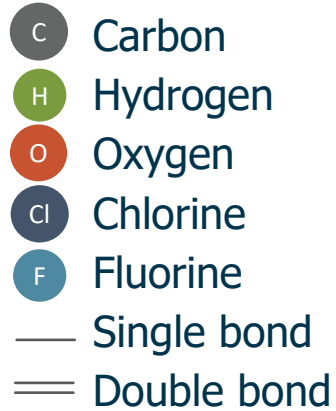
Check
In!

Some uses for PFAS include the following:
(check all that apply)

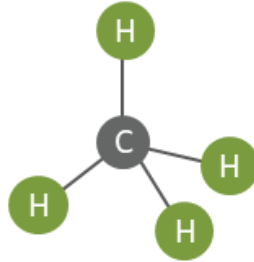
- a) Forest firefighting
- b) Metal plating
- c) Housefires
- d) Pharmaceuticals
- e) Food packaging
- f) Firefighting - flammable liquids



Organic chemistry refresher



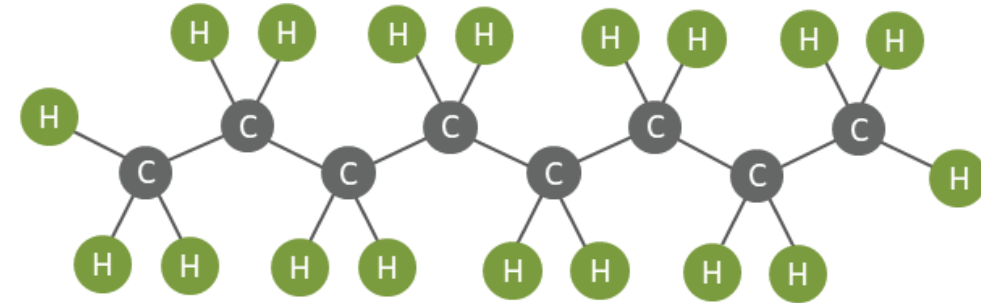
Methane



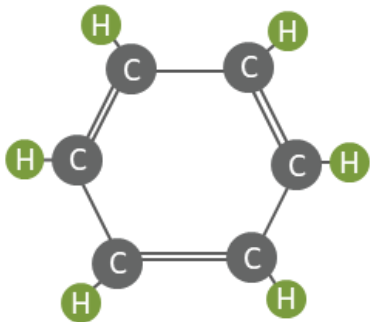
Carbon Dioxide



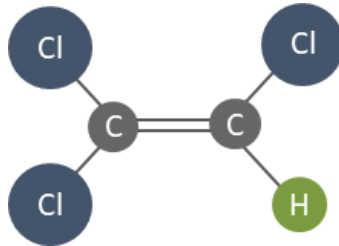
Octane



Benzene



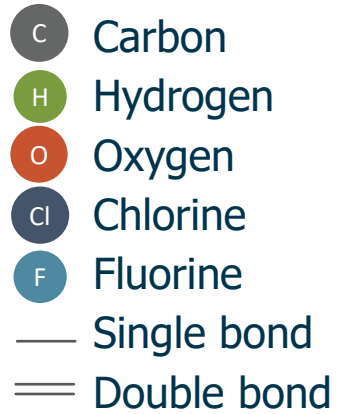
TCE (trichloroethene)



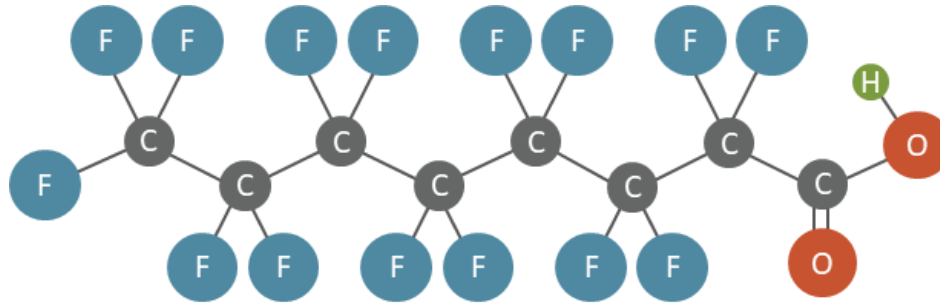
Organic chemistry principles

- Organic chemistry is all about carbon, but not all carbon is organic
- Covalent bonds: 4 for carbon (4 "lines")
- Chemical reactions – change in oxidation state, breaking/reforming bonds seeking a more stable configuration

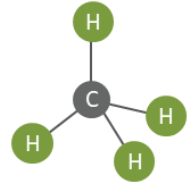
PFAS Chemistry



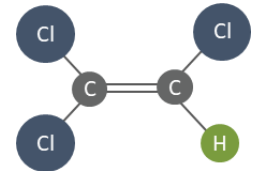
PFOA (perfluorooctanoic acid)



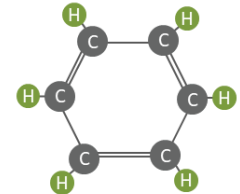
Methane



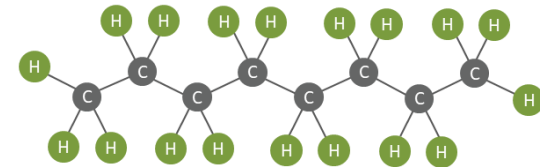
TCE (trichloroethene)



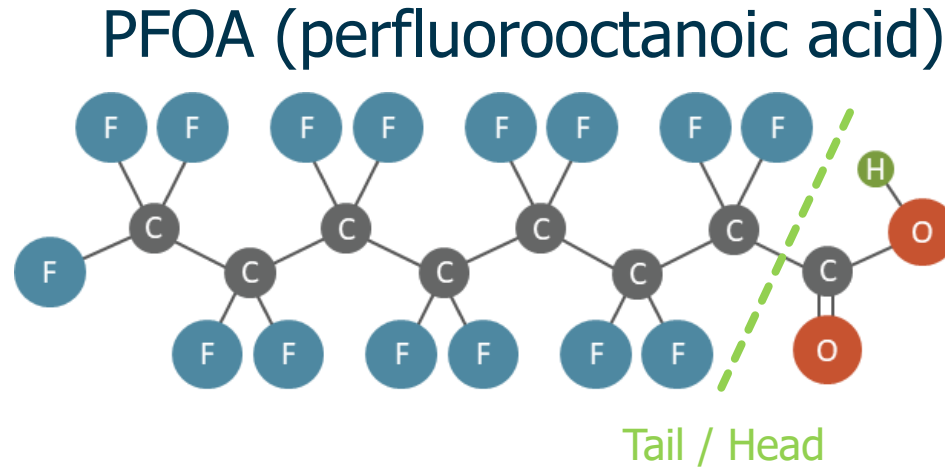
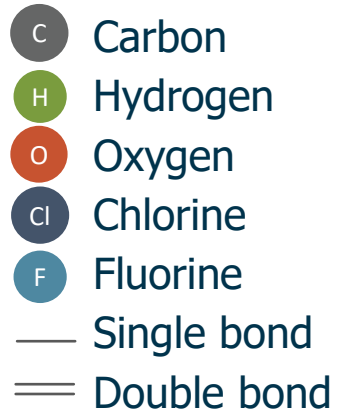
Benzene



Octane

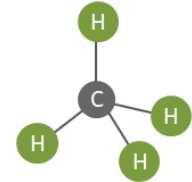


PFAS Chemistry

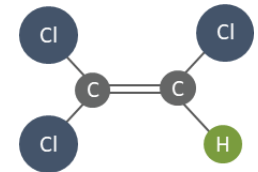


- **phobic** = repelling; **philic** = attracting
- **Tail:** hydrophobic ("water repelling") and lipophobic ("oil repelling")
- **Head:** hydrophilic ("water loving")

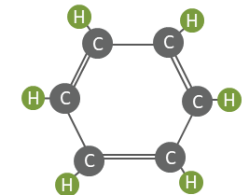
Methane



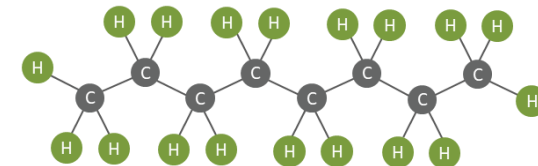
TCE (trichloroethene)



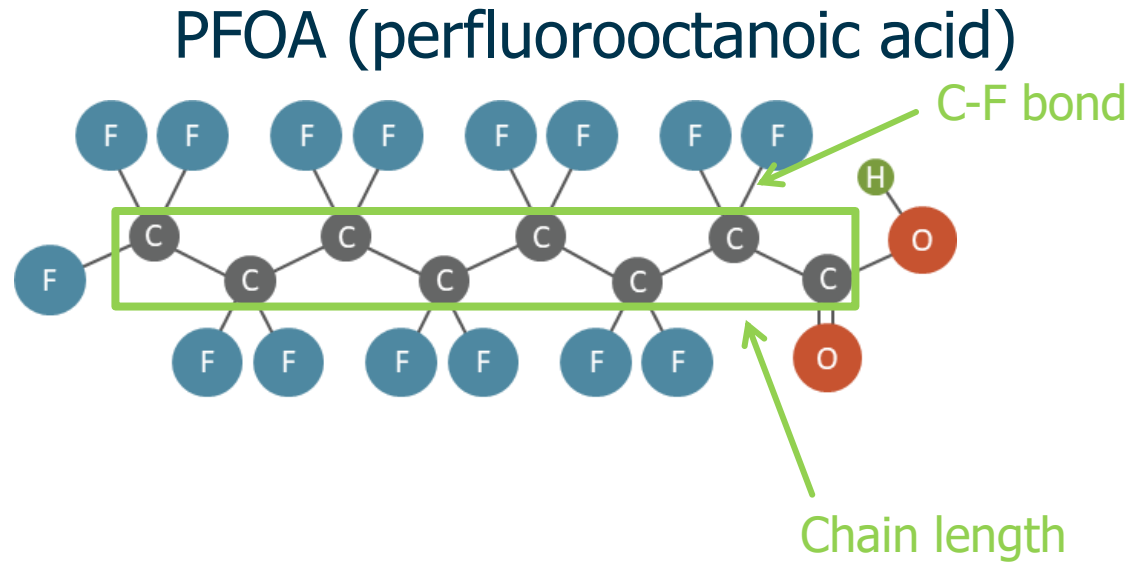
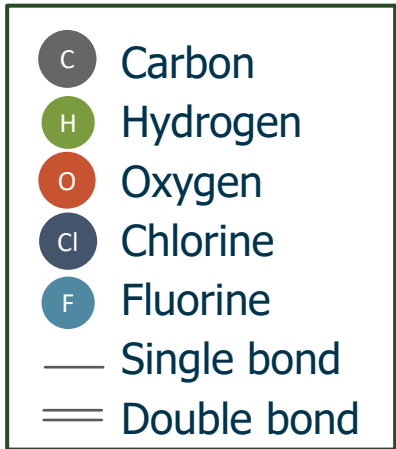
Benzene



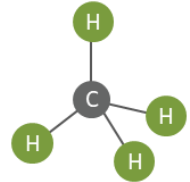
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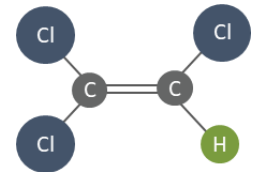
PFAS Chemistry



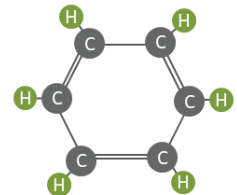
Methane



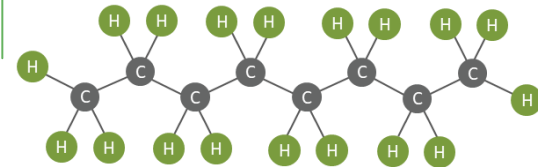
TCE (trichloroethene)



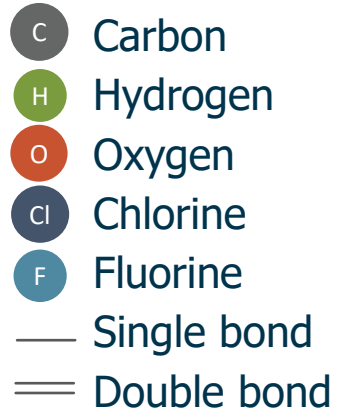
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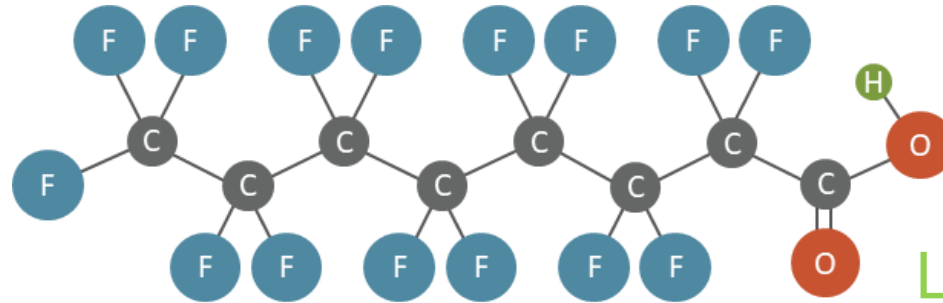
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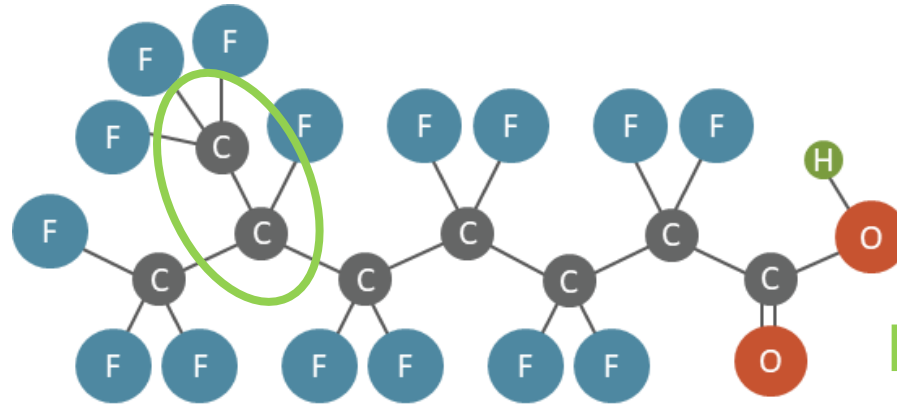
PFAS Chemistry



PFOA (perfluorooctanoic acid)

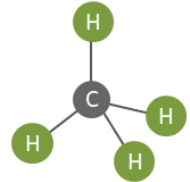


Linear isomer

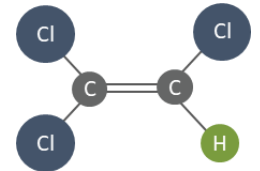


Branched isomer
(1 example)

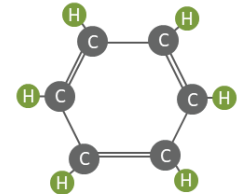
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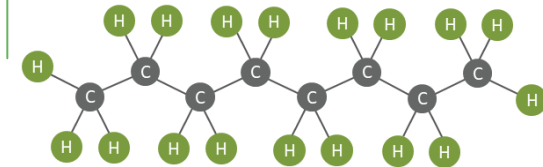
TCE (trichloroethene)



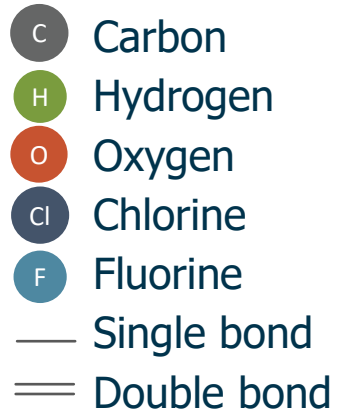
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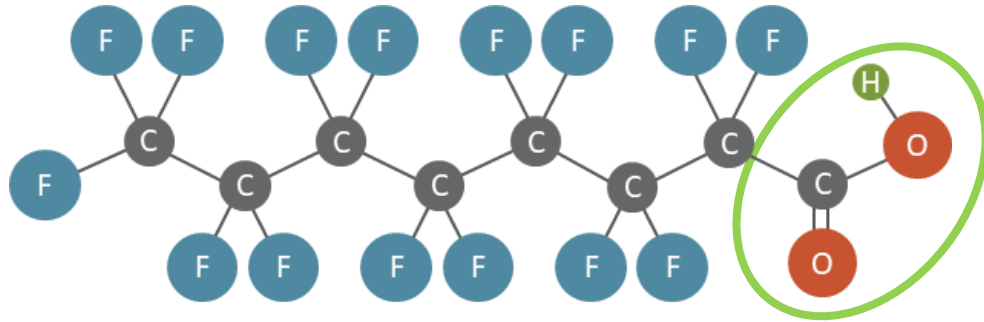
Octane



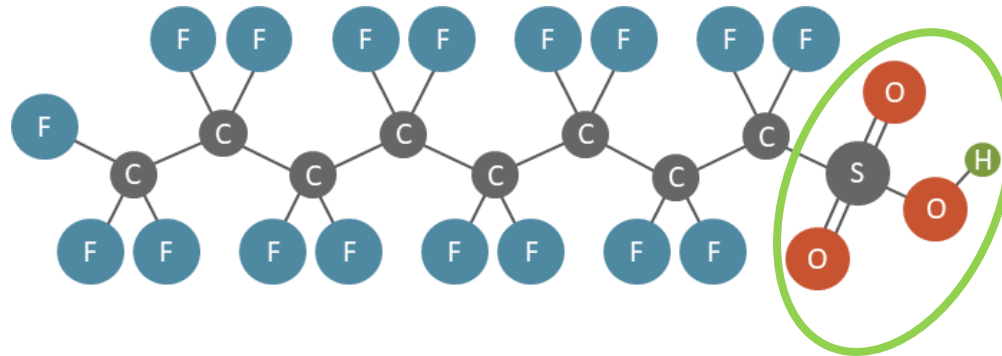
PFAS Chemistry



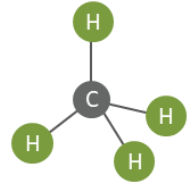
PFOA (perfluorooctanoic acid)



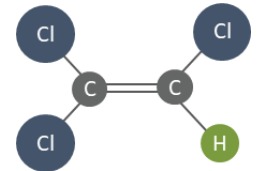
PFOS (perfluorooctane sulfonic acid)



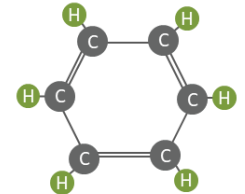
Methane



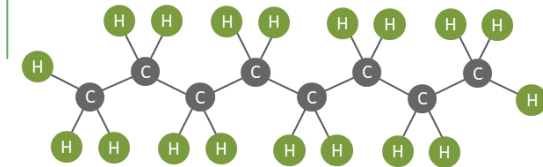
TCE (trichloroethene)



Benzene



Octane



Key Takeaways

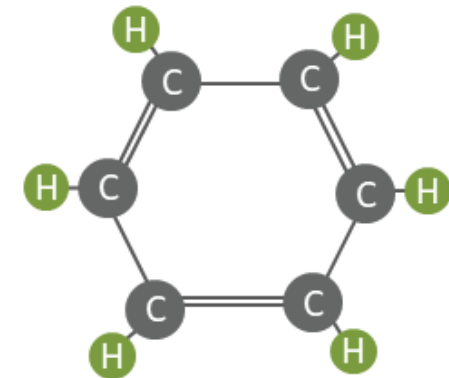
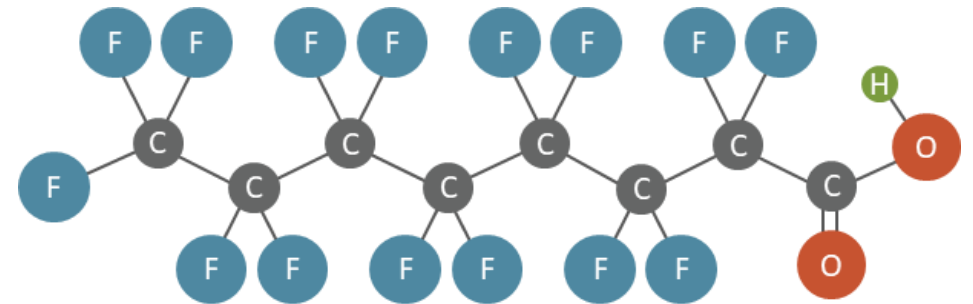
- History & Use
 - PFAS – manmade chemicals, widely produced since 1950s/1960s
 - Key uses: Class B firefighting foams, several industries, consumer products
- Organic chemistry
 - PFAS are different from organic contaminants
 - Characterized by carbon-fluorine (C-F) bond
 - Head – non-fluorinated - hydrophilic for many PFAS (PFOA & PFOS)
 - Tail – chain length/C-F bond – hydrophobic and lipophobic
 - Surfactant – polar/non-polar

Knowledge Check

Check
In!

Which of the following statements are true for PFOA and benzene? (select all that apply)

- a) Both are organic compounds
- b) Both have carbon-hydrogen bonds
- c) Both have carbon-fluorine bonds
- d) For both compounds, environmental releases typically involve a complex mixture with other chemicals





PFAS STRUCTURES AND NAMING CONVENTIONS

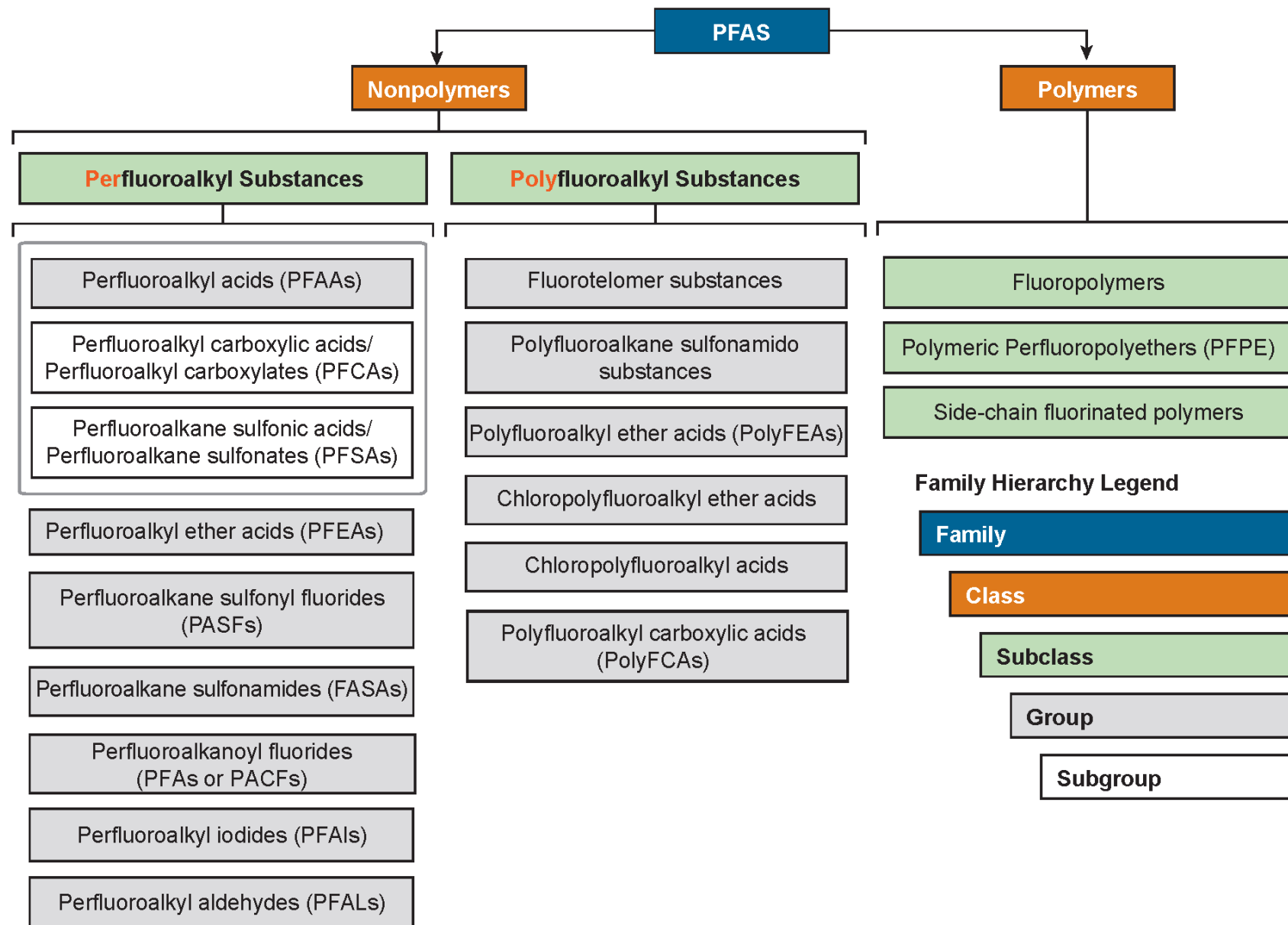
LIZ DENLY

PFAS Family Tree: Simple View

Two Major Classes

Nonpolymers

Polymers

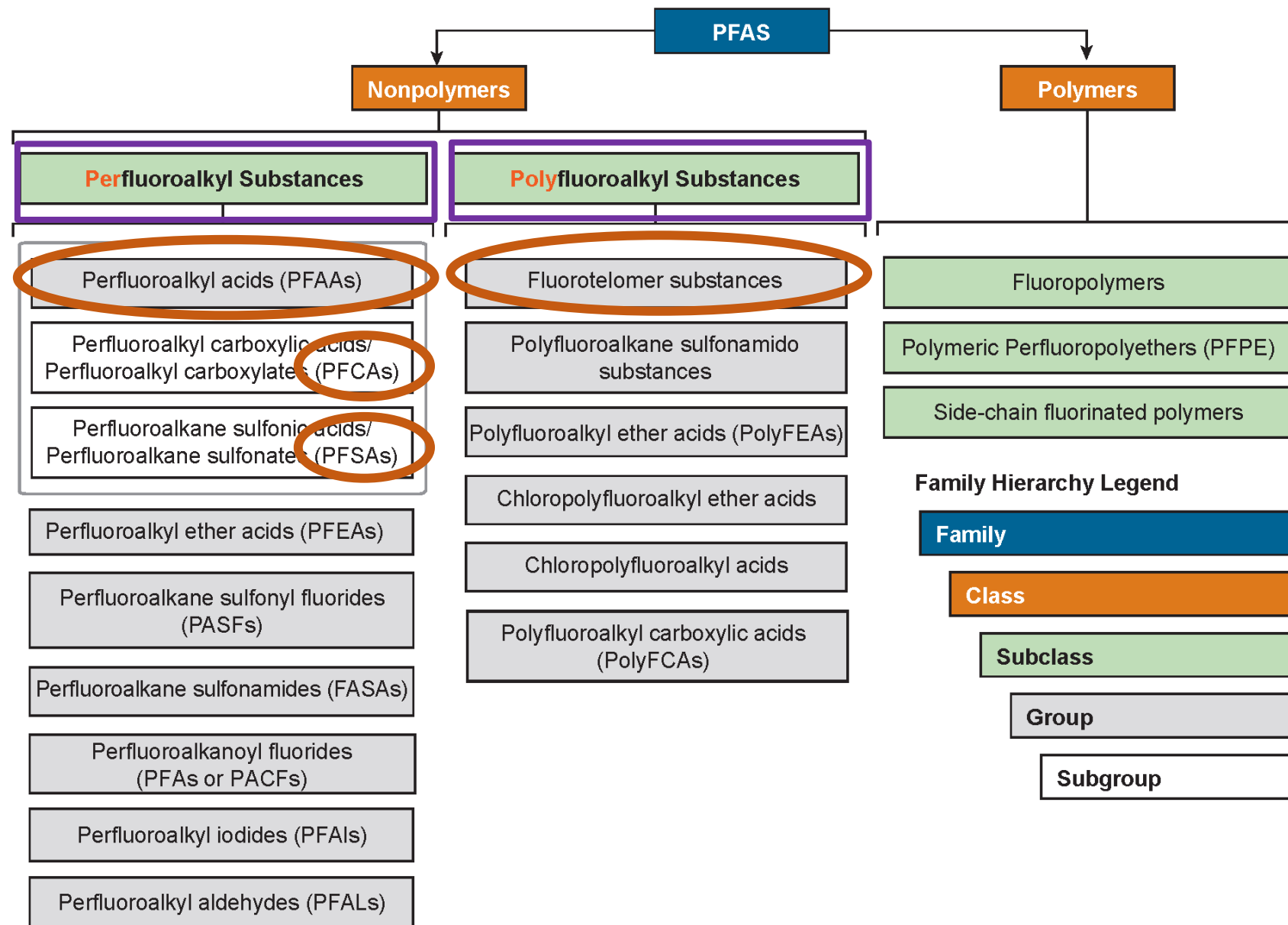


PFAS Family Tree: Simple View

Two Major Classes

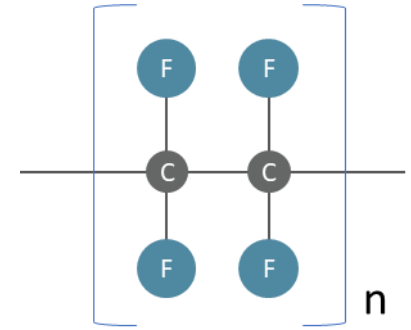
Nonpolymers

Polymers

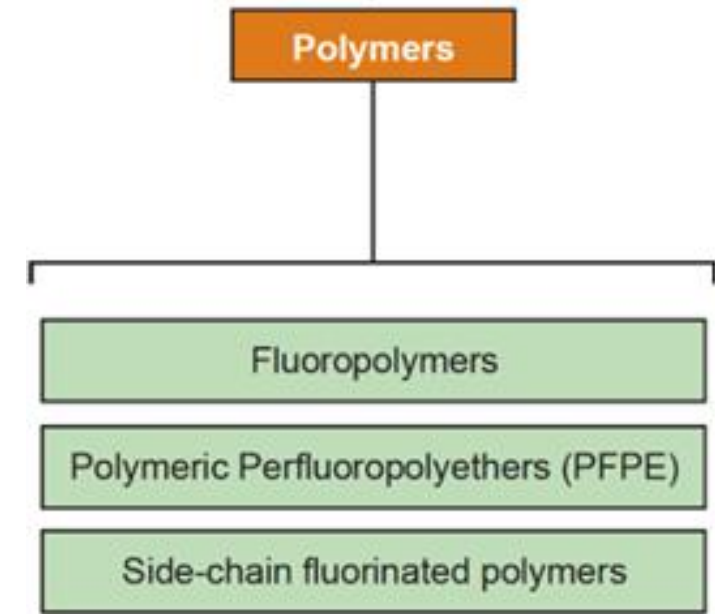


Polymer PFAS

- Polymers: large molecules formed by combining many identical smaller molecules (or monomers, which are shorter chain molecules with no repeating units) in a repeating pattern
- Fluoropolymers: carbon-only backbone with fluorine (F) attached to carbon (C)
 - Examples: polytetrafluoroethylene (PTFE), ethylene tetrafluoroethylene (ETFE)
 - Non-polymer PFAS used as processing aids
- Polymeric PFPE: carbon and oxygen backbone with F attached to C
- Side-chain Fluorinated Polymers: non-fluorinated polymer backbone with branched fluorinated side chains
 - Examples: fluorinated urethane, acrylate/methacrylate, or oxetane polymers
 - Can become precursors for perfluoroalkyl acids (PFAAs)

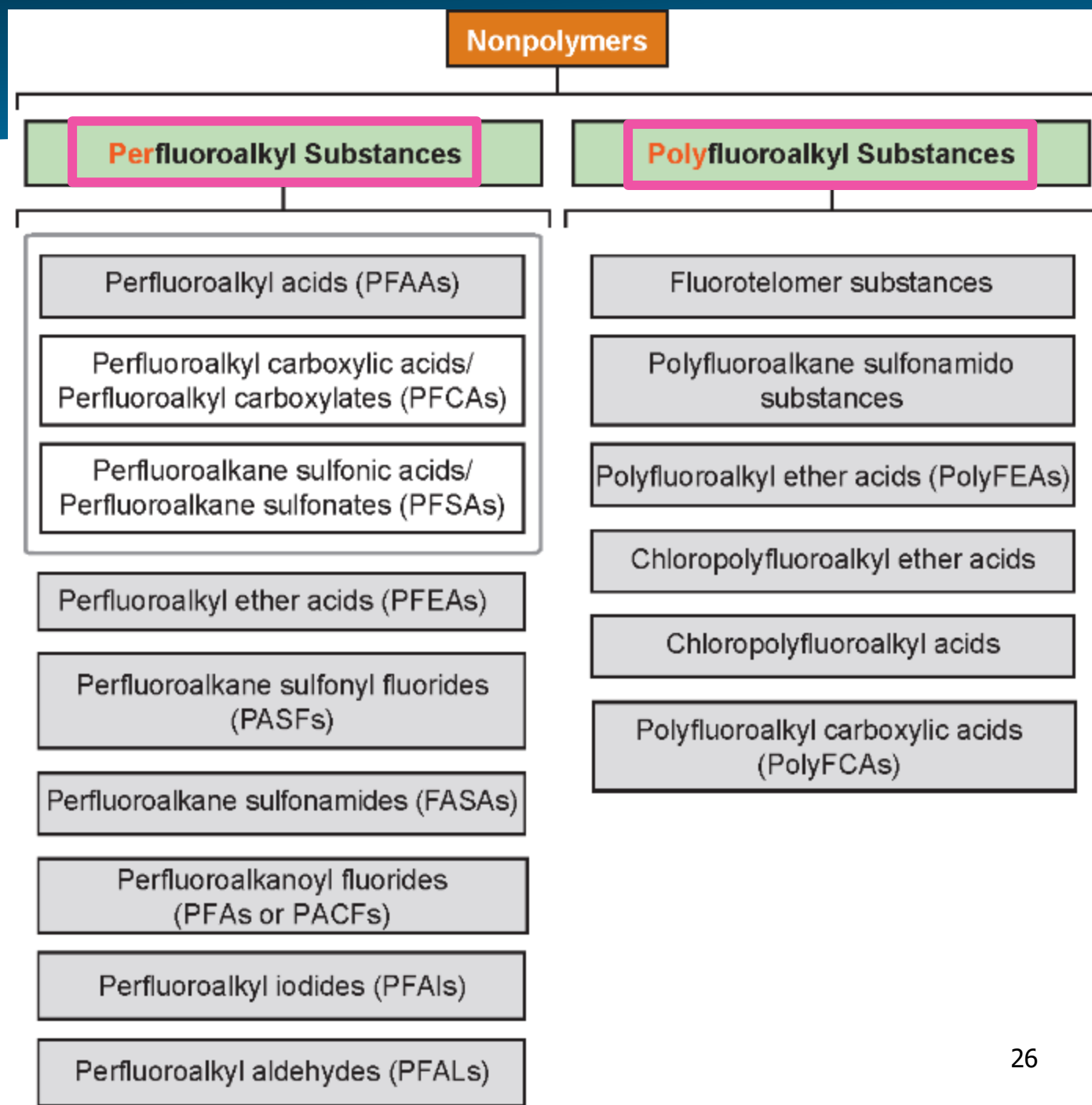


Monomer Example



Nonpolymer PFAS Class

- 2 Major Subclasses
 - Perfluoroalkyl Substances
 - Polyfluoroalkyl Substances
- Included on PFAS analytical method lists
- Most commonly detected
- Data available for human and ecological exposure
- State or federal guidance values exist



Knowledge Check

Check
In!

Two Major Classes of PFAS are:
(select one)

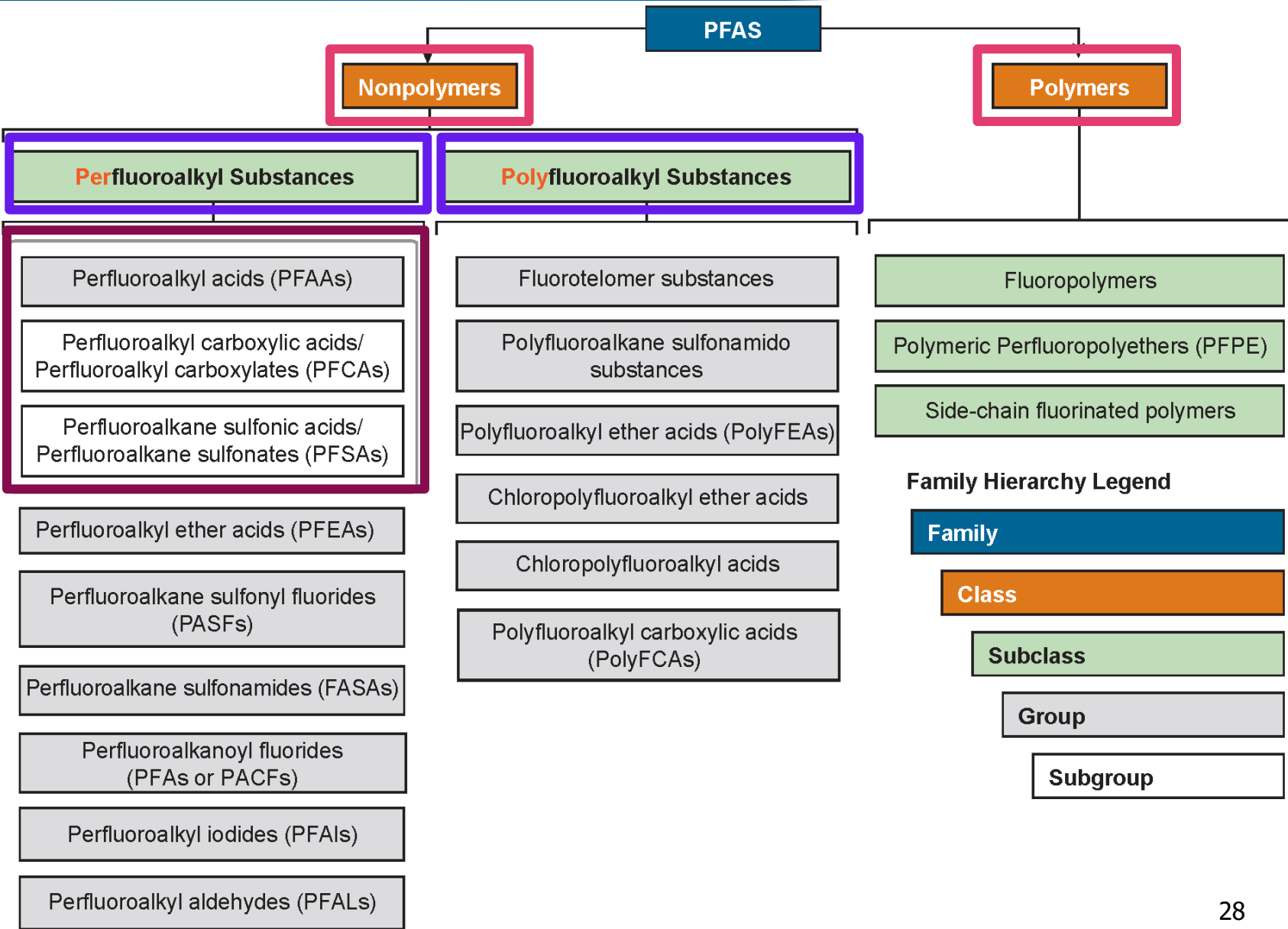
- a) PFOA and PFOS
- b) Perfluoroalkyl and Polyfluoroalkyl Substances
- c) Polymers and Nonpolymers
- d) Fluorinated Polymers and Side-chain Fluorinated Polymers



Knowledge Check Explained

Two Major Classes of PFAS are:
(select one)

- a) PFOA and PFOS
- b) Perfluoroalkyl and Polyfluoroalkyl Substances
- c) Polymers and Nonpolymers
- d) Fluorinated Polymers and Side-chain Fluorinated Polymers



Knowledge Check

Check
In!

PFAS Commonly Detected and Measured
in the Environment and Humans are:
(select one)

- a) Polymer PFAS
- b) Nonpolymer PFAS
- c) Side-chain Fluorinated Polymers
- d) Polytetrafluoroethylene (PTFE)



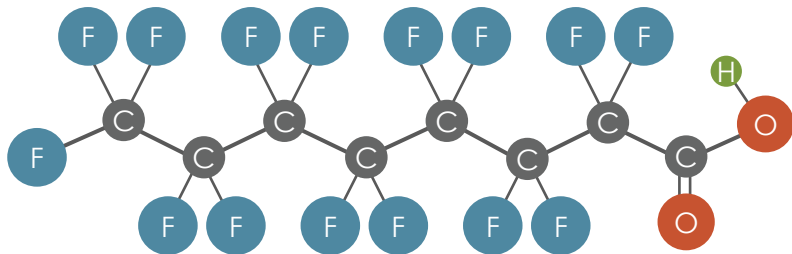
Perfluoroalkyl Substances & Polyfluoroalkyl Substances



Nonpolymer: Perfluoroalkyl Substances

Perfluoroalkyl substances: fully fluorinated alkyl tail

Perfluorooctanoic Acid (PFOA)



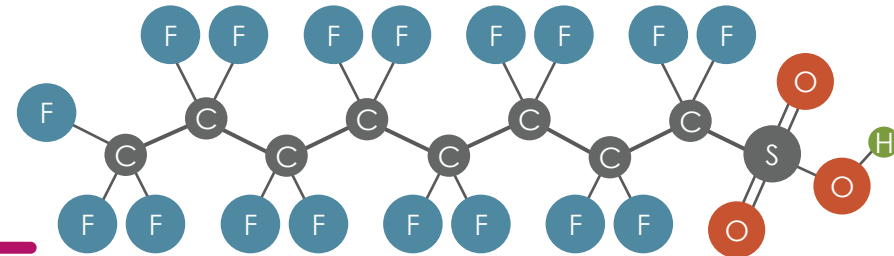
COOH = Head
Hydrophilic

- Alkyl tail, fully fluorinated
- C-F Bond
- Hydrophobic/lipophobic

Subgroup: Perfluoroalkane Sulfonic Acid (PFSA)

Subgroup: Perfluoroalkyl Carboxylic Acid (PFCA)

Perfluorooctane Sulfonic Acid (PFOS)



SO₃H = Head
Hydrophilic

- Alkyl tail, fully fluorinated
- C-F Bond
- Hydrophobic/lipophobic

Perfluoroalkyl Substances

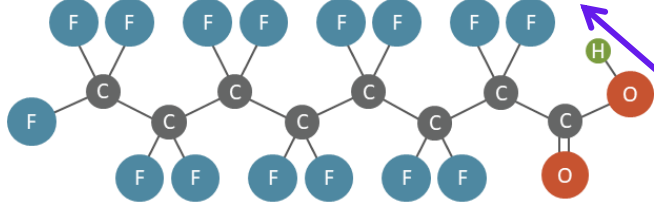
Perfluoroalkyl acids (PFAAs)

Perfluoroalkyl carboxylic acids/
Perfluoroalkyl carboxylates (PFCAs)

Perfluoroalkane sulfonic acids/
Perfluoroalkane sulfonates (PFSAs)

Perfluoroalkyl Acids (PFAAs) → PFCAs & PFSA

Perfluorooctanoic acid (PFOA)

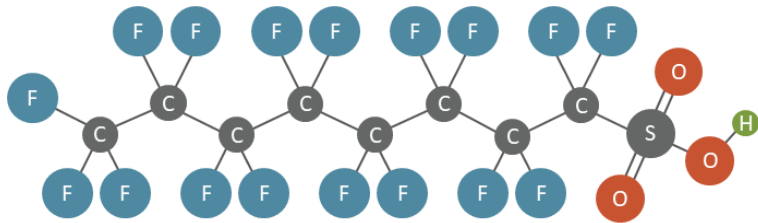


Other PFCA Examples:

Perfluorohexanoic Acid (PFHxA)

Perfluorononanoic Acid (PFNA)

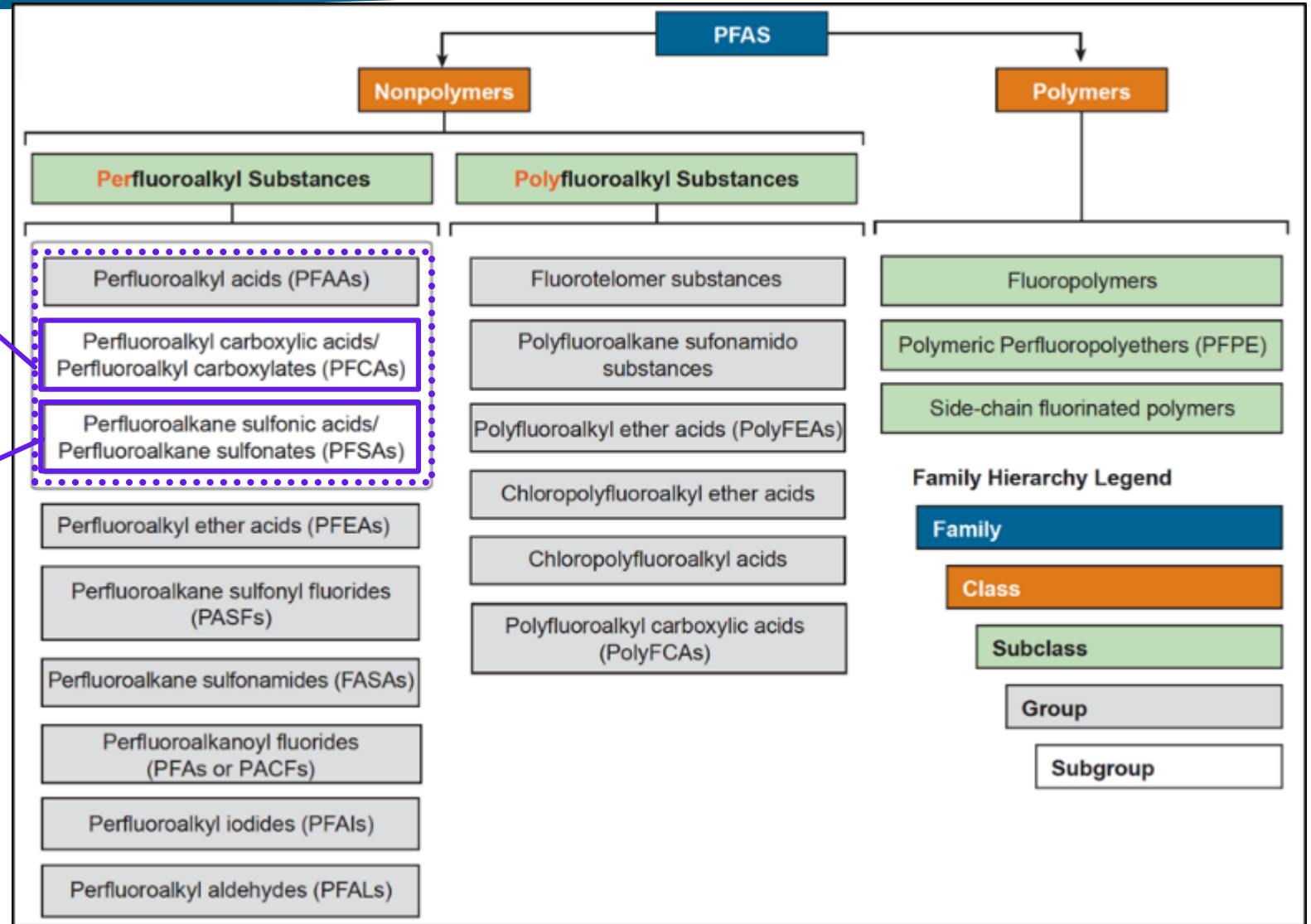
Perfluorooctane sulfonic acid (PFOS)



Other PFSA Examples:

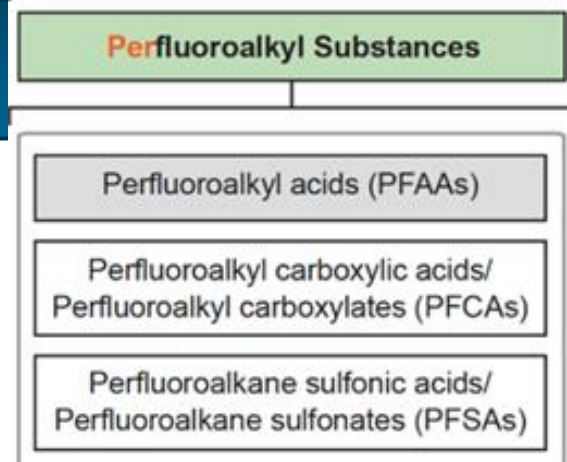
Perfluorobutane Sulfonic Acid (PFBS)

Perfluorohexane Sulfonic Acid (PFHxS)



Perfluoroalkyl Acids (PFAAs)

- Two major subgroups: PFCA & PFSA
- Non-degradable under normal environmental conditions
- “Terminal PFAS”
- Make up majority of PFAS included in commercial lab analyses
- Primary PFAS for which federal or state regulatory criteria exist
- Tend to drive site investigation and remediation decisions



PFCA = Perfluoroalkyl Carboxylic Acid
PFSA = Perfluoroalkane Sulfonic Acid

Knowledge Check

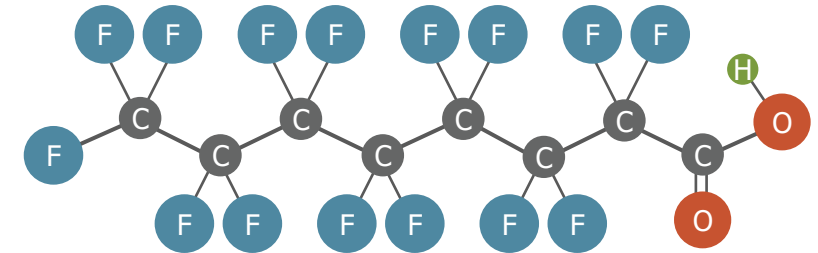
Check In!

An example of a Perfluoroalkyl Carboxylic Acid (PFCA) is:

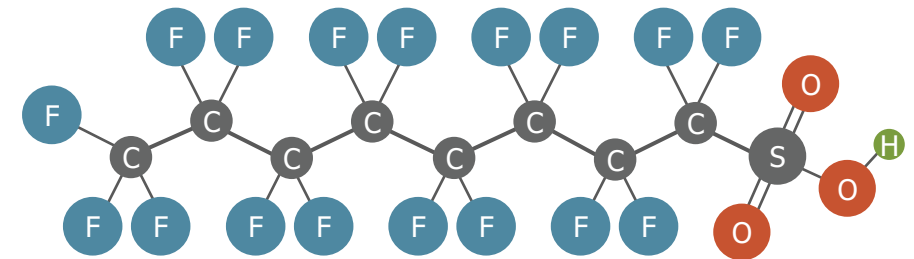
(select all that apply)

- a) Side-chain Fluorinated Polymer
- b) Perfluorobutanoic Acid (PFBA)
- c) Perfluorooctanesulfonic Acid (PFOS)
- d) Perfluorooctanoic Acid (PFOA)

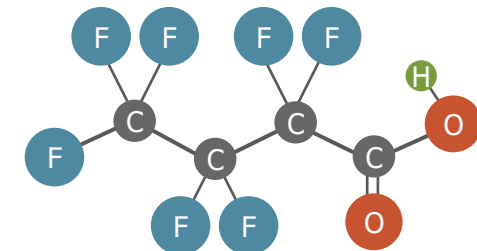
PFOA = Perfluorooctanoic Acid



PFOS = Perfluorooctanesulfonic Acid



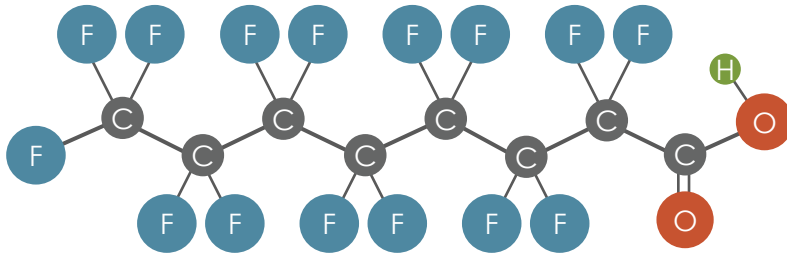
PFBA = Perfluorobutanoic Acid



Knowledge Check Explained

Remember: PFCAs Have Carboxylic Acid Head

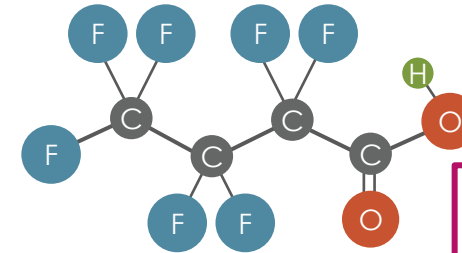
PFOA: Perfluorooctanoic Acid



COOH =
Carboxylic Acid
Head

Alkyl Tail, fully fluorinated

PFBA: Perfluorobutanoic Acid



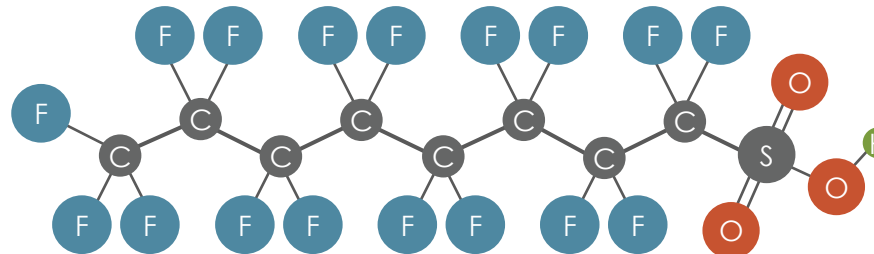
COOH = Carboxylic
Acid Head

Alkyl Tail, fully fluorinated

An example of a Perfluoroalkyl Carboxylic Acid (PFCA) is:
(select all that apply)

- a) Side-chain Fluorinated Polymer
- b) Perfluorobutanoic Acid (PFBA)
- c) Perfluorooctanesulfonic Acid (PFOS)
- d) Perfluorooctanoic Acid (PFOA)

PFOS: Perfluorooctane Sulfonic Acid



SO₃H = Sulfonic Acid
Head

Alkyl Tail, fully fluorinated

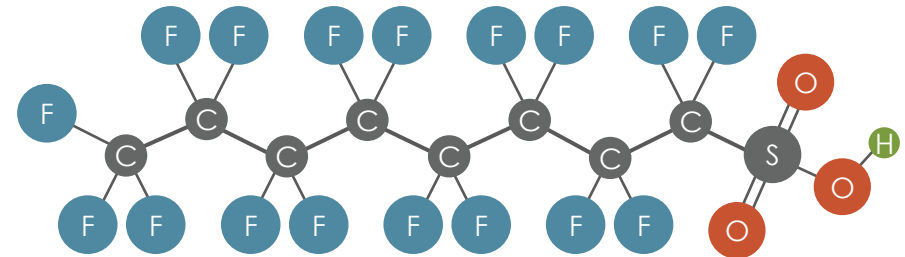
Knowledge Check

Check
In!

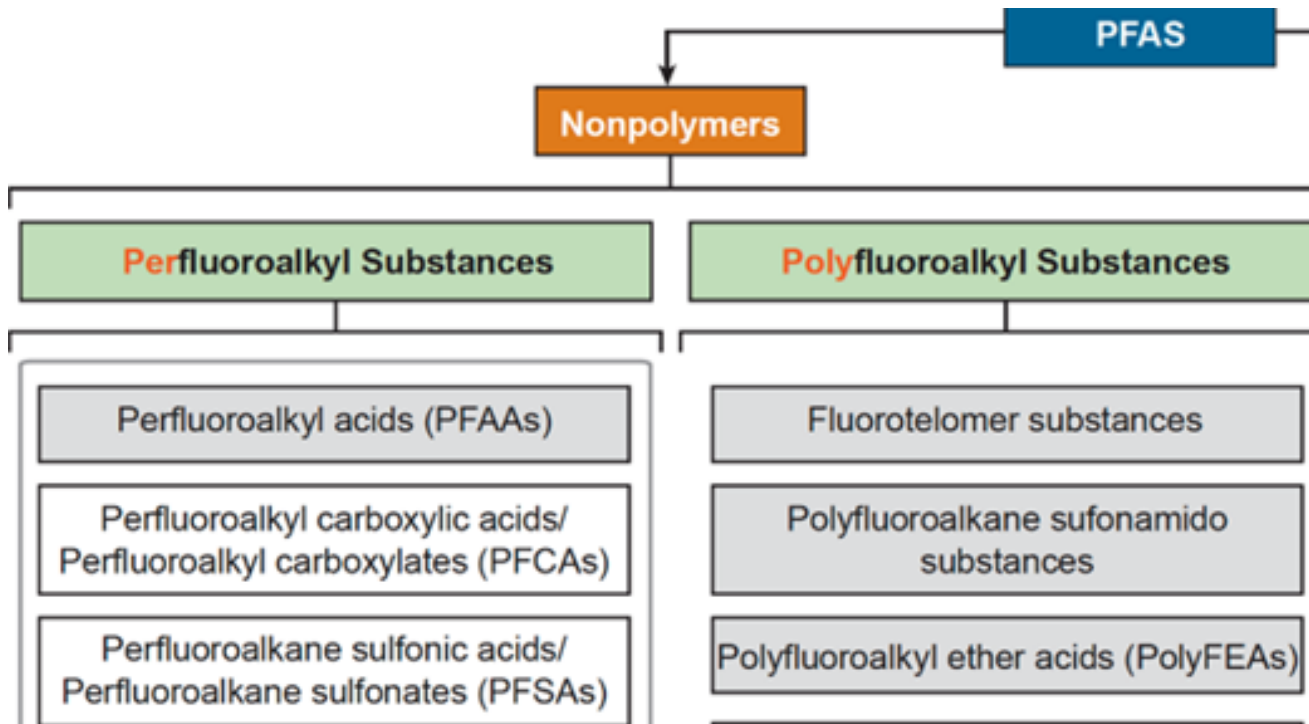
Perfluorooctane Sulfonic Acid (PFOS):
(select all)

- a) Is a Non-Polymer PFAS
- b) Has a partially fluorinated alkyl tail
- c) Is a Perfluoroalkyl Carboxylic Acid (PFCA)
- d) Is a Perfluoroalkane Sulfonic Acid (PFSA)

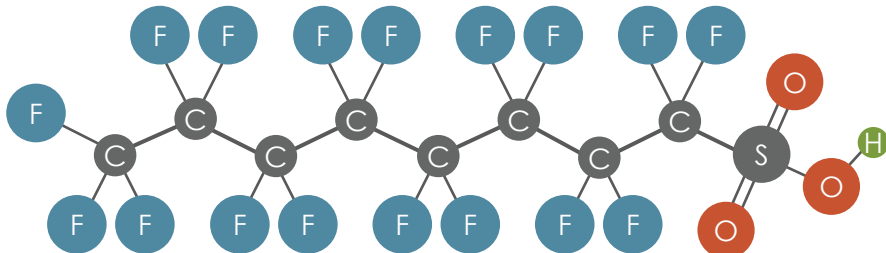
PFOS: Perfluorooctane Sulfonic Acid



Knowledge Check Explained



PFOS: Perfluorooctane Sulfonic Acid



SO₃H = Sulfonic Acid Head

- PFOS is a Perfluoroalkane Sulfonic Acid (PFSA)
- PFSAs are under the Perfluoroalkyl Substances
- Perfluoroalkyl Substances are Non-Polymers
- PFOS has a fully fluorinated alkyl tail

Perfluorooctane Sulfonic Acid (PFOS):
(select all)

- a) Is a Non-Polymer PFAS
- b) Has a partially fluorinated alkyl tail
- c) Is a Perfluoroalkyl Carboxylic Acid (PFCA)
- d) Is a Perfluoroalkane Sulfonic Acid (PFSA)

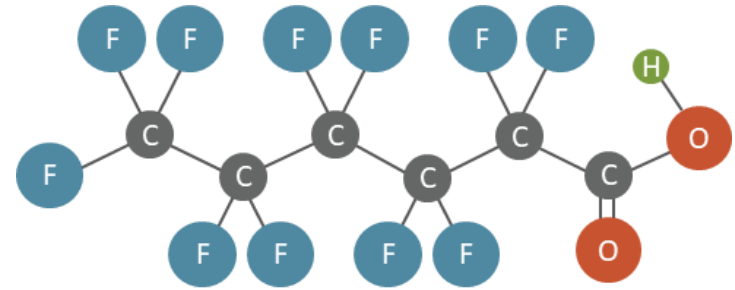
Knowledge Check

Check
In!

Perfluorohexanoic Acid (PFHxA) is persistent in the environment because:

- a) Carbon-fluorine bond
- b) It is a PFAS chemical
- c) It is a Perfluoroalkyl Carboxylic Acid (PFCA)
- d) It has 6 carbons

PFHxA: Perfluorohexanoic Acid



Knowledge Check

Check
In!

PFOA and PFOS are:
(select all that apply)

- a) Perfluoroalkyl acids (PFAAs)
- b) Polymer PFAS
- c) Most widely regulated
- d) All of the above



Perfluoroalkyl Acid (PFAA) Naming System

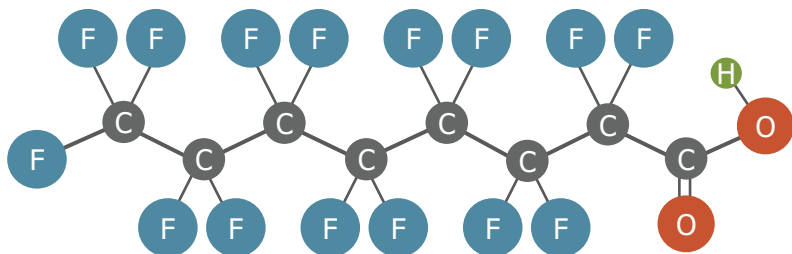
■ PFXY

- PF = perfluoro
- X = number of carbons
 - Same convention as hydrocarbons
 - Includes carbons in the carboxylate group
- Y = functional group
 - S = sulfonic acid (R-SO₃H)
 - A = carboxylic acid (R-COOH)

4	B	(buta-)
5	Pe	(penta-)
6	Hx	(hexa-)
7	Hp	(hepta-)
8	O	(octa-)
9	N	(nona-).....

Number of Carbons vs Number of Fluorinated Carbons

PFOA = Perfluorooctanoic Acid



PFOA: Perfluorooctanoic acid

- 8 Carbons (Octane)
- 7 Fluorinated Carbons
- Carboxylic Acid (COOH) Head

PF

PFO

PFOA

PF

PFO

PFOS

PF = Perfluoro

X = # Carbons = 8 = Octa = O

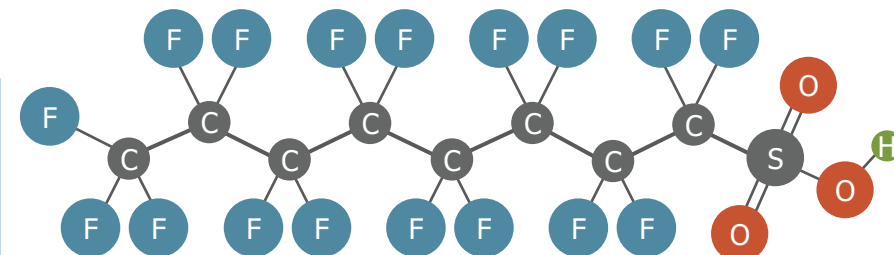
Y = Head (Carboxylic Acid = A and Sulfonic Acid = S)

PFOA

PFOS

PFOS: Perfluorooctane Sulfonic Acid

- 8 Carbons (Octane)
- 8 Fluorinated Carbons
- Sulfonic Acid (SO₃H) head



PFOS = Perfluorooctane Sulfonic Acid

PFAA Naming System

- **PF^XY**
 - PF = perfluoro
 - **X** = number of carbons
 - Same convention as hydrocarbons
 - Includes C in the carboxylate group
 - **Y** = functional group
 - S = sulfonic acid (R-SO₃H)
 - A = carboxylic acid (R-COOH)

Table 2-2 Basic naming structure and shorthand for PFAAs

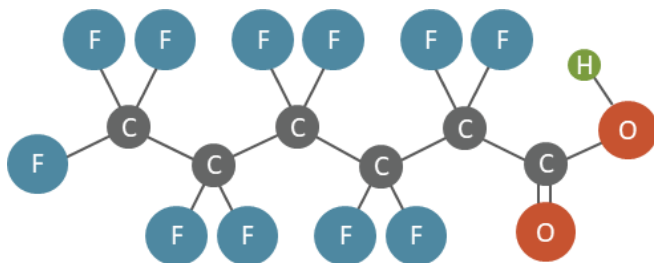
X	Y	Acronym	Name	Formula	CAS No.
B = buta (4 carbon)	A = Carboxylate or carboxylic acid	PFBA	Perfluorobutanoate	C ₃ F ₇ CO ₂ ⁻	45048-62-2
			Perfluorobutanoic acid	C ₃ F ₇ COOH	375-22-4
	S = Sulfonate or sulfonic acid	PFBS	Perfluorobutane sulfonate	C ₄ F ₉ SO ₃ ⁻	45187-15-3
			Perfluorobutane sulfonic acid	C ₄ F ₉ SO ₃ H	375-73-5
Pe = penta (5 carbon)	A = Carboxylate or carboxylic acid	PFPeA	Perfluoropentanoate	C ₄ F ₉ CO ₂ ⁻	45167-47-3
			Perfluoropentanoic acid	C ₄ F ₉ COOH	2706-90-3
	S = Sulfonate or sulfonic acid	PFPeS	Perfluoropentane sulfonate	C ₅ F ₁₁ SO ₃ ⁻	NA
			Perfluoropentane sulfonic acid	C ₅ F ₁₁ SO ₃ H	2706-91-4
Hx = hexa (6 carbon)	A = Carboxylate or carboxylic acid	PFHxA	Perfluorohexanoate	C ₅ F ₁₁ CO ₂ ⁻	92612-52-7
			Perfluorohexanoic acid	C ₅ F ₁₁ COOH	307-24-4
	S = Sulfonate or sulfonic acid	PFHxS	Perfluorohexane sulfonate	C ₆ F ₁₃ SO ₃ ⁻	108427-53-8
			Perfluorohexane sulfonic acid	C ₆ F ₁₃ SO ₃ H	355-46-4
Hp = hepta (7 carbon)	A = Carboxylate or carboxylic acid	PFHpA	Perfluoroheptanoate	C ₆ F ₁₃ CO ₂ ⁻	120885-29-2
			Perfluoroheptanoic acid	C ₆ F ₁₃ COOH	375-85-9
	S = Sulfonate or sulfonic acid	PFHpS	Perfluoroheptane sulfonate	C ₇ F ₁₅ SO ₃ ⁻	NA
			Perfluoroheptane sulfonic acid	C ₇ F ₁₅ SO ₃ H	375-92-8
O = octa (8 carbon)	A = Carboxylate or carboxylic acid	PFOA	Perfluorooctanoate	C ₇ F ₁₅ CO ₂ ⁻	45285-51-6
			Perfluorooctanoic acid	C ₇ F ₁₅ COOH	335-67-1
	S = Sulfonate or sulfonic acid	PFOS	Perfluorooctane sulfonate	C ₈ F ₁₇ SO ₃ ⁻	45298-90-6
			Perfluorooctane sulfonic acid	C ₈ F ₁₇ SO ₃ H	1763-23-1
N = nona (9 carbon)	A = Carboxylate or carboxylic acid	PFNA	Perfluorononanoate	C ₈ F ₁₇ CO ₂ ⁻	72007-68-2
			Perfluorononanoic acid	C ₈ F ₁₇ COOH	375-95-1
	S = Sulfonate or sulfonic acid	PFNS	Perfluorononane sulfonate	C ₉ F ₁₉ SO ₃ ⁻	NA
			Perfluorononane sulfonic acid	C ₉ F ₁₉ SO ₃ H	474511-07-4
D = deca (10 carbon)	A = Carboxylate or carboxylic acid	PFDA	Perfluorodecanoate	C ₉ F ₁₉ CO ₂ ⁻	73829-36-4
			Perfluorodecanoic acid	C ₉ F ₁₉ COOH	335-76-2
	S = Sulfonate or sulfonic acid	PFDS	Perfluorodecane sulfonate	C ₁₀ F ₂₁ SO ₃ ⁻	126105-34-8
			Perfluorodecane sulfonic acid	C ₁₀ F ₂₁ SO ₃ H	335-77-3

Nomenclature: Perfluoroalkyl Acids (PFAAs)

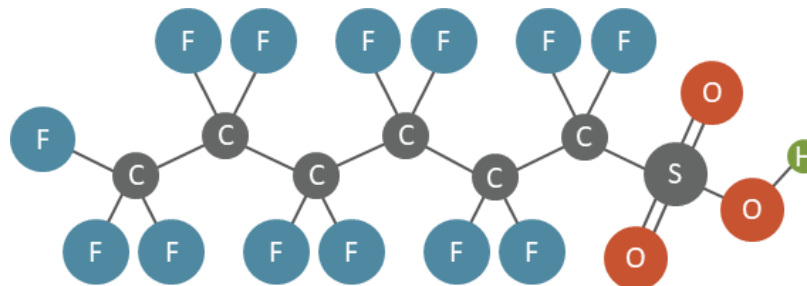
PFAS-1, Section 2.2.3.1 Perfluoroalkyl Acids (PFAAs).

Acronym	Compound Name	Carbon Chain Length	# Fluorinated Carbons	Functional Group
PFOA	<u>Per</u> fluoro <u>octa</u> noic acid	C8	7	Carboxylic acid
PFOS	<u>Per</u> fluoro <u>octane</u> sulfonic acid	C8	8	Sulfonic acid
PFBA	<u>Per</u> fluoro <u>buta</u> noic acid	C4	3	Carboxylic acid
PFBS	<u>Per</u> fluoro <u>butane</u> sulfonic acid	C4	4	Sulfonic acid
PFHxA	<u>Per</u> fluoro <u>hexa</u> noic acid	C6	5	Carboxylic acid
PFHxS	<u>Per</u> fluoro <u>hexane</u> sulfonic acid	C6	6	Sulfonic acid

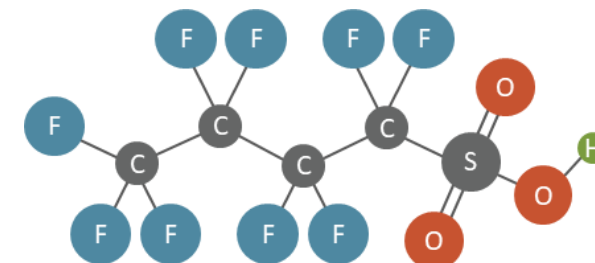
PFHxA



PFHxS



PFBS

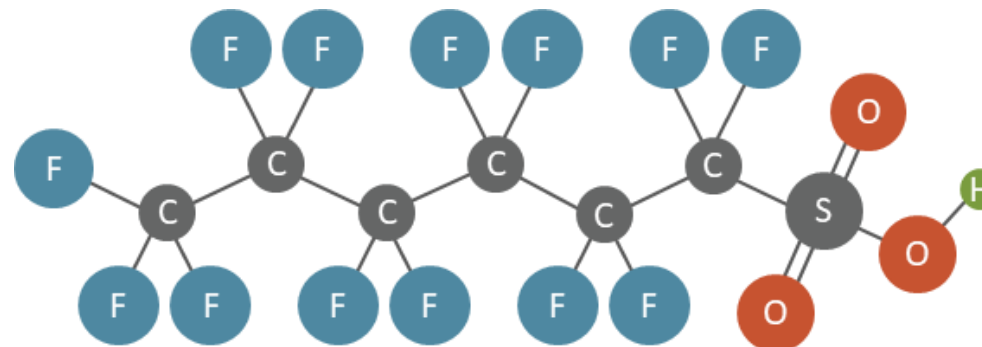


Knowledge Check

Check
In!

Name That PFAS!

Remember: Look at # carbons and functional group at head of molecule



- a) PFBS
- b) PFPeS
- c) PFBA
- d) PFHxS

4	B	(<u>buta</u> -)
5	Pe	(penta-)
6	<u>Hx</u>	(hexa-)
7	Hp	(hepta-)
8	O	(octa-)
9	N	(<u>nona</u> -).....

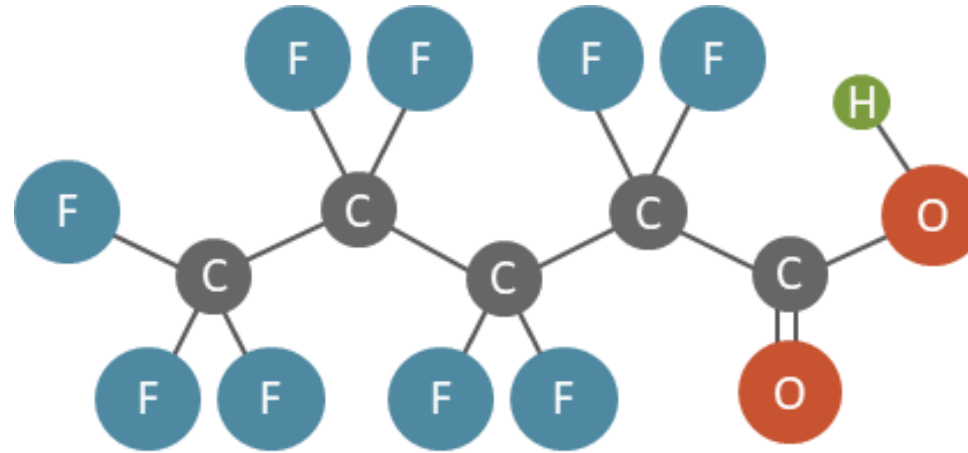


Knowledge Check

Check
In!

Name That PFAS!

Remember: Look at # carbons and functional group at head of molecule



- a) PFBS
- b) PFPeA
- c) PFBA
- d) PFPeS

4	B	(<u>buta</u> -)
5	Pe	(penta-)
6	<u>Hx</u>	(hexa-)
7	Hp	(hepta-)
8	O	(octa-)
9	N	(<u>nona</u> -).....



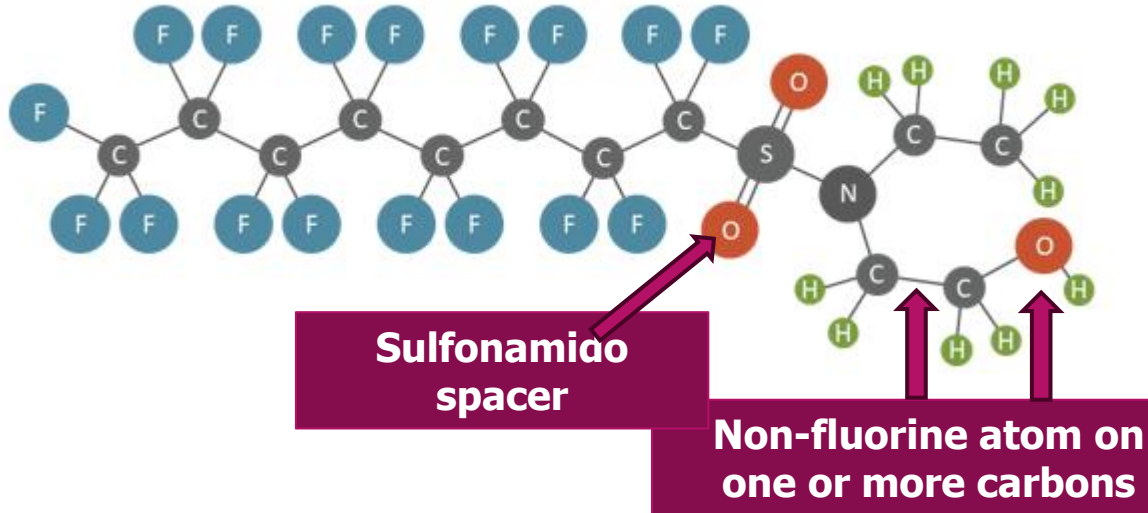
Nonpolymer: Polyfluoroalkyl Substances

PFAS-1, Section 2.2.4 Polyfluoroalkyl Substances.

Polyfluoroalkyl substances: partially fluorinated alkyl chain

Polyfluoroalkyl substances: non-fluorine atom (usually hydrogen [H] or oxygen [O]) attached to at least one carbon atom in the alkane chain

N-Ethylperfluorooctane sulfonamido ethanol (N-EtFOSE)



Polyfluoroalkyl substances may also be transformed (biotically or abiotically) to perfluoroalkyl substances (e.g., PFOS or PFOA):
PRECURSORS

Polyfluoroalkyl Substances

Fluorotelomer substances

Polyfluoroalkane sulfonamido substances

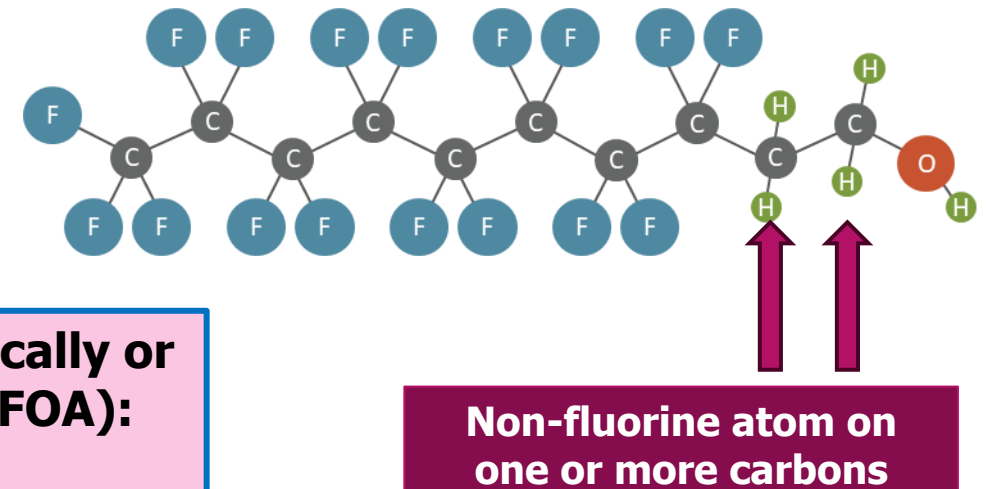
Polyfluoroalkyl ether acids (PolyFEAs)

Chloropolyfluoroalkyl ether acids

Chloropolyfluoroalkyl acids

Polyfluoroalkyl carboxylic acids (PolyFCAs)

8:2 Fluorotelomer Alcohol (8:2 FTOH)



Common Polyfluoroalkyl Substances

PFAS-1, Section 2.2.4.1 Fluorotelomer Substances; Section 2.2.4.2 Perfluoroalkane Sulfonamido Substances. Figure 2-5 expanded Family Tree

- **Fluorotelomers: commonly analyzed for by labs**

6:2 Fluorotelomer sulfonic acid (6:2 FTS)

8:2 FTS

5:3 Fluorotelomer carboxylic acid (5:3 FTCA)

- **Fluorotelomer alcohols: volatile PFAS; not commonly analyzed for by labs**

8:2 Fluorotelomer Alcohol (8:2 FTOH)

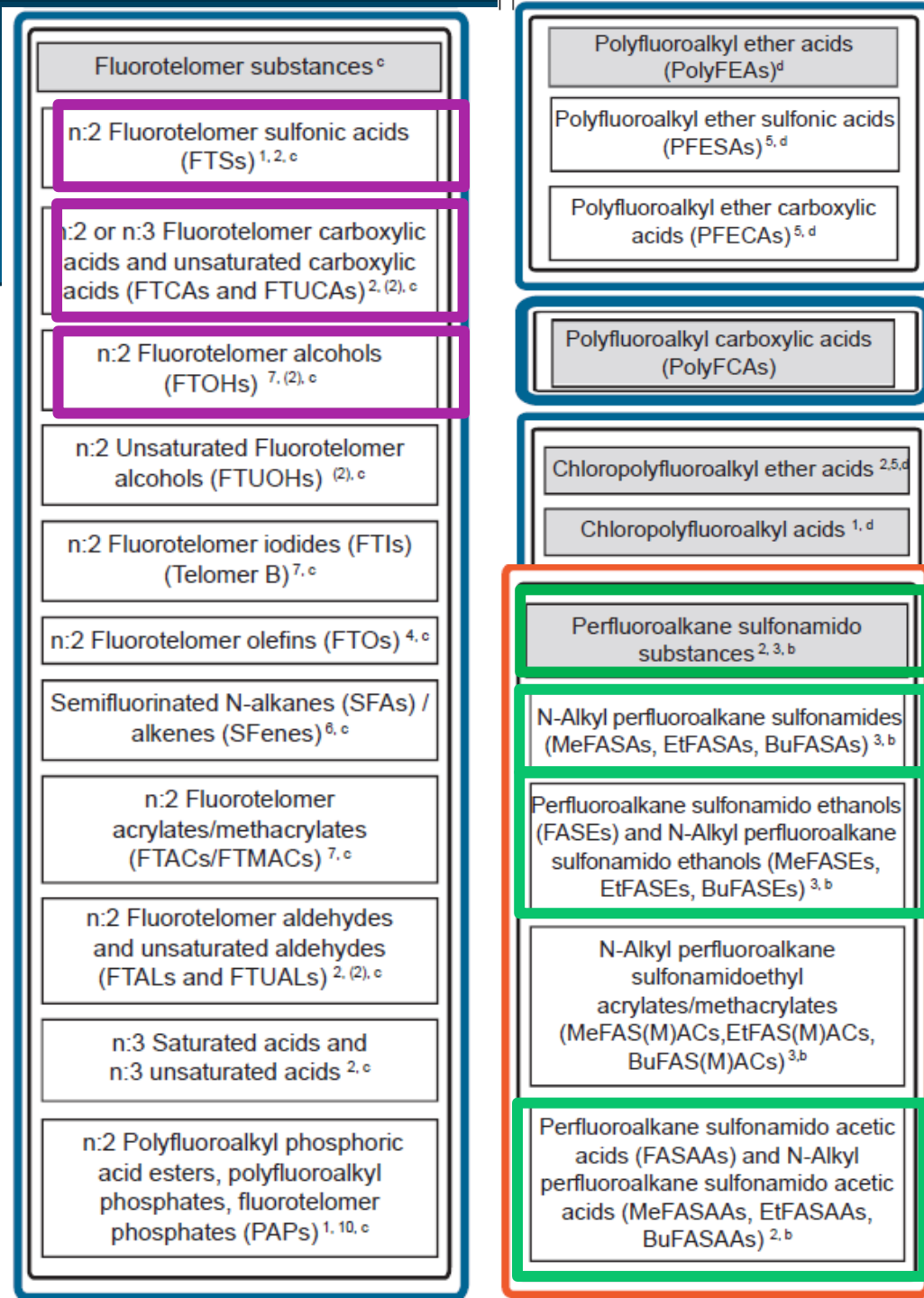
- **Perfluoroalkane sulfonamido substances: commonly analyzed for by labs**

Perfluorooctane sulfonamide (PFOSA)

N-Methyl perfluorooctane sulfonamido acetic acid (N-MeFOSAA)

N-Ethylperfluorooctane sulfonamido ethanol (N-EtFOSE)

N-Methylperfluorooctane sulfonamide (N-MeFOSA)

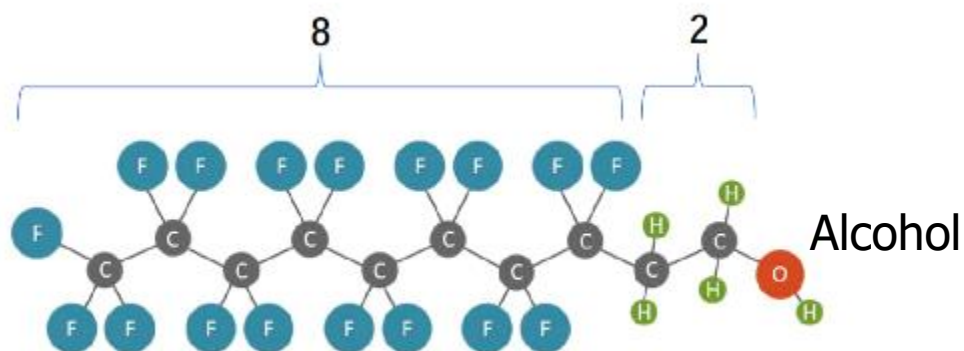


Polyfluoroalkyl Substances Currently Included in EPA Methods

Polyfluoroalkyl PFAS	EPA Method 1633A	EPA Method 537.1	EPA Method 533
4:2 FTS	X		X
6:2 FTS	X		X
8:2 FTS	X		X
PFOSA	X		
N-MeFOSA	X		
N-EtFOSA	X		
N-MeFOSAA	X	X	
N-EtFOSAA	X	X	
N-MeFOSE	X		
N-EtFOSE	X		
ADONA	X	X	X
9Cl-PF3ONS	X	X	X
11Cl-PF3OUdS	X	X	X
3:3 FTCA	X		
5:3 FTCA	X		
7:3 FTCA	X		

Fluorotelomers

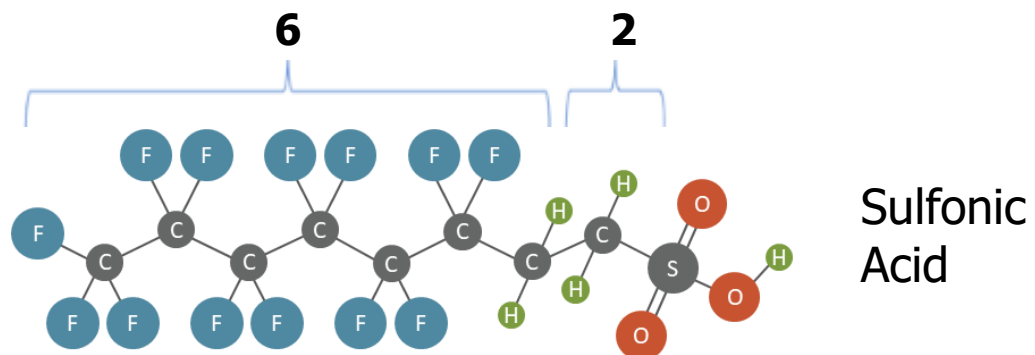
Acronym	Compound Name	Carbon Chain Length	# Fluorinated Carbons	# Non-Fluorinated Carbons	Functional Group
8:2 FTOH	8:2 Fluorotelomer Alcohol	C10	8	2	Alcohol
6:2 FTS	6:2 Fluorotelomer Sulfonic Acid	C8	6	2	Sulfonic acid



Fluorotelomers are often named using a “n:x” prefix (8:2 fluorotelomer alcohol, 8:2 FTOH)

n = number of fluorinated carbons (8)

X = number of non-fluorinated carbons (2)

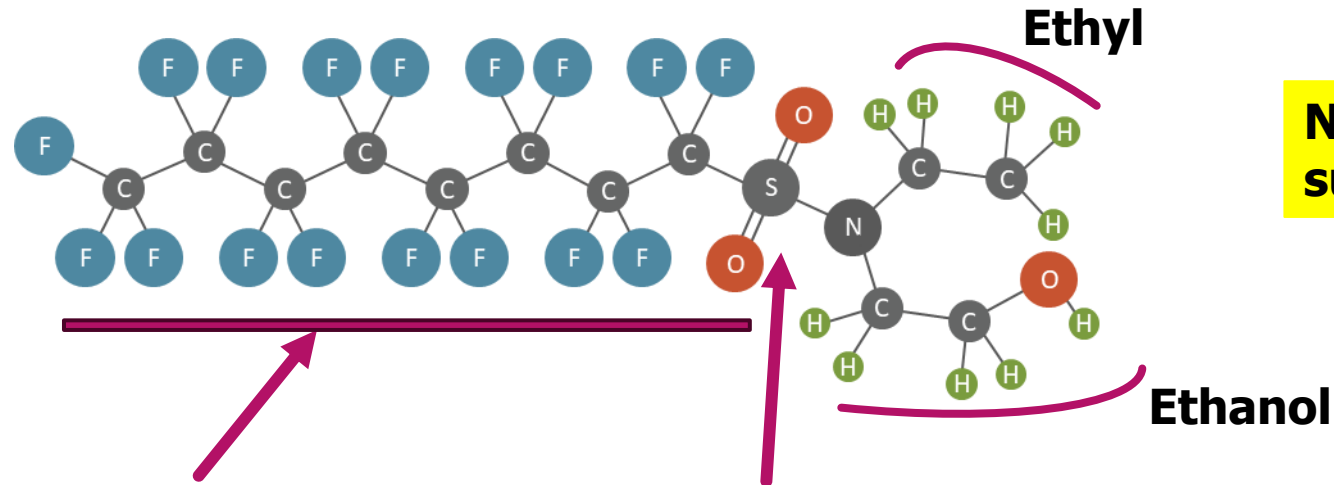


Fluorotelomers are often named using a “n:x” prefix (6:2 fluorotelomer sulfonic acid, 6:2 FTS)

n = number of fluorinated carbons (6)

X = number of non-fluorinated carbons (2)

Perfluoroalkane Sulfonamido Substances

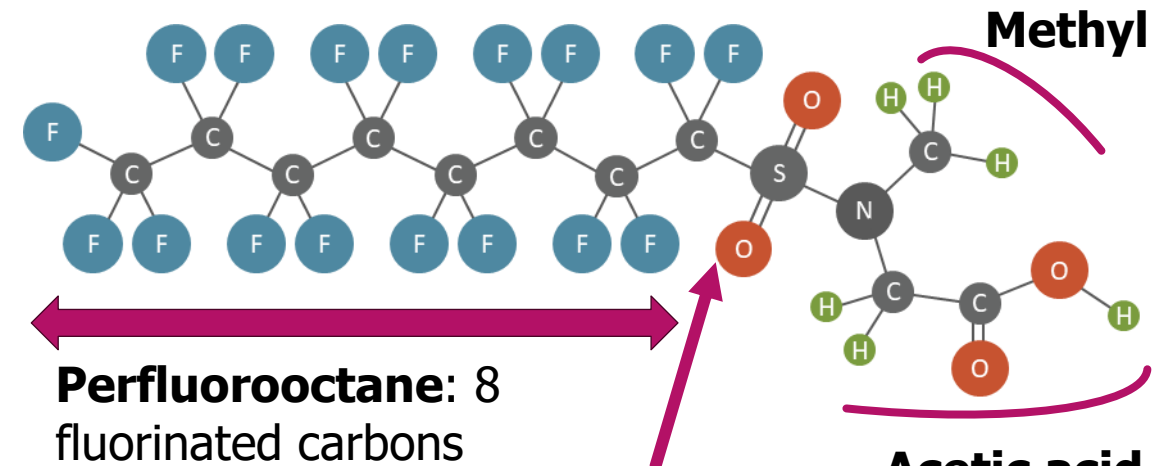


N-Ethyl perfluorooctane sulfonamido ethanol (N-EtFOSE)

Perfluorooctane: 8 fluorinated carbons

Sulfonamido Spacer
(SO₂ with N-CH₂CH₃: Ethyl group)

N-Methyl perfluorooctane sulfonamido acetic acid (N-MeFOSAA)



Sulfonamido Spacer
(SO₂ with N-CH₃: Methyl group)

Knowledge Check

Check
In!

Polyfluoroalkyl PFAS:
(Select all that apply)

- a) Are persistent in the environment
- b) Contain carbons that are not fluorinated
- c) Can transform into perfluoroalkyl PFAS

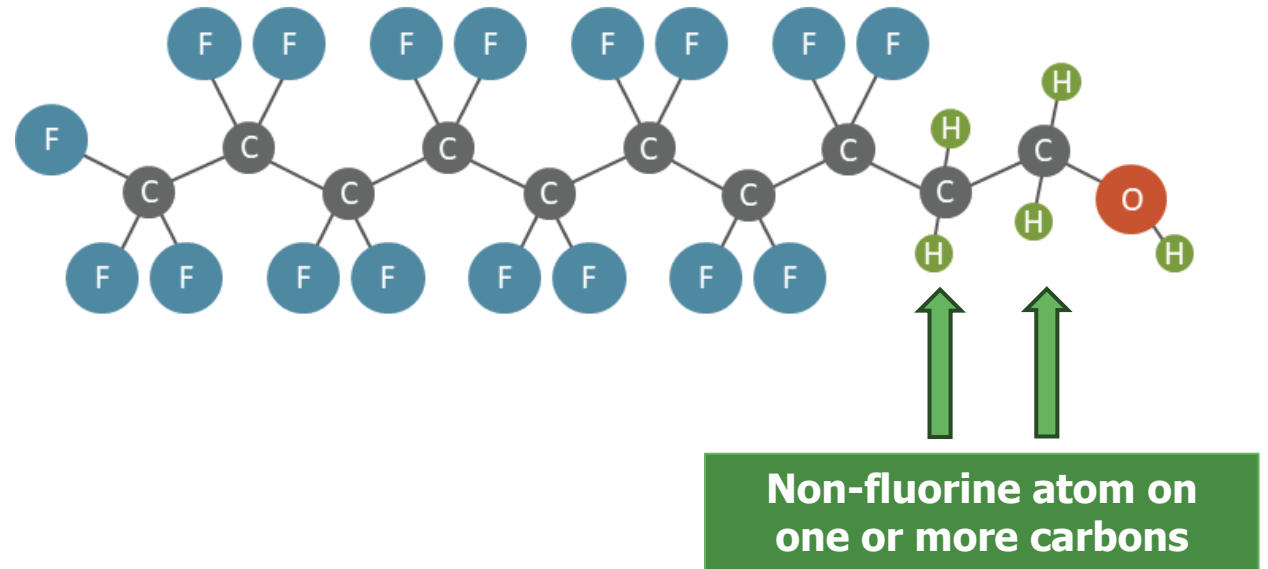


Knowledge Check Explained

Polyfluoroalkyl PFAS:

(Select all that apply)

- a) Are persistent in the environment
- b) Contain carbons that are not fluorinated
- c) Can transform into perfluoroalkyl PFAS

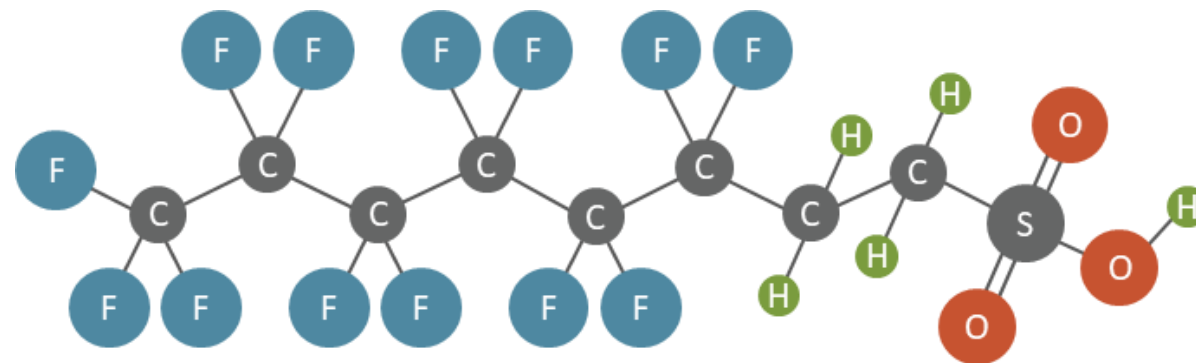


Knowledge Check

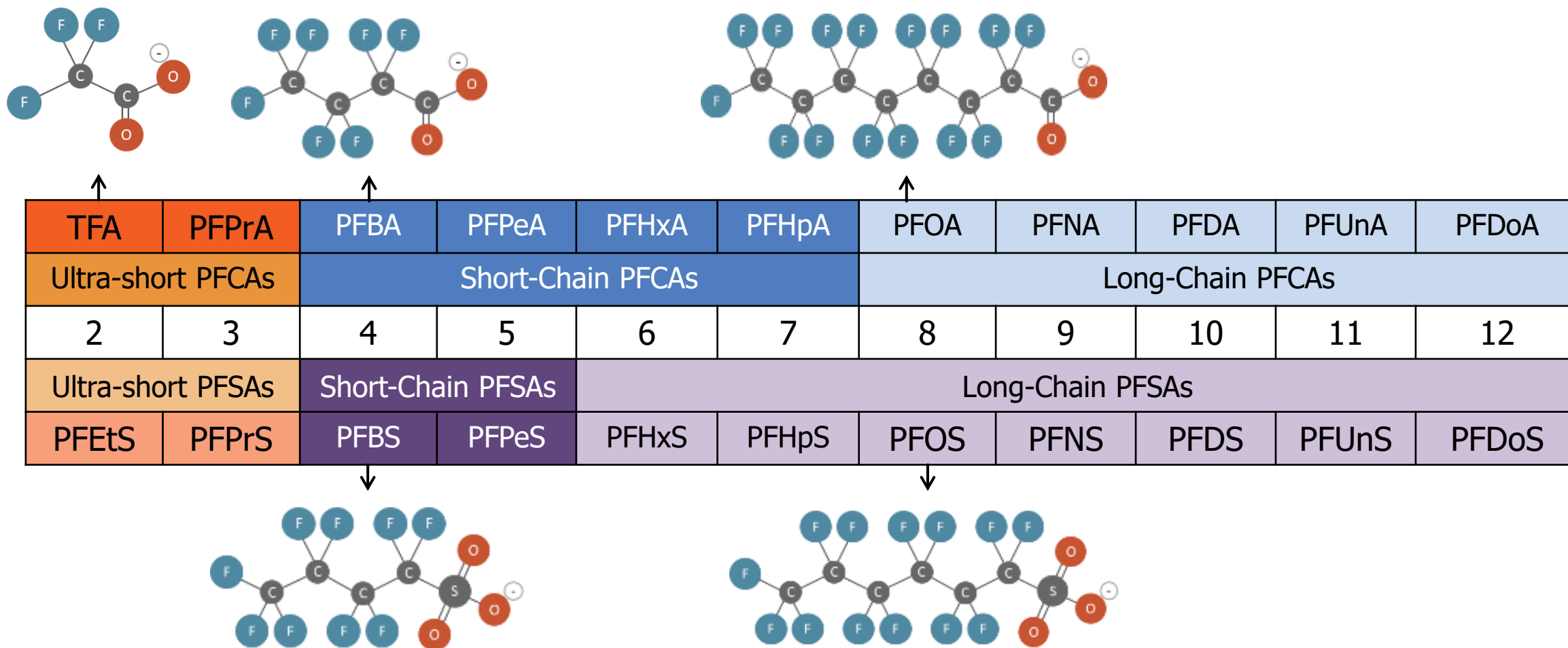
Check
In!

The fluorotelomer molecule shown here is:
(select all that apply)

- a) A perfluoroalkyl substance
- b) A polyfluoroalkyl substance
- c) 8:2 fluorotelomer sulfonic acid (8:2 FTS)
- d) 6:2 fluorotelomer sulfonic acid (6:2 FTS)
- e) PFOS

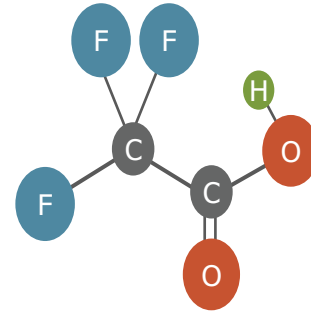


Long-Chain, Short-Chain, and Ultra-Short PFAs

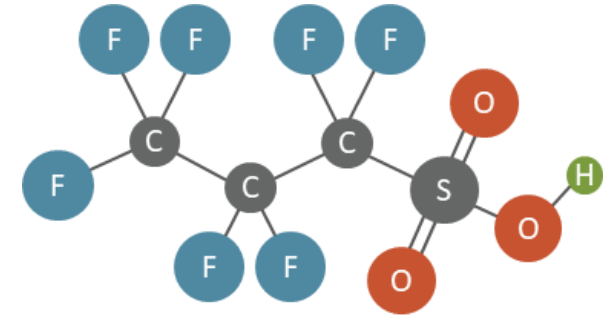


Ultrashort PFAS

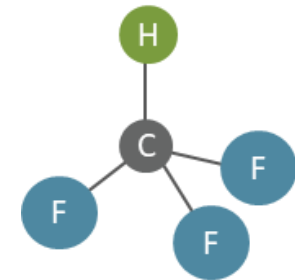
- ≤ 3 carbons
- Common examples:
 - Trifluoroacetic acid (TFA)
 - Perfluoropropanoic acid (PFPrA)
 - Perfluoropropanesulfonic acid (PFPrS)
- Some fluorinated gases considered ultra-short PFAS
- Not typically measured but gaining more interest



TFA



PFPrS



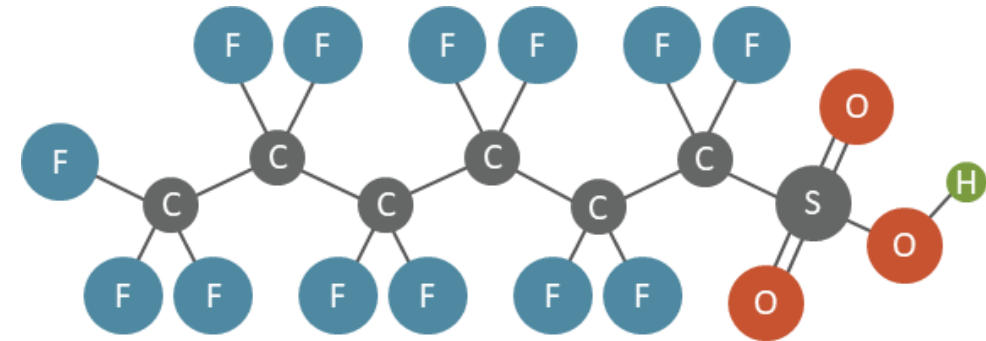
Trifluoromethane: Fluorinated Gas

Knowledge Check

Check
In!

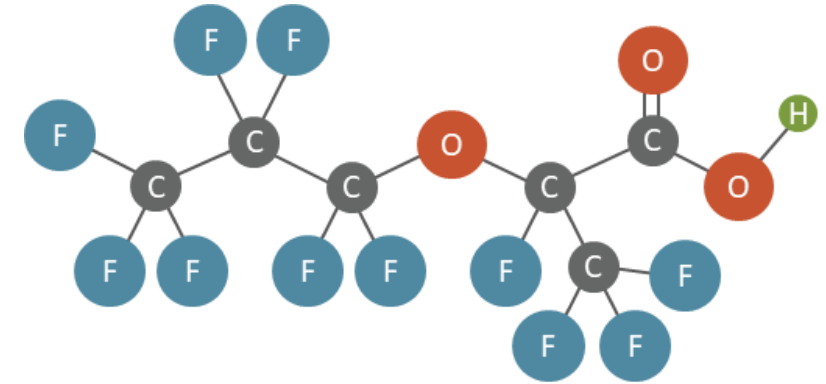
The Molecule Shown:
(select all that apply)

- a) Is long-chain
- b) Is PFPeS
- c) Is a Perfluoroalkane sulfonic acid (PFSA)
- d) Is PFHxS
- e) Has 6 fluorinated carbons



Replacement Chemistry

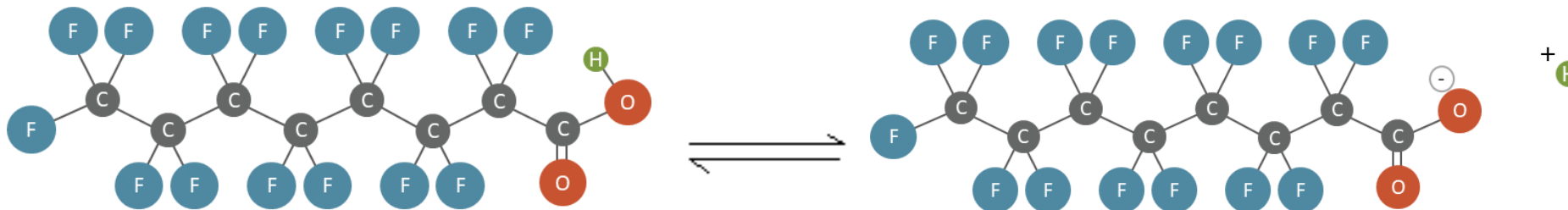
- 6:2 Fluorotelomers replace PFOS in metals plating
- Fluorotelomers replace PFOS and PFHxS in AFFF
- Shorter chain PFAAs replace PFOA: PFBA, PFPeA
- ADONA and HFPO-DA (GenX) are replacement chemicals for PFOA
- HFPO-DA (Hexafluoropropylene oxide dimer acid)
 - Component of GenX technology used by one manufacturer (USEPA 2018)
 - U.S. EPA MCL for HFPO-DA = 10 ppt



Chemical structure for HFPO-DA (GenX)
(hexafluoropropylene oxide dimer acid)

CAS Numbers and PFAS State

Every chemical substance has its own distinct Chemical Abstracts Service (CAS) Registry Number.

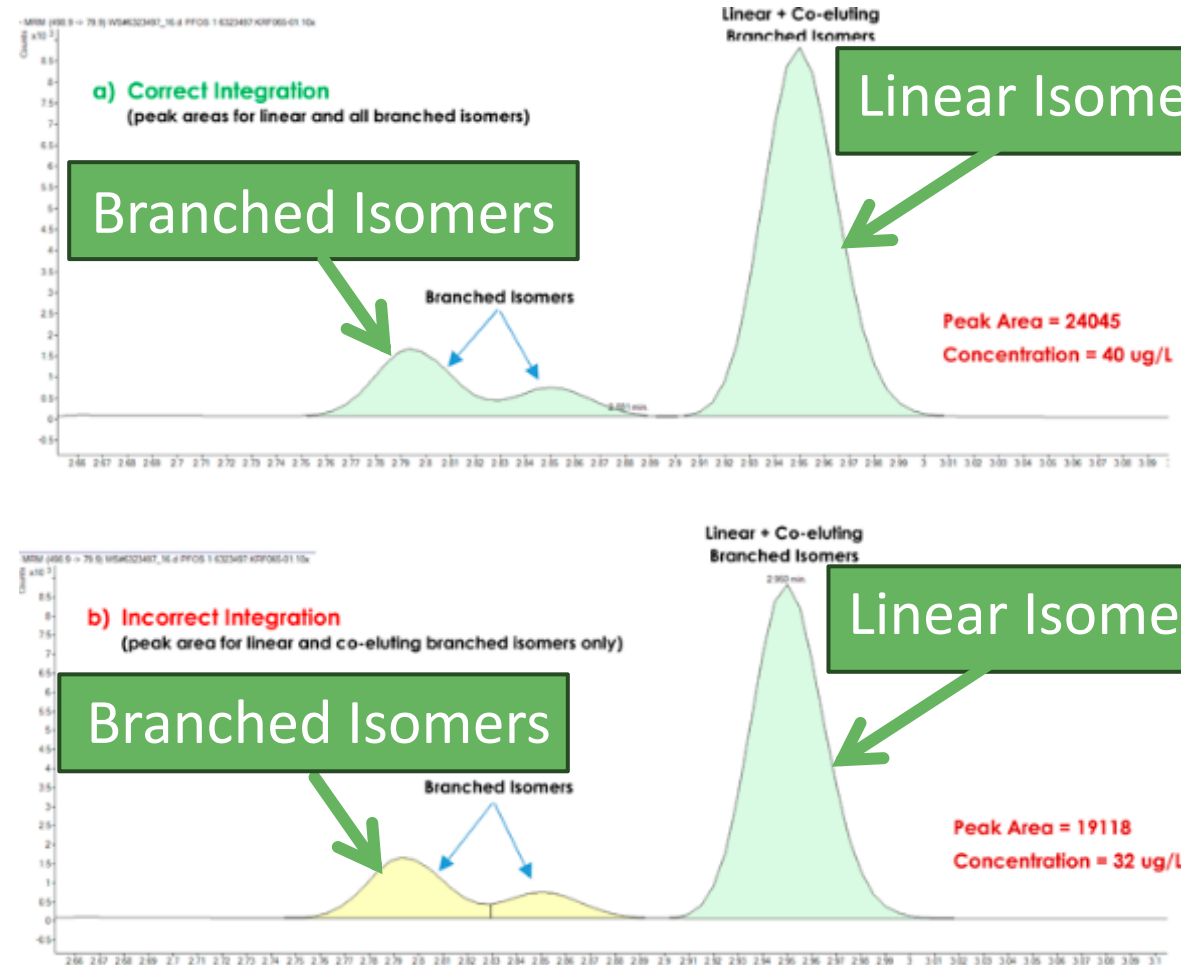


	PFAS State		Structure	CAS No.
PFOA	Anion	Perfluorooctanoate	$\text{C}_7\text{F}_{15}\text{CO}_2^-$	45285-51-6
	Acid	Perfluorooctanoic acid	$\text{C}_7\text{F}_{15}\text{COOH}$	335-67-1
PFOS	Anion	Perfluorooctane sulfonate	$\text{C}_8\text{F}_{17}\text{SO}_3^-$	45298-90-6
	Acid	Perfluorooctane sulfonic acid	$\text{C}_8\text{F}_{17}\text{SO}_3\text{H}$	1763-23-1

Why is this important?

Branched & Linear PFAS Isomers

- Branched and linear isomers of PFAS (including PFCAs) produced by ECF seen in consumer products, groundwater, sediment, soil, wastewater, landfills
- Observing branched isomers depends on chromatography
- If ignoring the branched peak, concentrations may be biased low
- Telomer chemistry theoretically produces predominantly linear PFAS, however, final product may contain branched isomers



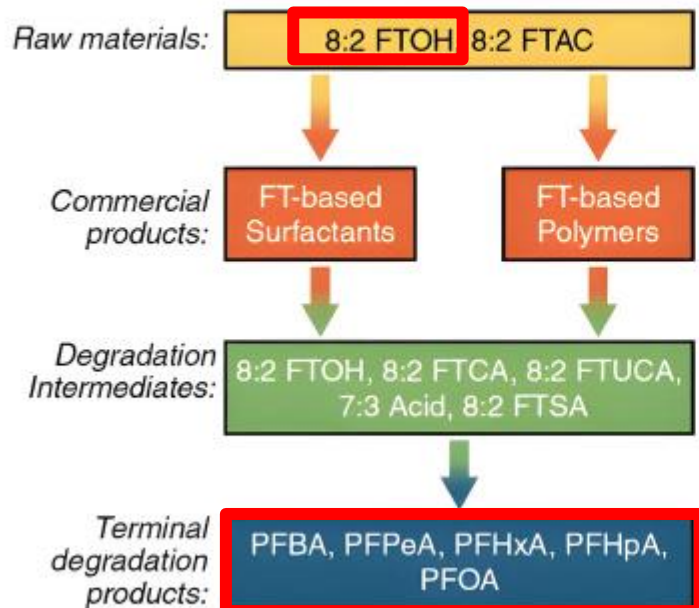
Currently labs reporting L&B consistently for: PFHxS, PFOS, PFOA, NMeFOSAA, NEtFOSAA

EPA 1633: also includes L&B for PFNA, PFOSA, NMeFOSA, NEtFOSA, NEtFOSE, NMeFOSE

Precursors: Transformation Pathways

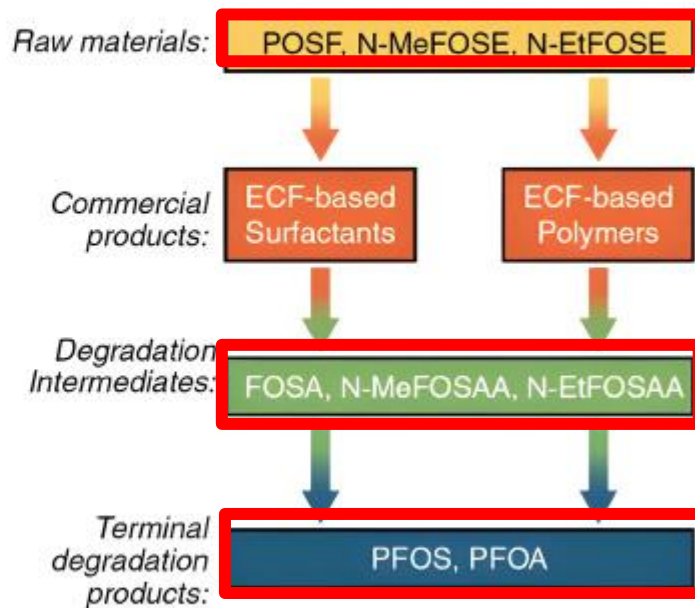
Fluorotelomer Degradation Pathway Overview

Example for 8:2 fluorotelomer homologue



ECF Degradation Pathway Overview

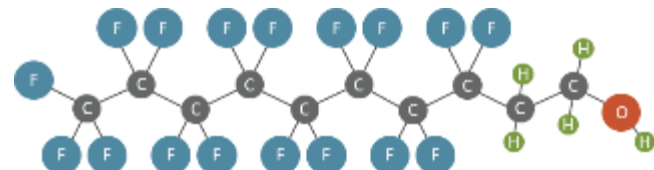
Example for perfluorooctane sulfonyl homologue



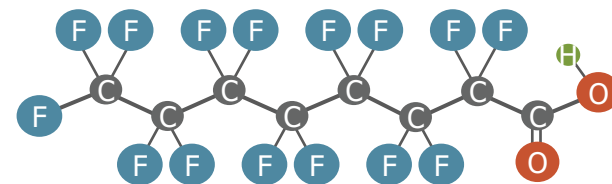
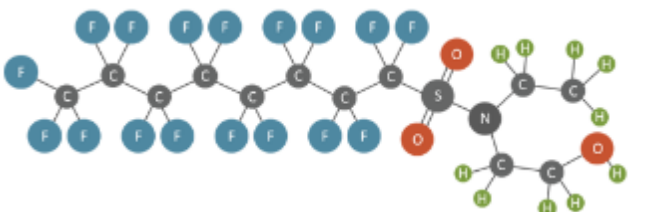
Takeaways:

- Polyfluoroalkyl PFAS precursors can transform into measurable regulated PFAS.
- Manufacturing process may dictate transformation pathway.
- Transformation can impact our decision-making on site investigations.

8:2 FTOH



N-EtFOSE



PFOA

PFAS-1, Figure 2-11 Example transformation pathways.
PFAS-1, Section 2.2.4 Polyfluoroalkyl Substances.

Precursors: Transformation Pathways

Manufacturing process can dictate potential transformation products of precursors.

Manufacturing Process	Commonly Found Polyfluorinated Substance (Precursors)	Potential PFAAs Produced
Fluorotelomerization	FTS ¹	Linear PFCAs ³
	FTCA ²	Linear PFCAs ³
	FTOH	Linear PFCAs ³
Electrochemical fluorination	FASE	Branched and linear PFCAs Branched and linear PFSAs
	FASAA	Branched and linear PFCAs Branched and linear PFSAs
¹ Fluorotelomer sulfonic acid: for example, may be found at AFFF sites ² Fluorotelomer carboxylic acids: for example, 5:3 FTCA may be found in landfill leachate ³ Under certain instances, can produce mixture of linear and branched PFCAs		

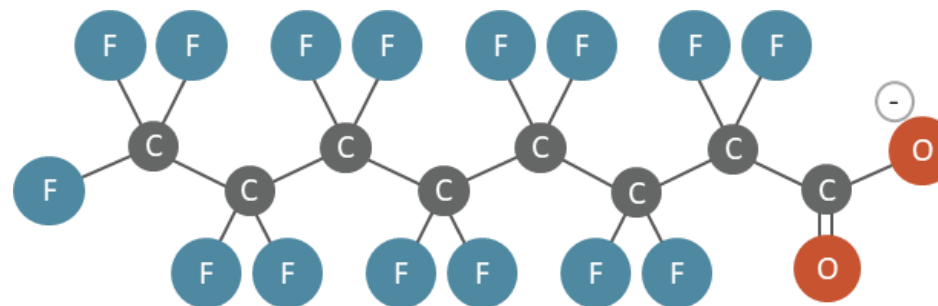
PFCA = Perfluoroalkyl Carboxylic Acids: Examples: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA

PFSA = Perfluoroalkane Sulfonic Acids: Examples: PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS

What is a PFAS? Definitions Vary

Source of Definition	Year Defined	Definition	Additional Comments
Buck et al. ^[156]	2011	"highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (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 $C_nF_{2n+1}-$."	Buck et al. (2011 ^[156]) is an open-access paper that provides a detailed explanation of PFAS terminology, classification, and origins, and recommends specific and descriptive terminology, names, and acronyms for PFAS.
OECD ^[2318]	2021	"fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is a PFAS."	OECD (2021 ^[2318]) expanded the Buck et al. (2011 ^[156]) definition to include chemicals that contain the $-C_nF_{2n}-$ moiety in addition to the $-CF_3$ and $-CF_2-$ moieties.
Gluge et al. ^[1939]	2020	In addition to substances containing functional groups on both ends of the chain, cycloaliphatic substances. A [excluding] non-polymeric substances, polyfluoroalkylether-based substances are included."	
TURA Program, Massachusetts (TURA 2023) ^[2795]	2023	"Certain PFAS not otherwise defined as PFAS in CCL5, including: (1) $CF_3-C_nF_{2n}-$, $n \geq 2$ or $-C_nF_{2n}OC_mF_{2m}-$ or $-C_nF_{2n}OC_mF_{2m}-$ may represent a straight or branched chain."	
USEPA OPPT ^[2813]	2021	"a structure that contains the perfluorinated moiety, branching, heteroatoms, and functional groups."	
NDAA, WA, CA, VT, ME	2019, 2020, 2021	Organic chemicals containing one or more fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is a PFAS."	
USEPA CCL5 ^[2718]	2022	"For the purposes of CCL5, one of these three structures: (1) $R-(CF_2)_n-CF(R')R''$, where R , R' , and R'' represent any functional group or atom except hydrogen (H). This includes perfluoroalkyl substances with $R-CF_2-CF_2-R'$ and CF_3-CF_2-R units or perfluoroalkyl ether substances with $R-CF_2-O-CF_2-R'$, and CF_3-O-CF_2-R units."	
MPART ^[2885]	2023	PFAS means per- and polyfluoroalkyl ether moiety, $R-(CF_2)_n-O-(CF_2)_m-R'$, where R , R' , and R'' represent any functional group or atom except hydrogen (H). This includes perfluoroalkyl substances with $R-CF_2-CF_2-R'$ and CF_3-CF_2-R units or perfluoroalkyl ether substances with $R-CF_2-O-CF_2-R'$, and CF_3-O-CF_2-R units."	This working description borrows from the OECD 2021 and the EPA TSCA definitions of PFAS. In 2024, the Subgroup is examining this working description closer and is considering physicochemical and toxicological properties.

OECD (2021): Fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is a PFAS.



Key Takeaways: What Did We Just Cover?

- PFAS Family Tree
- Polymer vs Non-Polymer
- Perfluoroalkyl Substances vs Polyfluoroalkyl Substances
- Perfluoroalkyl Acid (PFAA) Naming Conventions
- Fluorotelomer Naming Conventions
- Long Chain vs Short Chain PFAS
- Ultra-Short PFAS
- Replacement PFAS
- PFAS and CAS Numbers
- Linear & Branched PFAS Isomers
- Transformation Pathways of Polyfluoroalkyl Substances (Precursors)

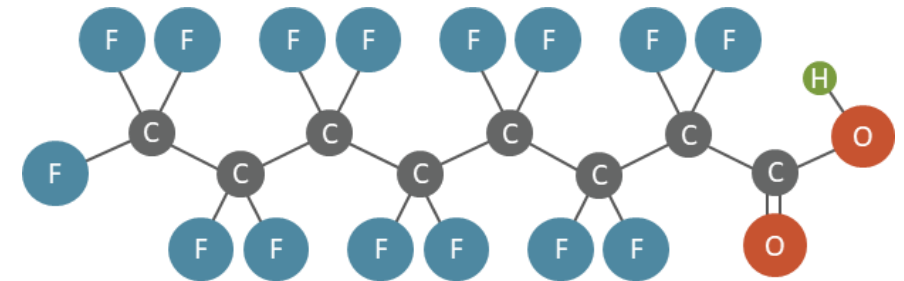


PHYSICAL AND CHEMICAL PROPERTIES

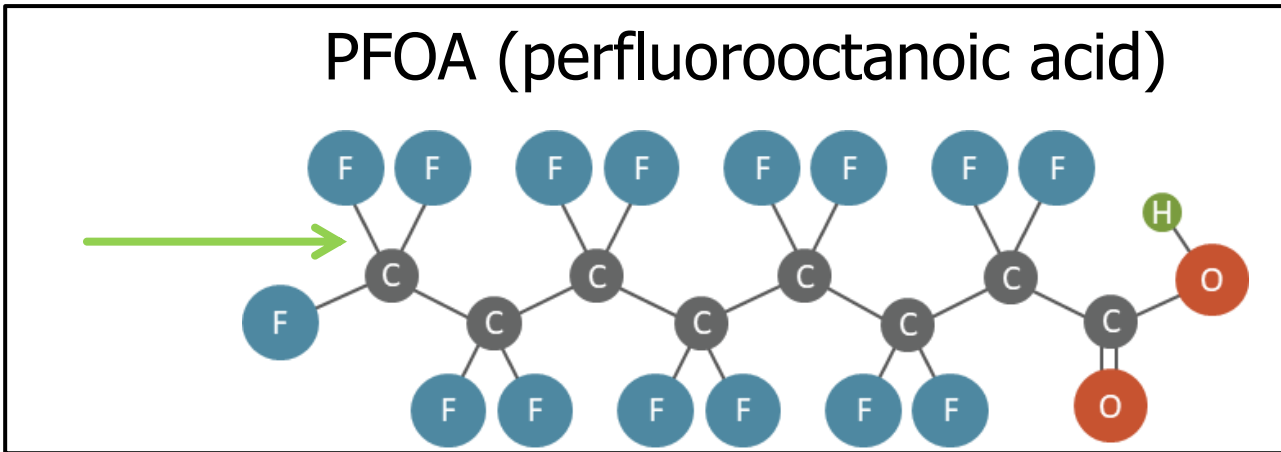
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PFAS Physical and Chemical Properties

- Chemical and physical properties – why are these important for PFAS in the environment?
 - C-F bond
 - Chain length
 - Functional group: PFAAs & precursors
 - Acid/base chemistry
 - Low Henry's constant
 - Mixed polarity (surfactant)



PFAS Physical and Chemical Properties



Key chemical property

- C-F bond
- Chain length
- Functional group: PFAAs & precursors
- Acid/base chemistry
- Low Henry's constant
- Mixed polarity (surfactant)

Physical properties & implications

- High thermal stability – destructive treatment is energy intensive
- High chemical stability – low reactivity, low biodegradability
- Weak intermolecular interactions – hydrophobic and lipophobic

PFAS Physical and Chemical Properties

Why is the C-F bond so strong?

strong?

1 H 1.008 Hydrogen	2 He 4.003 Helium																																			
3 Li 6.941 Lithium	4 Be 9.012 Beryllium	5 B 10.81 Boron	6 C 12.011 Carbon	7 N 14.007 Nitrogen	8 O 15.999 Oxygen	9 F 18.998 Fluorine	10 Ne 20.180 Neon																													
11 Na 22.990 Sodium	12 Mg 24.305 Magnesium	13 Al 26.982 Aluminum	14 Si 28.085 Silicon	15 P 30.974 Phosphorus	16 S 32.06 Sulfur	17 Cl 35.45 Chlorine	18 Ar 39.948 Argon																													
19 K 39.098 Potassium	20 Ca 40.078 Calcium	21 Sc 44.956 Scandium	22 Ti 47.88 Titanium	23 V 50.942 Vanadium	24 Cr 52.00 Chromium	25 Mn 54.938 Manganese	26 Fe 55.845 Iron	27 Co 58.933 Cobalt	28 Ni 58.69 Nickel	29 Cu 63.546 Copper	30 Zn 65.38 Zinc	31 Ga 69.723 Gallium	32 Ge 72.630 Germanium	33 As 74.922 Arsenic	34 Se 76.971 Selenium	35 Br 79.904 Bromine	36 Kr 83.796 Krypton																			
37 Rb 85.468 Rubidium	38 Sr 87.62 Strontium	39 Y 88.906 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.906 Niobium	42 Mo 95.94 Molybdenum	43 Tc 98.906 Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.91 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.87 Silver	48 Cd 112.414 Cadmium	49 In 114.818 Indium	50 Sn 118.710 Tin	51 Sb 121.760 Antimony	52 Te 127.60 Tellurium	53 I 126.904 Iodine	54 Xe 131.293 Xenon																			
55 Cs 132.905 Cesium	56 Ba 137.327 Barium	57 La 138.905 Lanthanum	58 Ce 140.12 Cerium	59 Pr 140.908 Praseodymium	60 Nd 144.24 Neodymium	61 Pm 144.913 Promethium	62 Sm 150.36 Samarium	63 Eu 151.964 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.925 Terbium	66 Dy 162.50 Dysprosium	67 Ho 164.930 Holmium	68 Er 167.26 Erbium	69 Tm 168.930 Thulium	70 Yb 173.054 Ytterbium	71 Lu 174.967 Lutetium	72 Hf 178.49 Hafnium	73 Ta 180.948 Tantalum	74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium	77 Ir 192.222 Iridium	78 Pt 195.084 Platinum	79 Au 196.967 Gold	80 Hg 200.59 Mercury	81 Tl 204.38 Thallium	82 Pb 207.2 Lead	83 Bi 208.980 Bismuth	84 Po 209 Polonium	85 At 210 Astatine	86 Rn 222 Radon					
87 Fr 223 Francium	88 Ra 226 Radium	89 Ac 227 Actinium	90 Th 232.038 Thorium	91 Pa 231.036 Protactinium	92 U 238.029 Uranium	93 Np 237.048 Neptunium	94 Pu 244.064 Plutonium	95 Am 243.061 Americium	96 Cm 247.07 Curium	97 Bk 247.07 Berkelium	98 Cf 251.08 Californium	99 Es 252.083 Einsteinium	100 Fm 257.10 Fermium	101 Md 258.10 Mendelevium	102 No 259.10 Nobelium	103 Lr 262.10 Lawrencium																				

9
F
18.998
Fluorine

17
Cl
35.45
Chlorine

35
Br
79.904
Bromine

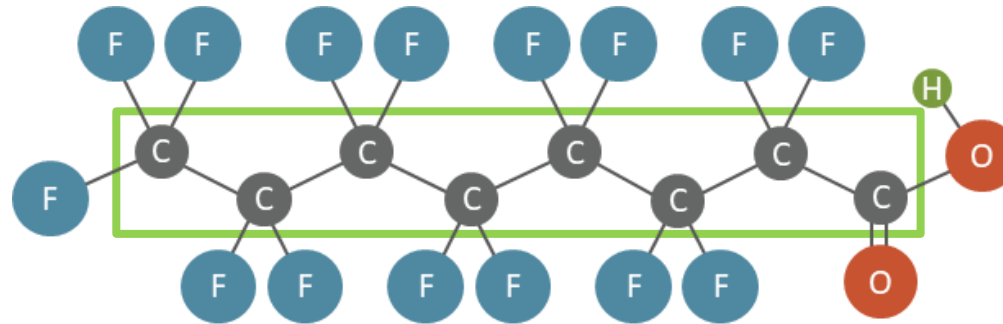
Key chemical property

- C-F bond
- Chain length
- Functional group: PFAAs & precursors
- Acid/base chemistry
- Low Henry's constant
- Mixed polarity (surfactant)

	Fluorine	Chlorine	Bromine
Atomic weight	19.0	35.5	79.9
Atomic radius (pm)	60	99	114
Electronegativity	3.98	3.16	2.96
Carbon bond strength (kJ/mol)	485	327	285

PFAS Physical and Chemical Properties

PFOA (perfluorooctanoic acid)



Key chemical property

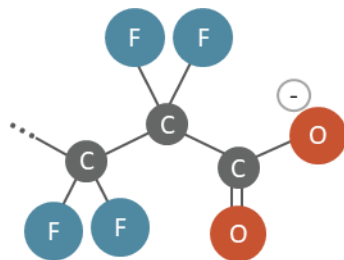
- C-F bond
- Chain length
- Functional group: PFAAs & precursors
- Acid/base chemistry
- Low Henry's constant
- Mixed polarity (surfactant)

Physical properties & implications

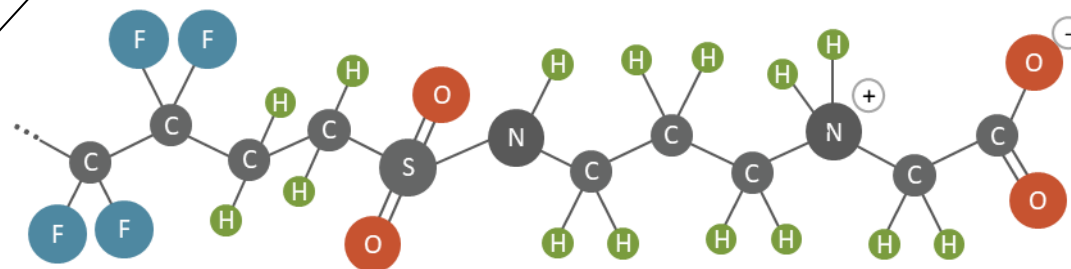
	Short Chain	Long Chain
Mobility in water	High mobility	Moderate
Treatability in water	Difficult to remove	More easily removed
Bioaccumulation	Less bioaccumulative	More bioaccumulative

PFAS Physical and Chemical Properties

Example PFAAs



Example zwitterions:
fluorotelomer sulfonamido betaines



Key chemical property

- C-F bond
- Chain length
- Functional group:
PFAAs & precursors
- Acid/base chemistry
- Low Henry's constant
- Mixed polarity
(surfactant)

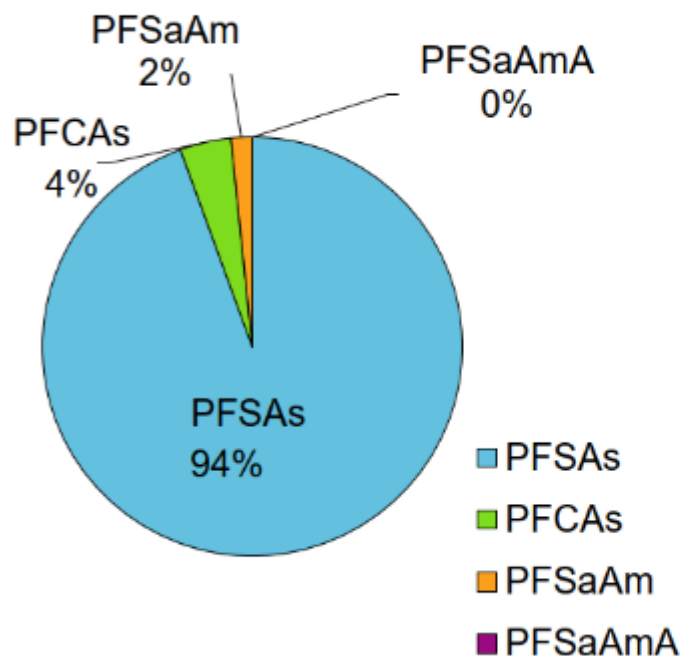
Physical properties & implications

- Precursors – may be cationic (+) or zwitterionic (+-), more sorptive to soils than anionic (-) PFAAs
- Precursors - biotransformation vs. biodegradation
- PFAAs – “terminal” end products

PFAS Physical and Chemical Properties

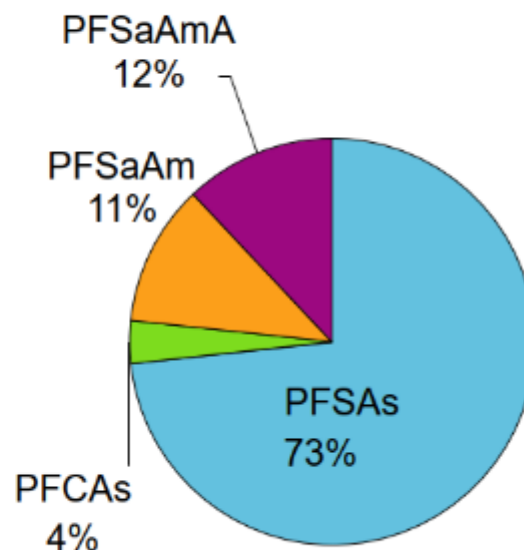
Evolving AFFF composition: PFAAs and precursors

1989 3M AFFF

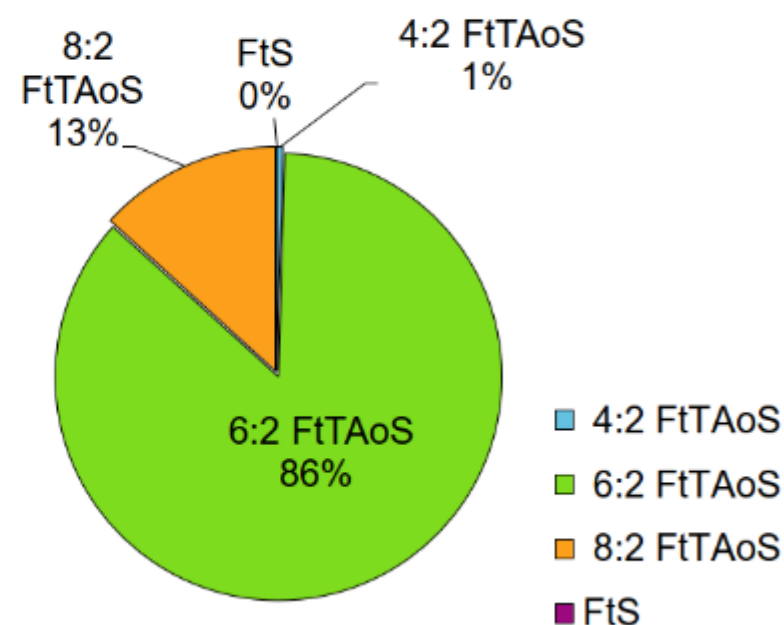


Electrochemical Fluorination

1993-2001 3M AFFF

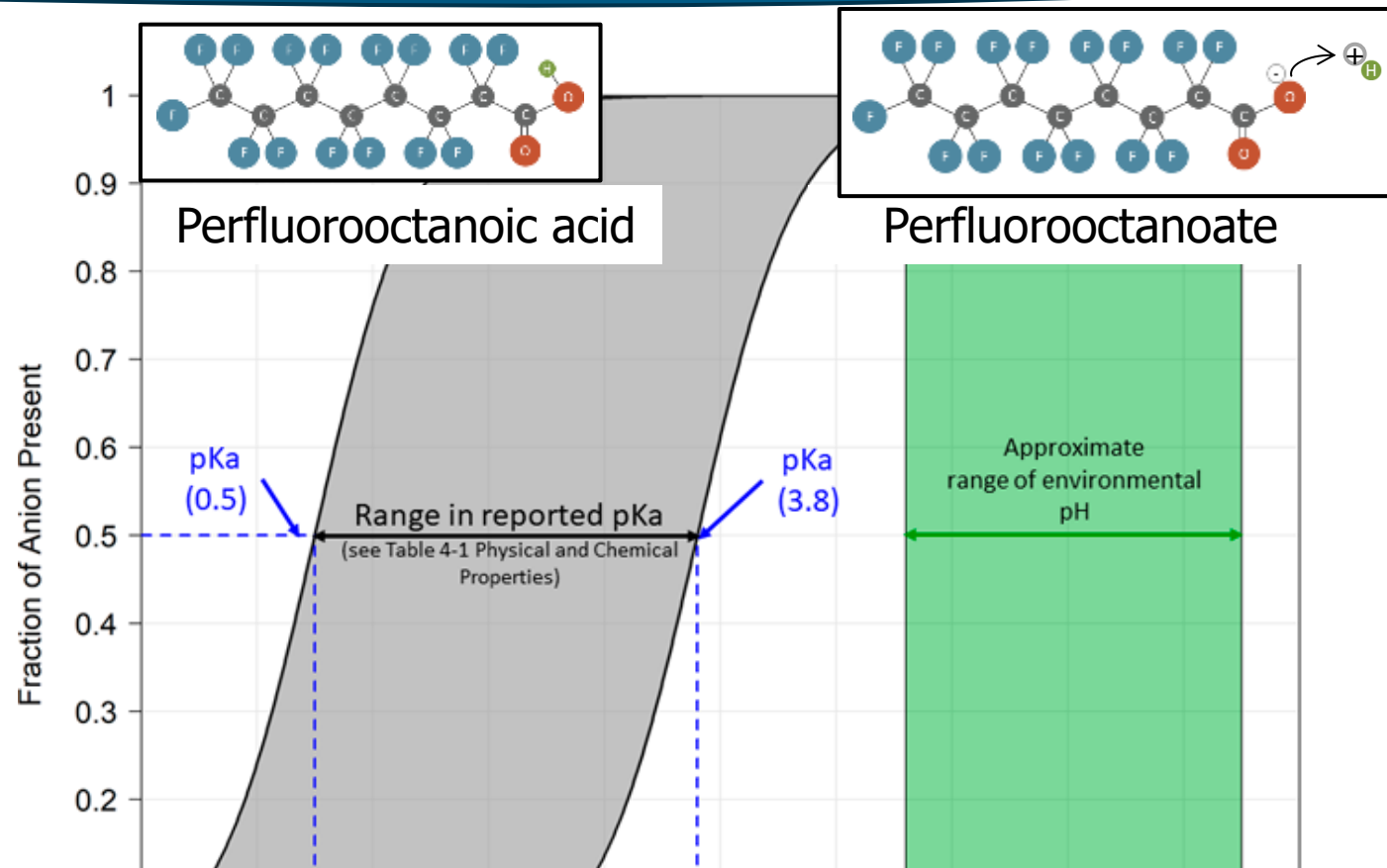


2008 Ansul AFFF



Fluorotelomerization

PFAS Physical and Chemical Properties



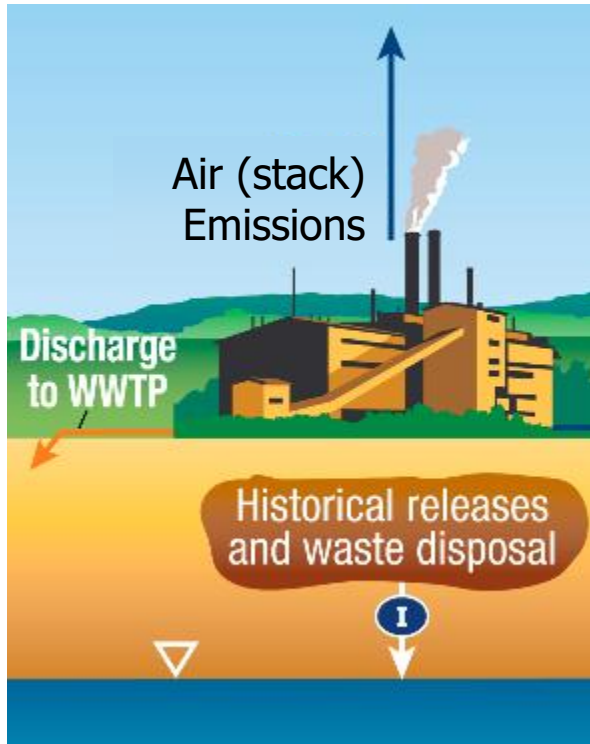
Physical properties & implications

- PFAAs are anionic (negatively charged) in most water systems
- Moderate to high water solubility – high potential mobility in water

Key chemical property

- C-F bond
- Chain length
- Functional group: PFAAs & precursors
- Acid/base chemistry
- Low Henry's constant
- Mixed polarity (surfactant)

PFAS Physical and Chemical Properties



Henry's constant:

$$\frac{\text{Vapor concentration}}{\text{Liquid concentration}}$$

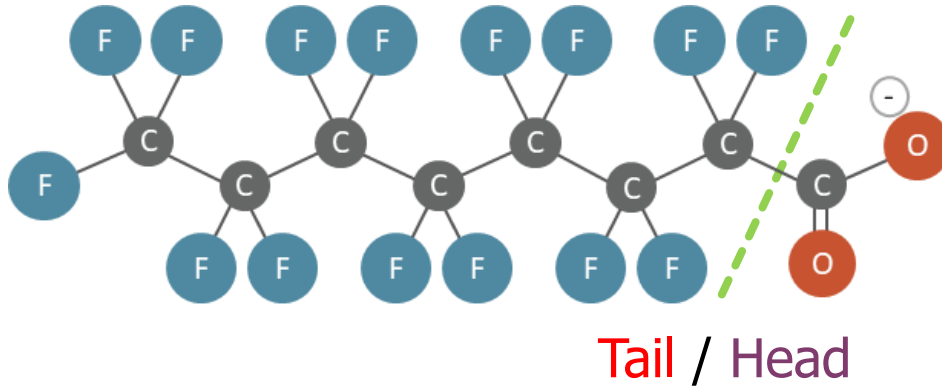
Physical properties & implications

- Limited volatility for many PFAS (including PFAAs)
- Conventional air stripping is not effective remediation*
- Nevertheless, PFAS may migrate via atmospheric transport

Key chemical property

- C-F bond
- Chain length
- Functional group: PFAAs & precursors
- Acid/base chemistry
- Low Henry's constant
- Mixed polarity (surfactant)

PFAS Physical and Chemical Properties



Physical properties & implications

- Tail is hydrophobic and lipophobic; head is hydrophilic
- Surfactant behavior - accumulation at air-water interface
- Elevated concentrations: micelles and foam formation

Key chemical property

- C-F bond
- Chain length
- Functional group: PFAAs & precursors
- Acid/base chemistry
- Low Henry's constant
- Mixed polarity (surfactant)

Knowledge Check

Check
In!

Which property contributes most to high chemical stability for PFAS?

- a) Chain length
- b) Acid/base
- c) Carbon-fluorine bond
- d) Henry's constant
- e) Surfactant

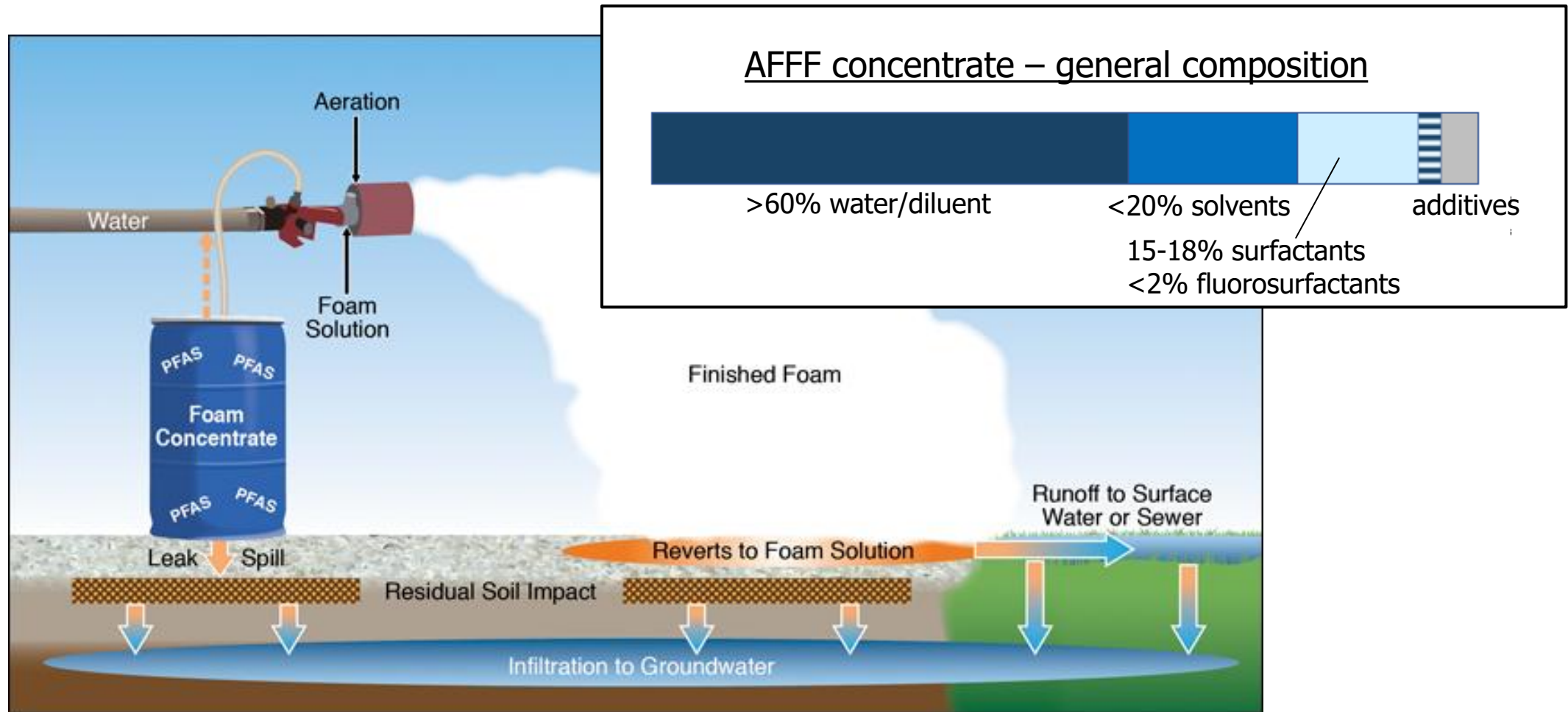




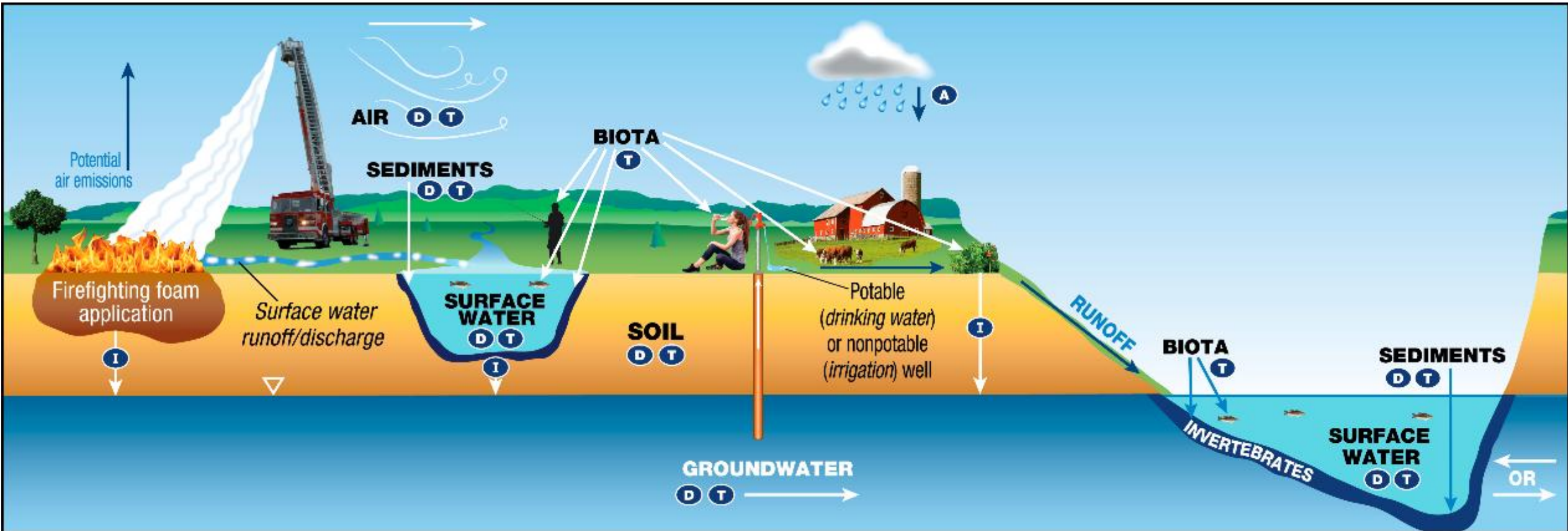
PFAS CHEMISTRY: IMPLICATIONS AND APPLICATIONS

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Aqueous Film Forming Foams (AFFF) Source Zones

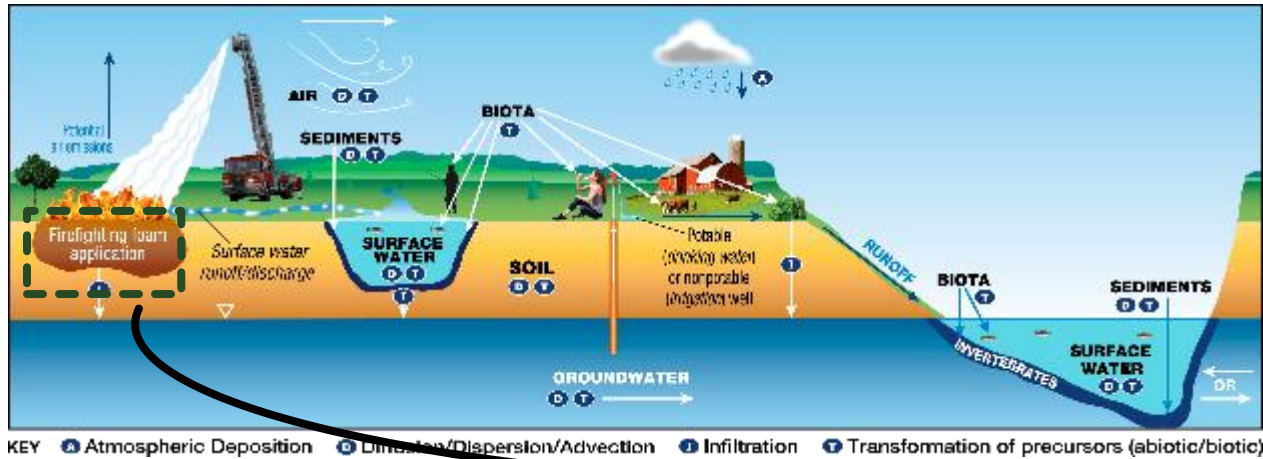


AFFF Fate and Transport



KEY **A** Atmospheric Deposition **D** Diffusion/Dispersion/Advection **I** Infiltration **T** Transformation of precursors (abiotic/biotic)

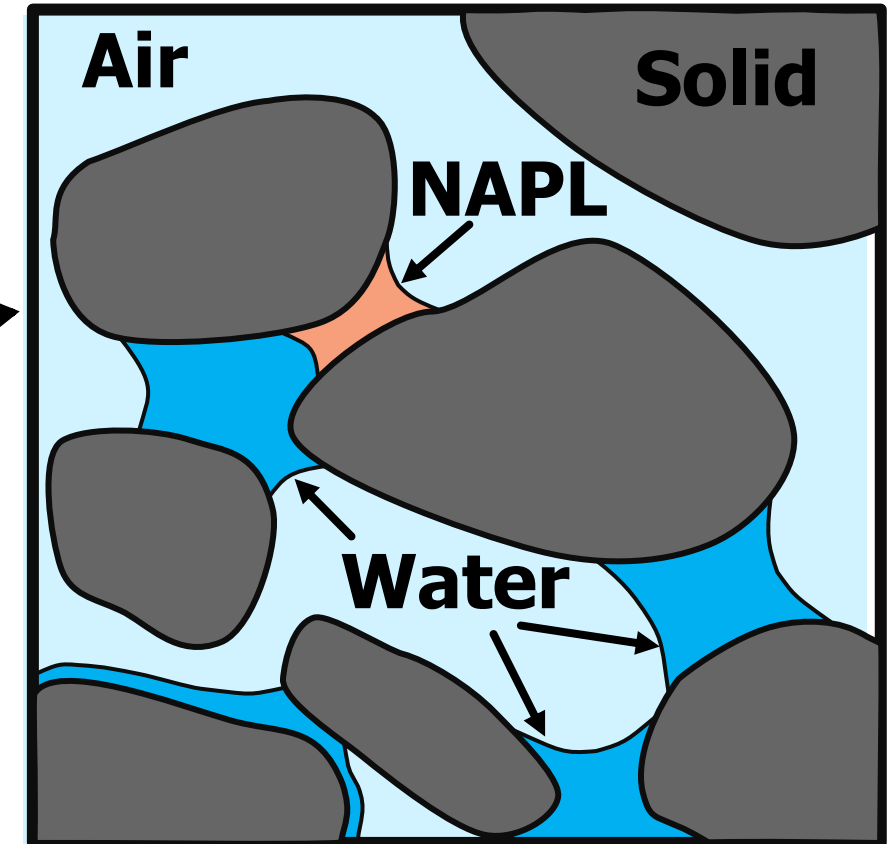
Micro-Scale Factors Influencing PFAS Retention



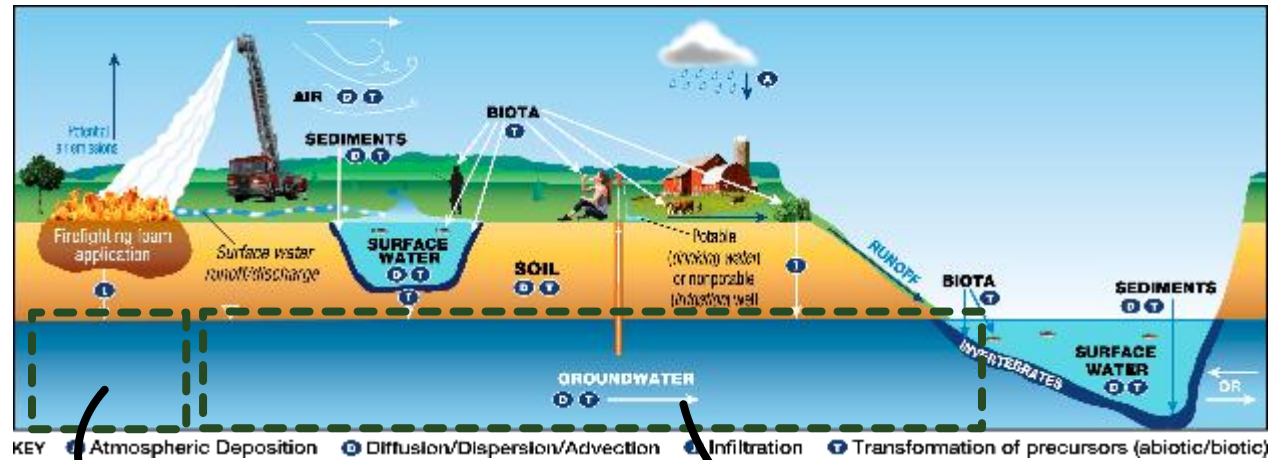
1. Sorption to organic matter
2. Air-water interface partitioning
3. Electrostatic interactions

Source areas:

- Multiple processes contribute to PFAS retention and mobility in shallow soils
- Rate of leaching to groundwater: determined by PFAS chemistry + site conditions (e.g., geology, climate)



Conceptual PFAS Fate and Transport at an AFFF site



Source Zone

- Mix of precursors and PFAAs
- Anaerobic & reducing
- Potential presence of co-contaminants

Groundwater Plume

- Fewer precursors, more PFAAs
- Short chain PFAS migrate faster
- Diminished concentrations of biodegradable co-contaminants

Oxidizing conditions (for example, via active remediation such as air sparging or chemical oxidation) may enhance precursor transformation

Knowledge Check

Check
In!

An aquifer is remediated for benzene via in situ chemical oxidation (ISCO) using persulfate. Subsequently, PFOA is found to increase in a downgradient monitoring well. What is a likely cause?

- a) PFOA contamination in persulfate
- b) PFOA in well construction materials
- c) Chemical oxidation resulted in transformation of precursors into PFOA
- d) Someone threw a fast food wrapper down the well



PFAS Treatment – Separation and Concentration

Technology	Mechanism	PFAS chemistry considerations
Granular Activated Carbon (GAC)	Hydrophobic sorption to organic matter	• Other organics outcompete PFAS for sorption sites – need for pretreatment • Long-chain PFAAs retained more effectively than short-chain
Ion Exchange (IX)	Anionic PFAS attracted to cationic sorption sites + hydrophobic sorption	• May require pretreatment • Long chain PFAAs > short, but IX may be more effective for short-chain PFAS than other techs
Foam Fractionation (FF)	Air-water interface attraction	• More selective for PFAS than GAC/IX • Long chain PFAAs > short
Reverse Osmosis (RO)	High pressure membrane filtration	• None (PFAS similar to other chems) • Removes short and long-chain PFAAs



All of these generate PFAS-concentrated media (solid or liquid) that requires disposal

PFAS Treatment – Destruction

Incineration



Hazardous waste incinerator in East Liverpool, Ohio,
Credit: Center for Land Use Interpretation/Creative Commons (CC BY-NC-SA 4.0)

Other Destructive Technologies (developing)

- Supercritical water oxidation
- Electrochemical oxidation
- Hydrothermal
- Sonolysis
- Plasma

Primary challenges:

- High energy input to overcome strong C-F bond
- Partial breakdown or mineralization?

Mineralization - breaking all of the C-F bonds

- Fluorine mass balance – confirming destruction versus other losses, such as sorption (primarily for lab or pilot studies)

Knowledge Check

**Check
In!**

Which technology relies on the surfactant properties of PFAS for treatment?

- a) Foam fractionation
- b) Anion exchange
- c) Activated carbon
- d) Incineration



Key Takeaways

- Physical/chemical properties
 - Carbon-fluorine bond
 - Chain length
 - PFAAs and precursors
 - Surfactants
- Fate and transport
 - **Source zones** – PFAS retention/mobility in shallow/unsaturated soils determined by PFAS chemistry as well as site conditions (geology, climate)
 - **Groundwater** – high potential mobility in saturated zone below water table; composition may change with time/distance (fewer precursors, more PFAAs)
 - **Other transport pathways** – atmospheric transport, stormwater runoff, others
- Treatment
 - **Separation/concentration** – technologies work with PFAS chemistry in unique ways
 - **Destruction** – high energy input to *mineralize* PFAS (break all C-F bonds)

- PFAS Introductory Training
- PFAS Chemistry Explained
- PFAS & Biosolids: Sources, Occurrence, Transport, and Treatment
- PFAS - Practical Approaches for PFAS Fate & Transport Evaluation
- PFAS Sorption Based Technologies for Separation & Concentration of PFAS from Water



PFAS Trainings



Questions

Please use the Q&A Pod to ask questions.



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

