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?
  - Fill out the online feedback form and check box for confirmation email and certificate

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/

ITRC – Shaping the Future of Regulatory Acceptance

Host Organization

Network - States, PR, DC

Federal Partners

DOE DOD EPA

ITRC Industry Affiliates Program

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Advancing Environmental Solutions

PFAS CHEMISTRY EXPLAINED

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

Training Topics

PFAS Background

PFAS Structure and Naming Conventions

Chemical Properties and Applications

TRAINING PURPOSE

Today's PFAS Trainers

Liz Denly
TRC Companies
edenly@trccompanies.com

Mitch Olson, Ph.D., P.E.
Colorado State University
mitchell.olson@colostate.edu

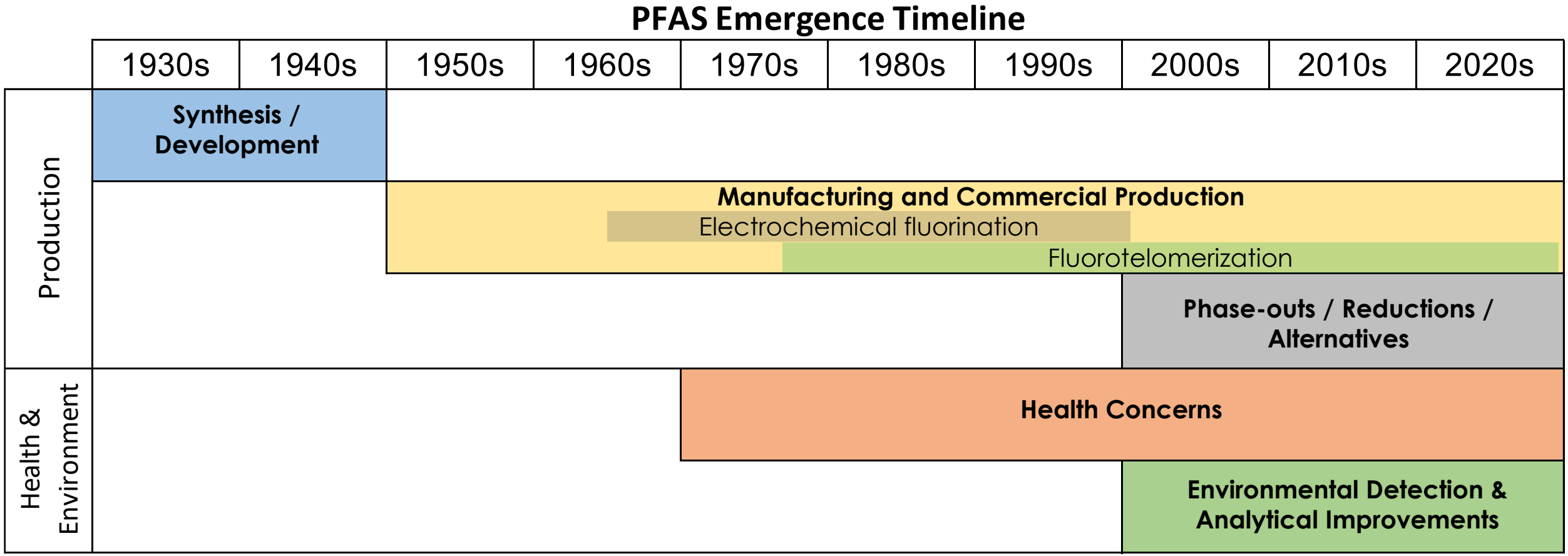
PFAS BACKGROUND

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-1, Section 2.0. Figure 2-1 General timeline of PFAS emergence and awareness.
Source: J. Hale, Kleinfelder. Used with permission.

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
- 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

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

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JJ Harrison, CC BY-SA 3.0, via Wikimedia Commons.

Iain Thompson / Cathkin Landfill Site, CC BY-SA 2.0, via Wikimedia Commons

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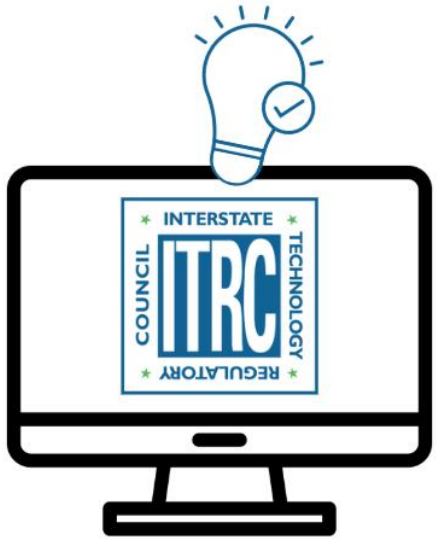
Knowledge Check

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

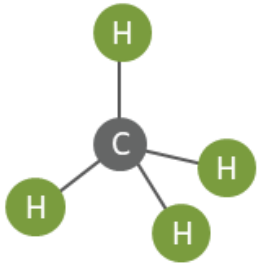
a) Forest firefighting
b) Metal plating
c) Housefires
d) Pharmaceuticals
e) Food packaging
f) Firefighting - flammable liquids



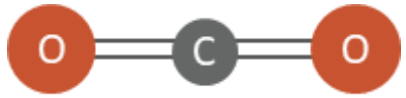
Organic chemistry refresher

- C Carbon
- H Hydrogen
- O Oxygen
- Cl Chlorine
- F Fluorine
- Single bond
- Double bond

Methane

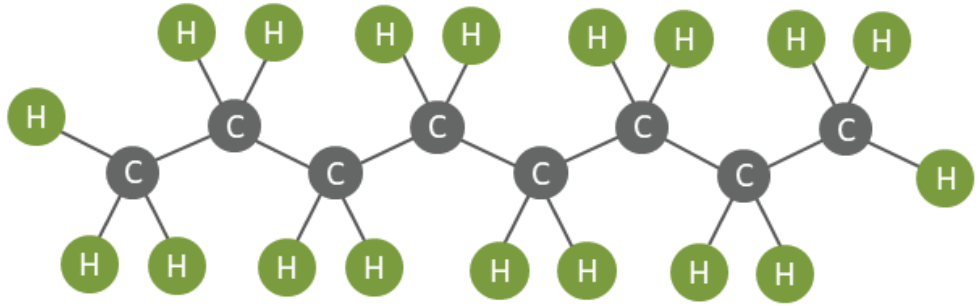


Carbon Dioxide

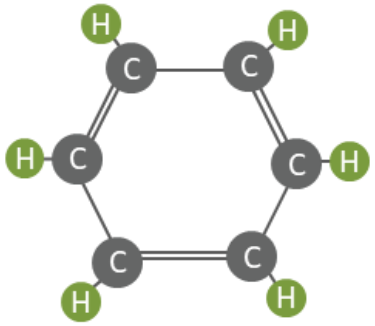


(inorganic carbon)

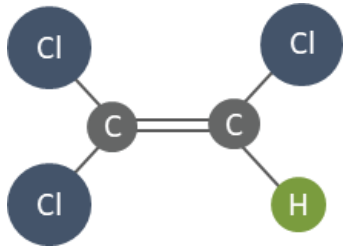
Octane



Benzene



TCE (trichloroethene)



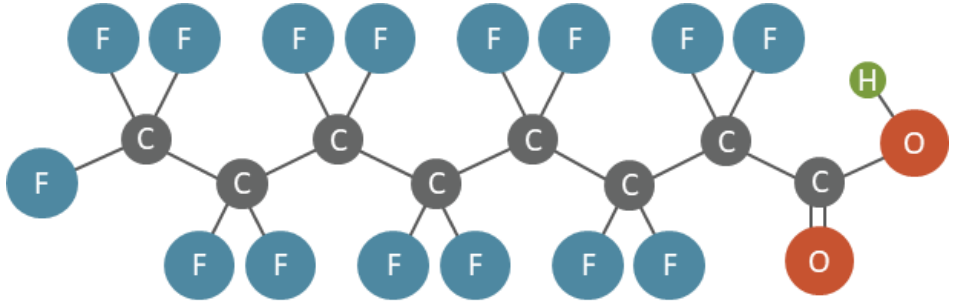
Organic chemistry principles

- 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

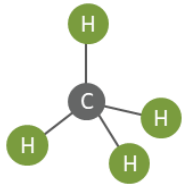
PFAS Chemistry

- C Carbon
- H Hydrogen
- O Oxygen
- Cl Chlorine
- F Fluorine
- Single bond
- Double bond

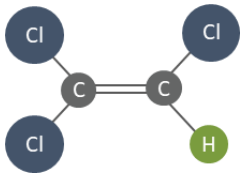
PFOA (perfluorooctanoic acid)



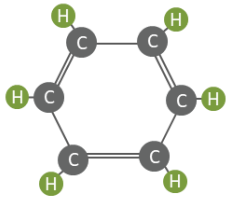
Methane



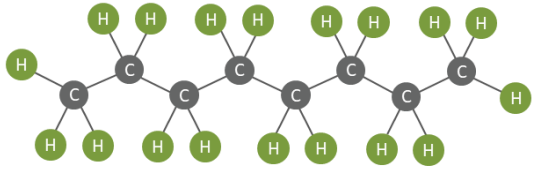
TCE (trichloroethene)



Benzene



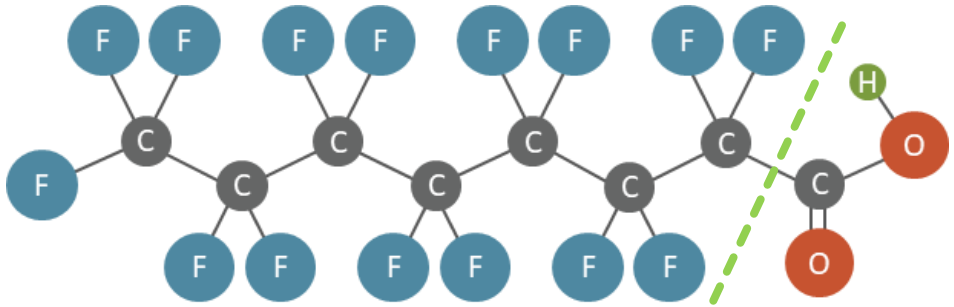
Octane



PFAS Chemistry

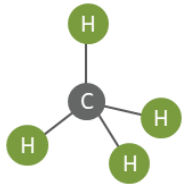
- C Carbon
- H Hydrogen
- O Oxygen
- Cl Chlorine
- F Fluorine
- Single bond
- Double bond

PFOA (perfluorooctanoic acid)

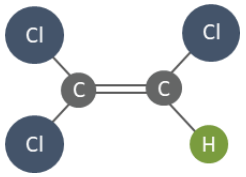


- **phobic** = repelling; **philic** = attracting
- **Tail**: hydrophobic ("water repelling") and lipophobic ("oil repelling")
- **Head**: hydrophilic ("water loving")

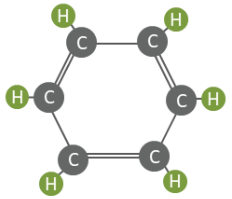
Methane



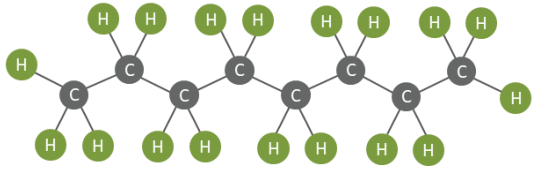
TCE (trichloroethene)



Benzene



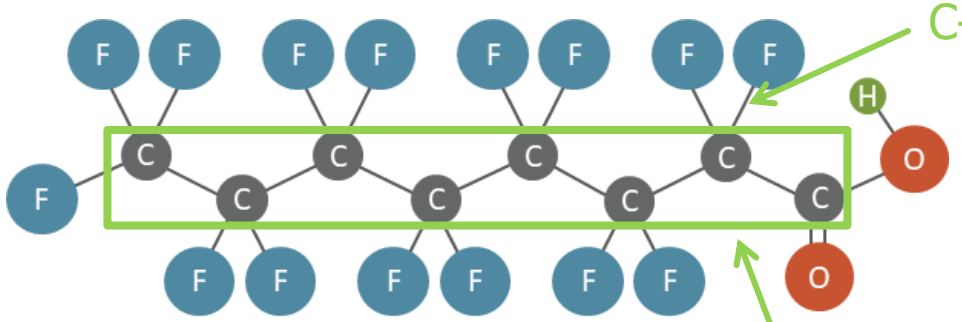
Octane



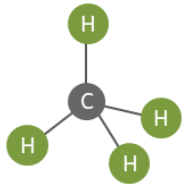
PFAS Chemistry

- C Carbon
- H Hydrogen
- O Oxygen
- Cl Chlorine
- F Fluorine
- Single bond
- Double bond

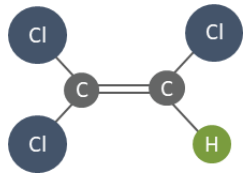
PFOA (perfluorooctanoic acid)



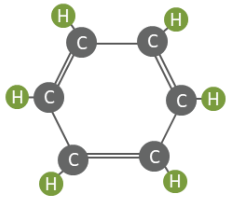
Methane



TCE (trichloroethene)



Benzene



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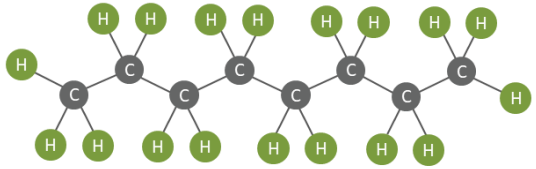
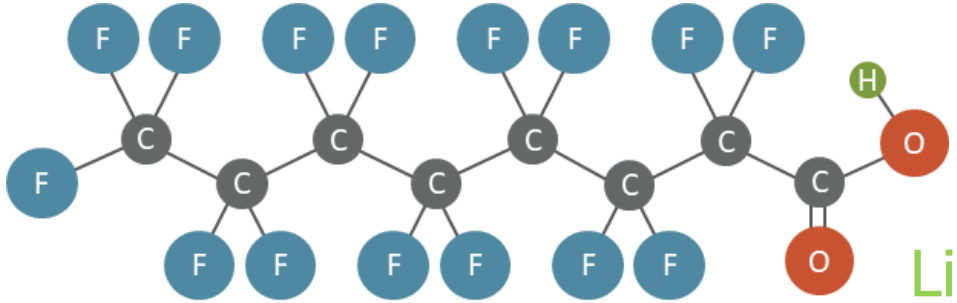


PFAS-1, Section 2.2.3.1 Perfluoroalkyl Acids (PFAAs).

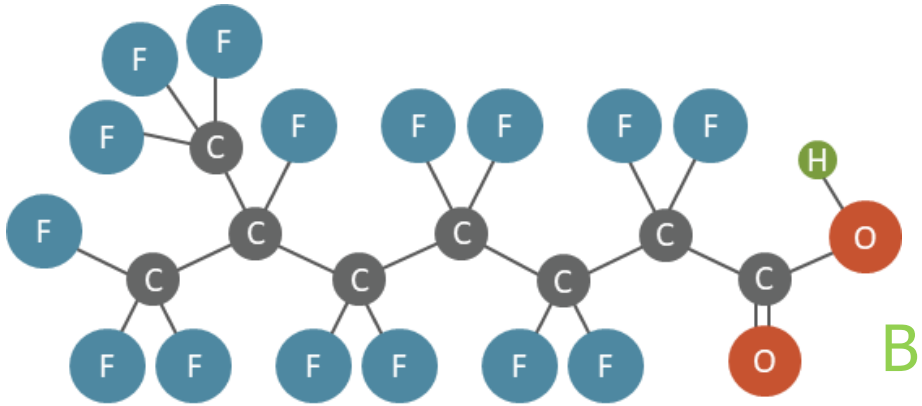
PFAS Chemistry

- Carbon
- Hydrogen
- Oxygen
- Chlorine
- Fluorine
- Single bond
- Double bond

PFOA (perfluorooctanoic acid)

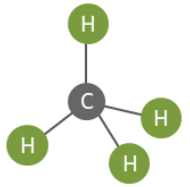


Linear isomer

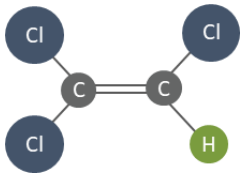


Branched isomer
(1 example)

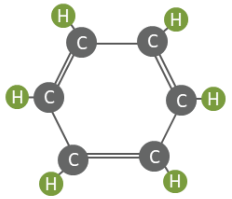
Methane



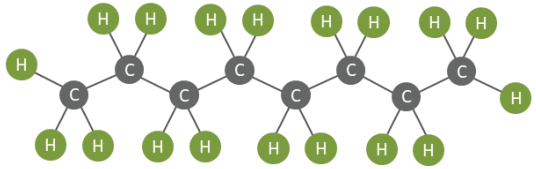
TCE (trichloroethene)



Benzene



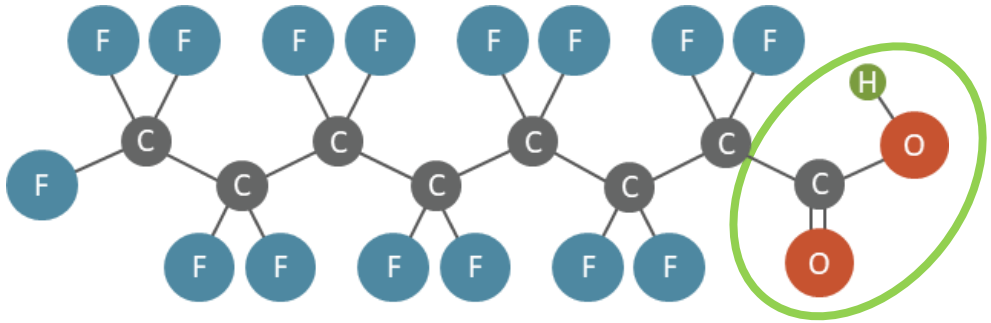
Octane



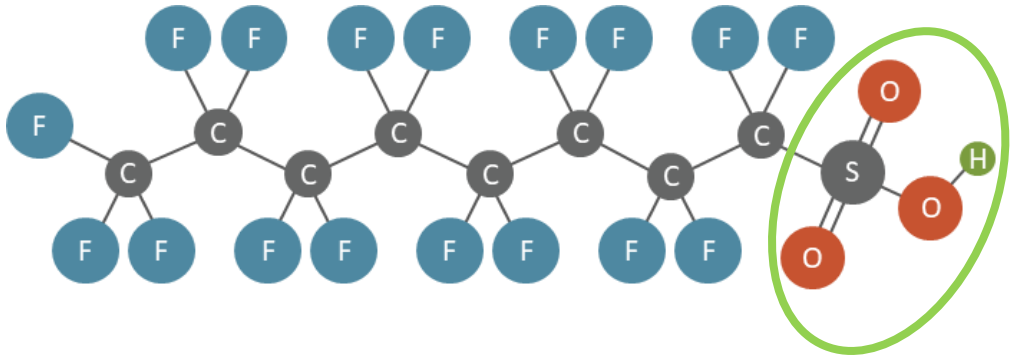
PFAS Chemistry

- Carbon
- Hydrogen
- Oxygen
- Chlorine
- Fluorine
- Single bond
- Double bond

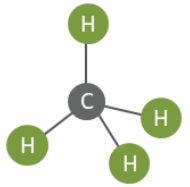
PFOA (perfluorooctanoic acid)



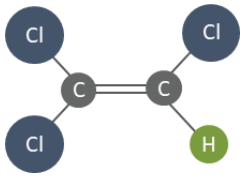
PFOS (perfluorooctane sulfonic acid)



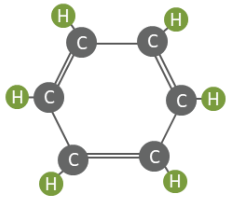
Methane



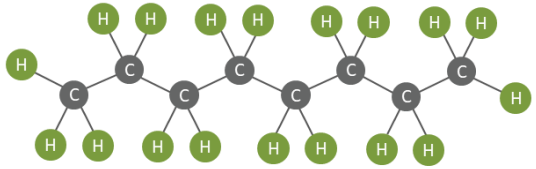
TCE (trichloroethene)



Benzene



Octane

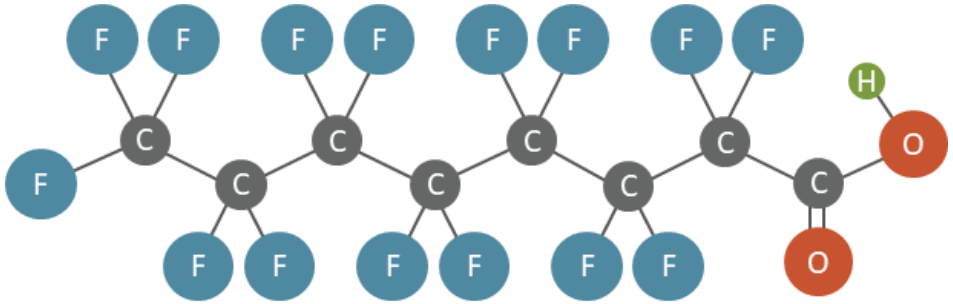


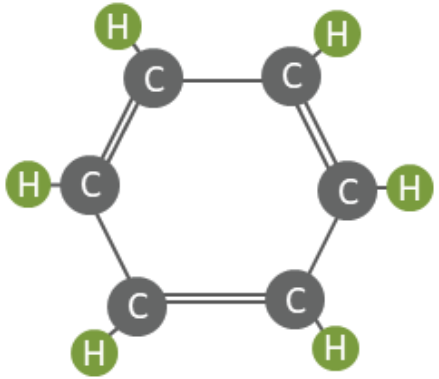
Knowledge Check

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) Environmental releases typically involve a complex mixture with other chemicals





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

PFAS STRUCTURES AND NAMING CONVENTIONS

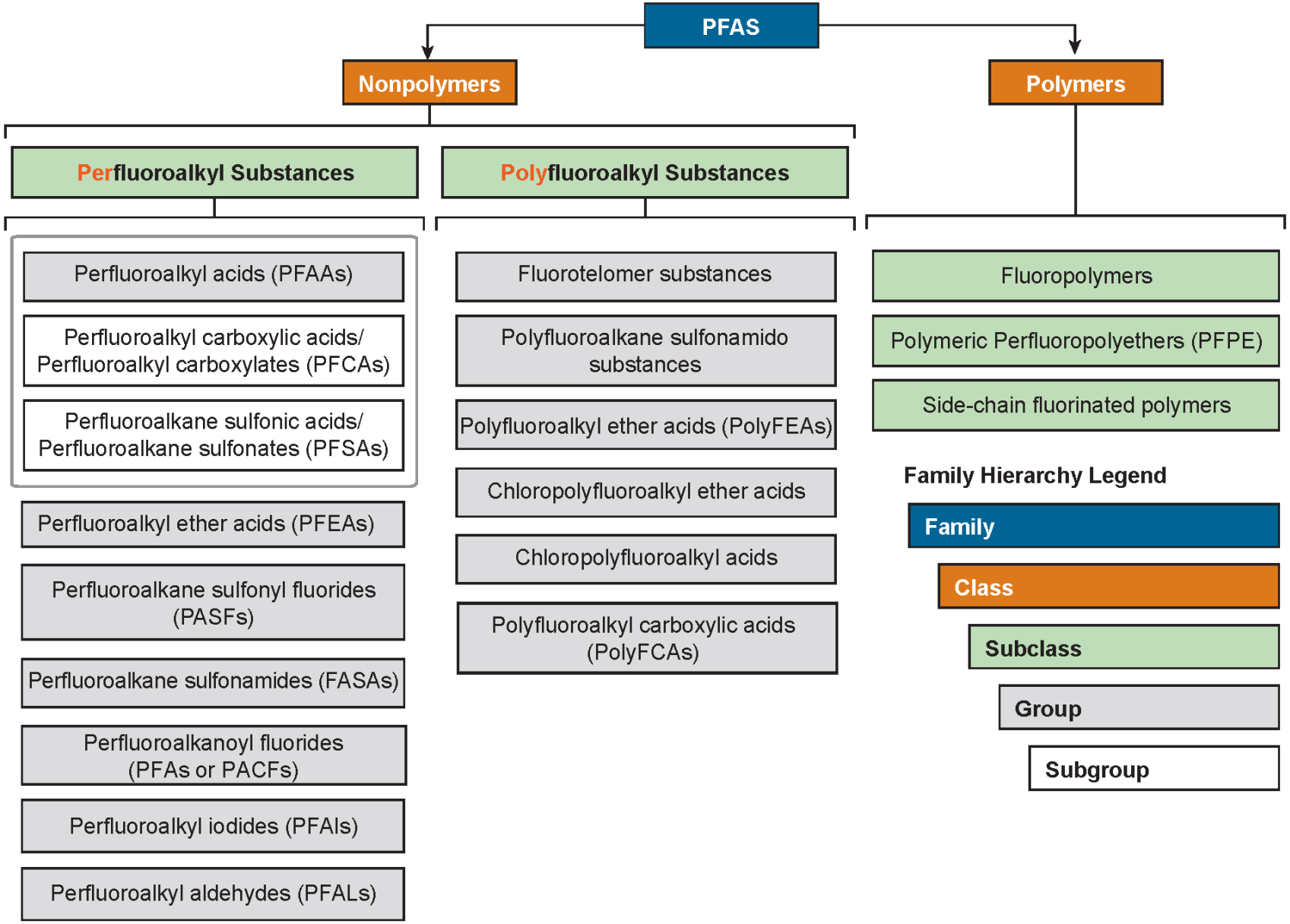
LIZ DENLY

PFAS Family Tree: Simple View

Two Major Classes

Nonpolymers

Polymers



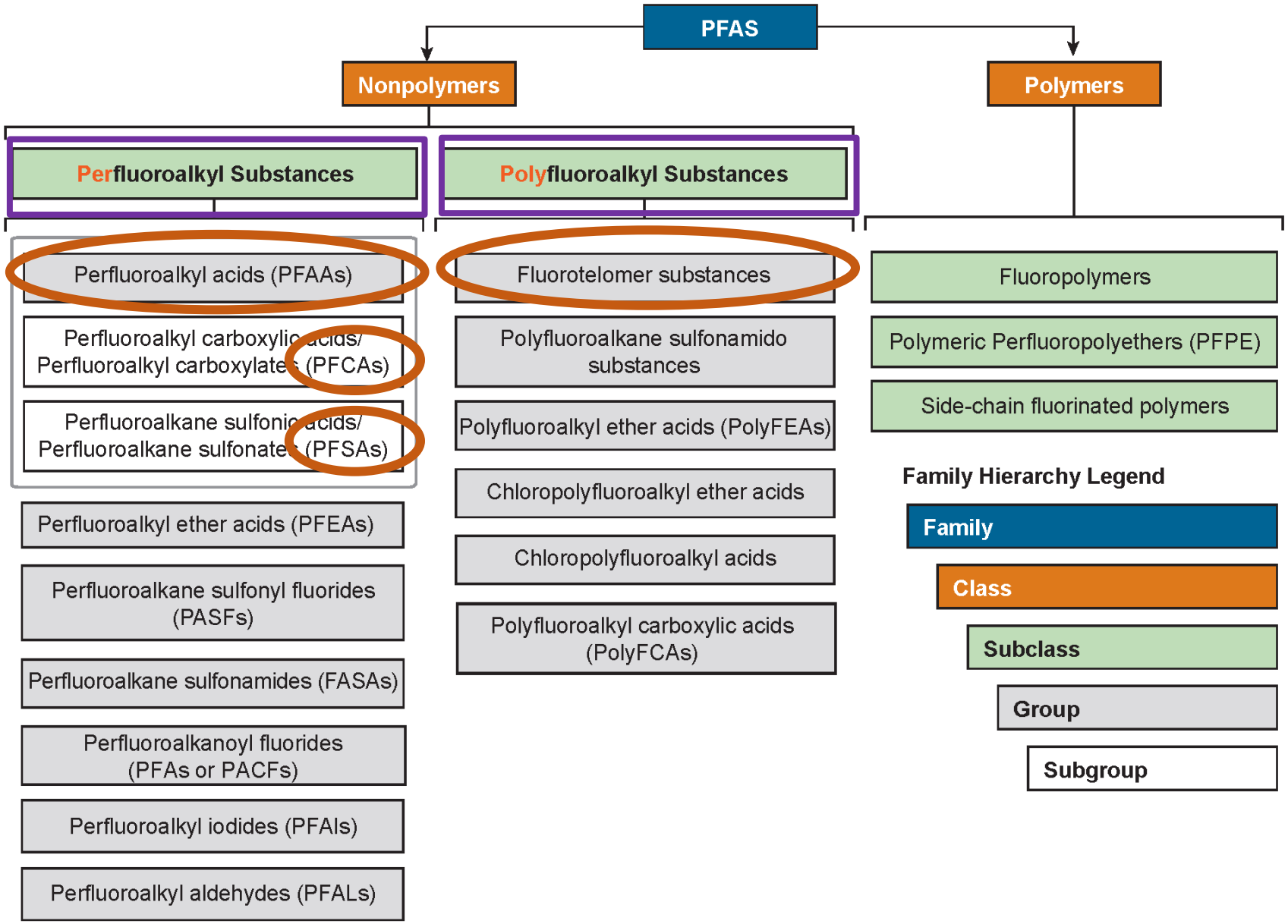
PFAS-1, Figure 2-4, The PFAS Family

PFAS Family Tree: Simple View

Two Major Classes

Nonpolymers

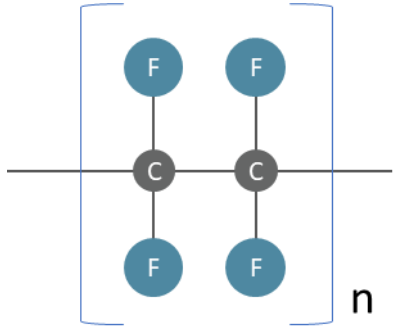
Polymers



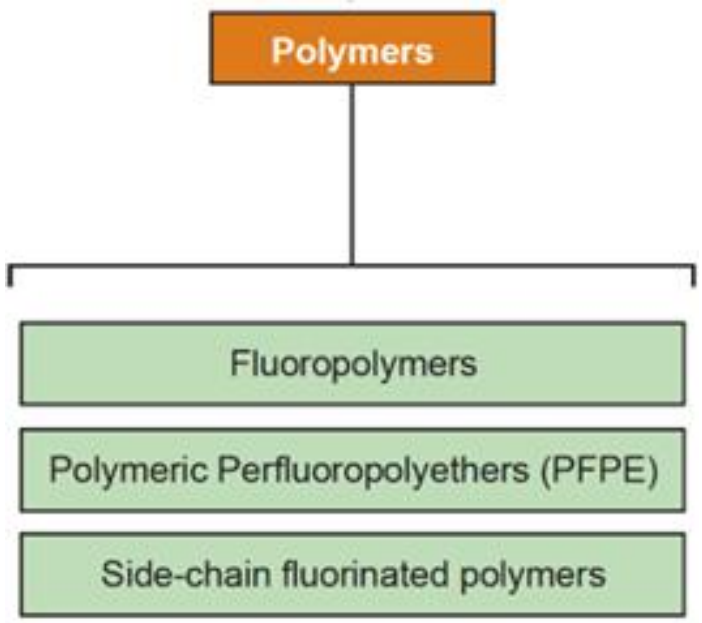
PFAS-1, Figure 2-4, The PFAS Family

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)

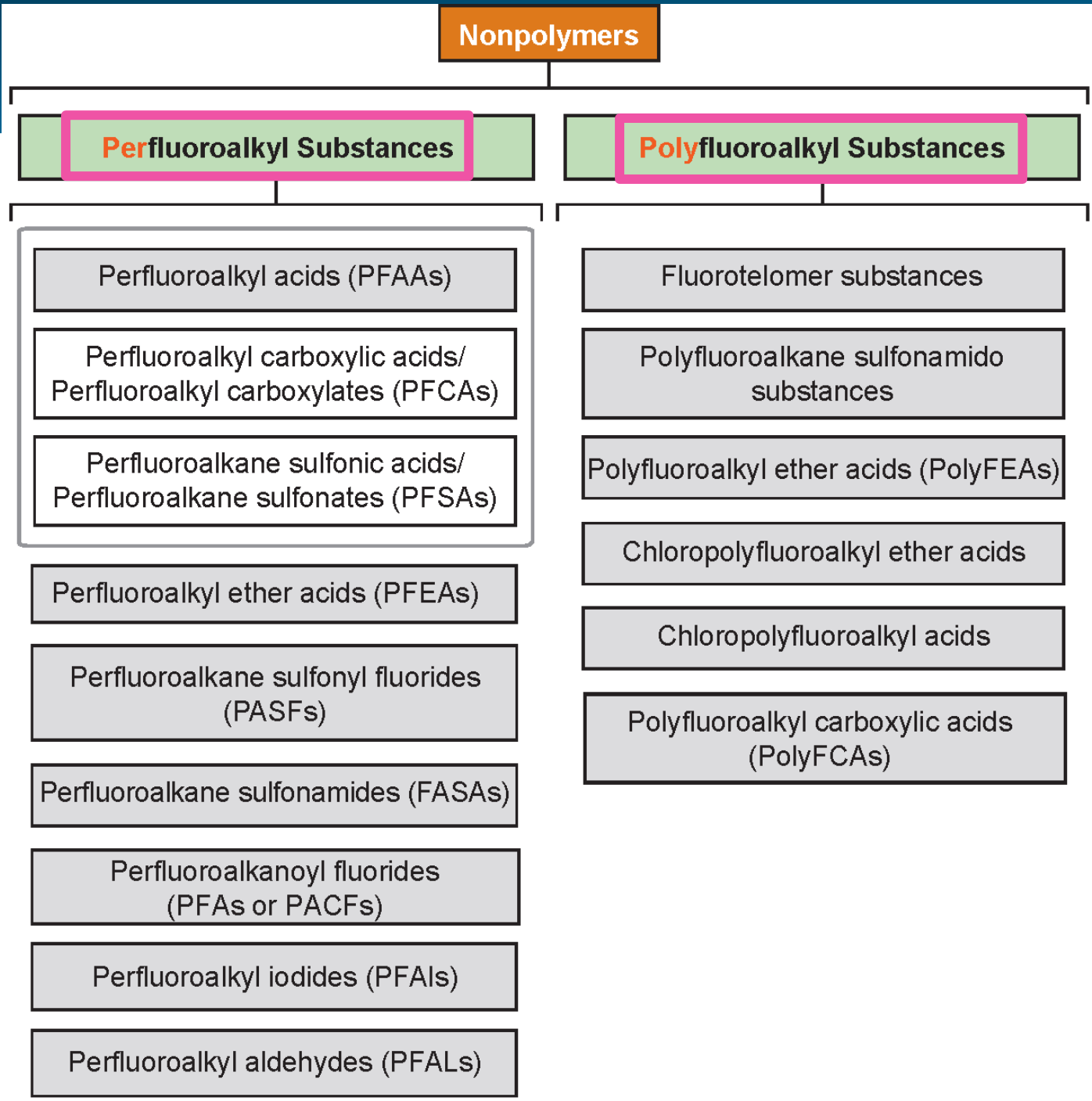


Monomer Example



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



PFAS-1, Section 2.2.2.2, Nonpolymer PFAS

Knowledge Check

Two Major Classes of PFAS are:

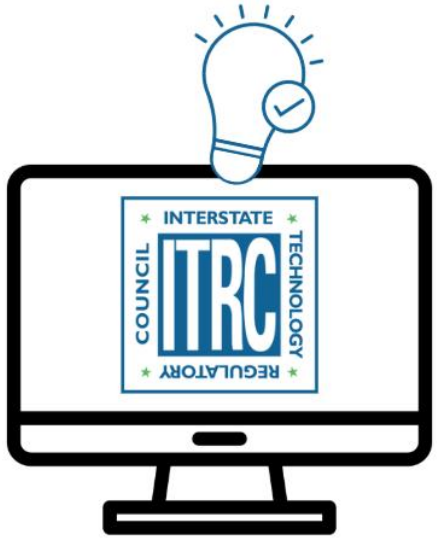
(select one)

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:

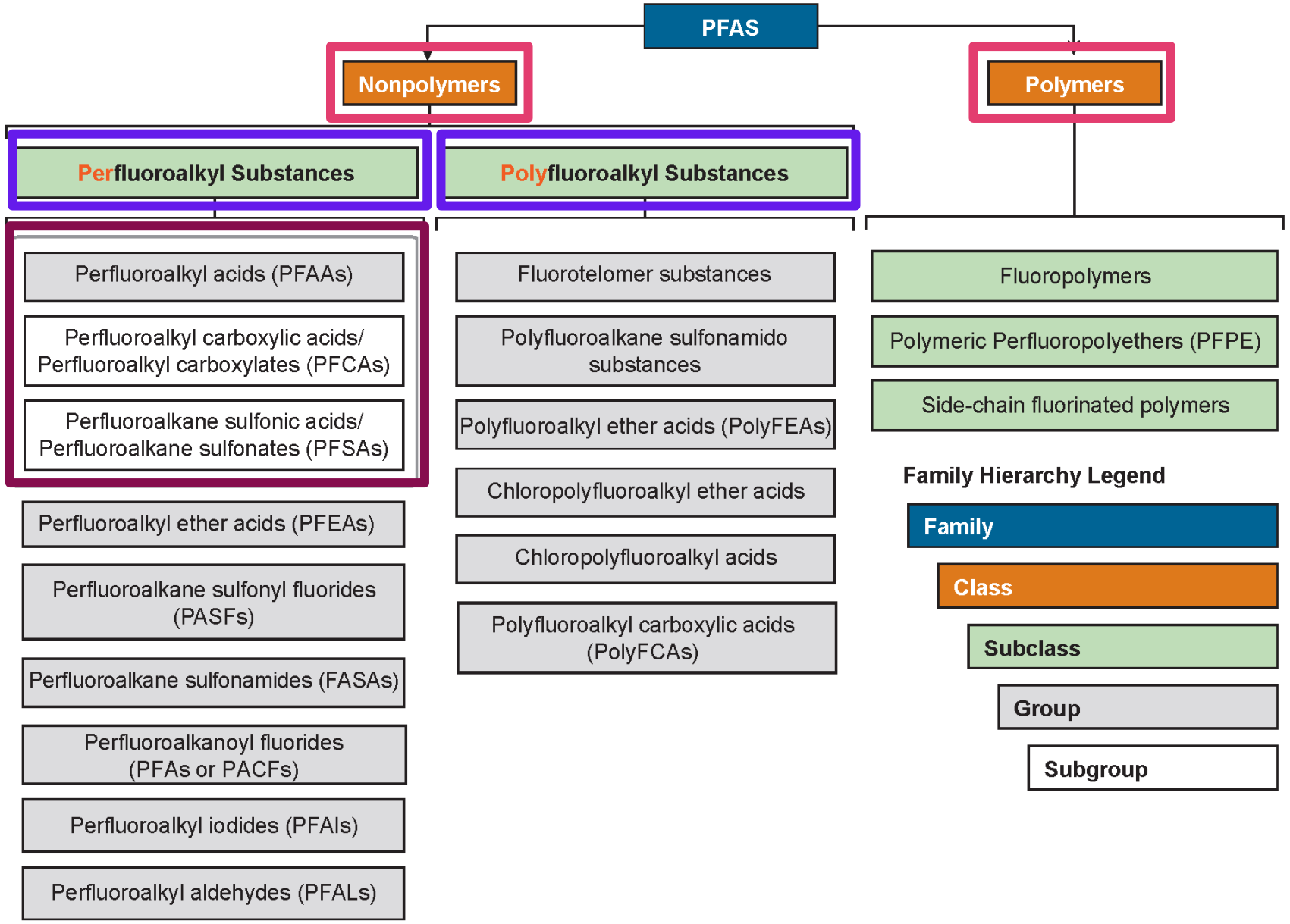
(select one)

a) PFOA and PFOS

b) Perfluoroalkyl and Polyfluoroalkyl Substances

c) Polymers and Nonpolymers

d) Fluorinated Polymers and Side-chain Fluorinated Polymers



Knowledge Check

PFAS Commonly Detected and Measured in the Environment and Humans are:

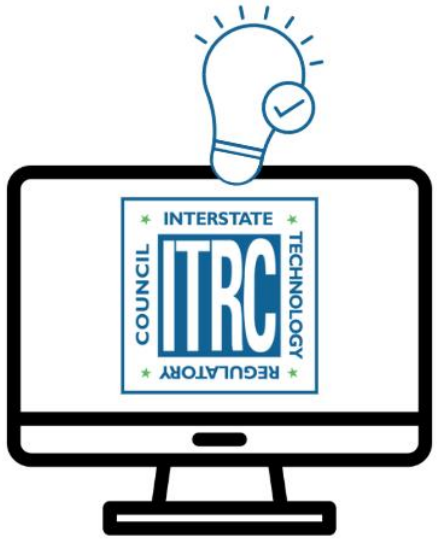
(select one)

a) Polymer PFAS

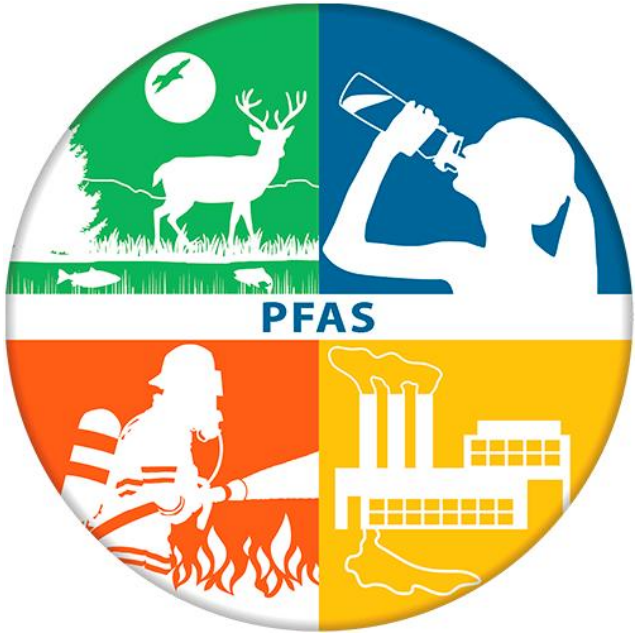
b) Nonpolymer PFAS

c) Side-chain Fluorinated Polymers

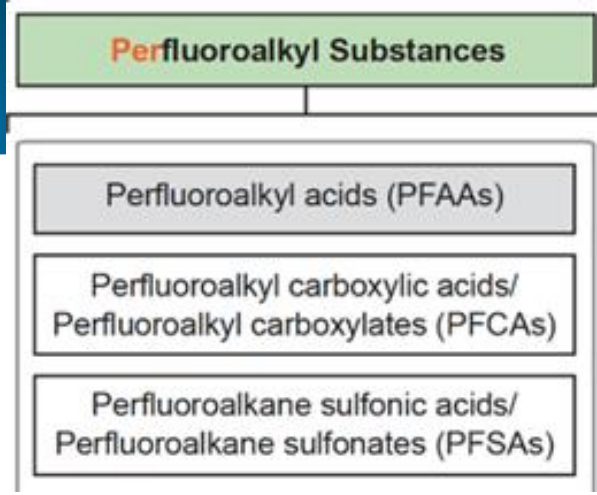
d) Polytetrafluoroethylene (PTFE)



Perfluoroalkyl Substances
&
Polyfluoroalkyl Substances

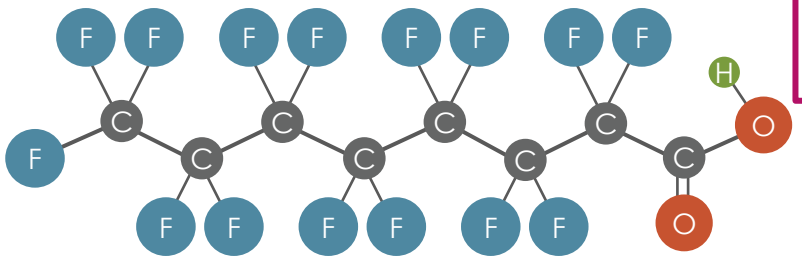


Nonpolymer: Perfluoroalkyl Substances



Perfluoroalkyl substances: fully fluorinated alkyl tail

Perfluorooctanoic Acid (PFOA)

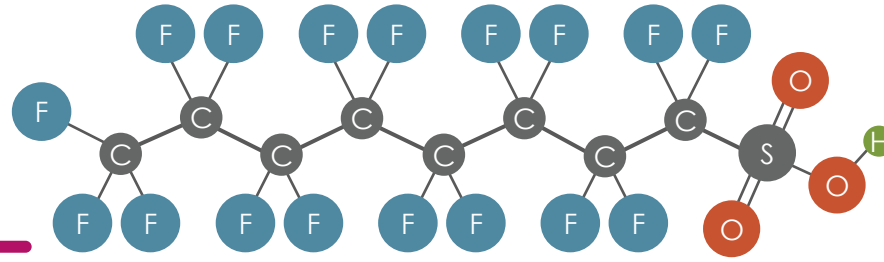


COOH = Head
Hydrophilic

Subgroup: Perfluoroalkyl Carboxylic Acid (PFCA)

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

Perfluorooctane Sulfonic Acid (PFOS)



SO_3H = Head
Hydrophilic

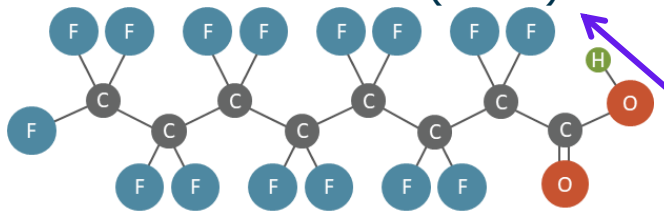
Subgroup: Perfluoroalkane Sulfonic Acid (PFSA)

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

PFAS-1, Section 2.2.3 and Figure 2-4 PFAS Family Tree

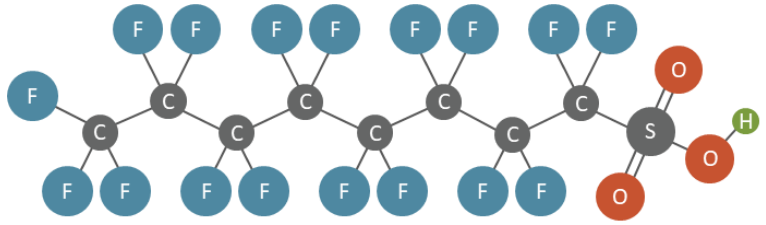
Perfluoroalkyl Acids (PFAAs) → PFCAs & PFSAs

Perfluorooctanoic acid (PFOA)

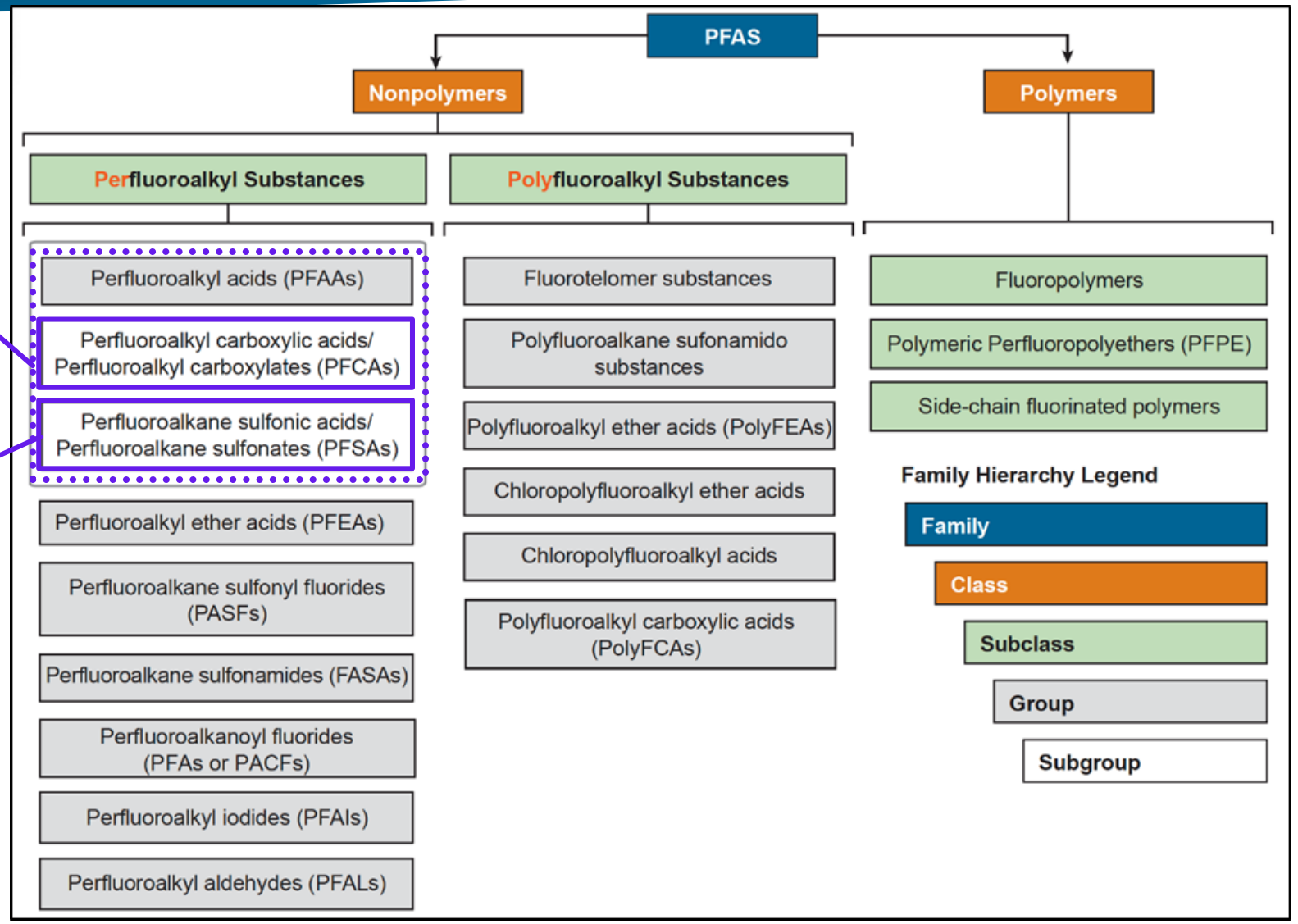


Other PFCA Examples:
Perfluorohexanoic Acid (PFHxA)
Perfluorononanoic Acid (PFNA)

Perfluorooctane sulfonic acid (PFOS)

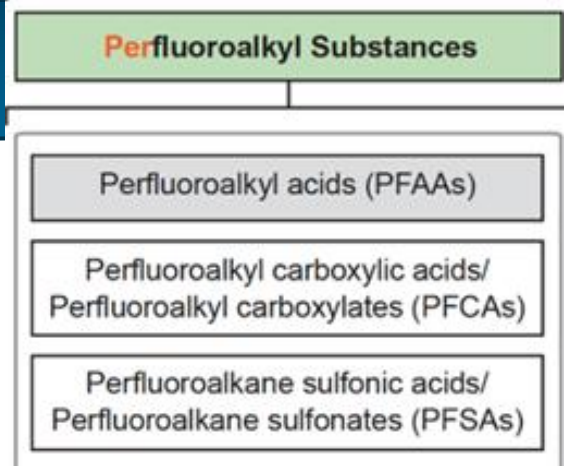


Other PFSA Examples:
Perfluorobutane Sulfonic Acid (PFBS)
Perfluorohexane Sulfonic Acid (PFHxS)



PFAS-1, Section 2.2.3.1 Figure 2-4 PFAS Family Tree

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)

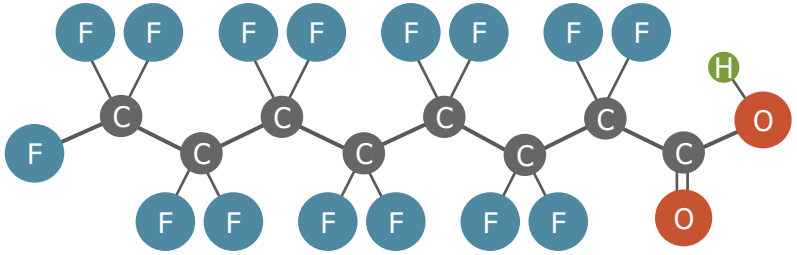
a) Side-chain Fluorinated Polymer

b) Perfluorobutanoic Acid (PFBA)

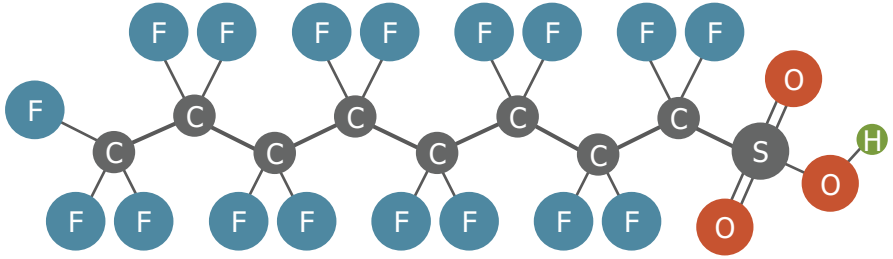
c) Perfluorooctanesulfonic Acid (PFOS)

d) Perfluorooctanoic Acid (PFOA)

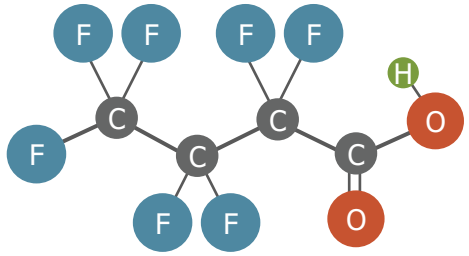
PFOA = Perfluorooctanoic Acid



PFOS = Perfluorooctanesulfonic Acid



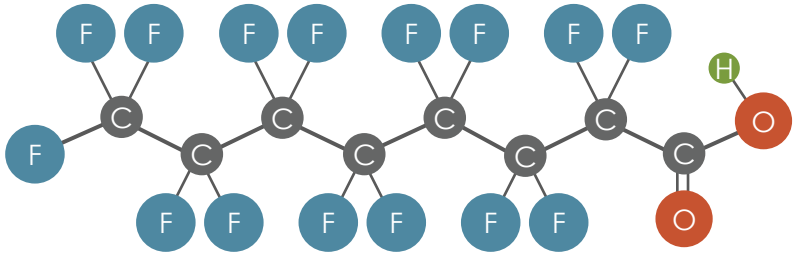
PFBA = Perfluorobutanoic Acid



Knowledge Check Explained

Remember: PFCAs Have Carboxylic Acid Head

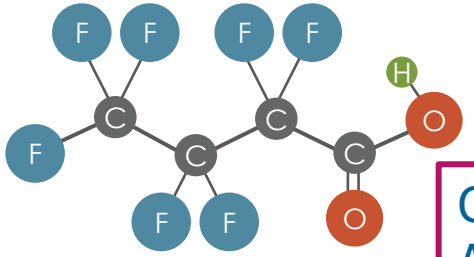
PFOA: Perfluorooctanoic Acid



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)

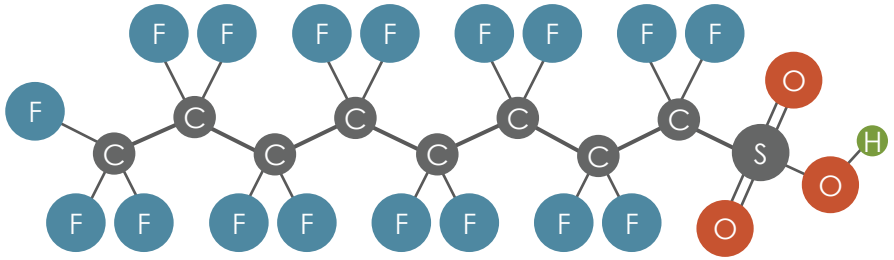
a) Side-chain Fluorinated Polymer

b) <u>Perfluorobutanoic Acid (PFBA)</u>

c) Perfluorooctanesulfonic Acid (PFOS)

d) <u>Perfluorooctanoic Acid (PFOA)</u>

PFOS: Perfluorooctane Sulfonic Acid



SO_3H = Sulfonic Acid Head

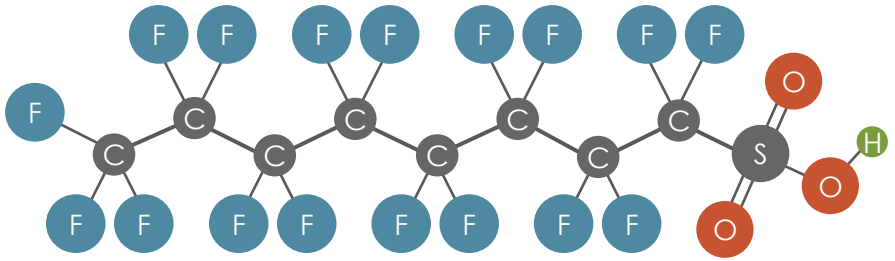
Alkyl Tail, fully fluorinated

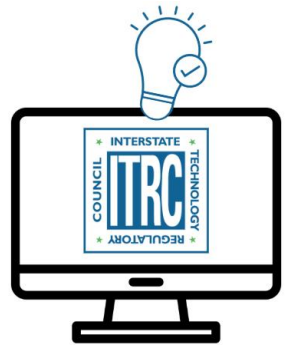
Knowledge Check

Perfluorooctane Sulfonic Acid (PFOS):
(select all)

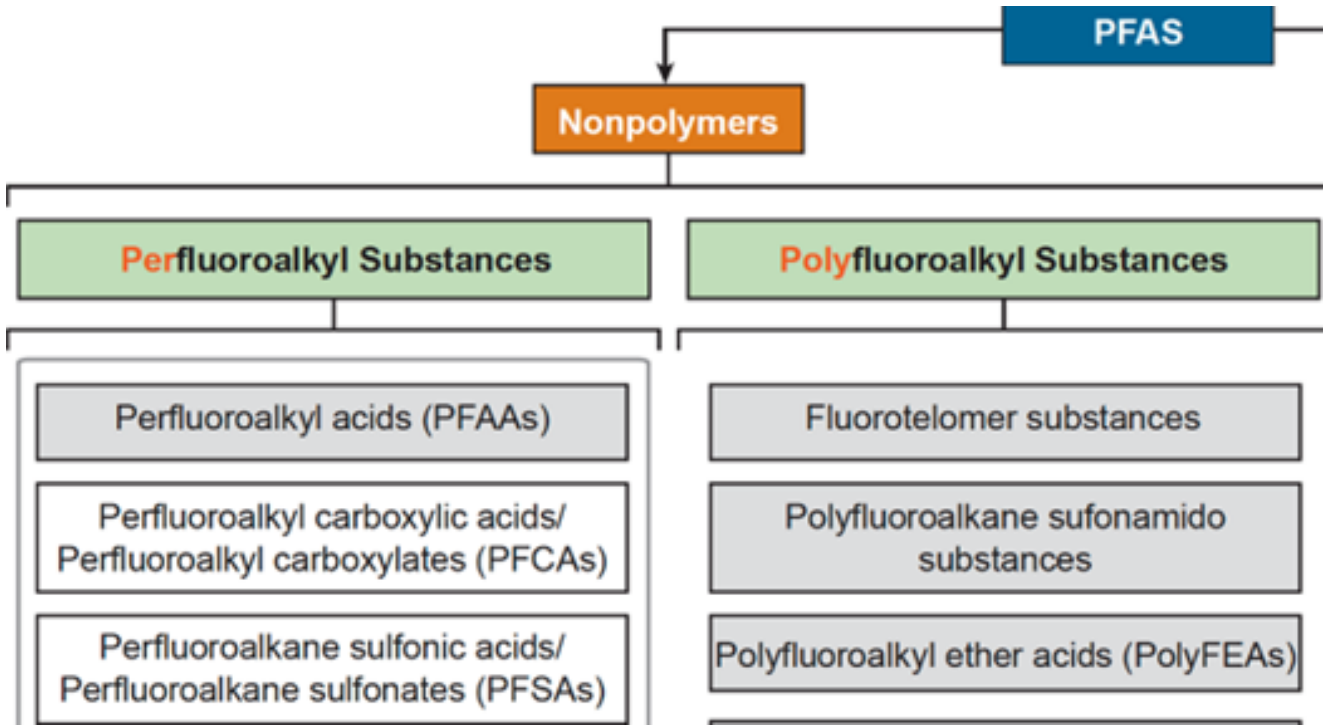
a) Is a Non-Polymer PFAS
b) Has a partially fluorinated alkyl tail
c) Is a Perfluoroalkyl Carboxylic Acid (PFCA)
d) Is a Perfluoroalkane Sulfonic Acid (PFSA)

PFOS: Perfluorooctane Sulfonic Acid

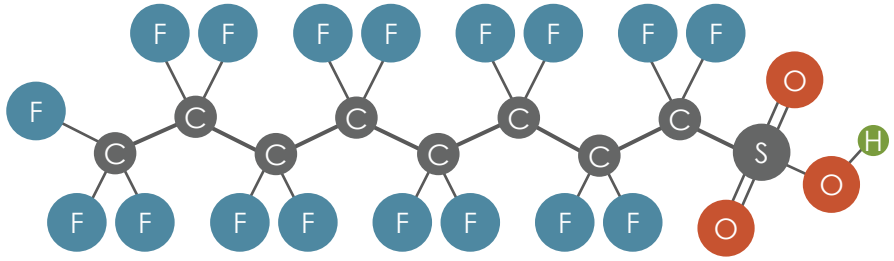




Knowledge Check Explained



PFOS: Perfluorooctane Sulfonic Acid



SO3H = Sulfonic Acid Head

Alkyl Tail, fully fluorinated

- 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)

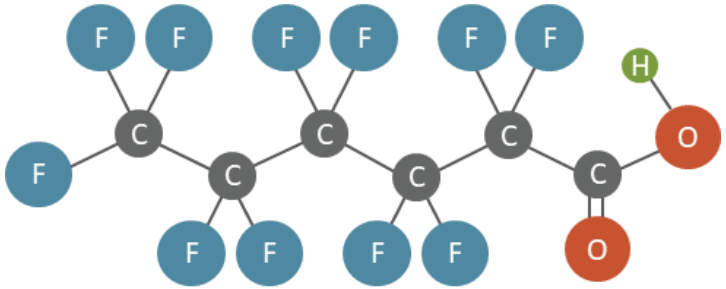
d) Is a Perfluoroalkane Sulfonic Acid (PFSA)

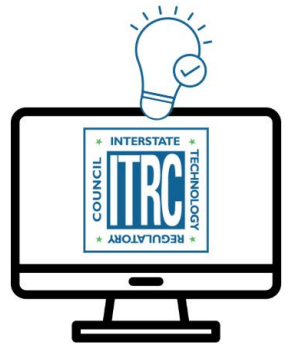
Knowledge Check

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



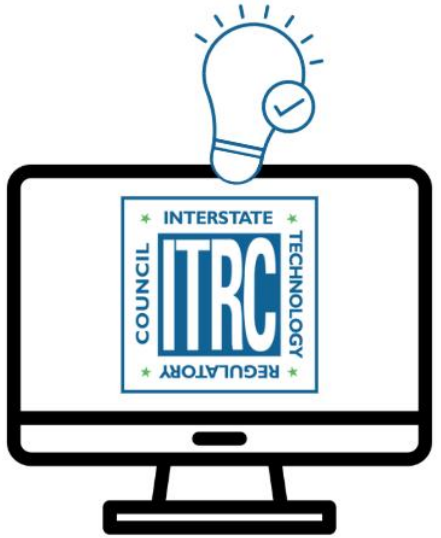


Knowledge Check

PFOA and PFOS are:

(select all that apply)

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



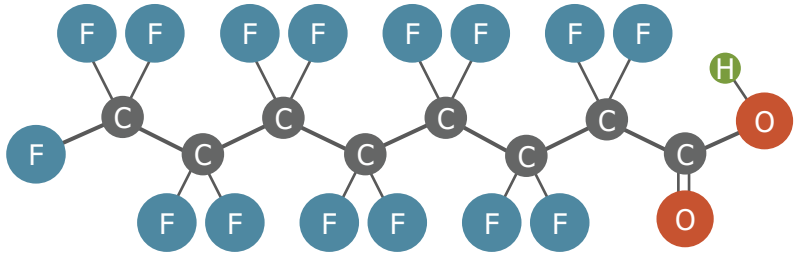
Perfluoroalkyl Acid (PFAA) Naming System

- PFXY
  - PF = perfluoro
  - X = number of carbons
    - Same convention as hydrocarbons
    - Includes carbons in the carboxylate group
  - Y = functional group
    - S = sulfonic acid (R-SO_3H)
    - 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



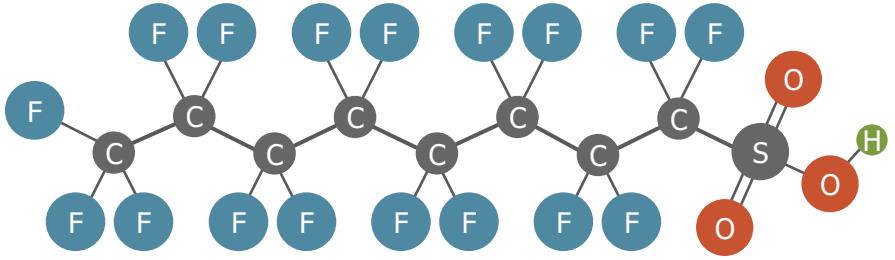
PFOA: Perfluorooctanoic acid
- 8 Carbons (Octane)
- 7 Fluorinated Carbons
- Carboxylic Acid (COOH) Head

PF | PFO | PFOA

PF = Perfluoro
X = # Carbons = 8 = Octa = O
Y = Head (Carboxylic Acid = A and Sulfonic Acid = S)
PFOA
PFOS

PF | PFO | PFOS

PFOS = Perfluorooctane Sulfonic Acid



PFOS: Perfluorooctane Sulfonic Acid
- 8 Carbons (Octane)
- 8 Fluorinated Carbons
- Sulfonic Acid (SO_3H) head

PFAA Naming System

- PFXY
  - PF = perfluoro
  - X = number of carbons
    - Same convention as hydrocarbons
    - Includes C in the carboxylate group
  - Y = functional group
    - S = sulfonic acid (R-SO_3H)
    - A = carboxylic acid (R-COOH)

Table 2-2 Basic naming structure and shorthand for PFAAs

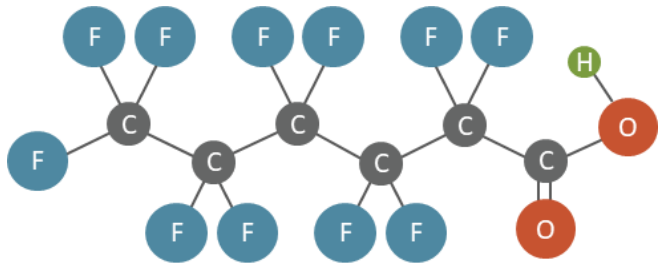
X	Y	Acronym	Name	Formula	CAS No.
B = buta (4 carbon)	A = Carboxylate or carboxylic acid	PFBA	Perfluorobutanoate	$C_3F_7CO_2^-$	45048-62-2
			Perfluorobutanoic acid	C_3F_7COOH	375-22-4
	S = Sulfonate or sulfonic acid	PFBS	Perfluorobutane sulfonate	$C_4F_9SO_3^-$	45187-15-3
			Perfluorobutane sulfonic acid	$C_4F_9SO_3H$	375-73-5
Pe = penta (5 carbon)	A = Carboxylate or carboxylic acid	PFPeA	Perfluoropentanoate	$C_4F_9CO_2^-$	45167-47-3
			Perfluoropentanoic acid	C_4F_9COOH	2706-90-3
	S = Sulfonate or sulfonic acid	PFPeS	Perfluoropentane sulfonate	$C_5F_{11}SO_3^-$	NA
			Perfluoropentane sulfonic acid	$C_5F_{11}SO_3H$	2706-91-4
Hx = hexa (6 carbon)	A = Carboxylate or carboxylic acid	PFHxA	Perfluorohexanoate	$C_5F_{11}CO_2^-$	92612-52-7
			Perfluorohexanoic acid	$C_5F_{11}COOH$	307-24-4
	S = Sulfonate or sulfonic acid	PFHxS	Perfluorohexane sulfonate	$C_6F_{13}SO_3^-$	108427-53-8
			Perfluorohexane sulfonic acid	$C_6F_{13}SO_3H$	355-46-4
Hp = hepta (7 carbon)	A = Carboxylate or carboxylic acid	PFHpA	Perfluoroheptanoate	$C_6F_{13}CO_2^-$	120885-29-2
			Perfluoroheptanoic acid	$C_6F_{13}COOH$	375-85-9
	S = Sulfonate or sulfonic acid	PFHpS	Perfluoroheptane sulfonate	$C_7F_{15}SO_3^-$	NA
			Perfluoroheptane sulfonic acid	$C_7F_{15}SO_3H$	375-92-8
O = octa (8 carbon)	A = Carboxylate or carboxylic acid	PFOA	Perfluorooctanoate	$C_7F_{15}CO_2^-$	45285-51-6
			Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1
	S = Sulfonate or sulfonic acid	PFOS	Perfluorooctane sulfonate	$C_8F_{17}SO_3^-$	45298-90-6
			Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	1763-23-1
N = nona (9 carbon)	A = Carboxylate or carboxylic acid	PFNA	Perfluorononanoate	$C_8F_{17}CO_2^-$	72007-68-2
			Perfluorononanoic acid	$C_8F_{17}COOH$	375-95-1
	S = Sulfonate or sulfonic acid	PFNS	Perfluorononane sulfonate	$C_9F_{19}SO_3^-$	NA
			Perfluorononane sulfonic acid	$C_9F_{19}SO_3H$	474511-07-4
D = deca (10 carbon)	A = Carboxylate or carboxylic acid	PFDA	Perfluorodecanoate	$C_9F_{19}CO_2^-$	73829-36-4
			Perfluorodecanoic acid	$C_9F_{19}COOH$	335-76-2
	S = Sulfonate or sulfonic acid	PFDS	Perfluorodecane sulfonate	$C_{10}F_{21}SO_3^-$	126105-34-8
			Perfluorodecane sulfonic acid	$C_{10}F_21SO_3H$	335-77-3

Nomenclature: Perfluoroalkyl Acids (PFAAs)

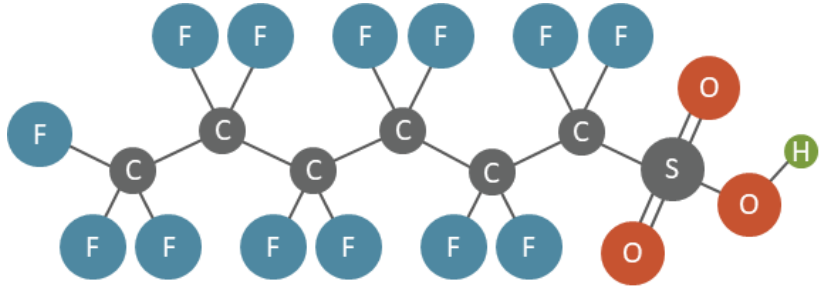
PFAS-1, Section 2.2.3.1 Perfluoroalkyl Acids (PFAAs).

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

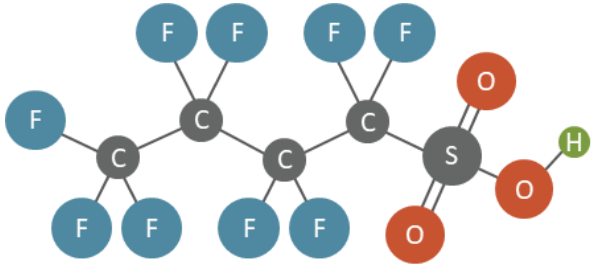
PFHxA



PFHxS



PFBS

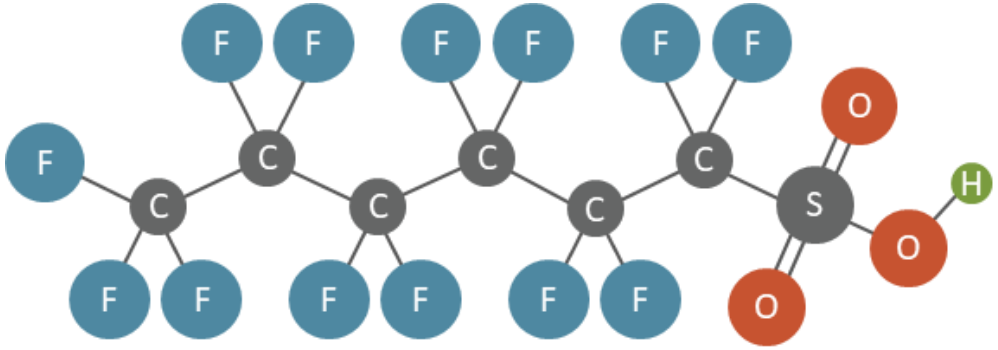


Knowledge Check

Check In!

Name That PFAS!

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



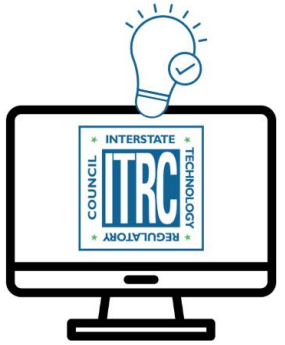
a) PFBS

b) PFPeS

c) PFBA

d) PFHxS

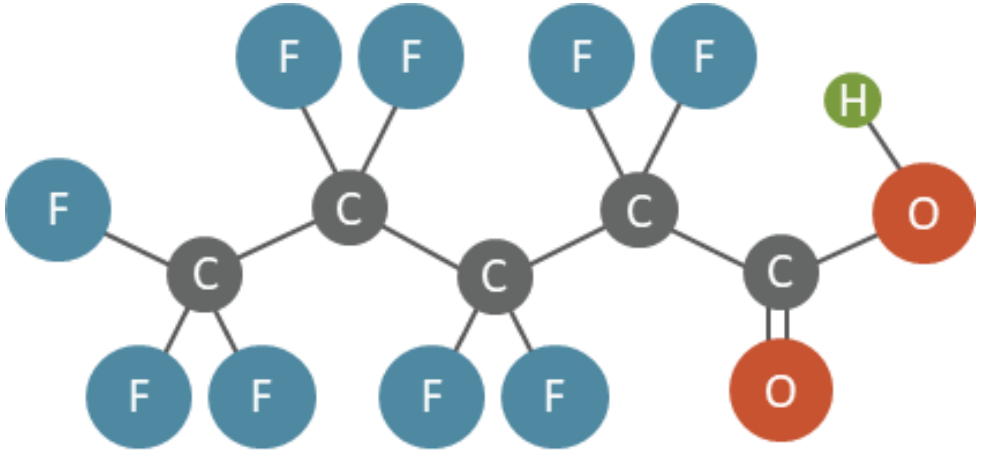
4	B	(buta-)
5	Pe	(penta-)
6	Hx	(hexa-)
7	Hp	(hepta-)
8	O	(octa-)
9	N	(nona-).....



Knowledge Check

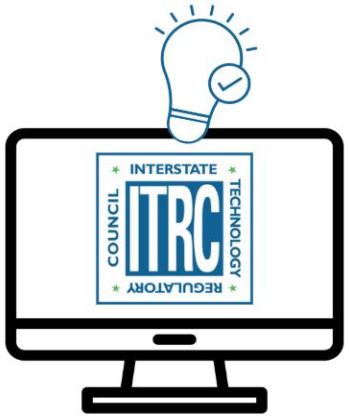
Name That PFAS!

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



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

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



Nonpolymer: Polyfluoroalkyl Substances

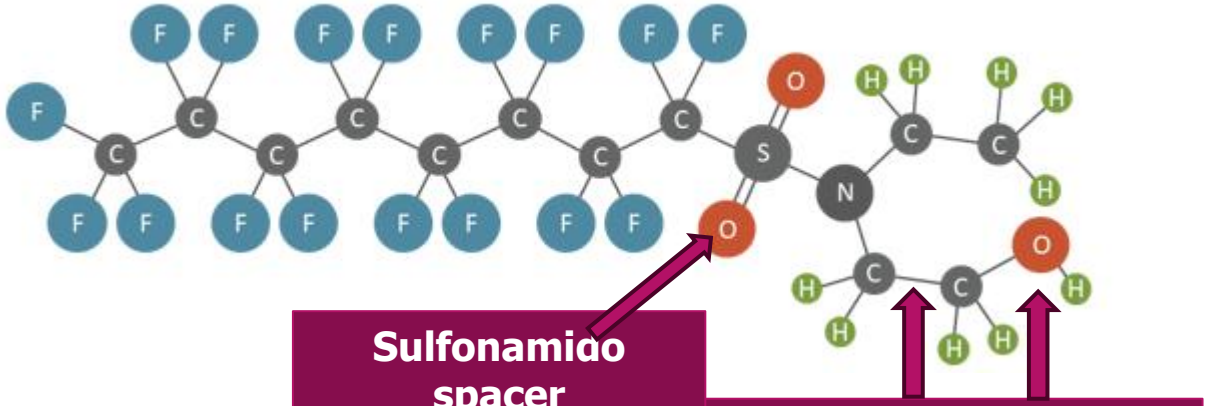
PFAS-1, Section 2.2.4 Polyfluoroalkyl Substances.

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

- Polyfluoroalkyl Substances
  - Fluorotelomer substances
  - Polyfluoroalkane sufonamido substances
  - Polyfluoroalkyl ether acids (PolyFEAs)
  - Chloropolyfluoroalkyl ether acids
  - Chloropolyfluoroalkyl acids
  - Polyfluoroalkyl carboxylic acids (PolyFCAs)

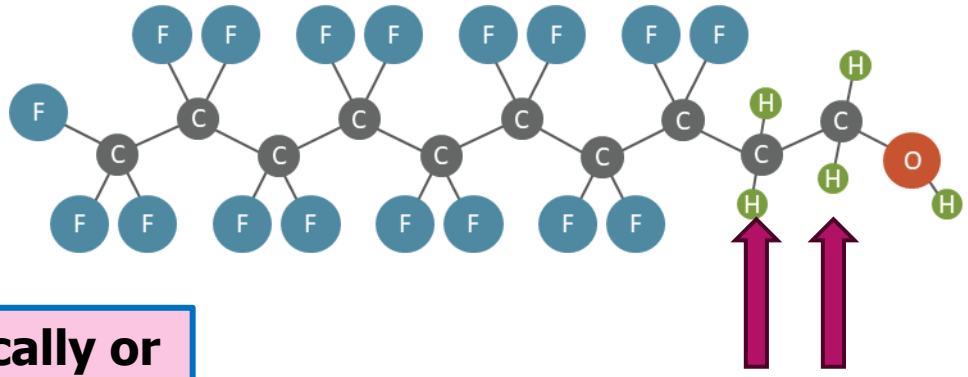
N-Ethylperfluorooctane sulfonamido ethanol (N-EtFOSE)



Sulfonamido spacer

Non-fluorine atom on one or more carbons

8:2 Fluorotelomer Alcohol (8:2 FTOH)



Non-fluorine atom on one or more carbons

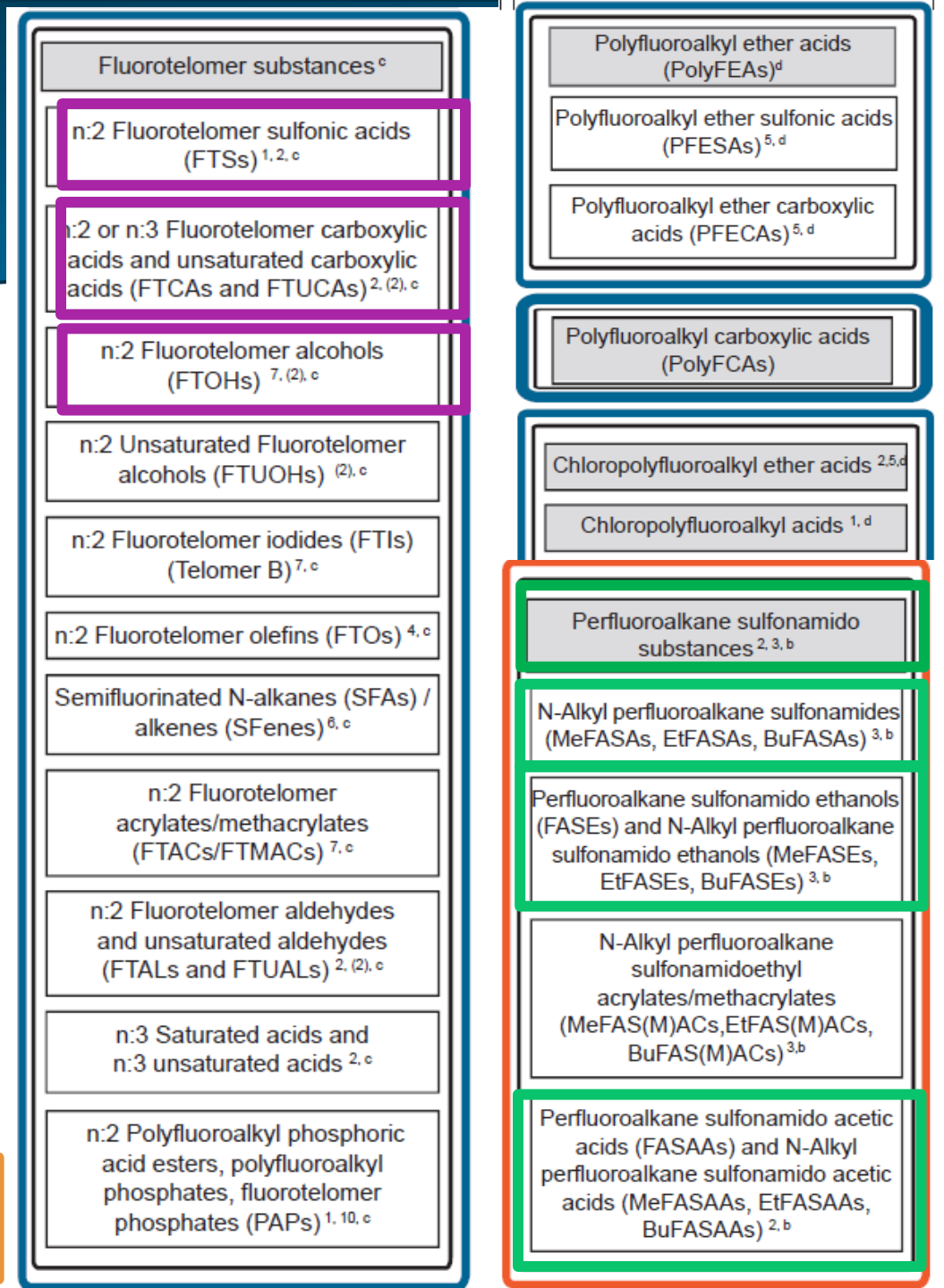
Polyfluoroalkyl substances may also be transformed (biotically or abiotically) to perfluoroalkyl substances (e.g., PFOS or PFOA): PRECURSORS

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)

Fluorotelomerization vs Electrochemical Fluorination (ECF)



Polyfluoroalkyl Substances Currently Included in EPA Methods

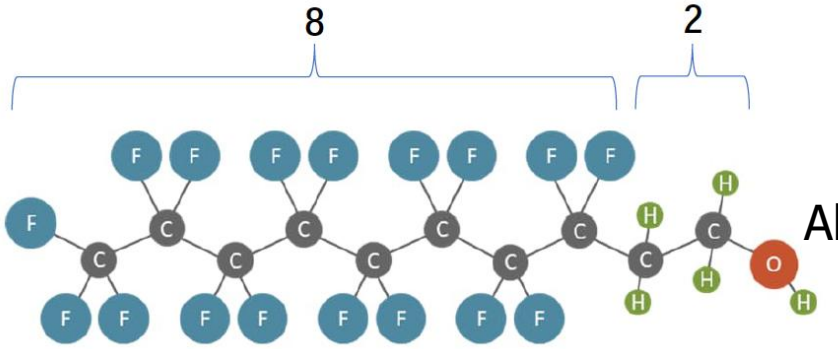
Polyfluoroalkyl PFAS	EPA Method 1633A	EPA Method 537.1	EPA Method 533
4:2 FTS	X		X
6:2 FTS	X		X
8:2 FTS	X		X
PFOSA	X		
N-MeFOSA	X		
N-EtFOSA	X		
N-MeFOSAA	X	X	
N-EtFOSAA	X	X	
N-MeFOSE	X		
N-EtFOSE	X		
ADONA	X	X	X
9Cl-PF3ONS	X	X	X
11Cl-PF3OUdS	X	X	X
3:3 FTCA	X		
5:3 FTCA	X		
7:3 FTCA	X		

PFAS-1, Table 2-5. USEPA PFAS Methods and PFAS Classifications.

Fluorotelomers

PFAS-1, Section 2.2.4.1 Fluorotelomer Substances.

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

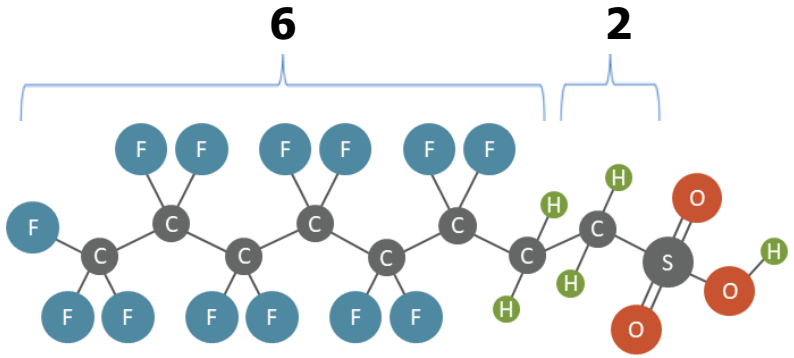


Alcohol

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)



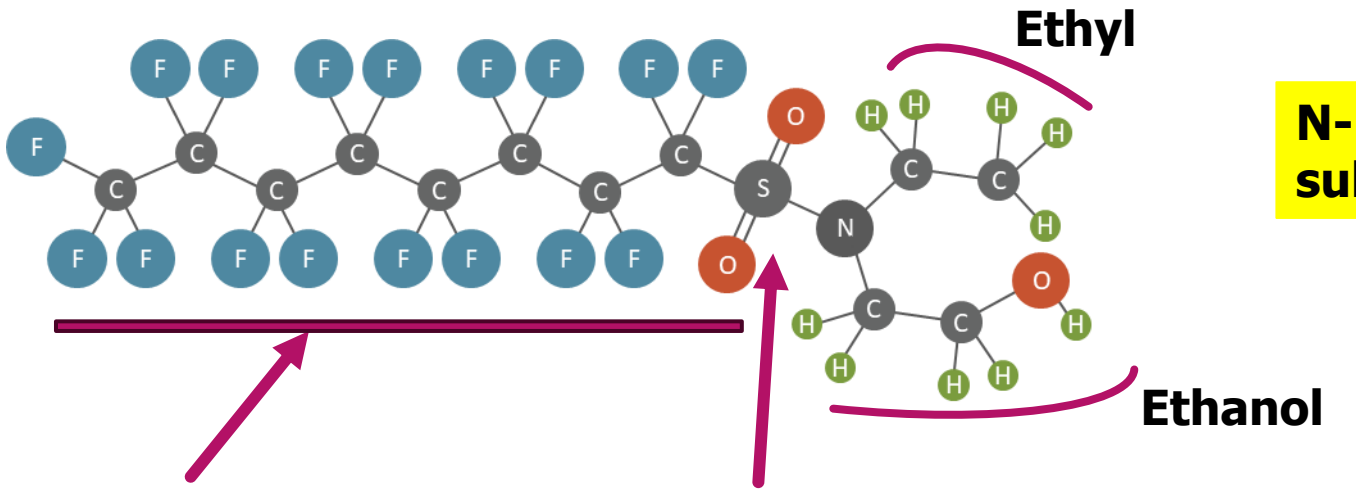
Sulfonic Acid

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)

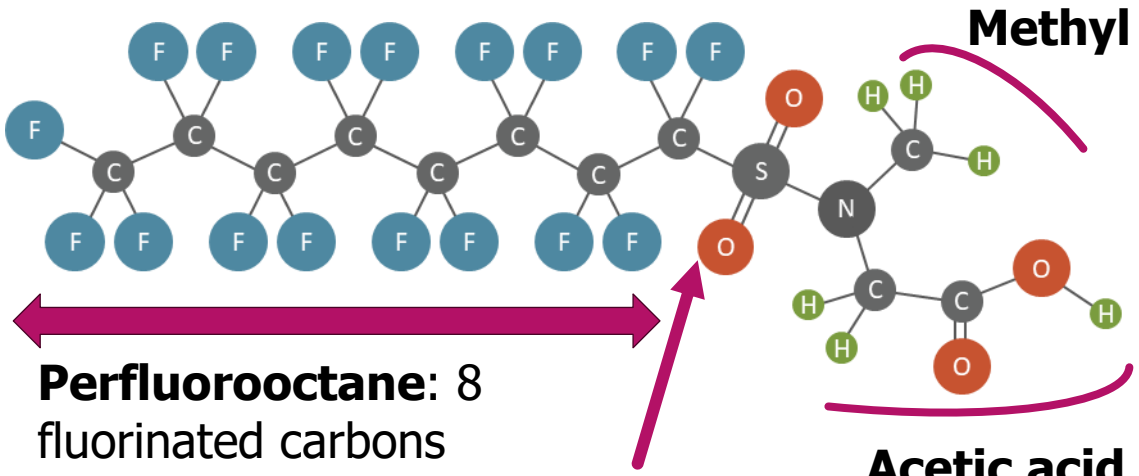
Perfluoroalkane Sulfonamido Substances



N-Ethyl perfluorooctane sulfonamido ethanol (N-EtFOSE)

Perfluorooctane: 8 fluorinated carbons

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



Perfluorooctane: 8 fluorinated carbons

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

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

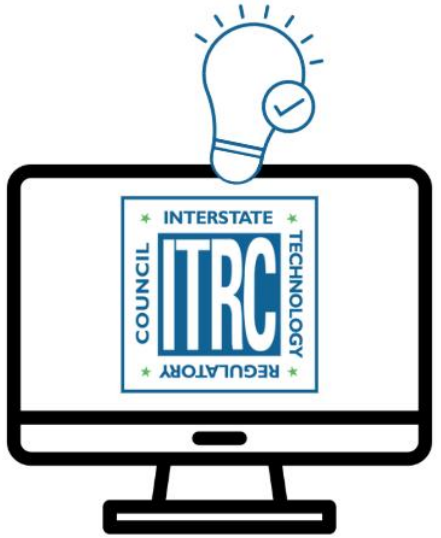
PFAS-1, Section 2.2.4.2 Perfluoroalkane Sulfonamido Substances.

Knowledge Check

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

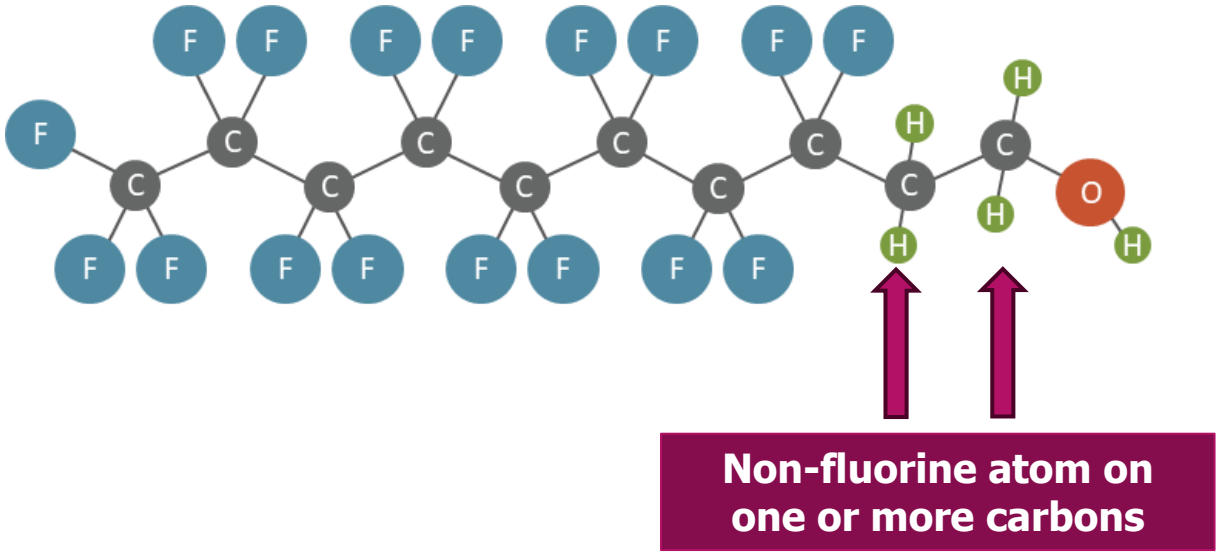
Polyfluoroalkyl PFAS:

(Select all that apply)

a) Are persistent in the environment

b) <u>Contain carbons that are not fluorinated</u>

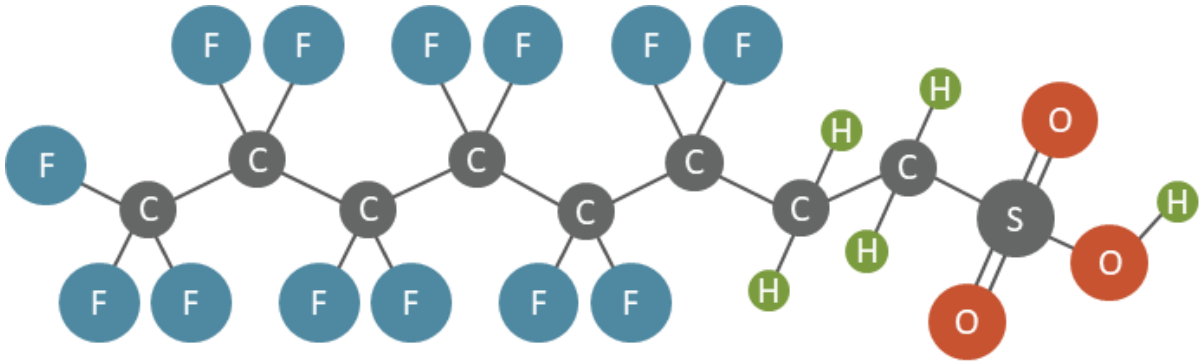
c) <u>Can transform into perfluoroalkyl PFAS</u>



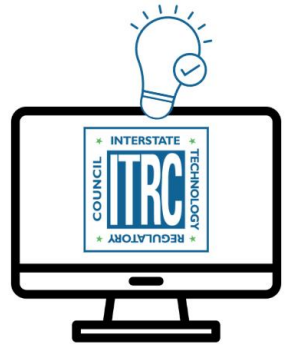
Knowledge Check

Check In!

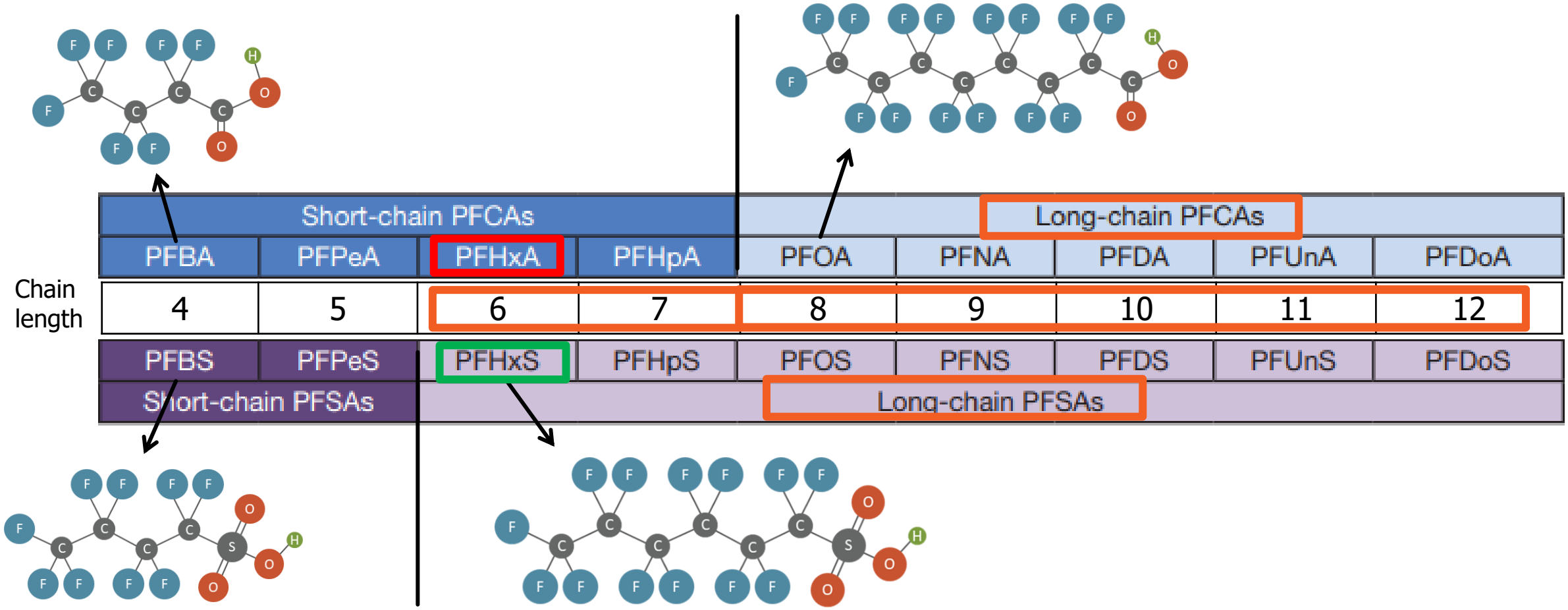
The fluorotelomer molecule shown here is:
(select all that apply)



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 vs Short-Chain PFAAs



PFAS-1, Section 2.2. Table 2-3 Short-chain and long-chain PFCAs and PFSAs.

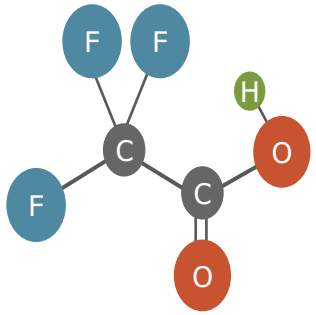
Ultrashort PFAS

- ≤3 carbons
- Common examples:

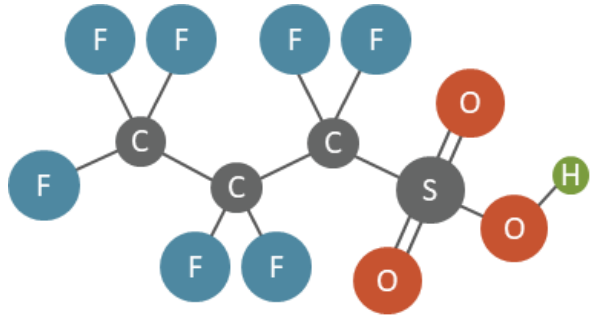
  Trifluoroacetic acid (TFA)

  Perfluoropropanoic acid (PFPrA)

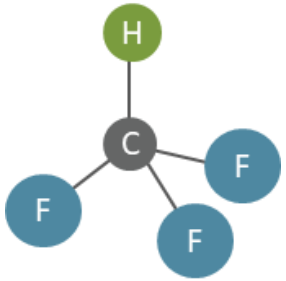
  Perfluoropropanesulfonic acid (PFPrS)
- Some fluorinated gases considered ultra-short PFAS
- Not typically measured but gaining more interest



TFA



PFPrS



Trifluoromethane: Fluorinated Gas

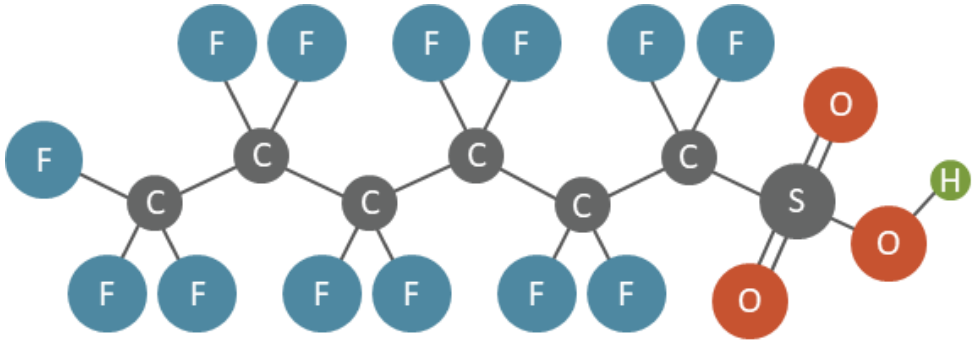
Knowledge Check

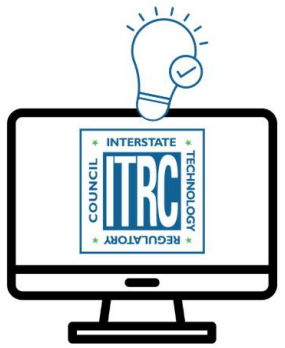
Check In!

The Molecule Shown:

(select all that apply)

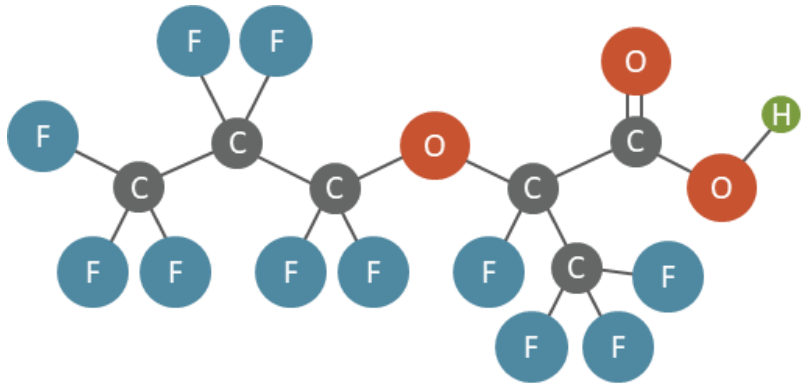
a) Is long-chain
b) Is PFPeS
c) Is a Perfluoroalkane sulfonic acid (PFSA)
d) Is PFHxS
e) Has 6 fluorinated carbons





Replacement Chemistry

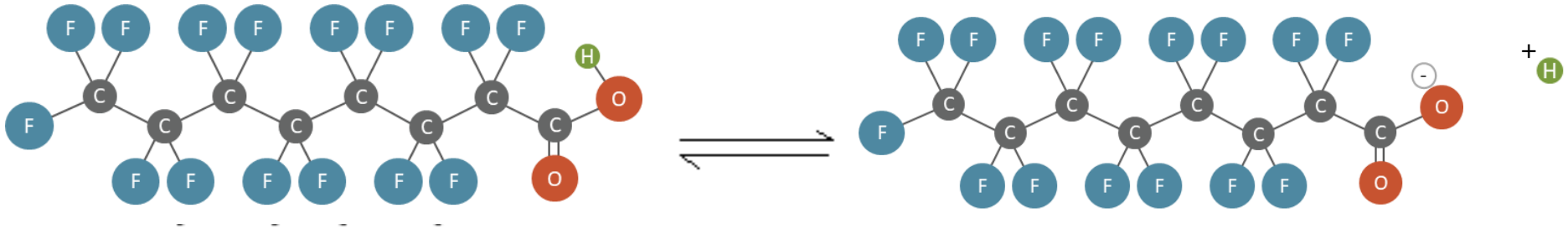
- 6:2 Fluorotelomers replace PFOS in metals plating
- Fluorotelomers replace PFOS and PFHxS in AFFF
- Shorter chain PFAAs replace PFOA: PFBA, PFPeA
- ADONA and HFPO-DA (GenX) are replacement chemicals for PFOA
- HFPO-DA (Hexafluoropropylene oxide dimer acid)
  - Component of GenX technology used by one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



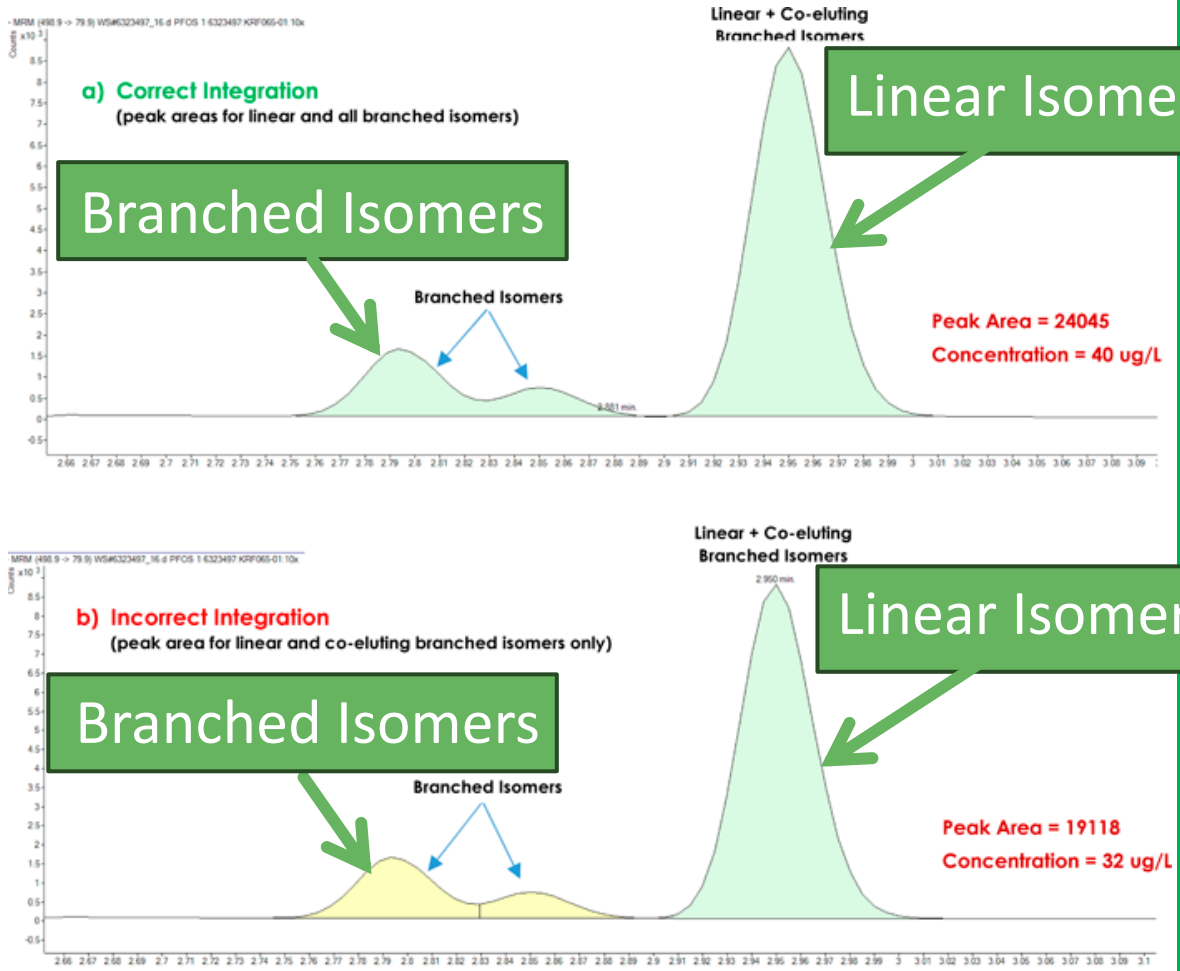
	PFAS State		Structure	CAS No.
PFOA	Anion	Perfluorooctanoate	$C_7F_{15}CO_2^-$	45285-51-6
	Acid	Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1
PFOS	Anion	Perfluorooctane sulfonate	$C_8F_{17}SO_3^-$	45298-90-6
	Acid	Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	1763-23-1

Why is this important?

PFAS-1, Section 2.2.1 Naming Convention Considerations.

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

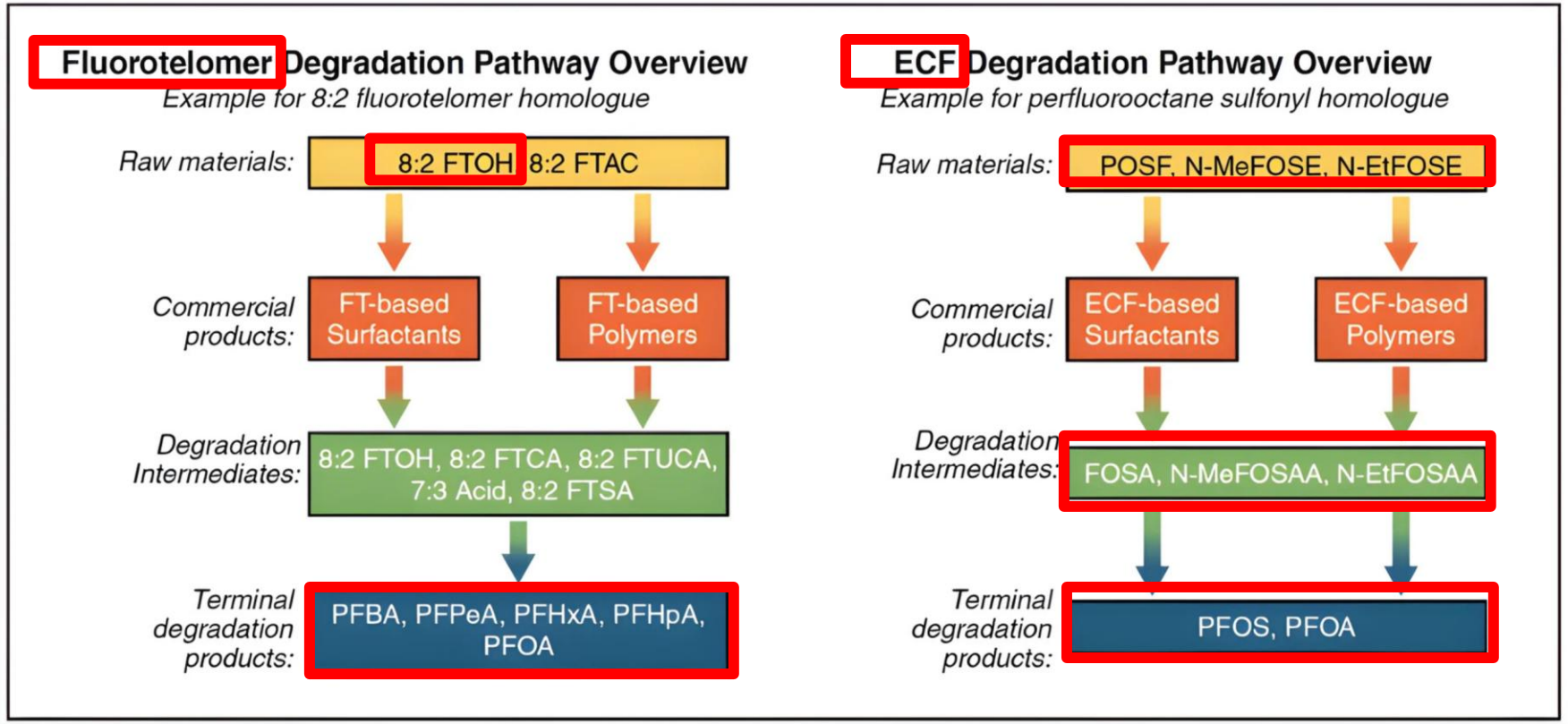


Currently labs reporting L&B consistently for: PFHxS, PFOS, PFOA, NMeFOSAA, NEtFOSAA

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

PFAS-1, Section 11.3.5 Linear and Branched Isomers
Figure 11-3, Source: Bureau Veritas Laboratories, Mississauga, Ontario, Canada. Used with permission.

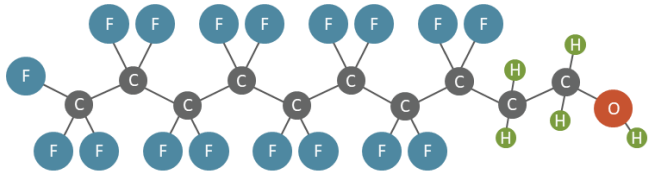
Precursors: Transformation Pathways



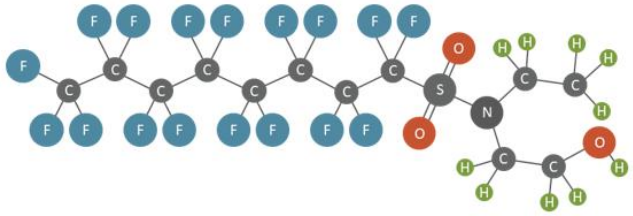
Takeaways:

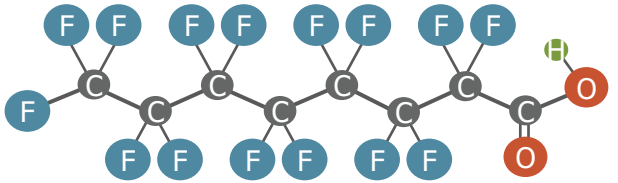
- Polyfluoroalkyl PFAS precursors can transform into measurable regulated PFAS.
- Manufacturing process may dictate transformation pathway.
- Transformation can impact our decision-making on site investigations.

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

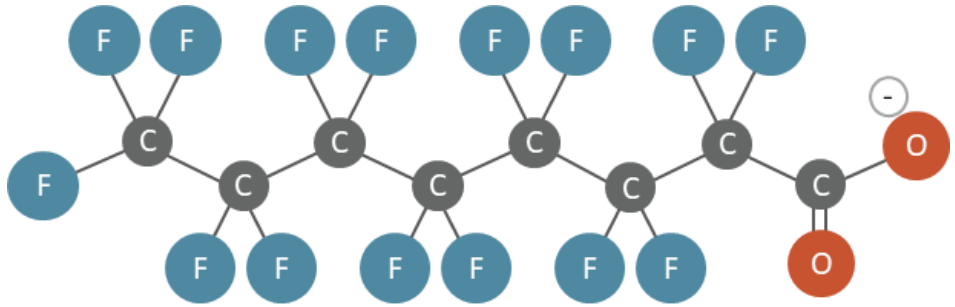
[1]Fluorotelomer sulfonic acid: for example, may be found at AFFF sites
[2]Fluorotelomer carboxylic acids: for example, 5:3 FTCA may be found in landfill leachate
[3]Under certain instances, can produce mixture of linear and branched PFCAs

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 ex ($–CF_2–$) 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
Gluge et al.[1939]	2020	In addition to substances co functional groups on both e cycloaliphatic substances. A [excluding] non-polymeric s polyfluoroalkylether-based s included."	
TURA Program, Massachusetts (TURA 2023[2795]**)**	2023	"Certain PFAS not otherwise 3; or $CF_3–C_nF_{2n}–$, n ≥ 2) or $–C_nF_{2n}OC_mF_{2m}–$ or $–C_nF_{2n}OC$ may represent a straight or	
USEPA OPPT[2813]	2021	"a structure that contains th branching, heteroatoms, an	
NDAA, WA, CA, VT, ME	2019, 2020, 2021	Organic chemicals containin	
USEPA CCL5[2718]	2022	"For the purposes of CCL5, t one of these three structure (1) $R–(CF_2)–CF(R')R''$, wher $CF_2OCF_2–R'$, where both the the carbons are saturated, a	
MPART[2885]	2023	PFAS means per- and polyflu C(F)(R')R", or perfluoroalkyl ether moiety, $R–(CF_2)–O–(CF)(R')R''$, 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.	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 propertie

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.



PFAS-1, Section 2.2, Table 2-1: Examples of PFAS definitions/Working Descriptions (Source: Hammel et al. 2022, iScience 25 (4):104020. Table 2, CC BY-NC-ND 4.0

Key Takeaways: What Did We Just Cover?

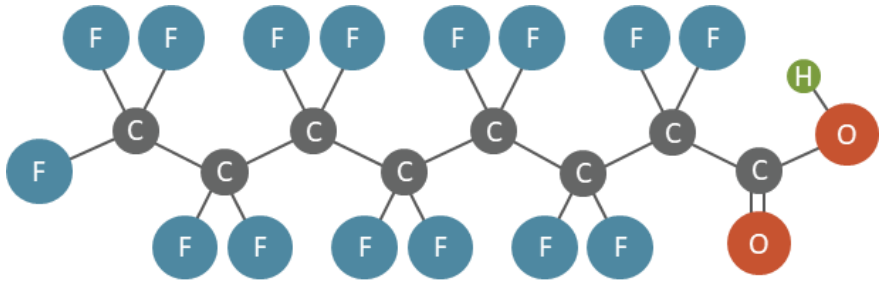
- PFAS Family Tree
- Polymer vs Non-Polymer
- Perfluoroalkyl Substances vs Polyfluoroalkyl Substances
- Perfluoroalkyl Acid (PFAA) Naming Conventions
- Fluorotelomer Naming Conventions
- Long Chain vs Short Chain PFAS
- Ultra-Short PFAS
- Replacement PFAS
- PFAS and CAS Numbers
- Linear & Branched PFAS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

PHYSICAL AND CHEMICAL PROPERTIES

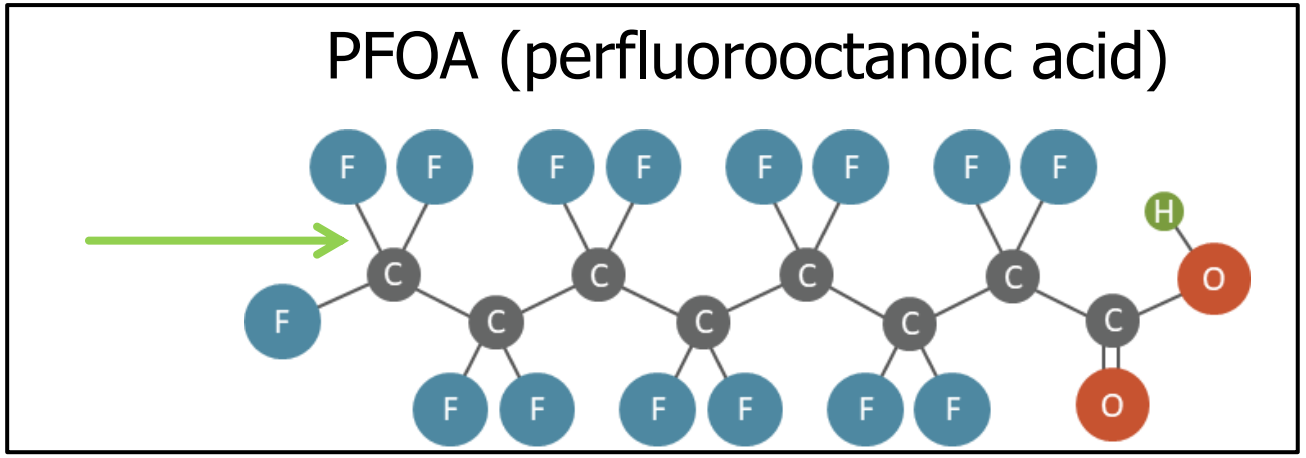
MITCH OLSON

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



Physical properties & implications

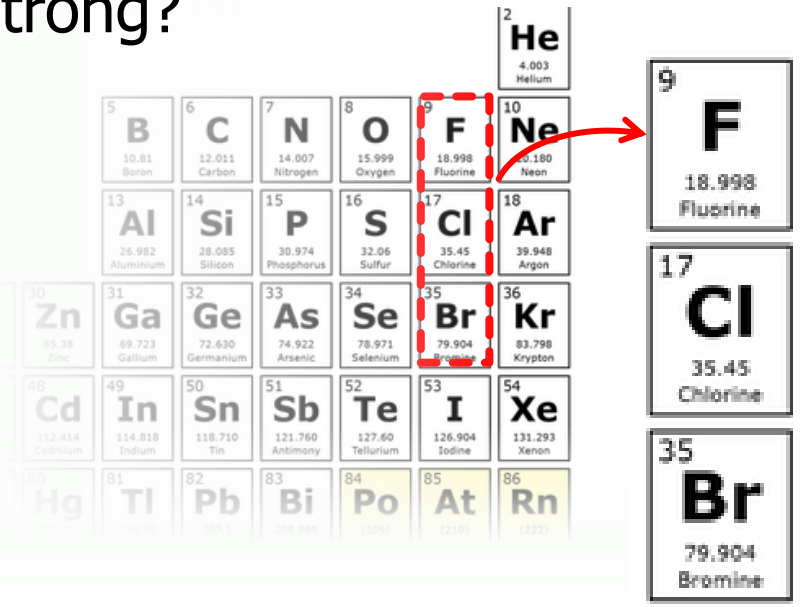
- High thermal stability – destructive treatment is energy intensive
- High chemical stability – low reactivity, low biodegradability
- Weak intermolecular interactions – hydrophobic and lipophobic

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

Why is the C-F bond so strong?



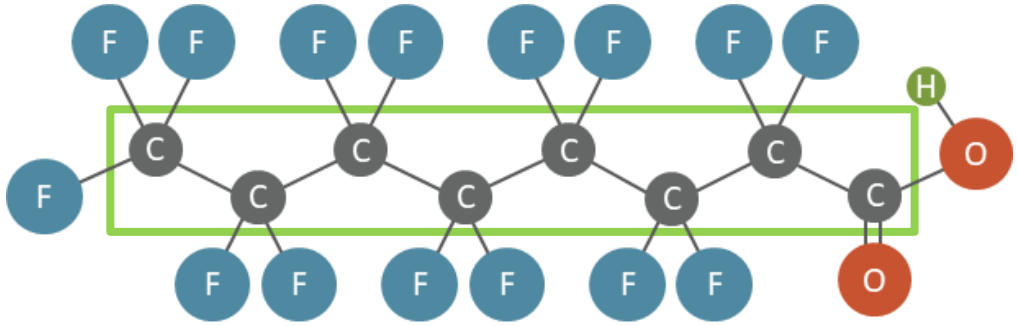
	Fluorine	Chlorine	Bromine
Atomic weight	19.0	35.5	79.9
Atomic radius (pm)	60	99	114
Electronegativity	3.98	3.16	2.96
Carbon bond strength (kJ/mol)	485	327	285

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

PFOA (perfluorooctanoic acid)



Physical properties & implications

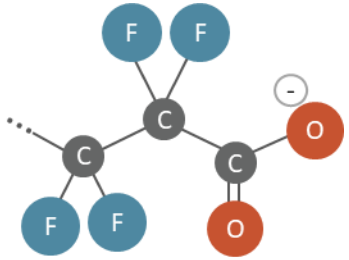
	Short Chain	Long Chain
Mobility in water	High mobility	Moderate
Treatability in water	Difficult to remove	More easily removed
Bioaccumulation	Less bioaccumulative	More bioaccumulative

Key chemical property

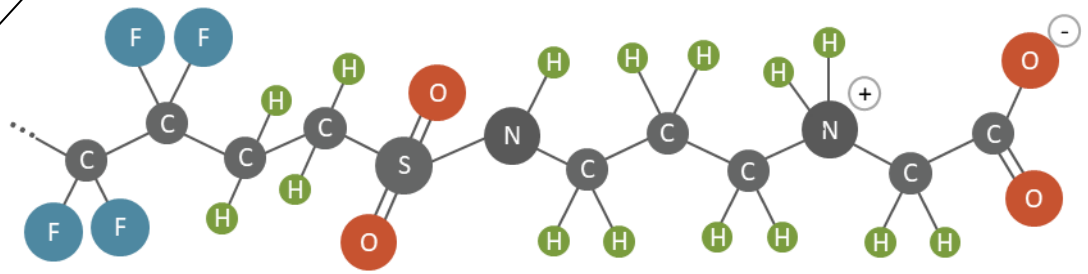
- C-F bond
- Chain length
- Functional group: PFAAs & precursors
- Acid/base chemistry
- Low Henry's constant
- Mixed polarity (surfactant)

PFAS Physical and Chemical Properties

Example PFAAs



Example zwitterions:
fluorotelomer sulfonamido betaines



Physical properties & implications

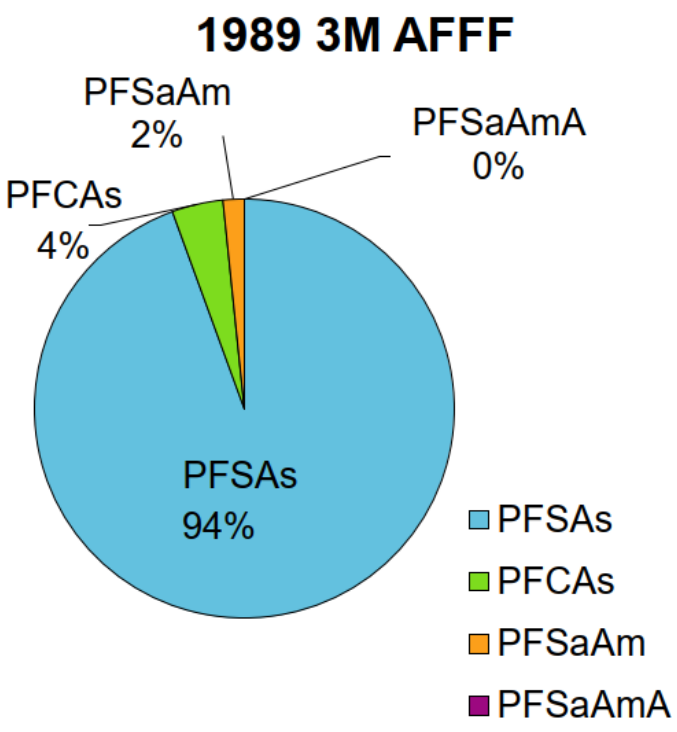
- Precursors – may be cationic (+) or zwitterionic (+-), more sorptive to soils than anionic (-) PFAAs
- Precursors - biotransformation vs. biodegradation
- PFAAs – "terminal" end products

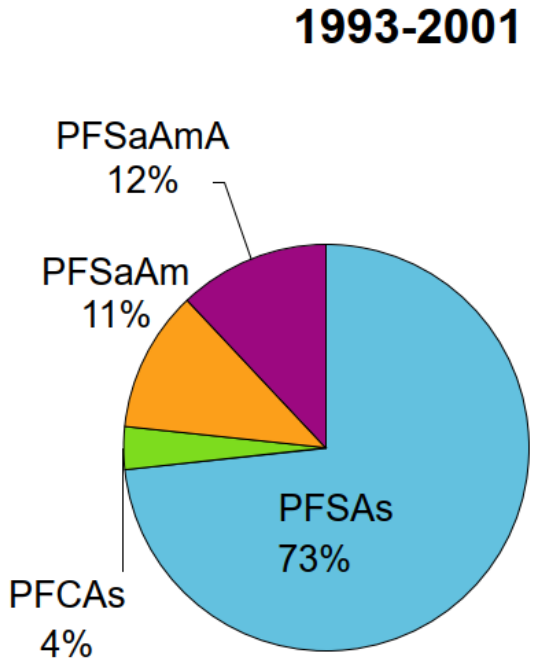
Key chemical property

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

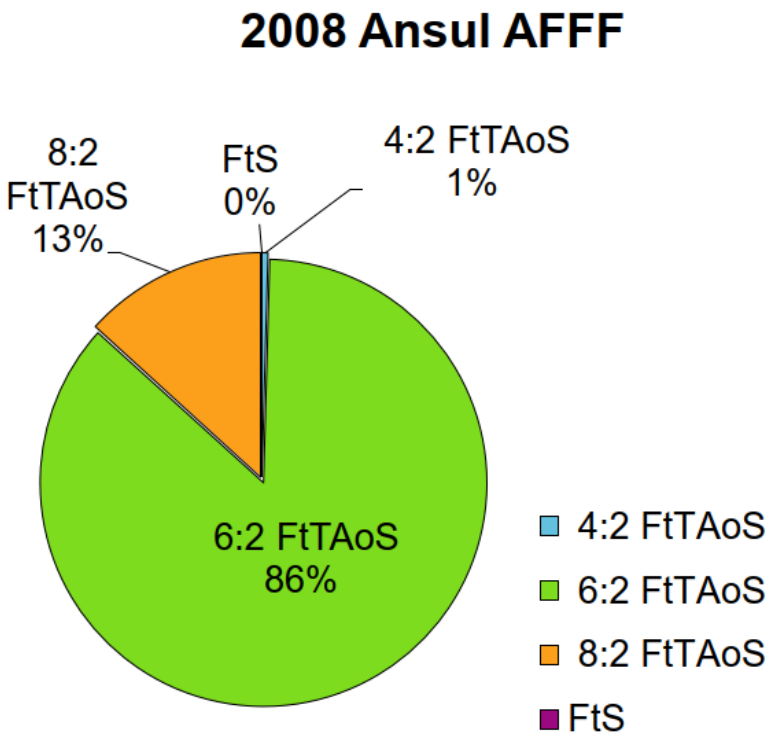
PFAS Physical and Chemical Properties

Evolving AFFF composition: PFAAs and precursors





Electrochemical Fluorination

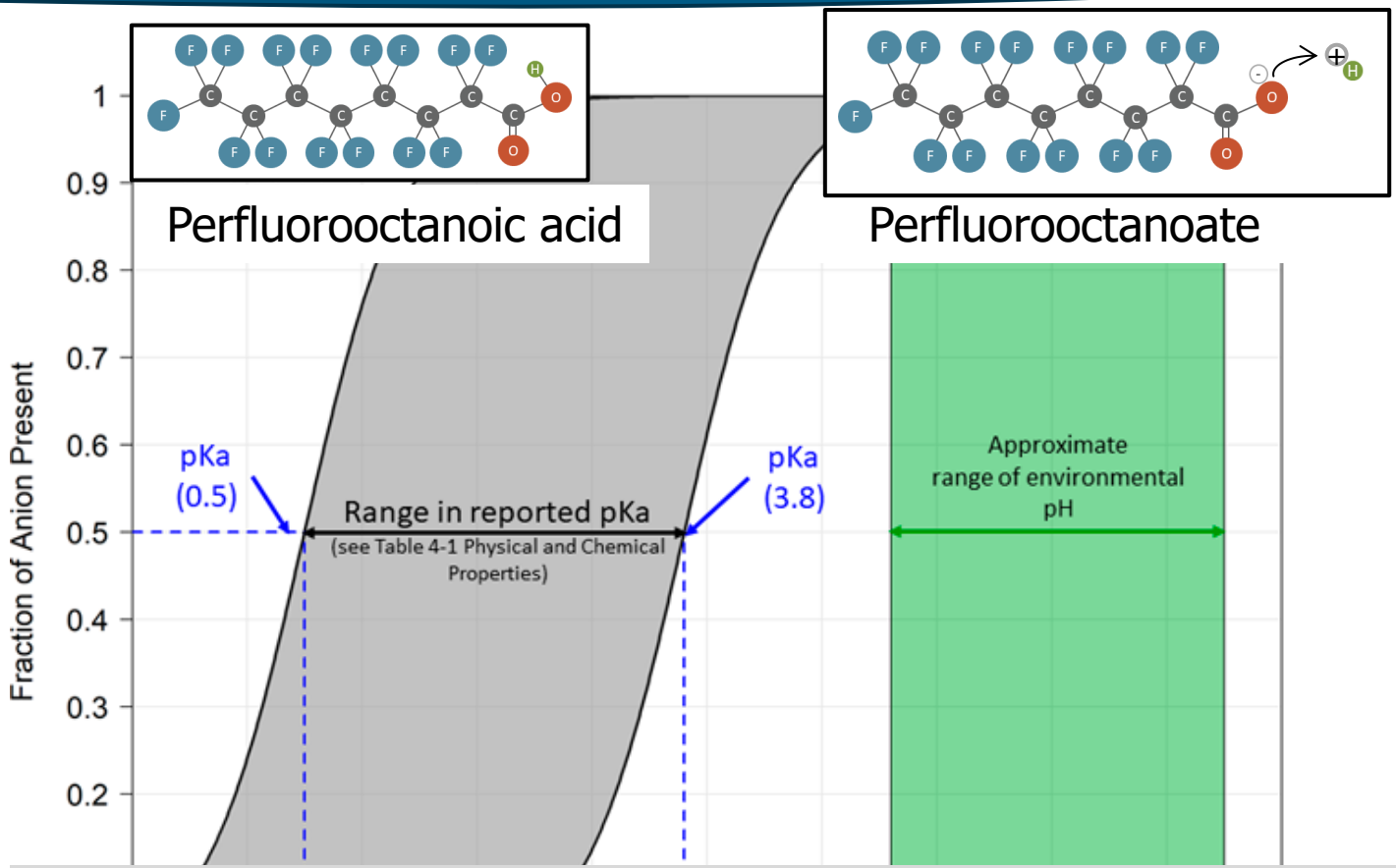


Fluorotelomerization

Barzen-Hanson et al. 2017. Environ Sci Technol 51: 2047-2057.
Figures used with permission from J. Field, Oregon State.

ITRC PFAS-1, Section 3.1, and Table 3-1.

PFAS Physical and Chemical Properties



Physical properties & implications

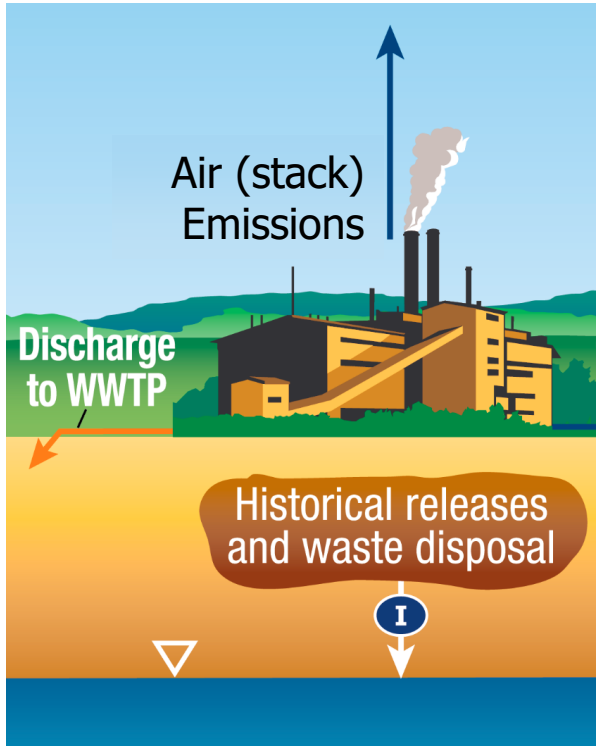
- PFAAs are anionic (negatively charged) in most water systems
- Moderate to high water solubility – high potential mobility in water

Key chemical property

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

PFAS-1, Figure 4-2 needs the source attribution Source: E. DiFilippo, S.S. Papadopulos & Associates, Inc. Used with permission.

PFAS Physical and Chemical Properties



$$Henry's\ constant: \quad \frac{Vapor\ concentration}{Liquid\ concentration}$$

Physical properties & implications

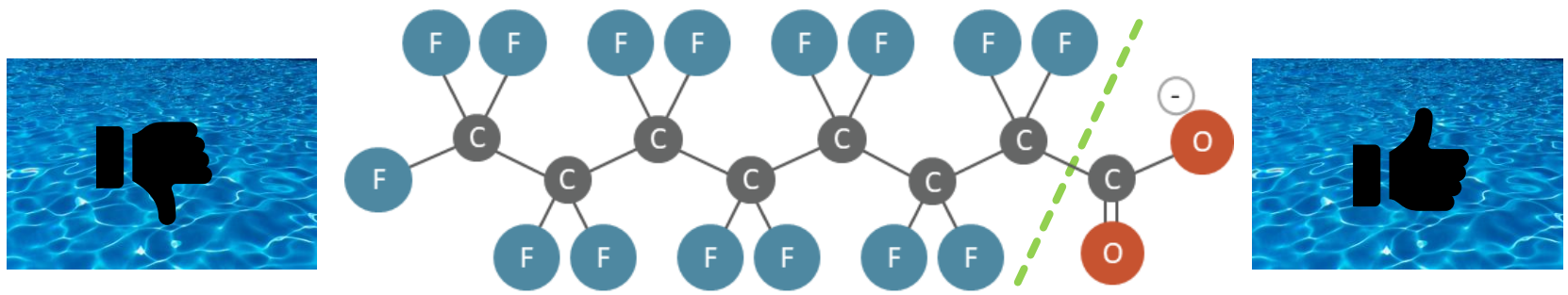
- Limited volatility for many PFAS (including PFAAs)
- Conventional air stripping is not effective remediation*
- Nevertheless, PFAS may migrate via atmospheric transport

Key chemical property

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

PFAS-1, Section 4.2.6, and Figure 2-20 CSM for industrial sites.
Source: Adapted from figure by L. Trozzolo, TRC, used with permission..

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

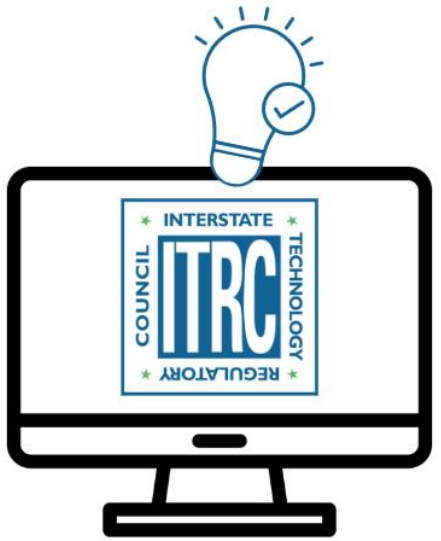
Key chemical property

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

Knowledge Check

Which property contributes most to high chemical stability for PFAS?

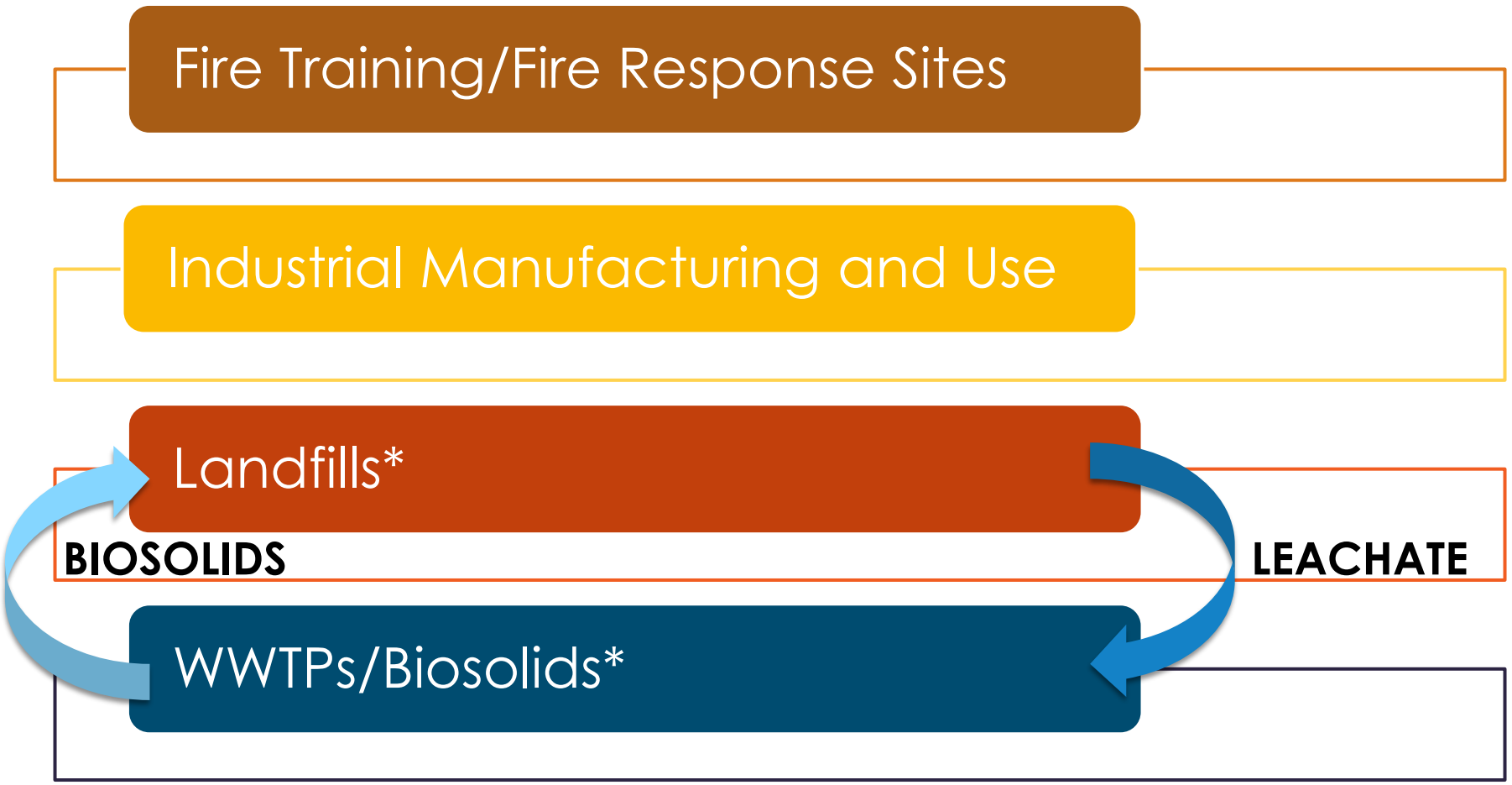
a) Chain length
b) Acid/base
c) Carbon-fluorine bond
d) Henry's constant
e) Surfactant



PFAS CHEMISTRY: IMPLICATIONS AND APPLICATIONS

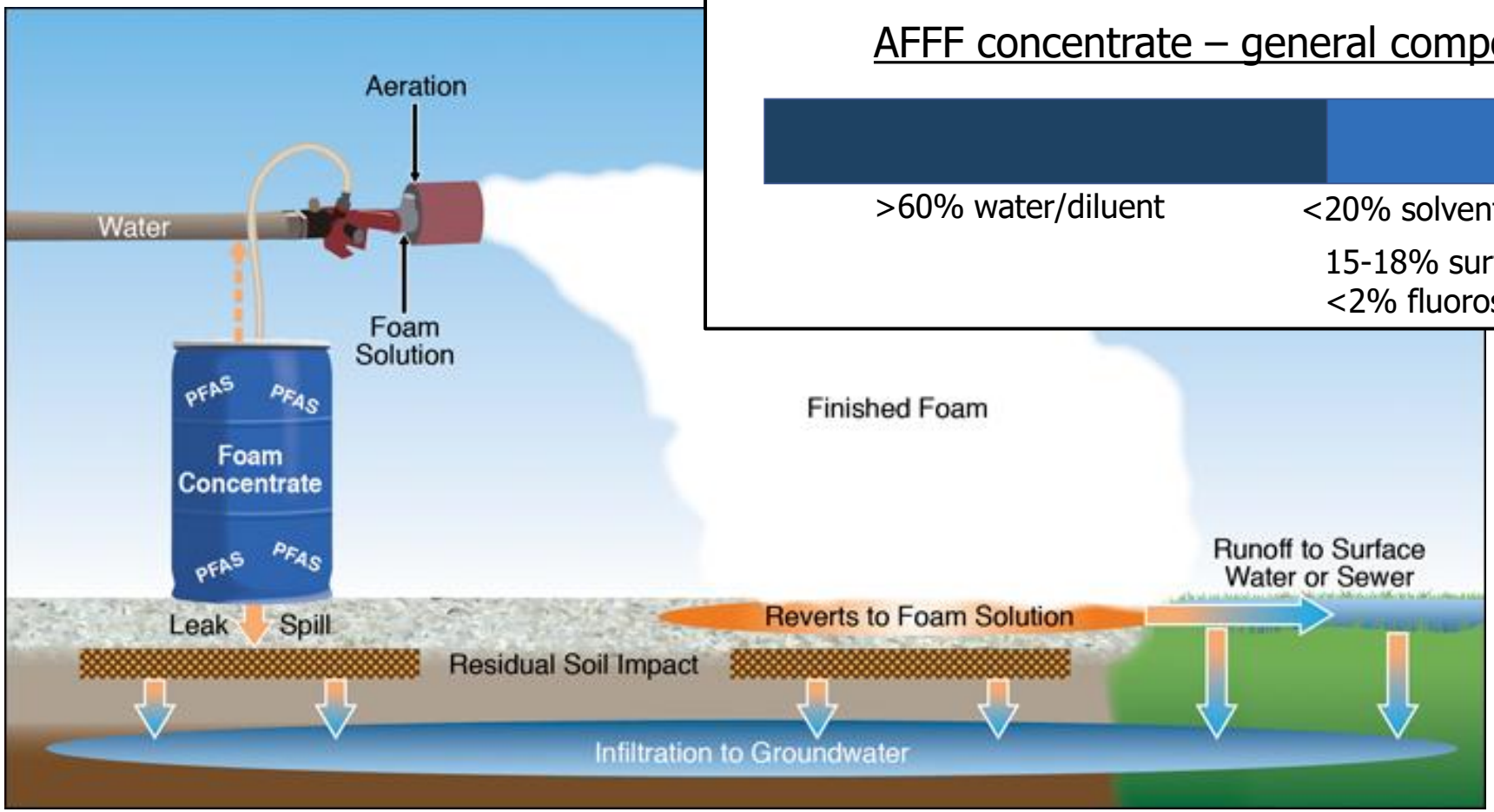
MITCH OLSON

Sources of PFAS Release to the Environment



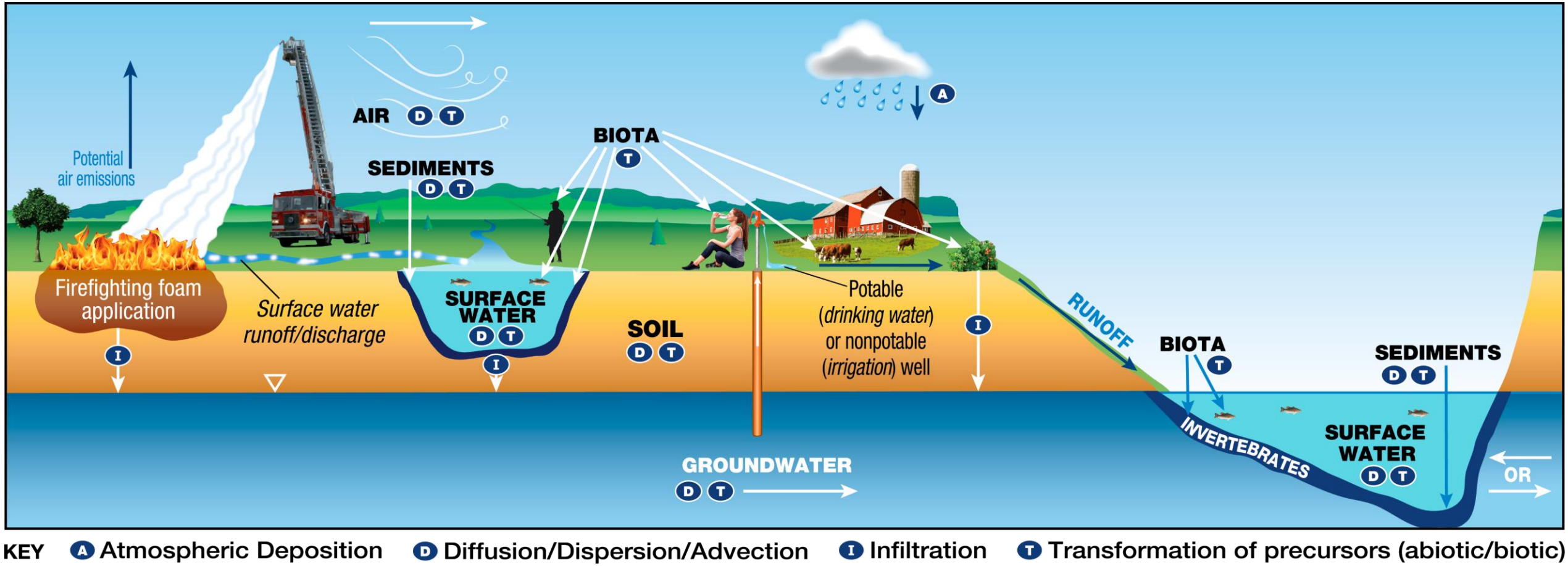
*Landfills and WWTPs are receivers of PFAS materials from domestic and industrial sources. PFAS concentrations vary widely depending on the waste stream accepted by facilities.

Aqueous Film Forming Foams (AFFF) Source Zones



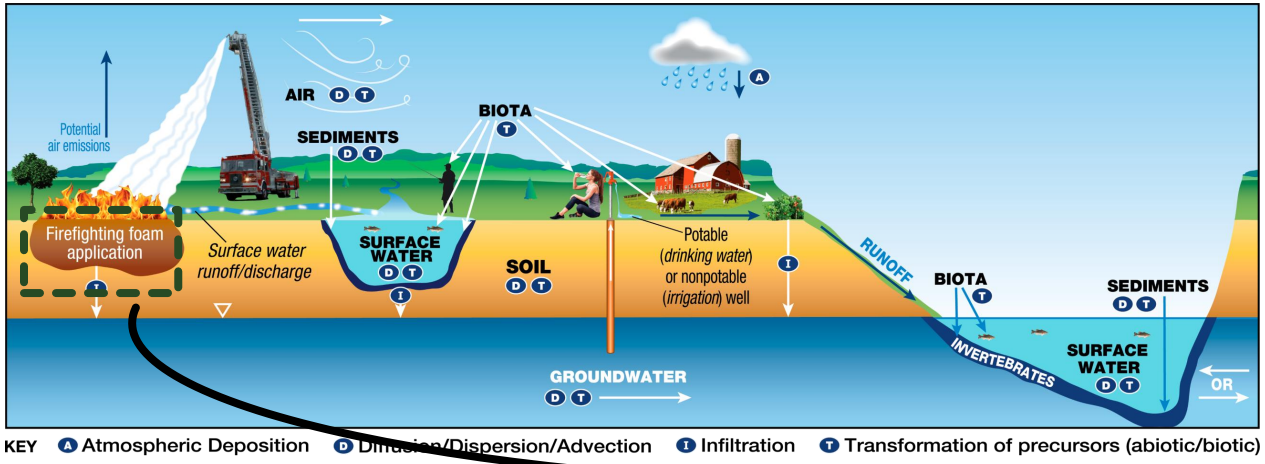
PFAS-1, Section 3.3 Mechanisms for Release to the Environment.
PFAS-1, Figure 3-3. Typical composition of 3% AFFF concentrate. Source: S. Thomas, Battelle. Adapted from Kempisty, Xing, and Racz 2018.
PFAS-1, Figure 3-4. Release of firefighting foam. Source: Adapted from figure by J. Hale, Kleinfelder, used with permission.

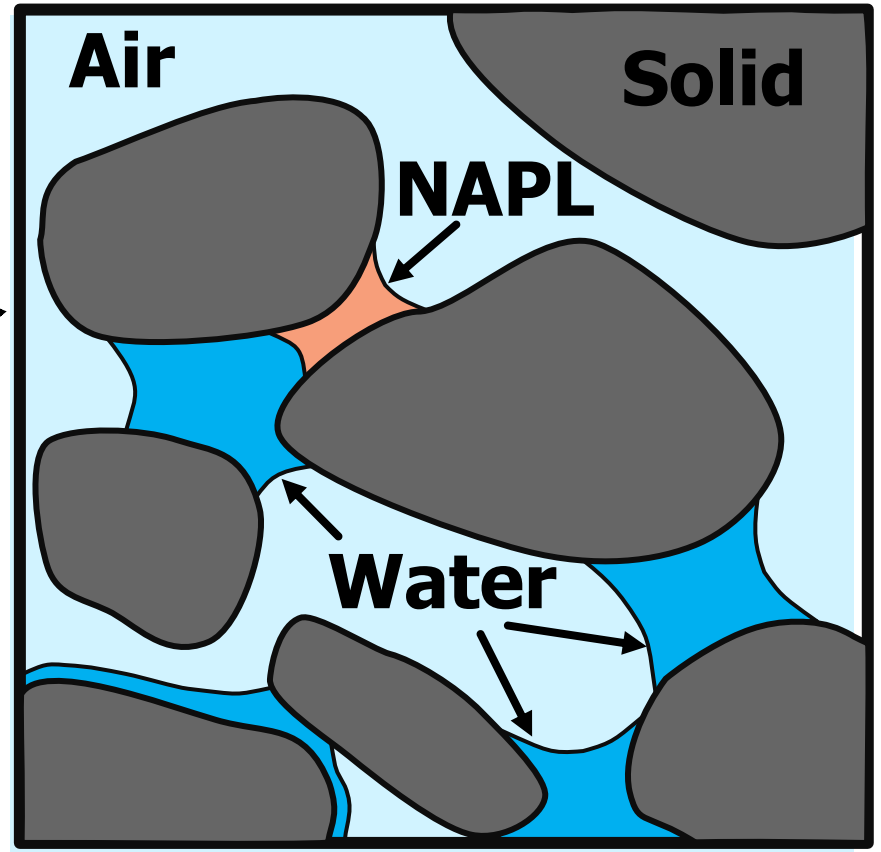
AFFF Fate and Transport



PFAS-1, Section 3.4 AFFF Fate and Transport.
PFAS-1, Figure 2-21 CSM for fire training areas. Figure Adapted from figure by L. Trozzolo, TRC, used with permission.

Micro-Scale Factors Influencing PFAS Retention





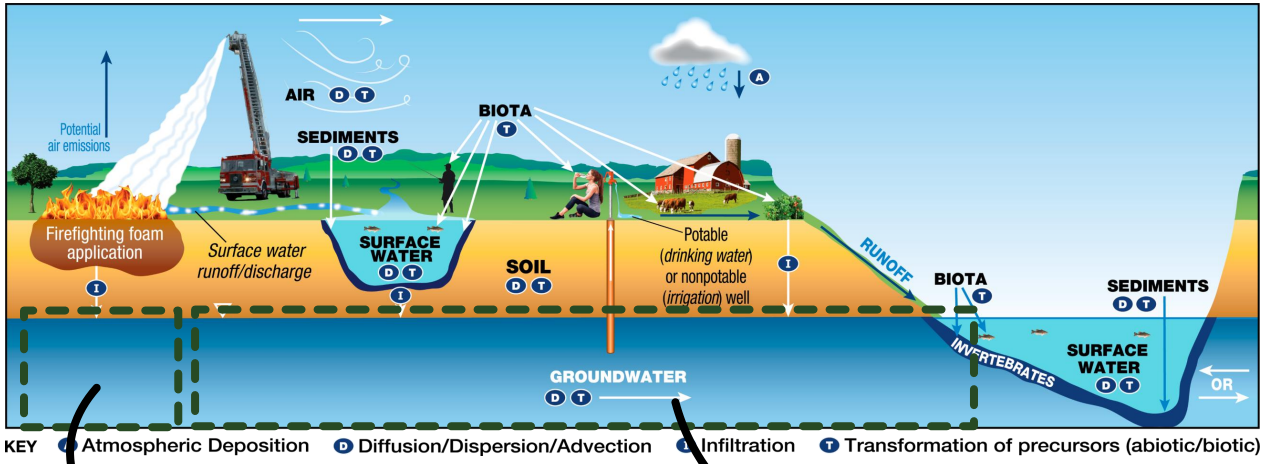
1. **Sorption to organic matter**
2. **Air-water interface partitioning**
3. **Electrostatic interactions**

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)

PFAS-1, Section 5.2.3
PFAS-1, Figure 2-21 CSM for fire training areas. Figure Adapted from figure by L. Trozzolo, TRC, used with permission.

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

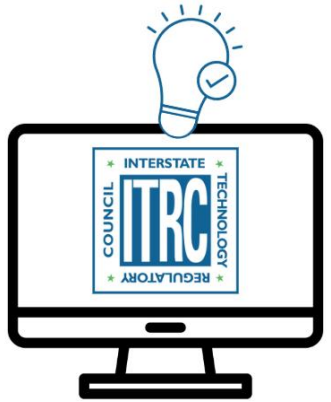
Oxidizing conditions (for example, via active remediation such as air sparging or chemical oxidation) may enhance precursor transformation

PFAS-1, Figure 2-21 CSM for fire training areas. Figure Adapted from figure by L. Trozzolo, TRC, used with permission.

Knowledge Check

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

Top photo used with permission, Francis Boodoo, Purolite. Bottom photo used with permission, Scott Grieco, Jacobs.

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!

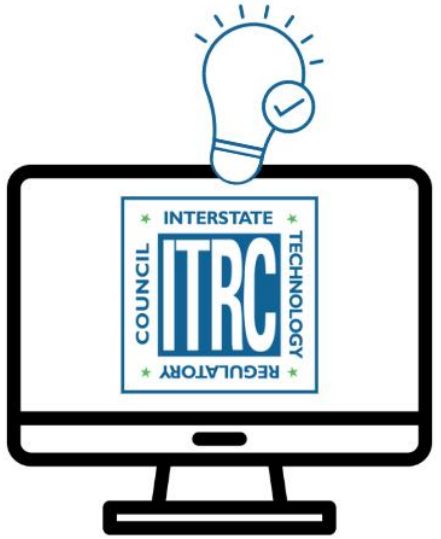
Which technology relies on the surfactant properties of PFAS for treatment?

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)

Questions

Please use the Q&A Pod to ask questions.

https://pfas-1.itrcweb.org