Basic Chemistry and Naming Conventions for Per- and Polyfluoroalkyl Substances (PFAS)

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What Are Per- and Polyfluoroalkyl Substances (PFAS)?

- Large class of surfactants (>3,000?) with unique chemical & physical properties that make many of them extremely persistent and mobile in the environment
- Used since 1940s in wide range of consumer and industrial applications











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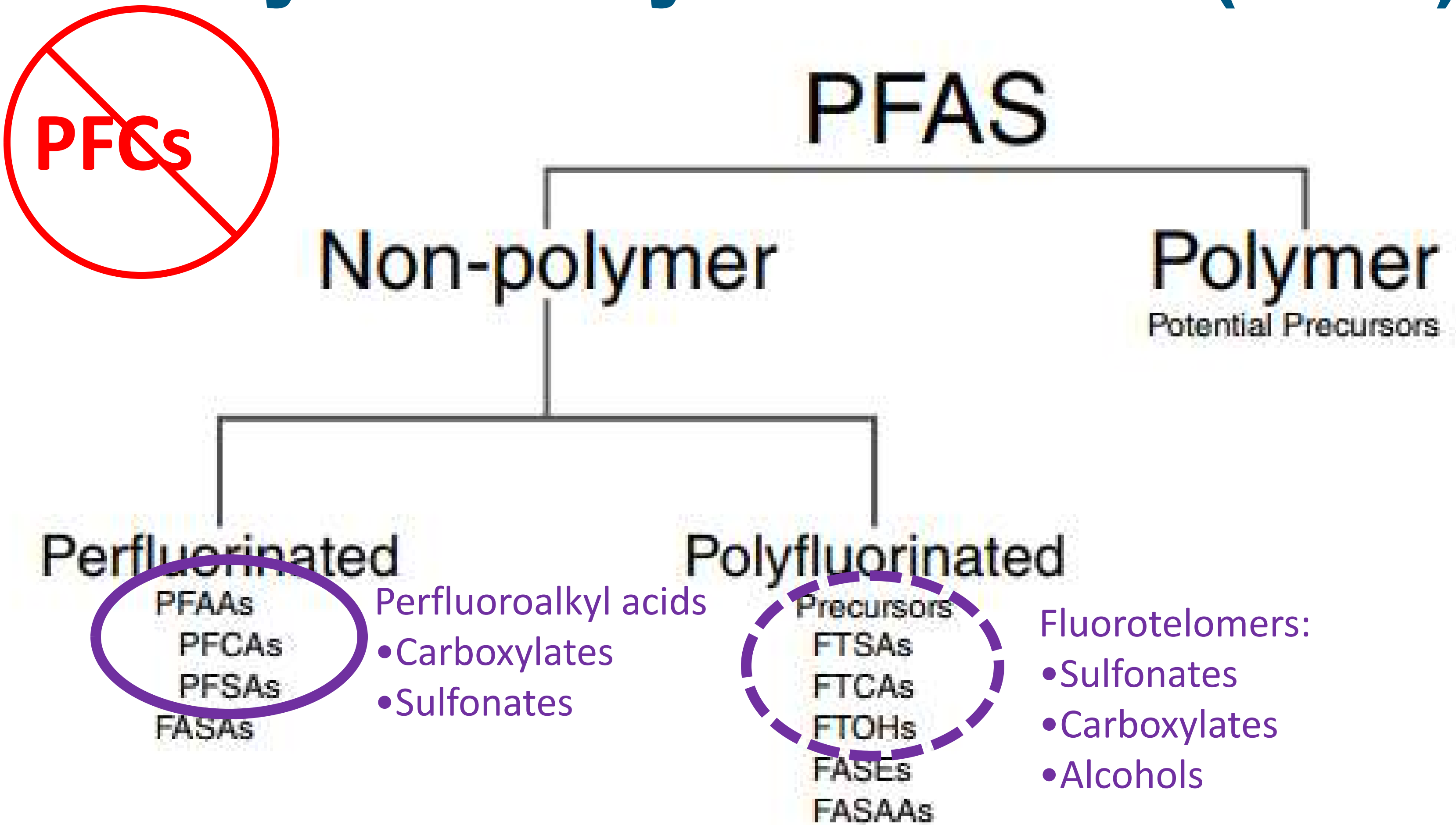
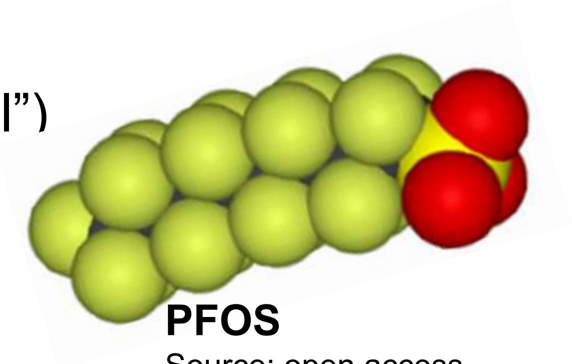
The General Classes of Per- and Polyfluoroalkyl Substances (PFAS)



Source: ITRC Naming Conventions and Physical Chemical Properties factsheet

Basic PFAA Structure

- Perfluoroalkyl Acids (PFAAs)
  - Fully fluorinated chain (2 or more carbon “tail”)
  - Functional group (“head”)
    - **PFCAs**: Carboxylate group (COO^-)
    - **PFSAs**: Sulfonate group (SO_3^-)



PFOS
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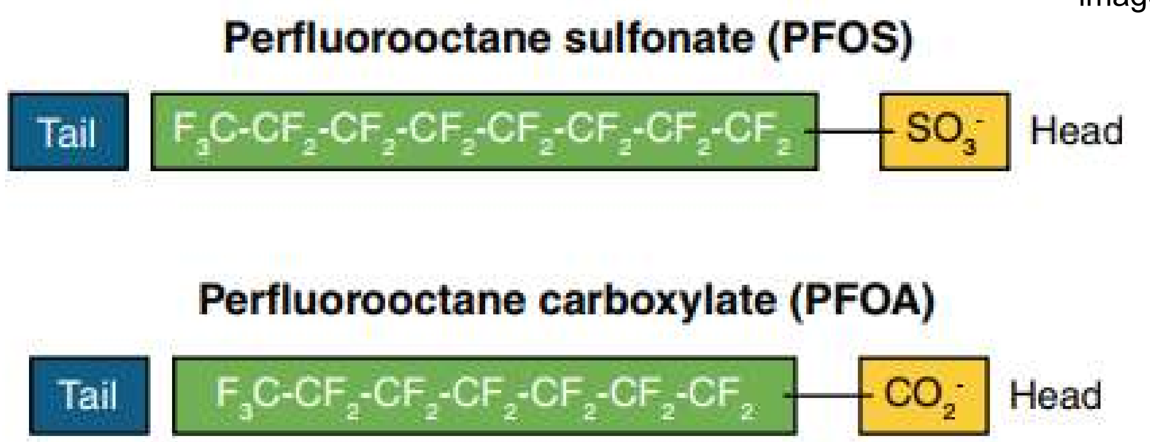

PFAA Naming System

- PFXY
  - PF = perfluoro
  - X = number of carbons
    - Same convention as hydrocarbons
    - Includes the "C" in the carboxylate group
  - Y = functional group
    - S = sulfonate
    - A = carboxylate
- Example:
  - X: 8 carbons = "octa"
  - Y: S = sulfonate

→ Perfluorooctane sulfonate (PFOS)

PFAA Naming System

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	$C_{10}F_{2}1SO_3H$	335-77-3

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Source: ITRC Naming Conventions and Physical Chemical Properties factsheet

Wait…Which PFAA Are We Talking About?

- Acid or Anion?
  - PFAS may exist in many ionic states (acids, anions, cations, zwitterions)
  - In the environment, most PFAAs exist in the anionic state (sulfonate, carboxylate, etc.)
  - Acid form of the name often used interchangeably (sulfonic acid and carboxylic acid)
  - Different CAS numbers & very different chemical and physical properties
- What Is The Lab Really Testing For?
  - Some labs report some or all PFAAs in the acid form
  - Depends on the standards used, which may be acids or salts of the PFAA (typically Na^+ or K^+)
  - The lab performs a calculation to account for the mass of the cation
    - For H+ in acids, this is essentially irrelevant in terms of the results
    - For salts, confirm the lab is accurately accounting for the cation mass (Section 7.2.3 of EPA Method 537)

Published Physical & Chemical Values

- Most values reported in the literature are for PFAA acids
  - PFAA acids not typically present in environment except at pH <3
  - Behavior of acids and anions are often VERY different
    - PFOA acid: low solubility, volatile / PFOA anion: highly soluble, non-volatile

Properties								Environmentally Relevant?
PFAA State	CAS No.	S_w	P^o	K_h	K_{ow}	K_{oc}	BCF and/or BAF	
Acid	Y	Y	Y	E	E	E	N	No
Cation:								No
NH_4^+	Y	Y	N	N	N	N	N	
Li^+	Y	Y	N	N	N	N	N	
Na^+	Y	Y	N	N	N	N	N	
Anion	M	N	N	N	N	Y	Y	Yes

S_w = solubility in water K_{oc} = org. carbon partition coefficient Y = data available
P^o = vapor pressure BAF = bioaccumulation factor N = no data available
K_h = Henry's Law constant BCF = bioconcentration factor M = data may be available
K_{ow} = octanol/water partition coefficient E = estimated

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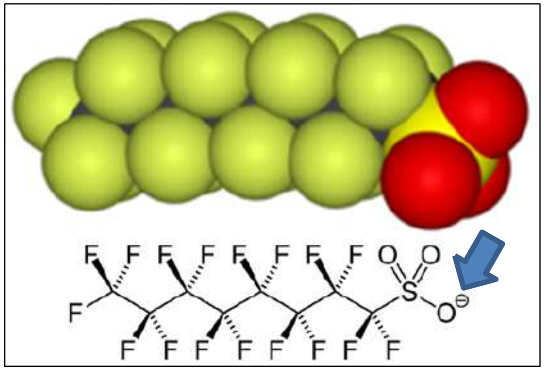
Highlights of PFAS Properties

- **C-F is the shortest and strongest bond in chemistry**
  - Small, highly electronegative fluorine atoms "shield" the carbon from chemical reactions
  - No biotic or abiotic degradation of PFAA under natural conditions
  - PFAAs thermally degrade only at high temperatures



Source: open access image - bing.com

- **Perfluoroalkyl acids (PFAAs) are negatively charged**
  - Interact and sorb on positively charged minerals
  - Mediated by pH, chain length, and functional group

High C-F Bond Energy

kJ/mol of bonds
C-F 485
C-H436
C-C346
C-Cl 339
C-N305
C-Br285
C-S272

Highlights of PFAS Properties

- **Surfactant properties are important**
  - Partitioning to interfaces (air-water, soil-water, NAPL-water) & micelles
  - PFCAs can be both hydrophobic & hydrophilic

- **Chain length and functional group generally determine bioaccumulation**
  - Longer chain and sulfonates tend to accumulate more than shorter chain and carboxylates
  - Some PFAS are "proteinphiles", so bioaccumlation process may be more complicated than for other environmental contaminants.
  - PFHxS breaks this "rule" – longer half-life in humans than PFOS

Highlights of PFAS Properties

- **PFAAs generally have low volatility**
  - Air transport may occur for PFAAs sorbed to particulates or dissolved in water droplets
  - May be formed from volatile precursors (e.g. FTOHs)
- **PFAAs may be linear or branched in form**
  - May affect partitioning and/or bioaccumulation - not well understood yet

$F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}SO_3^-$

Linear Perfluorooctane sulfonate (PFOS)

$F_3C\text{-}CF(CF_3)\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}SO_3^-$

Branched Perfluorooctane sulfonate (PFOS)

Polyfluorinated Substances

- Partially fluorinated
  - Non-fluorine atom (usually H or O) attached to at least one, but not all, of the carbon atoms in the "tail"
  - Creates a "weak link" susceptible to biotic or abiotic degradation
  - Often named using a "n:x" prefix
    - n = number of fully fluorinated carbons
    - x = number of non-fully fluorinated carbons

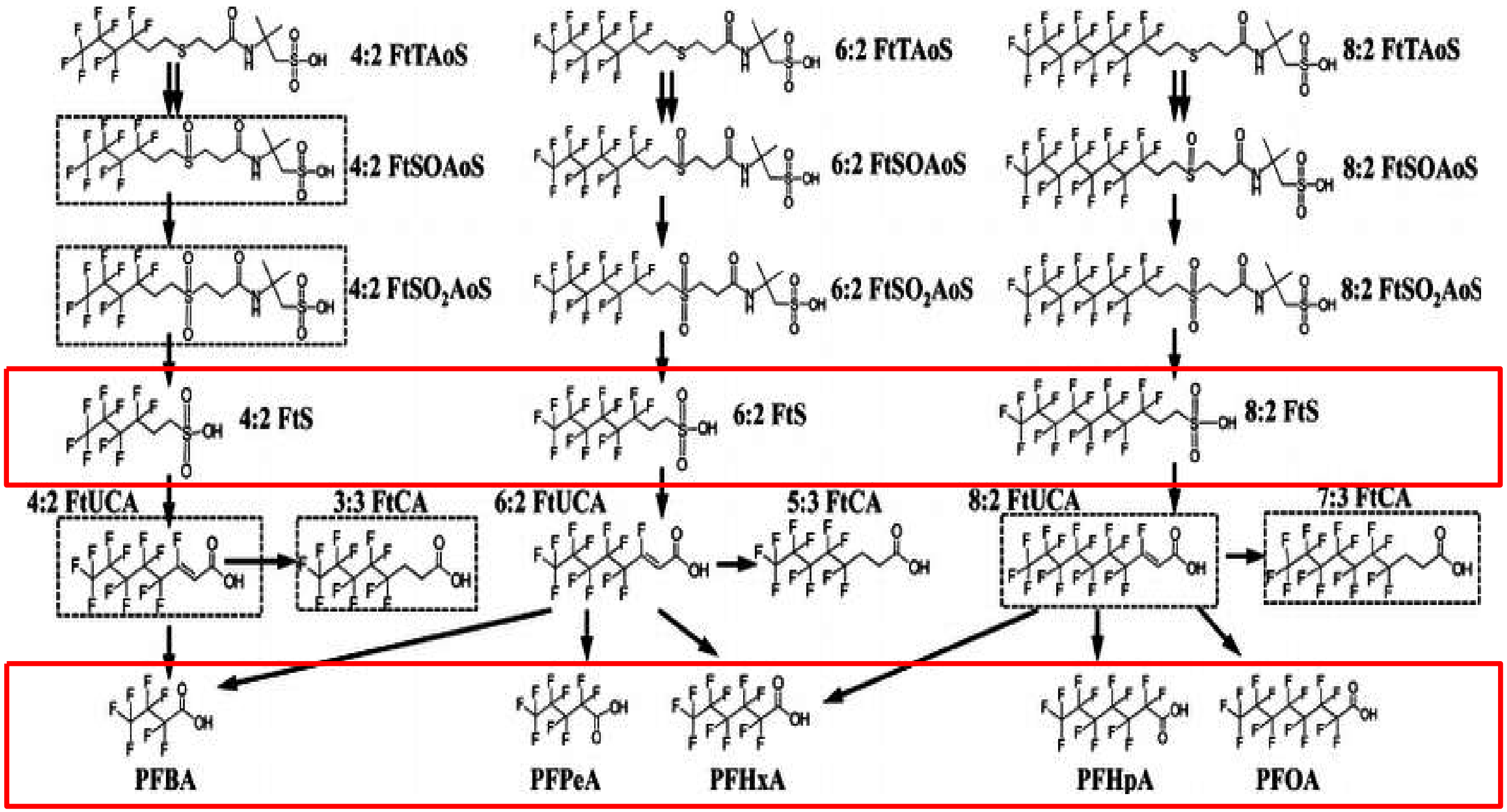
$$\underbrace{F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2}_{8}\text{-}\underbrace{CH_2CH_2}_{2}\text{-}OH$$

8:2 FTOH (8:2 fluorotelomer alcohol)

PFAA Precursors

- **Some polyfluorinated PFAS can degrade to PFAAs**
  - Referred to as "PFAA precursors"
  - Non-fluorine atom(s) attached to one or more carbons in the "tail" create a "weak link"
  - Resulting PFAAs sometimes referred to as "terminal perfluoroalkyl acids"
  - Some are cationic (+ charge) or zwitterionic (mixed charges) – less mobile than anionic PFAAs, so may be retained longer in source areas
- **Perfluoroalkane sulfonamides (FASAs)** — **May degrade to PFSAs**
- **Polyfluoroalkyl Substances**
  - **Fluorotelomers** — **May degrade to PFCAs**
    - Fluorotelomer alcohols (FTOH)
    - Fluorotelomer sulfonates (FTSA)
    - Fluorotelomer carboxylates (FTCA)
  - **Perfluoroalkyl sulfonamido ethanols (FASE) & acetic acids (FASAA)** — **May degrade to PFCAs or PFSAs**

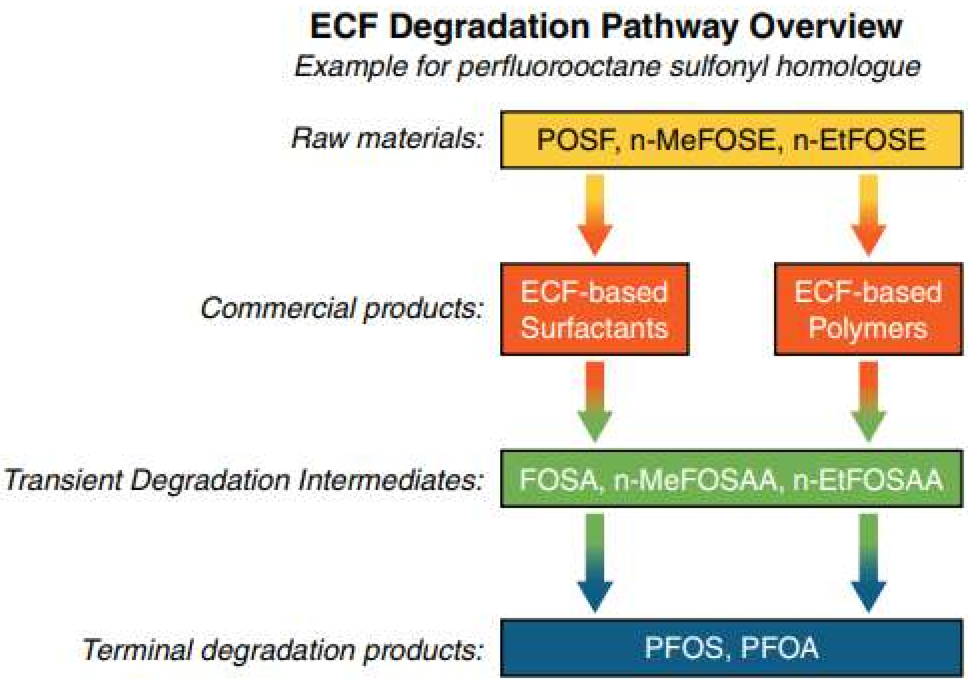
Precursor Biotransformation

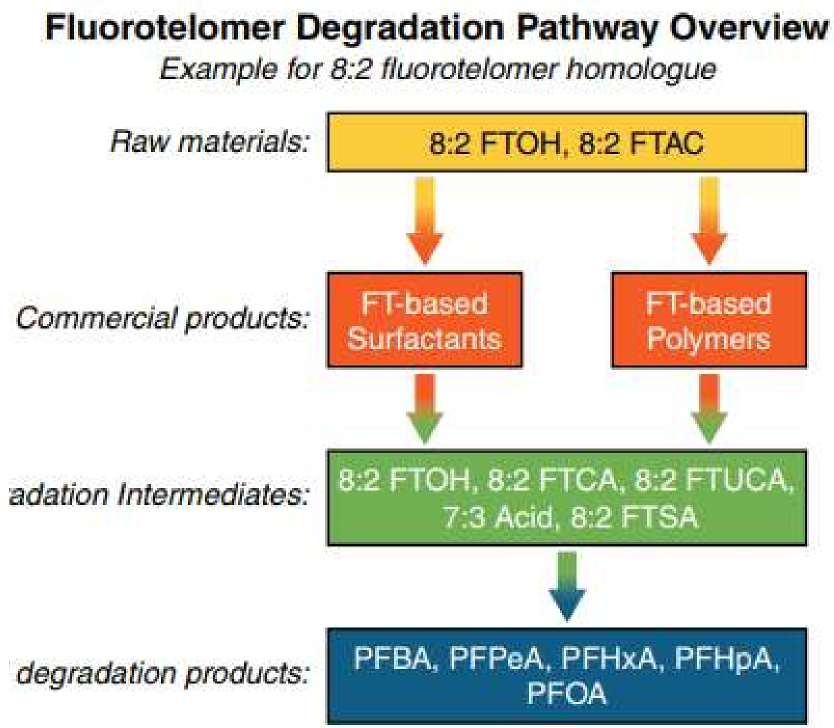


Can be analyzed using USEPA 537 Mod

Figure 4 from Harding-Marjanovic et al., 2015

ECF vs Telomerization Origin Predicts Degradation Products





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Questions?