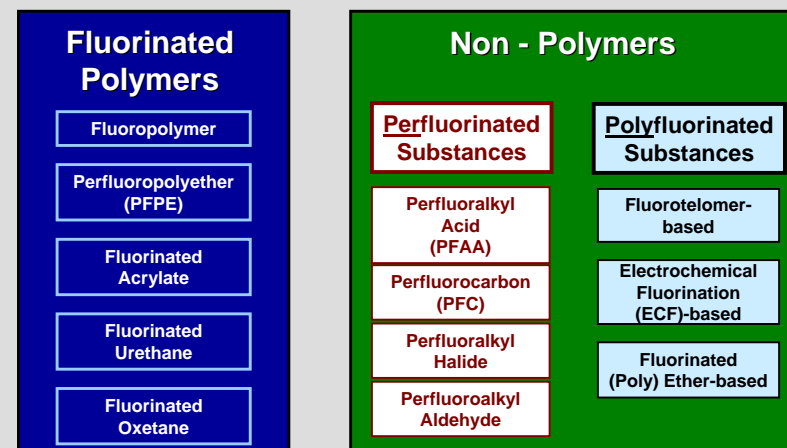


## Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in the environment: terminology, classification and origins

Robert C. Buck, James Franklin, Urs Berger, Jason M. Conder, Ian T. Cousins, Pim de Voogt, Allan Astrup Jensen, Kurunthachalam Kannan, Scott Mabury and Stefan P. J. van Leeuwen

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## Per(poly)fluoroalkyl Substances (PFASs)



## Background

- The discovery of fluorinated substances such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in the environment has prompted an expansive increase in research and publications on these and related substances.

## Background

- Concomitantly, authors have created new words and acronyms to describe these and like substances.
  - Unfortunately this has resulted in multiple names and acronyms that describe the same substances and broad names to describe a wide array of substances that may in fact not really be like one another.
  - For example, what does the acronym "PFC" describe?*

## “PFC” What does it mean?

- Perfluorocarbon
- Perfluorinated chemical
- Perfluorinated compound
- Polyfluorinated chemical
- Perfluorocarboxylate
- Polyfluorocarboxylate
- Perfluoroalkyl chemical

*These substances may be VERY different from one another !*

## Nomenclature Matters

- Structural differences make a BIG difference in physical, chemical and biological properties
  - # Carbons: Methane vs. Decane:  $\text{CF}_4$  vs.  $\text{C}_{10}\text{F}_{22}$
  - # Fluorinated Carbons:  $\text{FCH}_2\text{COOH}$  vs.  $\text{FCF}_2\text{COOH}$
- **Fluorinated substances are NOT all the same, they are very different**
  - “PFC’s are.....persistent and bioaccumulative”
    - Factually correct ? No.
    - Confusing ? Definitely.
- **The solution is to be clear, specific and descriptive of the substance(s) you are talking about. Do not use indeterminate broad terms.**

*Convinced we need common nomenclature to eliminate confusion?*

## Objective

- To provide an overview of “perfluoroalkyl and polyfluoroalkyl substances” (PFASs) detected in the environment, wildlife and humans and recommend clear, specific and descriptive terminology, names and acronyms for PFASs.
- To unify and harmonize communication on PFASs by offering terminology for use by the global scientific, regulatory and industrial communities.

- Emphasis is placed on *long-chain perfluoroalkyl acids, substances related to the long-chain perfluoroalkyl acids, and substances intended as alternatives* to the use of the long-chain perfluoroalkyl acids or their precursors.

## Long chain\* vs. Short chain

**Perfluoroalkyl acids (PFAAs)**

<b>Long Chain</b> $n \geq 6$ PFDS, PFOS, PFHxS	Perfluoroalkane sulfonate <b>PFSA</b> $C_n F_{2n+1} SO_3(H)$	<b>Short Chain</b> $n \leq 5$ PFBS
$x \geq 8$ PFDA, PFNA, PFOA	Perfluoroalkyl carboxylate <b>PFCA</b> $C_x F_{2x-1} O_2(H)$	$x \leq 7$ PFHxA, PFPeA, PFBA

\* As defined by U.S. EPA Long-Chain Perfluorinated Chemicals Action Plan, April 2010 and by OECD

## Key Terms

- Fluorochemical (aka fluorinated chemical / substance)
- Fluorosurfactant
  - aka Fluorinated Surfactant, Fluorinated Tenside
- Perfluorinated and Polyfluorinated
- Per- and Poly-fluoroalkyl Substances (PFASs)
- Perfluorocarbon (PFC)

## A first definition....

- Fluorochemical / Fluorinated Chemical / Fluorinated Substance
  - Synonymous general, non-specific, broad names for substances containing the element fluorine.
  - Describes *a universe of substances* with vastly different physical, chemical, and biological properties.



{
 Fluorosurfactant  
 Fluorinated Surfactant  
 Fluorinated Tenside

***synonymous names***

- General, non-specific, names for a surface active substance which contains fluorinated carbon atoms.
- Describes a universe of substances with vastly different physical, chemical, and biological properties.
- Surfactants...a general definition (from wikipedia)
  - Are amphiphilic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads")
  - Reduce surface and interfacial tension

## • Perfluorinated (alkyl substances)

- Aliphatic substances for which all of the hydrogen atoms attached to carbon atoms in the non-fluorinated substance from which they are notionally derived have been replaced by fluorine atoms, except those hydrogen atoms whose substitution would modify the nature of any functional groups present.
- Examples
  - $C_8F_{17}SO_3^-$
  - $C_4F_9I$
  - $C_6F_{14}$

## • Polyfluorinated (alkyl substances)

- aliphatic substances for which all hydrogen atoms attached to at least one (but not all) carbons have been replaced by fluorine atoms, in such a manner that they contain the perfluoroalkyl moiety  $C_nF_{2n+1}-$  (e.g.,  $C_8F_{17}CH_2CH_2OH$ ).
- The general chemical concept of “polyfluorination” embraces compounds containing “scattered” multiple fluorine atoms (such as in  $CH_2FCHFCHFCH_2OH$ ), as well as “grouped” ones (such as in  $CF_3CF_2CH_2COOH$ )
- We consider that **only those polyfluorinated substances having at least one perfluoroalkyl moiety  $C_nF_{2n+1}-$  belong to the PFAS family.**

## Per- and Poly-fluoroalkyl Substances (PFASs)

- **Highly fluorinated aliphatic substances that contain one or more carbon atoms on which all the hydrogen substituents (present in the non-fluorinated analogs from which they are notionally derived) have been replaced by fluorine atoms, in such a manner that they contain the perfluoroalkyl moiety  $C_nF_{2n+1}-$ .**
- **These compounds are hereafter referred to as the “perfluoroalkyl and polyfluoroalkyl substances” and denoted by the acronym PFASs**

## Origin of the acronym PFAS

### Perfluoroalkylated substances

Aquatic environmental assessment

Report RIKZ/2002.043

1 July 2002

#### Authors:

University of Amsterdam  
F.M. Helkster  
P. de Voogt

RIKZ  
A.M.C.M. Pijnenburg  
R.W.F.M. Laane

University of Amsterdam  
Environmental and Toxicological Chemistry  
Nieuwe Achtergracht 166  
1018 WV Amsterdam  
Tel. 31 20 5256504  
Fax: 31 20 5256522

RIKZ  
Kortenaarkade 1  
P.O. Box 20907  
2500 EX Den Haag  
Tel. 31 70 3114311  
Fax: 31 70 3114330

Perfluoroalkylated substances - aquatic environmental assessment.

Rijksinstituut voor Kust en Zee (RIKZ), 2002.

### Environmental and Toxicity Effects of Perfluoroalkylated Substances

Floris M. Helkster, Remi W.P.M. Laane, and Pim de Voogt

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#### I. Introduction

Various publications on the occurrence of perfluorinated chemicals in the natural as well as the work environment (Gilliland and Mandel 1993; Key et al. 1997; Ghiesy and Kuttan 2001; Kissa 2001) recently have raised scientific and political interest in these compounds. Most of the studies on perfluorinated compounds have focused on perfluorooctyl sulfonate (PFOS) and perfluorooctanoic acid (PFOA). These two chemicals (Fig. 1) are the most important degradation products of the perfluoroalkylsulfonates, which form, together with the perfluoroalkylethylates, the vast majority of the perfluoroalkylated substances (PFAS).

**Environmental and toxicity effects of perfluoroalkylated substances.**

Rev Environ Contam Toxicol., 2003, 179, 99-121.

## Perfluorocarbon (PFC)

- Perfluorocarbons – meaning fully fluorinated hydrocarbons – are one of the groups of compounds regulated under the Kyoto Protocol on greenhouse gases, where they are designated in official documents as PFCs.
- A substance derived from a hydrocarbon by replacing all the hydrogen atoms with fluorine atoms.
- Perfluorocarbons (PFCs) contain only carbon and fluorine atoms.**
  - e.g.,  $F(CF_2)_nF$
  - Those PFCs that have a perfluoroalkyl moiety ( $C_nF_{2n+1}$ -) constitute a subset of PFASs.

Clear, specific, descriptive nomenclature and acronyms for fluorinated substances is needed and will be enormously useful.

- So how do we begin?
- How about we think about two groups, a polymer and a substance that is not a polymer?

## Per(poly)fluoroalkyl Substances (PFAS)

### Fluorinated Polymers

Fluoropolymer

Perfluoropolyether (PFPE)

Fluorinated Acrylate

Fluorinated Urethane

Fluorinated Oxetane

### Non - Polymers

#### Perfluorinated Substances

Perfluoroalkyl Acid (PFAA)

Perfluorocarbon (PFC)

Perfluoroalkyl Halide

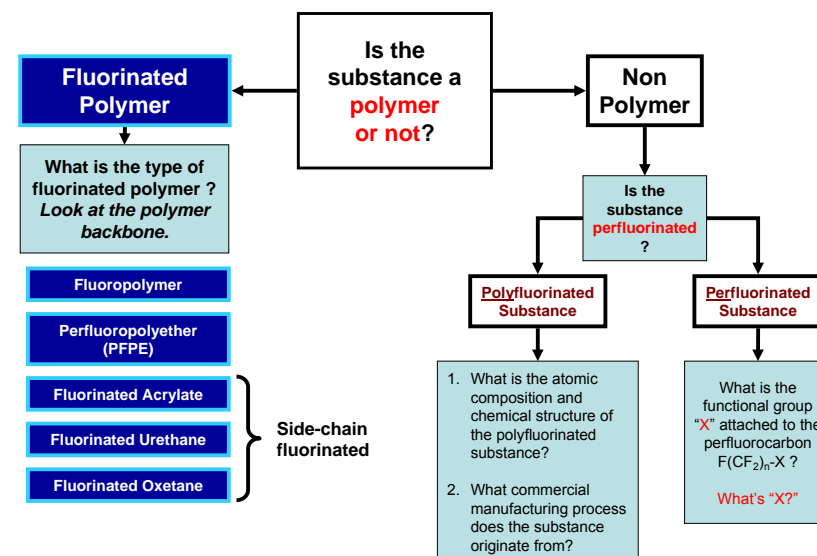
Perfluoroalkyl Aldehyde

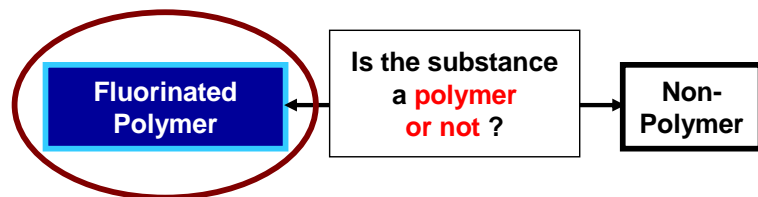
#### Polyfluorinated Substances

Fluorotelomer-based

Electrochemical Fluorination (ECF)-based

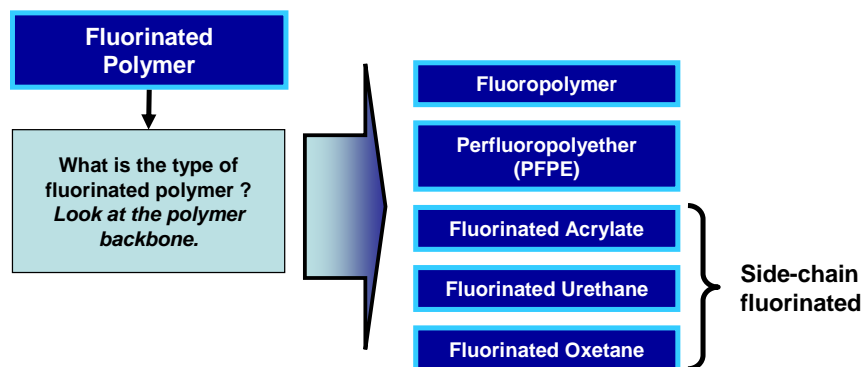
Fluorinated (Poly) Ether-based





## Fluorinated Polymer Definition

*A general term for a polymer in which one or more of the monomer units contains fluorine.*



## Fluoropolymer Definition

Fluoropolymer

- A distinct subset of fluorinated polymers that is made from the (co)polymerization of olefinic monomers, at least one of which contains fluorine bound to one or both of the olefinic carbons, to form a carbon-only polymer backbone.

## Fluoropolymers

### Fluoropolymer

- Tetrafluoroethylene (TFE)  $\text{CF}_2=\text{CF}_2$ 
  - polymers: PTFE, ETFE
- Vinylidene Fluoride (VDF)  $\text{CH}_2=\text{CF}_2$ 
  - Polymer: PVDF
- Vinyl Fluoride (VF)  $\text{CH}_2=\text{CHF}$ 
  - Polymer: PVF
- Hexafluoropropene (HFP)  $\text{CF}_2=\text{CFCF}_3$ 
  - Polymer: FEP

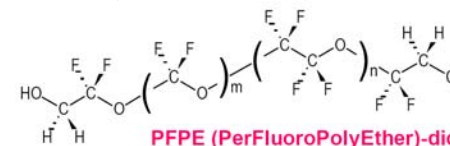
Fluorine bound to the carbon(s) that react to form a carbon-only polymer backbone

### Fluoropolymer

## Perfluoropolyethers (PFPE)

### Perfluoropolyether (PFPE)

- Perfluoropolyethers are a class of fluorinated polymers whose backbone consists of perfluorinated carbon atoms linked by ether bonds.
  - e.g., A proprietary process, involving UV-assisted copolymerization of TFE with oxygen obtains this fluorinated backbone.
    - An example:  $\text{CF}_3(\text{OCF}_2)_m(\text{OCF}_2\text{CF}_2)_n\text{OCF}_3$
  - A functionalized perfluoropolyether polymer is:
    - $\text{X-CF}_2\text{O}-(\text{CF}_2\text{CF}_2\text{O})_m-(\text{CF}_2\text{O})_n-\text{CF}_2\text{-X}$
    - where X is a generic functional group, such as  $-\text{CH}_2\text{OH}$



## Monomer / Reactant examples

- **Acrylate Monomer**
  - $\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{R})=\text{CH}_2$
  - $\text{F}(\text{CF}_2)_4\text{SO}_2\text{N}(\text{R})\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{R})=\text{CH}_2$
- **Oxetane Monomer**
  - Oxetane monomer from fluorinated alcohol  $\text{R}_f\text{CH}_2\text{-OH}$ 
    - $\text{R}_f = -\text{CH}_2\text{CF}_3, -(\text{CH}_2)_2(\text{CF}_2)_x\text{F}$  (x = 2, 3, 4)
- **Alcohol Reactant**
  - $\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OH}$
  - $\text{F}(\text{CF}_2)_4\text{SO}_2\text{N}(\text{R})\text{CH}_2\text{CH}_2\text{OH}$

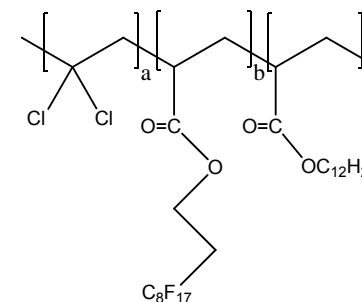
### Fluorinated Acrylate

### Fluorinated Oxetane

### Fluorinated Urethane

## Fluorinated Polymers

- **Fluorinated acrylate polymer**
  - Fluorinated acrylate monomer
  - $\text{R}_f\text{-X-O-C}(\text{O})\text{CR}=\text{CH}_2$ 
    - $\text{R}_f$  = carbon chain that contains fluorinated carbons (e.g.,  $\text{F}(\text{CF}_2)_n-$ )
    - X = linking group such as  $-\text{CH}_2\text{-CH}_2-$
    - R = H, or alkyl (e.g., )Me, Et, Bu

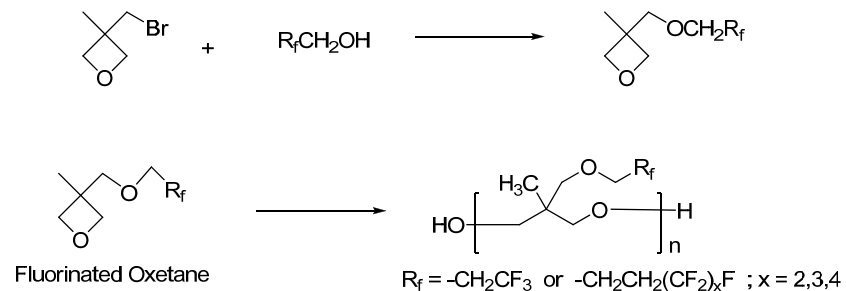


### Fluorinated Acrylate

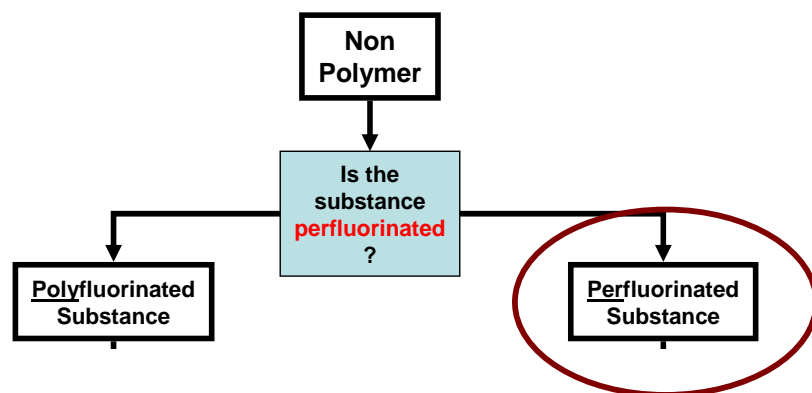
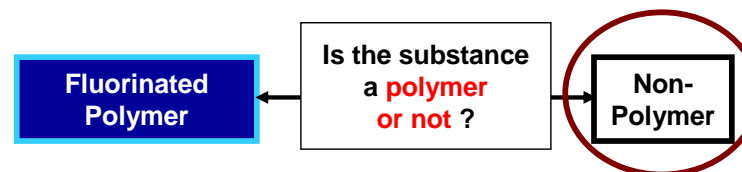
## Fluorinated Oxetane Polymers

Fluorinated Oxetane

- Ring-opening polymerization of a fluorinated oxetane



## How to determine nomenclature – an Overview



## Perfluoroalkyl Substance (PFAS)

### Non - Polymers

#### Perfluorinated Substances

Perfluoroalkyl Acid (PFAA)

Perfluorocarbon (PFC)

Perfluoroalkyl Halide

Perfluoroalkyl Aldehyde

#### Polyfluorinated Substances

Fluorotelomer Based

Electrochemical Fluorination (ECF) Based

Fluorinated (Poly) Ether Based



Perfluorinated  
Substance

What is the functional group  
"X" attached to the  
perfluoroalkyl chain  
 $C_nF_{2n+1}X$  ?

What's "X"?

X = F  
Perfluorocarbon

X = C, P, or S oxidized  
Perfluoroalkyl Acid

X = I, Cl, Br  
Perfluoroalkyl Halide

X = CHO  
Perfluoroalkyl Aldehyde

## Perfluoroalkyl Acid - PFAA

- A substance that contains a perfluoroalkyl ( $C_nF_{2n+1}^-$ ) moiety directly bound to an acid functionality, e.g., carboxylate, sulfonate, sulfinic acid, phosphonate, phosphinate.
  - PFAAs may be used commercially as their salts, e.g. ammonium, sodium and potassium salts.
- X – bound to the perfluoroalkyl chain is
  - Carbon (C) – Carboxylate
  - Sulfur (S) – Sulfinic acid, Sulfonate
  - Phosphorous (P) - Phosphinate, Phosphonate

## Perfluorinated Alkyl Acids (X = Carbon, C)

- Carbon (C) general nomenclature
  - $CO_2^-$  Carboxylate PFCa perfluoroalkyl carboxylate (anion)
    - e.g.,  $F(CF_2)_8CO_2^-$  PFOA perfluorooctanoate
  - $CO_2H$  Carboxylic Acid PFCa perfluoroalkyl carboxylic acid
    - e.g.,  $F(CF_2)_8CO_2H$  PFOA perfluorooctanoic acid
  - $CO_2F$  Acid Fluoride PAF perfluoroalkanoyl fluoride
    - e.g.,  $F(CF_2)_8CO_2F$  POF perfluorooctanoyl fluoride

Note: if specifically discriminating the protonated and anionic forms, please be clear; for example, PFO is used for the anionic form and PFOA for the protonated acid form. If not discriminating between the two forms, PFOA is used.

## Perfluorinated Alkyl Acids (X= Sulfur, S)

- Sulfur (S) general nomenclature
  - $SO_2^-$  Sulfinic acid PFSIA perfluoroalkane sulfinic acid (anion)
    - e.g.,  $F(CF_2)_8SO_2^-$  PFOSI perfluorooctane sulfinic acid
  - $SO_2F$  Sulfonyl Fluoride PASF perfluoroalkane sulfonyl fluoride
    - e.g.,  $F(CF_2)_8SO_2F$  POSF perfluorooctane sulfonyl fluoride
  - $SO_3^-$  Sulfonate PFSA perfluoroalkane sulfonate (anion)
    - e.g.,  $F(CF_2)_8SO_3^-$  PFOSA perfluorooctane sulfonate
  - $SO_3H$  Sulfonic Acid PFSA perfluoroalkane sulfonic acid
    - e.g.,  $F(CF_2)_8SO_3H$  PFOSA perfluorooctane sulfonic acid

## Perfluorinated Alkyl Acids (X = Phosphorus, P)

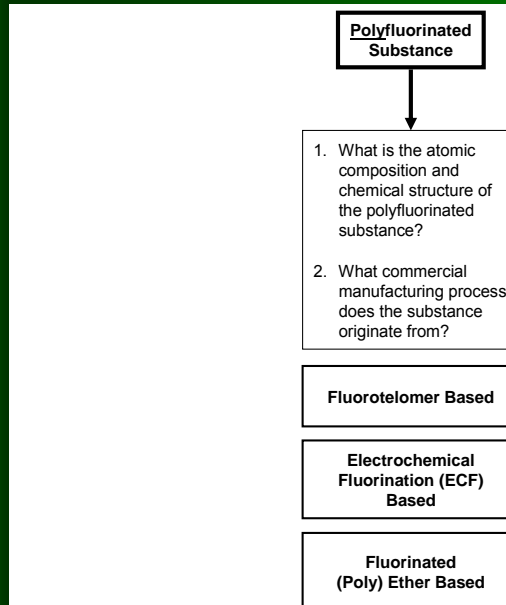
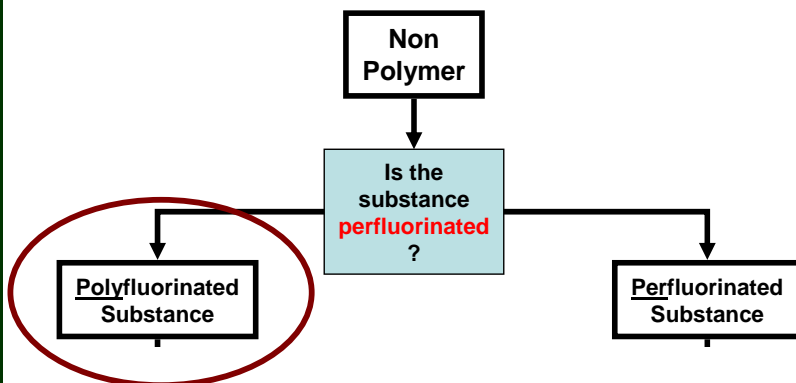
### • Phosphorus (P)

- $\text{RPO}_3^-$  Phosphonate (anion) PFPA perfluoroalkyl phosphonic acids
- $\text{RPO}_3\text{H}_2$  Phosphonic acid PFPA
  - e.g.,  $\text{F}(\text{CF}_2)_8\text{PO}_3^{2-}$  C8-PFPA perfluorooctyl phosphonate
- $\text{RR}'\text{PO}_2^-$  Phosphinate (anion) PFPIA perfluoroalkyl phosphinic acids
- $\text{RR}'\text{PO}_2\text{H}$  Phosphinic acid PFPIA
  - e.g.,  $[\text{F}(\text{CF}_2)_8]_2\text{PO}_2^-$  C8/C8-PFPIA bis-perfluorooctyl phosphinate
- R and R' are perfluoroalkyl moieties,  $\text{C}_n\text{F}_{2n+1}^-$

## Perfluorinated Substances

Perfluorinated Substances

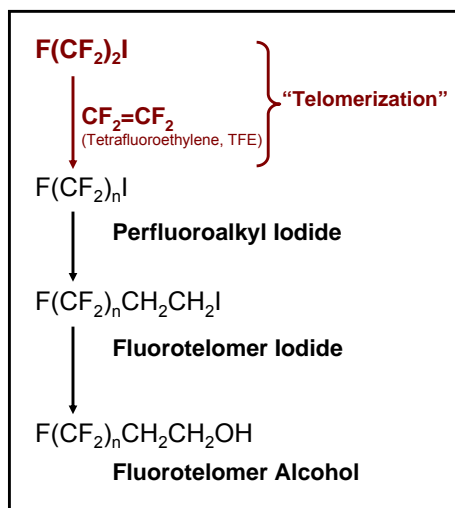
- Perfluorocarbon PFC Perfluorocarbon (PFC)
- Perfluoroalkyl Acid PFAA Perfluoroalkyl Acid (PFAA)
  - Carboxylic Acid PFCA
  - Sulfinic Acid PFSIA
  - Sulfonic Acid PFSA
  - Phosphonic Acid PFPA
  - Phosphinic Acid PFPIA
- Perfluoroalkyl Halide Perfluoroalkyl Halide
- Perfluorinated Aldehyde PFAL Perfluoroalkyl Aldehyde



## Polyfluorinated - Fluorotelomer

- A process technology used to manufacture fluorinated substances where a perfluoroalkyl iodide (e.g., pentafluoroethyl iodide,  $C_2F_5I$ , telogen) is reacted with tetrafluoroethylene (TFE,  $CF_2=CF_2$ , taxogen) to yield even carbon-numbered perfluoroalkyl iodides.

Note: "telomere" is a biology term and should not be used or confused with the term "telomer"

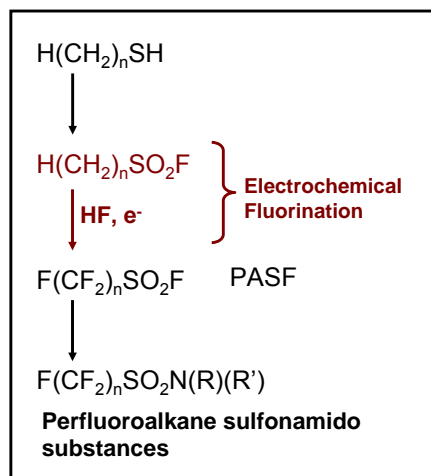


## Nomenclature for Polyfluorinated degradation products from Fluorotelomer substances

- A:B designation**
  - A = number of fluorinated carbons
  - B = number of non-fluorinated carbons
  - Examples
    - $F(CF_2)_7CH_2CH_2CO_2H$  7:3 Acid
    - $F(CF_2)_8CH_2CO_2H$  8:2 Acid
    - $F(CF_2)_7CF=CHCO_2H$  8:2 Unsaturated Acid
    - $F(CF_2)_7CH(OH)CH_3$  7:2 secondary alcohol

## Polyfluorinated – Electrochemical Fluorination (ECF)

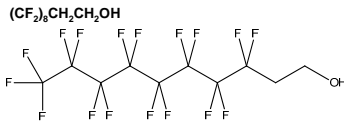
- A process technology used to manufacture fluorinated substances where an organic raw material is dissolved in hydrogen fluoride and electrolyzed, resulting in the replacement of hydrogens with fluorine.
  - The free-radical nature of the process leads to rearrangement resulting in a product mixture of linear and branched isomers of multiple carbon chain lengths.

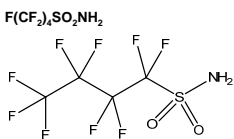


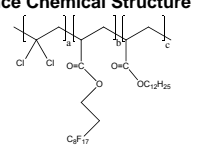
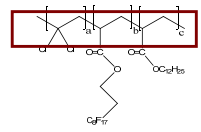
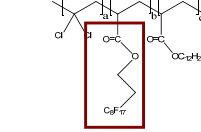
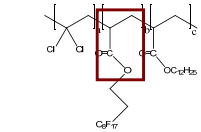
## Fluorinated Ether Based

- Polyfluoroalkyl (poly)ether carboxylic acids**
  - Fluoropolymer processing aids
- E.g.,  $CF_3OCF_2CF_2CF_2OCHF_2COOH$ 
  - Polyfluoroalkyl polyether carboxylate

Let's work through a few examples

Substance Chemical Structure	Question	Conclusion
$(CF_2)_8CH_2CH_2OH$ 	<b>Polymer or Non-Polymer?</b>	Non Polymer
$F(CF_2)_8CH_2CH_2OH$	<b>Perfluorinated?</b> <i>No. The substance has a perfluoroalkyl chain, <math>F(CF_2)_8</math>, but all hydrogen on carbons are not replaced with fluorine.</i>	Polyfluorinated
$F(CF_2)_8CH_2CH_2OH$	<b>Process Origin?</b> <i>Perfluoroalkyl chain with an ethylene spacer (<math>-CH_2CH_2-</math>). Fluorotelomer origin.</i>	Fluorotelomer origin
$F(CF_2)_8CH_2CH_2OH$	<b>Functionality.</b> Alcohol	Fluorotelomer Alcohol (FTOH)
$F(CF_2)_8CH_2CH_2OH$	<i>Eight fluorinated carbons, two non-fluorinated carbons, therefore 8:2.</i>	8:2 Fluorotelomer Alcohol (8:2 FTOH)

Substance Chemical Structure	Question	Conclusion
$F(CF_2)_4SO_2NH_2$ 	<b>Polymer or Non-Polymer?</b>	Non Polymer
$F(CF_2)_4SO_2NH_2$	<b>Perfluorinated?</b> <i>Yes. All hydrogens on all four carbons are replaced with fluorine. Perfluorobutyl.</i>	Perfluorinated
$F(CF_2)_4SO_2NH_2$	<b>Perfluoroalkyl Acid (PFAA)?</b> <i>No. Has no acid functionality.</i>	
$F(CF_2)_4SO_2NH_2$	<b>Process Origin?</b> <i>Perfluoroalkyl chain with a sulfone, <math>-SO_2-</math>, spacer. Electrochemical fluorination (ECF) origin.</i>	ECF origin
$F(CF_2)_4SO_2NH_2$	<b>Functionality.</b> Sulfonamide	Perfluorobutanesulfonamide (FBSA)

Substance Chemical Structure	Question	Conclusion
	<b>Polymer or Non-Polymer?</b>	Polymer
	<b>Fluoropolymer?</b> <i>No. The polymer backbone contains no fluorine bound to carbon.</i>	
	<b>Side-chain fluorinated?</b> Yes.	Side-chain fluorinated polymer
	<b>Polymer Type?</b> Acrylate.	Side-chain fluorinated acrylate polymer

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### Supplemental Data

- 42 families and sub-families of PFASs and....
- 268 selected individual compounds, providing recommended names and acronyms, and structural formulas, as well as CAS registry numbers.

Manuscript accepted for publication in  
*Integrated Environmental Assessment and Management (IEAM)*. A SETAC Journal

## Summary:

Use of clear, specific, descriptive nomenclature and acronyms for fluorinated substances will be enormously useful.

- Let's agree and use the proposed Nomenclature and Acronyms going forward.

## Per(poly)fluoroalkyl Substances (PFAS)

### Fluorinated Polymers

Fluoropolymer

Perfluoropolyether (PFPE)

Fluorinated Acrylate

Fluorinated Urethane

Fluorinated Oxetane

### Non - Polymers

#### Perfluorinated Substances

Perfluoroalkyl Acid (PFAA)

Perfluorocarbon (PFC)

Perfluoroalkyl Halide

Perfluoroalkyl Aldehyde

#### Polyfluorinated Substances

Fluorotelomer-based

Electrochemical Fluorination (ECF)-based

Fluorinated (Poly) Ether-based

Thank You : )

Questions welcomed