

The PFAS Universe: Uses, Classification & Degradation

Webinar for IC2 & MA TURI

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30 January 2019



FluoroCouncil
Global Industry Council
for FluoroTechnology

Meeting Agenda

- **PFAS Universe** (50-60min)
 - Introduction
 - Description, Two Categories, Five Classes
 - Current Uses
 - TURI Focus
 - Q&A
- **PFAS Degradation Pathways** (20-30 min)
 - for PFAS Currently in Use Q&A
- **Group Discussion** (10 min)
 - on Webinar Content and Follow Up Items

PFAS: Uses, Occurrence, Messages

- In industrial and consumer products manufactured in U.S. and globally
- In manufacturing and processing
- Produced as intermediates and raw materials
- Occur as byproducts, as metabolites and via degradation

PFAS: BE CLEAR, SPECIFIC AND DESCRIPTIVE



PFAS Introduction

Description, Two Categories, Five Classes



Aliphatic Hydrocarbons, C-H Substances

A Big Universe of Very Different Substances

SOLID



Polyethylene
Milk Jug

LIQUID



Ethyl Alcohol
 $\text{CH}_3\text{CH}_2\text{OH}$

GAS



Propane

Hydrocarbons C-H

SOLID



Polyethylene
Milk Jug

LIQUID



Ethyl Alcohol
 $\text{CH}_3\text{CH}_2\text{OH}$

GAS



Propane

Fluorocarbons C-F

SOLID



Polytetrafluoroethylene
PTFE Plastic

LIQUID

Fluorotelomer

Alcohol



GAS



HFC-134a
Refrigerant

Fluorocarbons – Also, a Big Universe of Very Different Substances

WHY are we talking about PFAS?

- PFOS and PFOA found globally in the environment.
- A need to identify their origin – where did they come from?
 - and substances that break down in the environment to form them - precursors.
- More broadly, on homologues, longer and shorter, and their origins.
 - and more recently, additional highly fluorinated substances found in the environment.
- The PFAS terminology was created to help define the group of relevant substances and establish a common lexicon.
 - it is very important to use common terms and to use terms that are clear, specific and descriptive.

PFAS

Per- and Poly- Fluoroalkyl Substances

- The substances included in the term “PFAS” are a wide universe of substances with very different physical, chemical, environmental and biological properties.
- “PFAS” is a very broad term and should be used only when talking about all substances in the group.
 - It is very important to use common terms and to use terms that are clear, specific and descriptive.

Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins

PFAS Definition*

aliphatic
substance that
contain the
perfluoroalkyl
moiety



“highly fluorinated aliphatic substances that contain 1 or more C atoms on which all the H substituents have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety $\text{C}_n\text{F}_{2n+1}-$. These compounds are hereafter referred to as “perfluoroalkyl and polyfluoroalkyl substances” and denoted by the acronym PFASs...”

*IEAM 2011, 7(4):513-541.

Open access: <http://dx.doi.org/10.1002/ieam.258>

PFAS – What's included? Not?

PFAS

Non-Polymer:

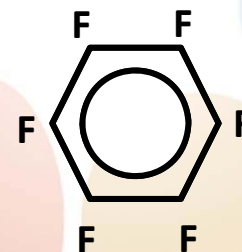
- Perfluoroalkyl
- Polyfluoroalkyl

Polymer:

- Fluoropolymer
- Perfluoropolyether Polymers
- Side-Chain Fluorinated Polymers

Fluorinated Substances that are not PFAS

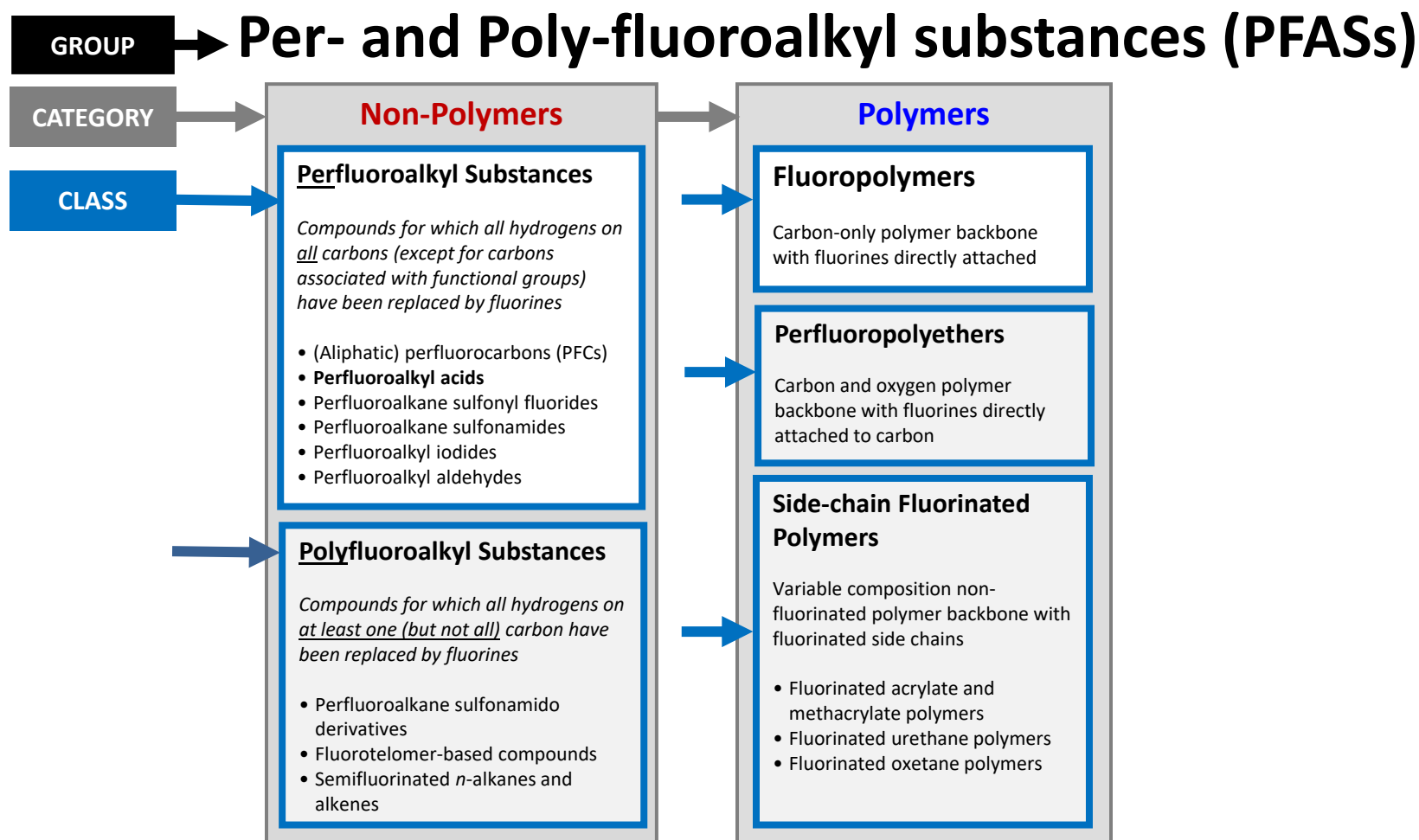
- Fluorochemicals
 - Refrigerants
- Fluorinated aromatics
 - hexafluorobenzene



Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins

Open access:

<http://dx.doi.org/10.1002/ieam.258>



BE CLEAR, SPECIFIC AND DESCRIPTIVE

PFAS - Uses

RM

C

TD

Raw Material

RM

- Telomer Iodides
- Telomer Alcohols
- Perfluoroalkyl sulfonyl fluorides
- Tetrafluoroethylene

Commercial Product

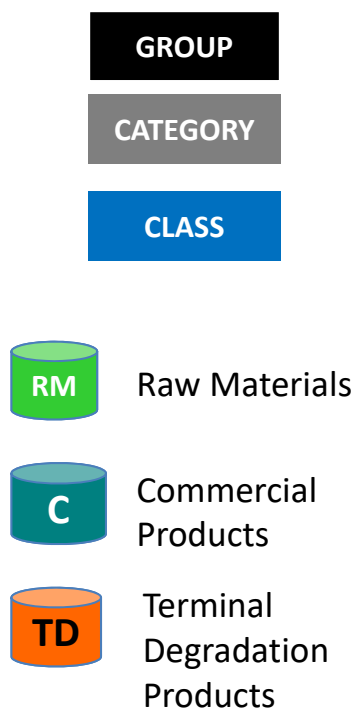
C

- Polytetrafluoroethylene (PTFE)
- Side-chain fluorinated polymers
- Fluorosurfactants

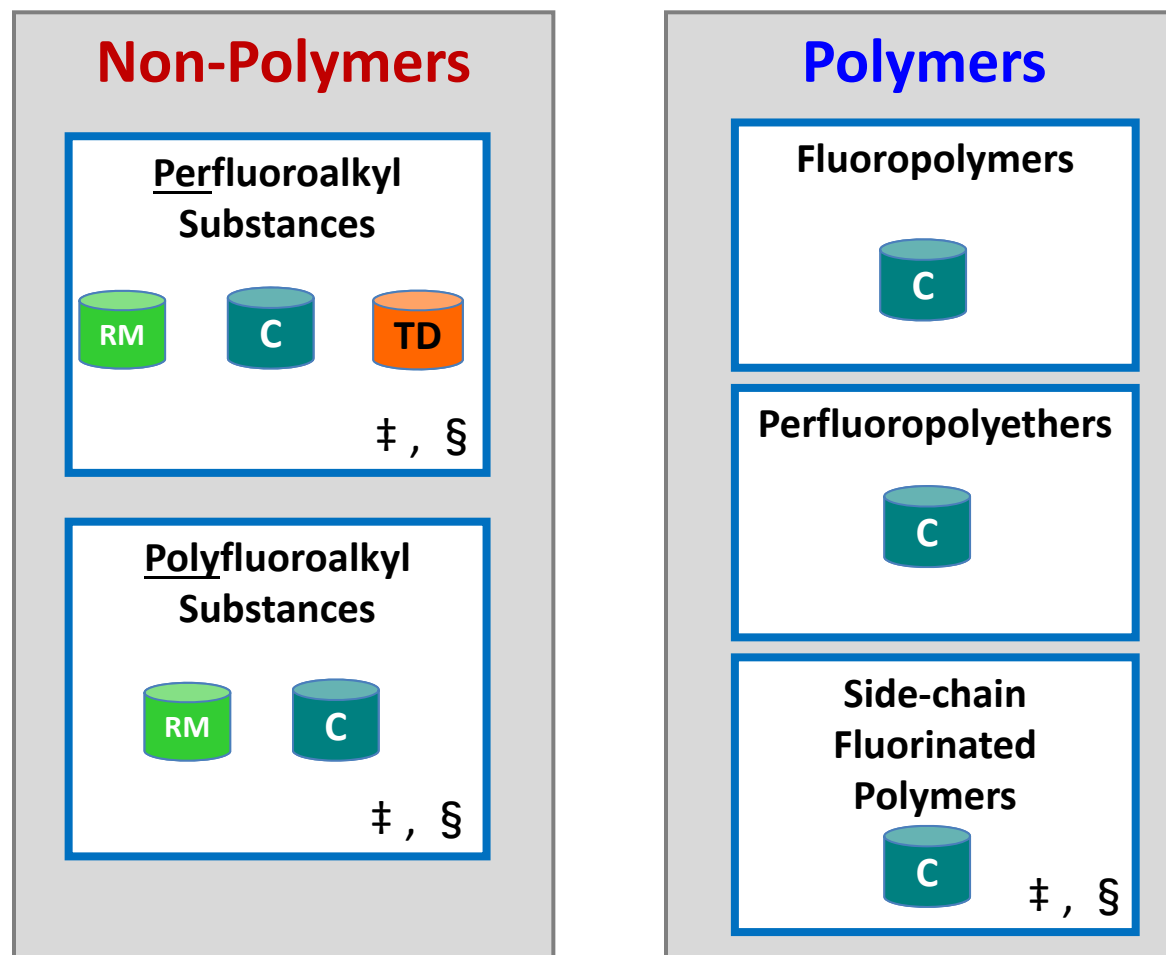
Terminal Degradation Product

TD

PFCAs – e.g., PFOA
PFSA – e.g., PFOS



Per- and Poly-fluoroalkyl substances (PFASs)



Main Manufacturing Technologies:

‡ - Electrochemical Fluorination (ECF)

§ - Fluorotelomer (FT)

GROUP

CATEGORY

CLASS

RM

C

TD

Per- and Poly-fluoroalkyl substances (PFASs)

Non-Polymers

Perfluoroalkyl
Substances

Polyfluoroalkyl
Substances

Polymers

Fluoropolymers

Perfluoropolyethers

Side-chain
Fluorinated
Polymers

Map these
substances
in to the
classes

PFOS

C TD

PFOA

C TD

HFPO-DA

C

ADONA

C

TFE

RM

PTFE

C

FTOH

RM

C

FT Acrylate Polymer

C

ECF Urethane Polymer

GROUP

CATEGORY

CLASS

RM

C

TD

Per- and Poly-fluoroalkyl substances (PFASs)

Non-Polymers

Perfluoroalkyl Substances

C PFOS, PFOA TD
TFE
RM HFPO-DA

Polyfluoroalkyl Substances

C ADONA
FTOH RM

Polymers

Fluoropolymers

PTFE C

Perfluoropolyethers

D- PFPE C

Side-chain Fluorinated Polymers

C FT Acrylate
ECF Urethane

PFOS C TD

PFOA C TD

HFPO-DA C

ADONA C

TFE RM

PTFE C

FTOH RM

C FT Acrylate Polymer

C ECF Urethane Polymer

C D-PFPE

Non-
Polymers

are a

Focus
PFAS
Category

FOCUS PFAS CATEGORY

Non-Polymers

Perfluoroalkyl
Substances



Polyfluoroalkyl
Substances



Specific Focus
on

Perfluoroalkyl
Acids -

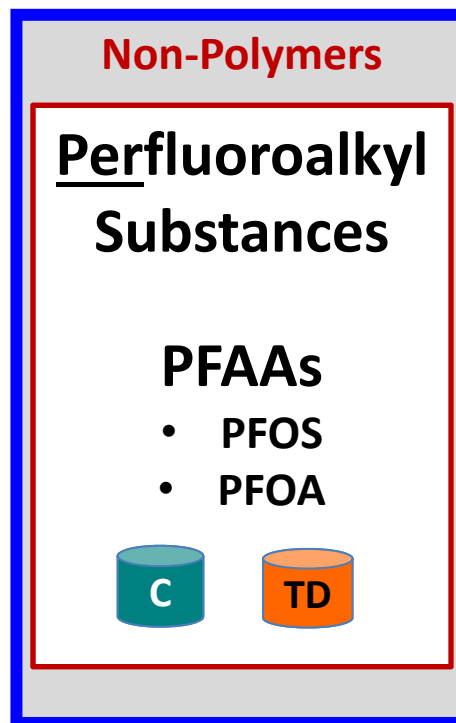
PFAAs

such as

PFOA and PFOS

And substances that may
degrade in the environment
to form them

30 January 2019



PFSA – Perfluoroalkane Sulfonic Acid ($-\text{SO}_3\text{H}$)
e.g., **PFOS**, PFH_xS , PFBS

PFCA – Perfluorocarboxylic Acid ($-\text{CO}_2\text{H}$)

e.g., **PFOA**, PFH_xA , PFBA

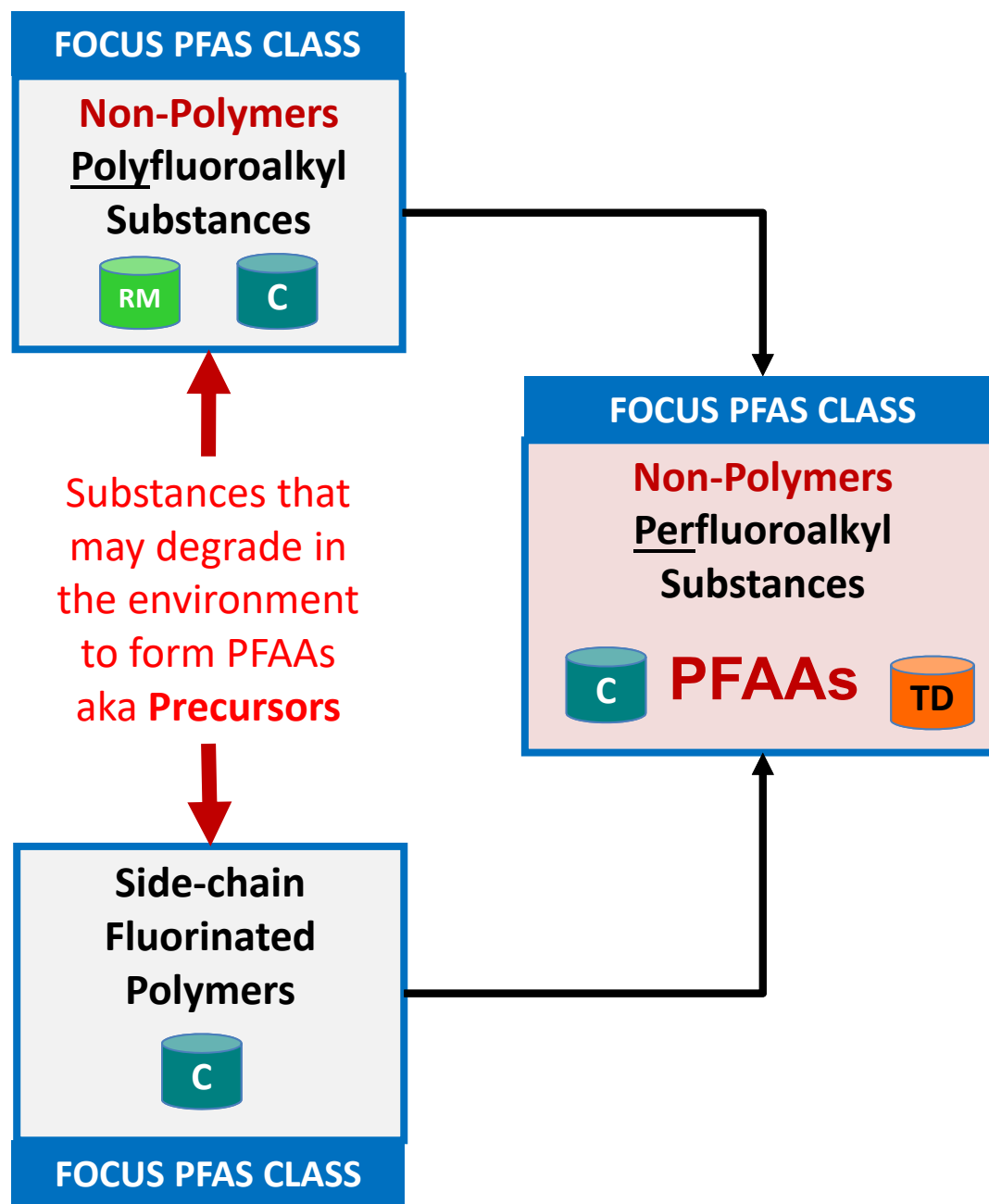
See ITRC Fact Sheet

https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_naming_conventions_3_16_18.pdf

Focus on PFAAs

and

Substances
that may
degrade in the
environment
to form them



Non-Polymer
Per-and
Polyfluoroalkyl
Substances

and

Side-Chain
Fluorinated
Polymers

are the
Focus PFAS
Classes

FOCUS PFAS CLASSES

Perfluoroalkyl Substances



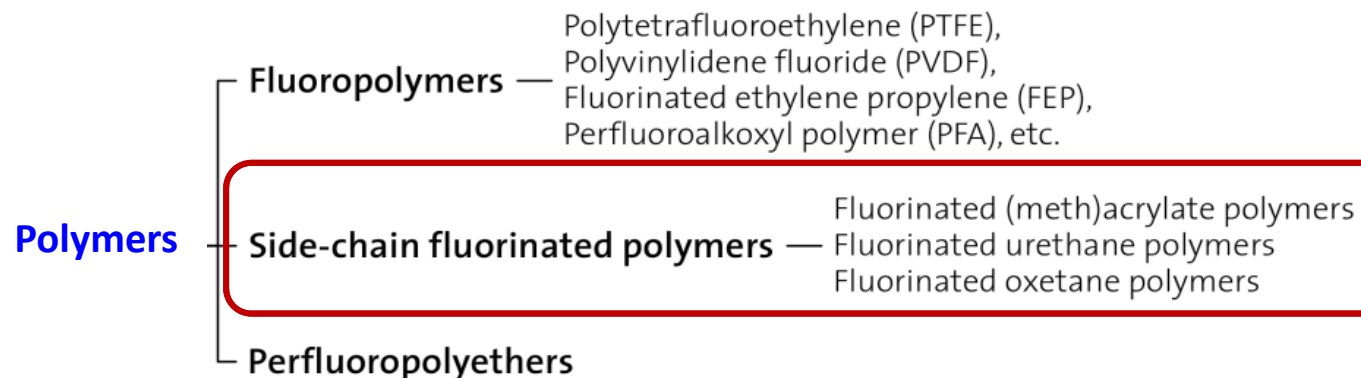
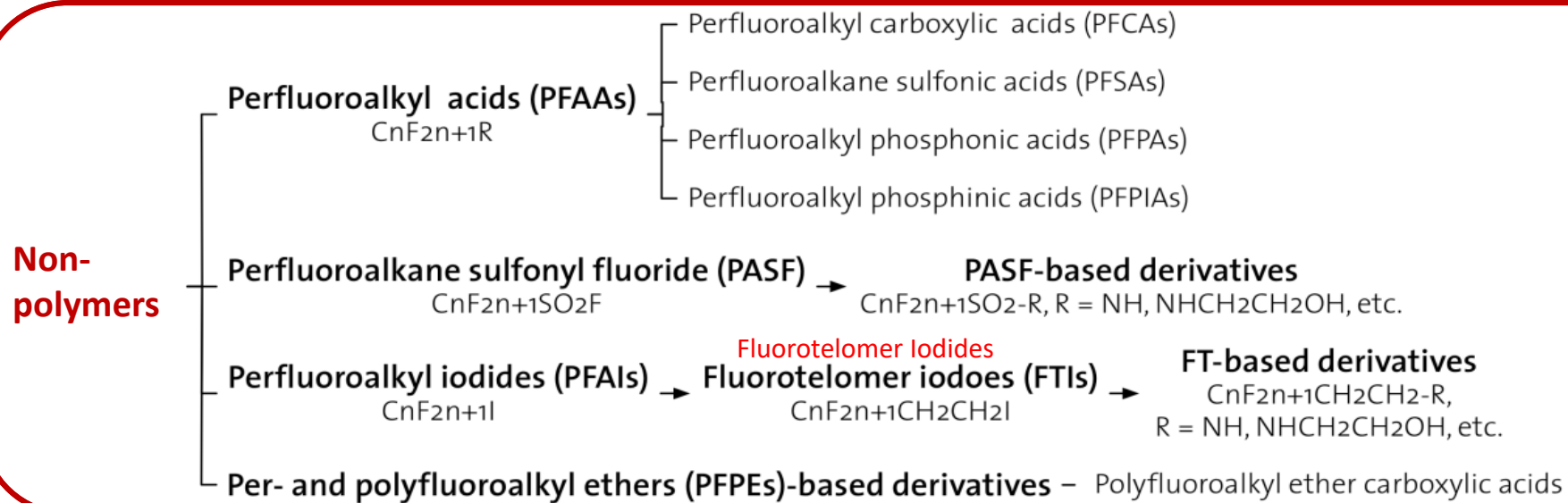
Side-chain Fluorinated Polymers



Polyfluoroalkyl Substances



OECD PFAS Map



A New View

PFAS to FOCUS ON

including
impurities and
use of non-
polymer PFAS
such as PFECAs
as PPAs in
manufacturing
Polymers

High molecular
weight polymers
themselves are
not the FOCUS

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PFAS to FOCUS ON

Perfluoroalkyl Substances



Polyfluoroalkyl Substances



Side-chain Fluorinated Polymers



Polymers

Fluoropolymers



Perfluoropolyethers

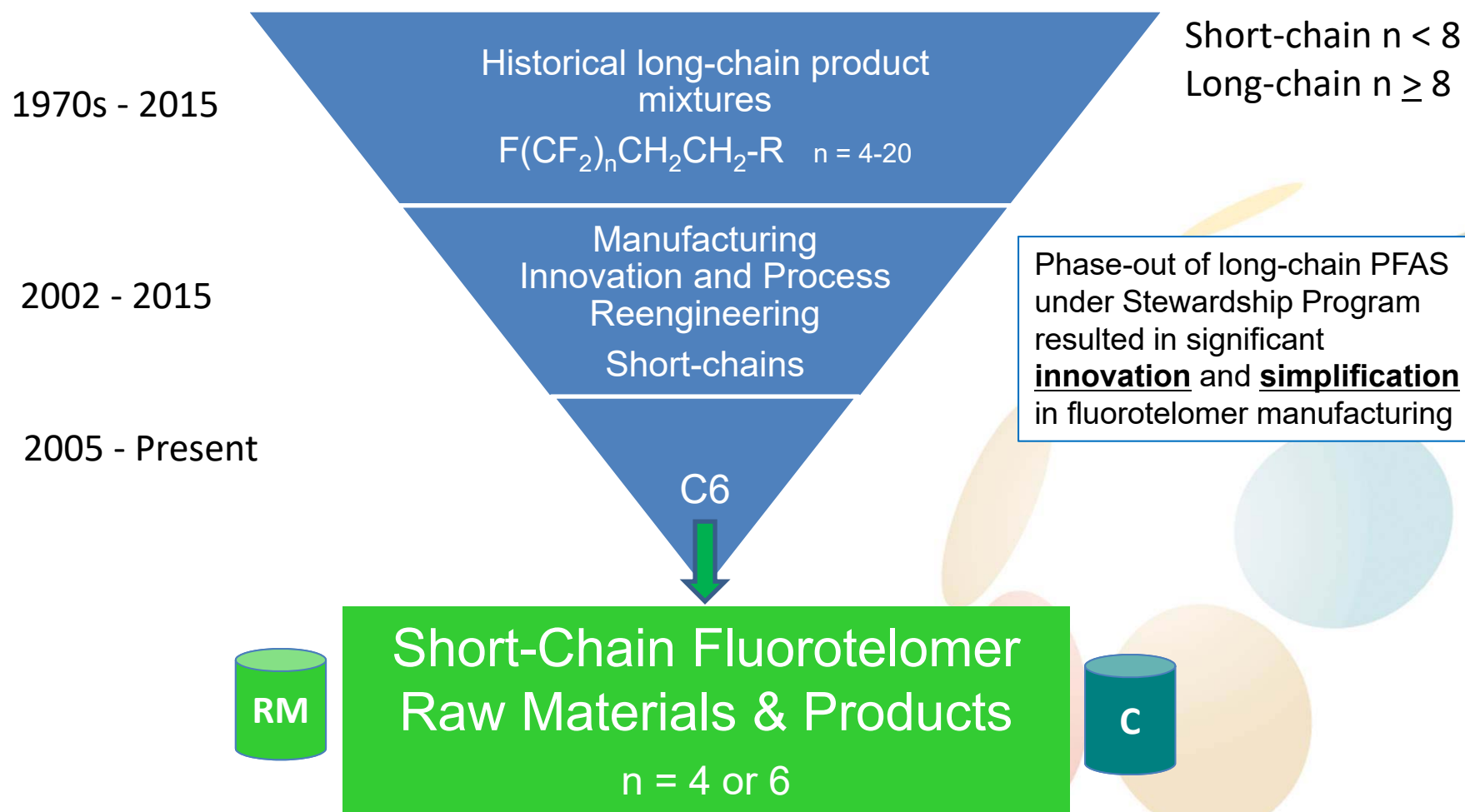


High molecular
weight, inert
polymers of low
concern

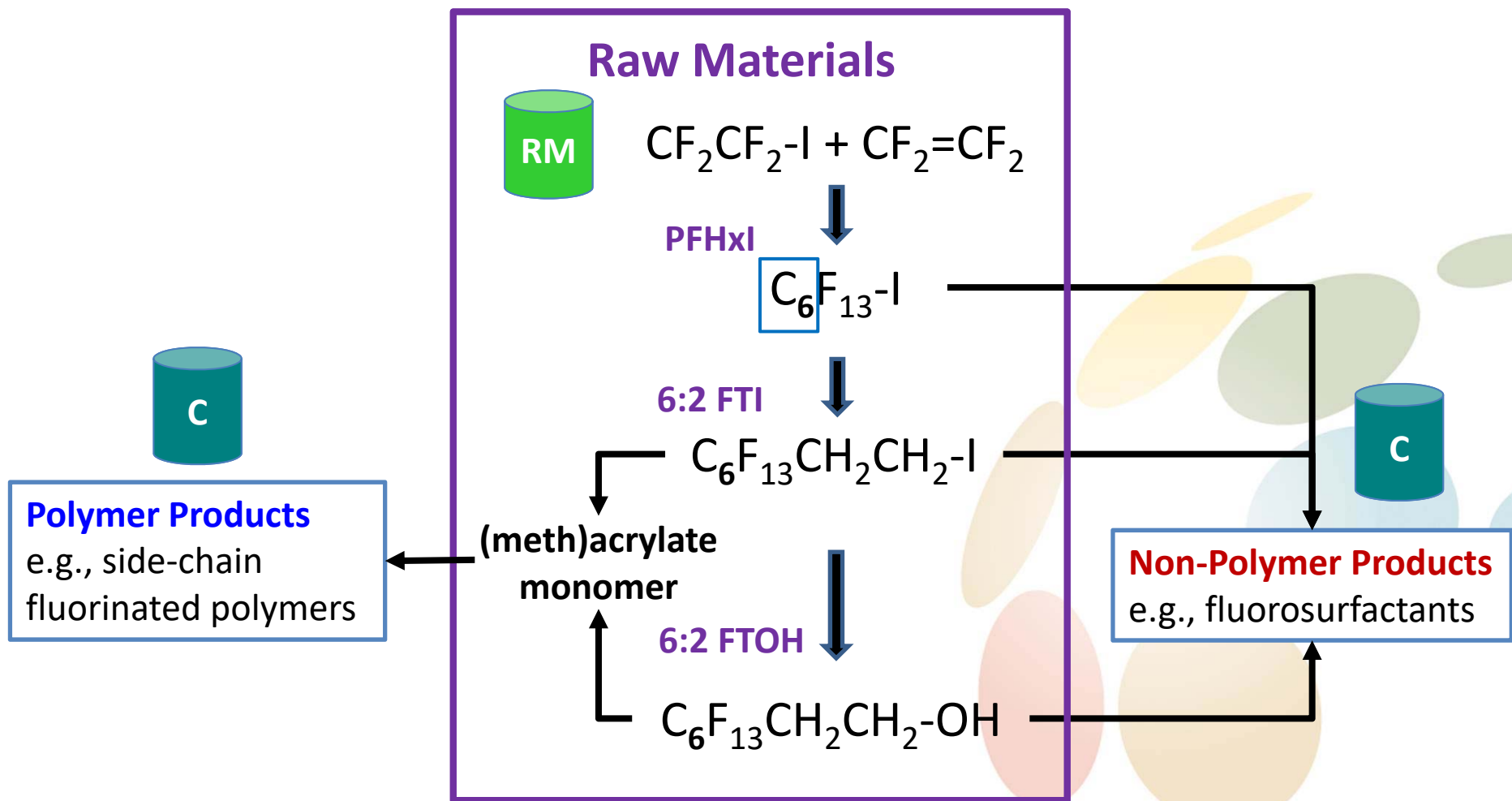
Specific topics

- Fluorotelomers
- ECF
- PPAs (polymer polymerization aids)
- Fluoropolymers
- PFPE Polymers

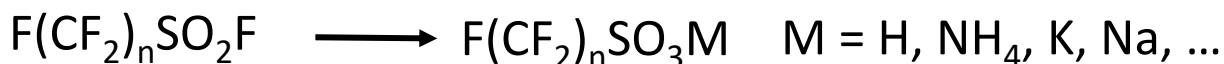
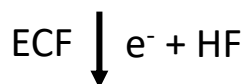
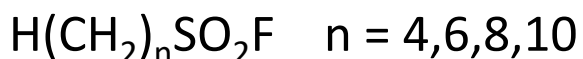
Fluorotelomer Manufacturing: Shift to Short-Chains



Short-chain Fluorotelomers - C6



Electrochemical Fluorination (ECF)



Perfluoroalkane sulfonyl fluoride

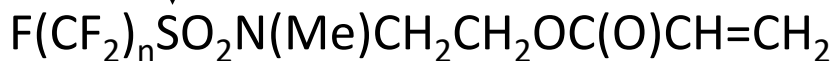
Perfluoroalkane sulfonate



Perfluoroalkane sulfonamide



N-Methyl Perfluoroalkane sulfonamido alcohol (MeFASE)



Acrylate monomer

Non-Polymer Products
e.g., fluorosurfactants

Polymer Products
e.g., side-chain fluorinated polymers

Short-chain $n < 6$
Long-chain $n \geq 6$

ECF produced materials have up to 30% branched perfluoroalkyl chains and contain odd and even carbon chain lengths.

Polymer Polymerization Aids - PPA's

Per- and Poly- fluoroalkyl ether carboxylates

PFAS CATEGORY

Non-Polymers

Perfluoroalkyl ether carboxylates



HFPO-DA;
①

HFPO-DA, CAS# 62037-80-3
 $\text{F}_3\text{C}-\text{CF}_2\text{CF}_2-\text{O}-\text{CF}(\text{CF}_3)-\text{CO}_2^-$

① CAS# 908020-52-0
 $\text{F}_3\text{C}-\text{CF}_2-\text{O}-\text{CF}_2\text{CF}_2-\text{O}-\text{CF}_2\text{CO}_2^-$

Polyfluoroalkyl ether carboxylates



ADONA;
②

ADONA, CAS# 958445-44
 $\text{F}_3\text{C}-\text{O}-\text{CF}_2\text{CF}_2\text{CF}_2-\text{O}-\text{CFHCF}_2-\text{CO}_2^-$

② CAS# 329238-24-6
 $\text{ClC}_3\text{F}_6-\text{O}-[\text{CF}_2\text{CF}(\text{CF}_3)\text{O}]_n-[\text{CF}(\text{CF}_3)-\text{O}]_m-\text{CF}_2-\text{CO}_2^-$

Fluoropolymers

Integrated Environmental Assessment and Management — Volume 14, Number 3—pp. 316–334

316

Received: 26 September 2017 | Returned for Revision: 16 January 2018 | Accepted: 30 January 2018

<http://dx.doi.org/10.1002/ieam.4035>

Critical Review

A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers

PTFE, FEP, ETFE,
PFA, etc.

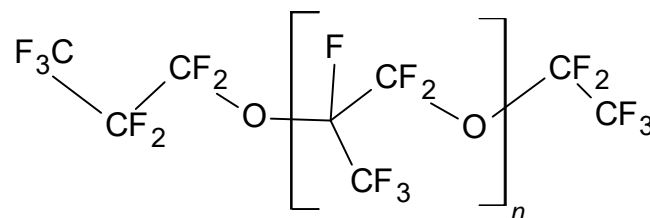
- Fluoropolymers have thermal, chemical, photochemical, hydrolytic, oxidative, and biological stability.
- Fluoropolymers are practically insoluble in water and not subject to long-range transport.
- With a molecular weight well over 100 000 Da, fluoropolymers cannot cross the cell membrane. Fluoropolymers are not bioavailable or bioaccumulative
- Clinical studies of patients receiving permanently implanted PTFE cardiovascular medical devices demonstrate no chronic toxicity or carcinogenicity and no reproductive, developmental, or endocrine toxicity.
- Degrade to form HF and CO₂ under municipal waste incineration conditions.

PFPE Polymers - Basics

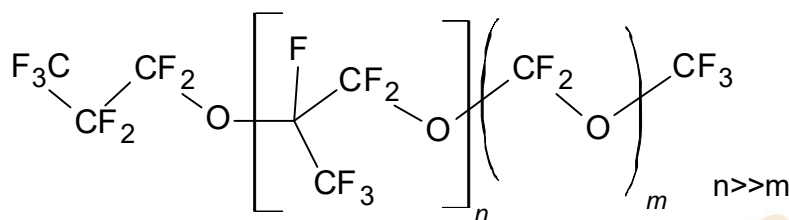
- PFPE's are unique polymers which have excellent thermal stability, chemical inertness, as well as being liquids over a wide range of molecular weights
 - There are also products based on PFPE oligomers
- They are characterized as containing only Carbon, Fluorine and Oxygen, with differing amounts of Carbon and Oxygen
- Commercial products containing PFPEs are oils and greases used as lubricants where high thermal and chemical stability is critical for service and service lifetime.
 - Applications include:
 - Bearings
 - including Sealed for Life Applications
 - Vacuum Pump Fluids

Commercial Perfluoropolyethers - PFPEs

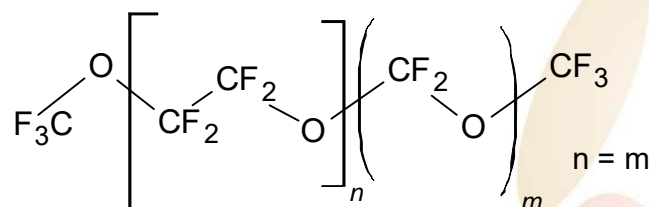
PFPE- K



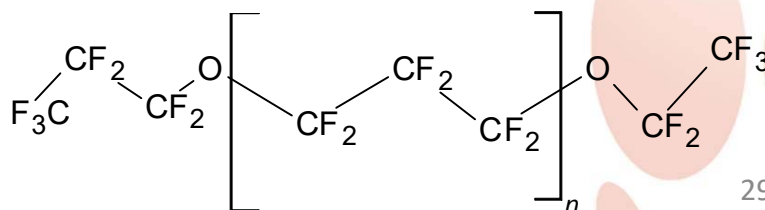
-Y



-M / Z



-D



Perfluoroalkylpolyethers.
*Synthetics, Mineral Oils,
 and Bio-Based Lubricants:
 Chemistry and Technology*
 Rudnik, L. R., Ed.
 CRC Press, **2005**.
 pp 158-174



PFAS: Current Uses

Societal Value and Benefits of Fluorotechnology

- **The use and variation of the carbon-fluorine bond gives FluoroTechnology its distinct properties of strength, durability, heat-resistance and stability.**
 - **These properties are critical to the reliable and safe function of myriad products that industry and consumer rely on every day**

PFAS Uses & Occurrence*

- In industrial and consumer products manufactured in U.S. and globally
- In manufacturing and processing
- Produced as intermediates and raw materials
- Occur as byproducts, as metabolites and via degradation

*Sources: ITRC Fact Sheets; OECD Synthesis Paper; FluoroCouncil Infographic and Website

FluoroTechnology Benefits and Supported Industries

- **Durability**

- Building and Construction
- Industrial and Institutional Floor Care
- Paints and Coatings
- Cookware
- Outdoor Apparel/Equipment
- Leather (Footwear and Furniture)
- Professional Textiles



- **Emissions Reduction/(Alternative) Energy**

- Automotive, Trucks, Buses
- Oilfield and Mining
- Alternative Energy



FluoroTechnology Benefits and Supported Industries

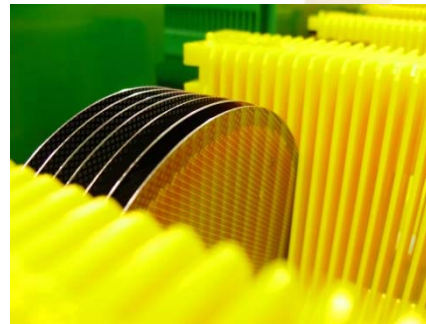
- **Safety: Workers, Consumers, Environment**

- Chemical and Pharmaceutical Manufacturing
- Food Processing
- Personal Protection and Worker Safety
- Safety Equipment
- Healthcare/Hospitals
- Metal Plating
- Aerospace
- Wire & Cable in Buildings
- Paper and Packaging



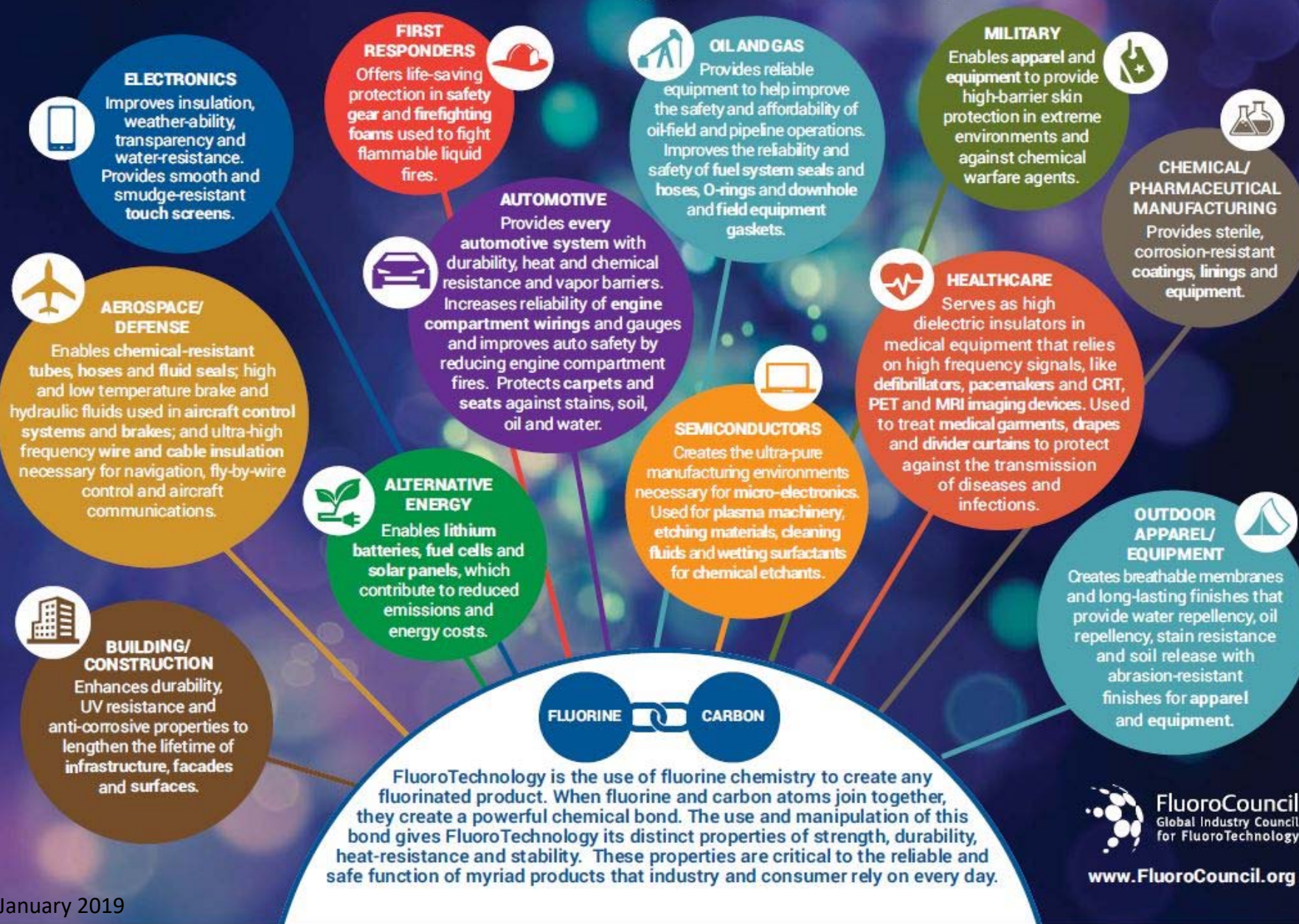
- **Electronic Equipment**

- Semiconductors and Electronics






FLUOROTECHNOLOGY MAKES IMPORTANT PRODUCTS FOR VITAL INDUSTRIES POSSIBLE

FluoroCouncil member companies voluntarily committed to a global phase-out of long-chain fluorochemistries by the end of 2015, resulting in the transition to alternatives, such as short-chain fluorochemistries that offer the same high-performance benefits, but with improved environmental and health profiles.

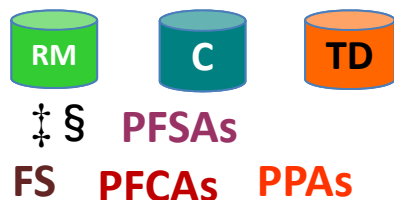


Fluorotechnologies: Legend

- **FP: Fluoropolymers**
 - **PFPE: Perfluoropolyethers**
 - **SC FP: Side-chain fluoropolymers**
 - **FS: Fluorosurfactants**
 - **PFCAs: Perfluoro carboxylic acids**
 - **PFECAs: Perfluoroalkylether carboxylic acids (e.g., HFPO-DA)**
 - Polyfluoroalkyl ether carboxylic acids (e.g., ADONA)
 - **PFSAs: Perfluoroalkane sulfonic acids**
-
- **Terminal Degradation Products** 
 - **Raw Materials** 
 - **Commercial Products** 

PFAS to FOCUS ON

Perfluoroalkyl Substances



Polyfluoroalkyl Substances



Side-chain Fluorinated Polymers



Polymers

Fluoropolymers



Perfluoropolyethers



High molecular
weight, inert polymers
of low concern

† - Electrochemical
Fluorination (ECF)
§ - Fluorotelomer (FT)

Commercial Products

- **FP: Fluoropolymers**
- **PFPE: Perfluoropolyethers**
- **SC FP: Side-chain fluoropolymers**
- **FS: Fluorosurfactants**
- **PFCAs: Perfluoro carboxylic acids**
- **PPAs: PFECAs- Perfluoroalkylether carboxylic acids (e.g., HFPO-DA); Polyfluoroalkyl ether carboxylic acids (e.g., ADONA)**
- **PFSAs: Perfluoroalkane sulfonic acids**

Fluorotechnology Uses (1)

- **Electronics**

- insulation, weatherability, transparency, water-resistance; smudge-resistant touch screens

- **FP**; **PFPE**

- **Aerospace/Defense/Aviation**

- chemical-resistant tubes & hoses, fluid seals; UHF wire & cable insulation; extreme temperature & conditions lubrication; brake & hydraulic fluids

- **FP**; **PFPE**; **FS**

- **Building/Construction**

- exterior durability, UV resistance, anti-corrosive properties; wire & cable; paints & coatings

- **FP**; **PFPE**; **FS**

Fluoropolymers



FP

Perfluoropolyethers



PFPE

Polyfluoroalkyl Substances



FS

Fluorotechnology Uses (2)

- **First Responders**

- protective turnout gear; AFFF for high-hazard Class B fires

— **FP**; **FS**; **SC FP**

- **Alternative Energy**

- lithium batteries, fuel cells, solar panels; membranes & protective coatings

— **FP**; **PFPE**; **FS**

- **Automotive**

- heat & chemical resistant tubes, hoses, seals, wiring; carpet & seat protection (see next chart)

— **FP**; **SC FP**

Fluoropolymers



FP

Side-chain
Fluorinated Polymers



SC FP

Polyfluoroalkyl
Substances



FS

Perfluoropolyethers



PFPE

Automotive Uses of Fluoropolymers

Steering Systems:

- Gear Seals
- PTFE Bearings
- Column Adjusters
- Pump Seals
- Gear Mounts
- Steering Rack

Environmental Systems:

- Hood, Door, & Trunk Hinges
- PTFE Bearings
- Push/Pull Cables
- Power Door Lock Seal
- Seat Adjustment Systems
- Active Headlight Seal

Engines:

Suspension/Brakes:

- Corrosion Inhibitors
- Oxygen Sensors
- Filler
- Seals

Electronics:

- Engine Wiring
- Transmission Wiring
- Under-hood Wiring
- Fiber Optic Cables

Transmissions:

- E Seals
- E Bearings
- on Seals
- ft Seals
- s
- s
- Transfer Seals
- Modules

Fluorotechnology Uses (3)

- **Military**

- protective gear/armor, helmets and equipment for extreme environments and against chemical warfare agents; AFFF for Class B fires

— **FP**; **FS**; **SC FP**

- **Semiconductors**

- ultra pure environments; etching materials; cleaning fluids; wetting surfactants; lubrication

— **FP**; **PFPE**; **FS**

- **Oil & Gas**

- equipment for oil-field, downhole and pipelines; fuel system seals, hoses, O-rings, gaskets; oil well and NG stimulation; lubrication

— **FP**; **PFPE**; **FS**

Fluoropolymers



FP

Side-chain Fluorinated Polymers



SC FP

Perfluoropolyethers



PFPE

Polyfluoroalkyl Substances



FS

Fluorotechnology Uses (4)

- **Healthcare & Medical**

- high dielectric insulators in defibrillators, pacemakers and imaging devices; surface protection treatments for medical garments, drapes

— **FP**; **SC FP**

- **Chemical/Pharma/Food Processing/General Manufacturing**

- sterile, corrosion-resistant coatings, linings and equipment; lubrication in extreme environments

— **FP**; **PFPE**

- **Outdoor Apparel & Equipment**

- breathable membranes and long-lasting finishes for high-performance uses: water/oil/stain/soil resistance

— **FP**; **SC FP**

Fluoropolymers



FP

Side-chain Fluorinated Polymers



SC FP

Perfluoropolyethers



PFPE

Fluorotechnology Uses (5)

- **Paper & Packaging**

- surface coatings for oil and grease repellency / protection in food-contact uses and non-food applications: boxes, masking papers, carbonless forms

- SC FP; PolyFPE oligomers

- **I&I and HH Cleaning Products**

- provides wetting, leveling in floor polishes and other cleaning products

- FS; SC FP

- **Biocides & Pesticides:** used as active ingredient in pesticides, formulations

- FS (ECF only)

Side-chain
Fluorinated Polymers



SC FP

Polyfluoroalkyl
Substances



PolyFPE
oligomers

Polyfluoroalkyl
Substances



FS

Fluorotechnology Uses (6)

- **Polymer Polymerization**

- used as a polymerization surfactant to make various high molecular weight fluoropolymers

- **PFCAs; PFECAs; FS**

- **Metal Plating & Etching**

- corrosion prevention; wetting agent; fume suppression in electroplating for chrome, copper, nickel and tin

- **FS**

- **Carpet, Textile, Leather, Apparel**

- coatings applied to provide water, oil, soil and stain repellency and in some cases impart soil release properties

- **SC FP; PolyFPE oligomers**

**Polyfluoroalkyl
Substances**

FS, PPA's, PolyFPE
Oligomers



**Perfluoroalkyl
Substances**

FS, PFCAs, PPA's



**Side-chain Fluorinated
Polymers**

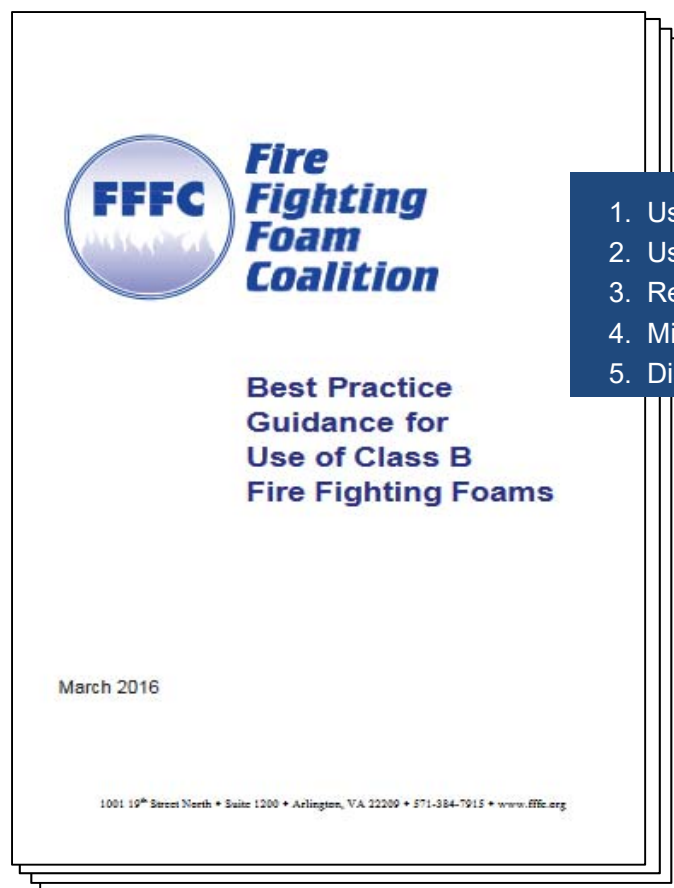
SC FP



Fluorotechnology Uses & PFAS Classification

Use Areas	/ Classification			NP = Non-polymer		
Electronics	FP: Fluoropolymers			PFPE: Perfluoropolyethers		
Aerospace/Aviation	FS: Fluorosurfactants (NP)			FP	PFPE	
Building/Construction	FP	PFPE	FS			
First Responders	FP	FS	SC FP: Side-chain fluoropolymers			
Automotive	FP	SC FP				
Alternative Energy	FP	PFPE	FS			
Military	FP	SC FP	FS			
Semiconductors	FP	PFPE	FS			
Oil & Gas	FP	PFPE	FS			
Healthcare/Medical	FP	SC FP				
Chemical/Pharma/Food Processing	FP	PFPE				
Outdoor Apparel & Equipment	FP	SC FP				
Paper & Packaging	SC FP	PolyPFPE Oligomers				
I&I and HH Cleaning	FS	SC FP				
Biocides & Pesticides	FS (ECF)					
Polymer Polymerization	PFECAs: Perfluoroalkylether carboxylic acids (e.g., HFPO-DA) (NP)					
	Polyfluoralkyl ether carboxylic acids (e.g., ADONA)					
	PFCAs: Perfluoro carboxylic acids (NP)					FS
Metal Plating & Etching	FS					
Carpet/Textile/Leather/Apparel	SC FP	PFPE				

Industry Best Practices - Reduces Environmental Release and Potential For Exposure



1. Use the product only when necessary
2. Use only what you need
3. Reuse/recycle residual liquids if possible
4. Minimize waste and emissions
5. Dispose of all chemicals properly



Links: <https://fluorocouncil.com/PDFs/Guidance-for-Best-Environmental-Practices-BEP-for-the-Global-Apparel-Industry.pdf>
<https://fluorocouncil.com/PDFs/Best-Practice-Guide-for-Use-of-Class-B-Fire-Fighting-Foams-PDF.pdf>



PFAS Universe: TURI Focus

TURI Request for Information

- TURI Current Focus:
 - Non-Polymer: Fluoroethers and polymerization aids
 - » Perfluoroalkyl (e.g. HFPO-DA)
 - » Polyfluoroalkyl (e.g., Adona[®])
 - Non-Polymer, PFAAs:
 - » Perfluoroalkyl Phosphonic Acids (PFPAs)
 - » Perfluoroalkyl Phosphinic Acids (PFPIAs)
- EPA's new chemicals program
 - Discuss EPA's PMN/TSCA program and approvals

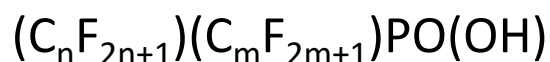
PFPAs and PFPIAs - Primer

- Less well known, studied and used acids
- Manufactured by multiple companies historically
- Current manufacture and uses expected to be minor, if at all
- Reported to be used as defoamers in pesticide formulations and wetting agents in some consumer products*
- Structures:

Perfluoroalkyl Phosphonic Acids (PFPAs)



Perfluoroalkyl Phosphinic Acids (PFPIAs)



*See Z. Wang et al, *Environment International* 89-90 (2016) 235-247

EPA's PFAS PMN/TSCA Approval Process*

- Historically EPA took an integrated testing approach that involved a matrix of data needs
- Testing and data submission were required before PFAS alternatives (i.e. short chains) PMNs were approved
 - Work required on notified substance and/or degradant
- EPA's hazard and fate requirements included
 - Health and metabolism and Environmental fate
 - Half-life in animals and Human biomonitoring
- EPA issued Consent Orders (5e) that required testing on alternatives and are still effective and enforceable
 - Alternatives testing continues even today



Q&A on Universe of Substances & Uses

TURI Request for Information

- Global restriction limits, agreements, actions, residuals, exemptions, regulations and/or proposals – review/highlight aka REACH and others
- TURI has been using May 2018 OECD diagram of PFAS compounds from: *TOWARD A NEW COMPREHENSIVE GLOBAL DATABASE OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs): SUMMARY REPORT ON UPDATING THE OECD 2007 LIST OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs)*. Review current work plan with OECD to re-define/classify/broaden published PFAS list as noted
- Discuss request for annotated OECD spreadsheet of substances indicating which CAS #s/specific chemicals are in use in US and for which uses. There are approx. 100 CAS #'s that indicate reported in 2016 TSCA inventory. Note part of effort in b. Work in progress. Timing?



Degradation Pathways for PFAS Currently in Use



TURI Ask for Information

- Perfluoropolyether polymers, fluoropolymers, side-chain fluorinated polymers, fluorosurfactants: per- and polyfluoroalkyl
- Experimental degradation data for chemicals in use and intermediates
 - Half-lives and rough percentages of breakdown products
 - Ultimate breakdown products
 - how many and which compounds are terminal end products?
 - Biotic pathways
 - Abiotic pathways (hydrolysis, oxidation or photolysis)

Degradation Pathways

Biotic

aerobic [O]
anaerobic

Abiotic

thermal (heat)
light
chemical
mechanical
hydrolysis

reasonably
foreseeable use
and
environmental
conditions

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PFAS to FOCUS ON

Perfluoroalkyl Substances



‡, §

Polyfluoroalkyl Substances



‡, §

Side-chain Fluorinated Polymers



‡, §

Polymers

Fluoropolymers



Perfluoropolyethers



High molecular
weight, inert
polymers of low
concern

Consider
each PFAS
class

Incineration (thermal)

reasonably
foreseeable use
and
environmental
conditions

- Under typical municipal or medical waste incineration conditions, PFAS substances are destroyed forming HF and CO₂.

Degradation Pathways

Fluorotelomer-based substances

ECF-based substances

reasonably foreseeable use and environmental conditions

Non-Polymers

Perfluoroalkyl Substances



‡, §

Polyfluoroalkyl Substances



‡, §

Polymers

Side-chain Fluorinated Polymers



‡, §

Manufacturing Technologies:

‡ - Electrochemical Fluorination (ECF)

§ - Fluorotelomer (FT)

Degradation Pathways

Fluorotelomer-based substances

reasonably foreseeable use and environmental conditions

PFAS to FOCUS ON

Perfluoroalkyl Substances



Polyfluoroalkyl Substances



Side-chain Fluorinated Polymers



Examples

Perfluorohexyl Iodide - PFHxI



PFHxA



6:2 Fluorotelomer Iodide

6:2 Fluorotelomer Alcohol (FTOH)

6:2 Fluorotelomer surfactants



6:2 Fluorotelomer-based polymers



Short-chain Fluorotelomer – C6 Biodegradation Pathway



Short-chain Fluorotelomer-based Products and Raw Materials



Transient Biodegradation Intermediates

e.g., 6:2 FTOH, 6:2 FTSA, 6:2 FTCA, 6:2 FTUCA, 5:3 Acid



Short-chain PFCA Terminal Degradation Products

PFCAs

PFBA

PFPeA

PFHxA

PFHpA

Degradation products formed and yields vary by substance,
matrix (e.g., soil, sediment, air,) and mode (biotic vs. abiotic)

Degradation Pathways

ECF-based substances

reasonably foreseeable use and environmental conditions

PFAS to FOCUS ON

Perfluoroalkyl Substances



Polyfluoroalkyl Substances



Side-chain Fluorinated Polymers



Examples

Perfluorooctanesulfonyl fluoride (POSF)



PFOS
PFBS



nEtFOSE



ECF Surfactants



Perfluorobutanesulfonamido-based acrylic polymers



Short-chain ECF Biodegradation Pathway



**ECF-based Products
and Raw Materials**



Transient Biodegradation Intermediates

e.g., FASA, FASE, FASAA, etc.



PFSA and PFCA Terminal Degradation Products

PFSA_s

PFBS

PFPeS

PFHxS

PFHpS

PFOS

PFCA_s

PFBA

PFPeA

PFHxA

PFHpA

PFOA

Degradation products formed and yields vary by substance,
matrix (e.g., soil, sediment, air,) and mode (biotic vs. abiotic)

Degradation Pathways

Perfluoroalkyl Acids - PFAAs

reasonable
foreseeable use and
environmental
conditions

PFAS to FOCUS ON

Perfluoroalkyl
Substances



PFCA

carboxylate

PFSA

sulfonate

PFPA

phosphonate

PFPiA

phosphinate

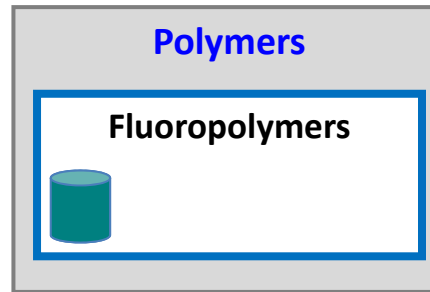
Perfluoroalkyl acids are not known to degrade in the environment or metabolize in living systems.

Degradation Pathways

Fluoropolymers are stable and do not degrade

under reasonable foreseeable use and environmental conditions

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- Fluoropolymers have thermal, chemical, photochemical, hydrolytic, oxidative, and biological stability.
- Fluoropolymers are practically insoluble in water and not subject to long-range transport.
- With a molecular weight well over 100 000 Da, fluoropolymers cannot cross the cell membrane. Fluoropolymers are not bioavailable or bioaccumulative
- Clinical studies of patients receiving permanently implanted PTFE cardiovascular medical devices demonstrate no chronic toxicity or carcinogenicity and no reproductive, developmental, or endocrine toxicity.
- Degrade to form HF and CO₂ under municipal waste incineration conditions.

A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers.
Integrated Environmental Assessment and Management
2018, 14(3):316-334. <http://dx.doi.org/10.1002/ieam.4035>

Fluoropolymers

- Proper use and handling
 - “Polymer Fume Fever”
 - Adequate ventilation must be used during industrial use and processing
 - Do not heat above decomposition temperature

<https://www.plasticseurope.org/en/resources/publications/108-guide-safe-handling-fluoropolymer-resins>

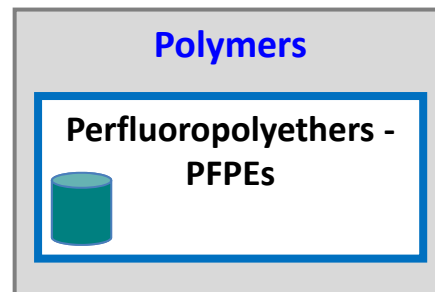


Degradation Pathways

Perfluoropolyethers

PFPEs

reasonably foreseeable use and environmental conditions



- Perfluoropolyether polymers (PFPEs) have thermal, chemical, photochemical, hydrolytic, oxidative, and biological stability.
- PFPEs are practically insoluble in water and hydrocarbons and not subject to long-range transport.



Q&A on Degradation Pathways and Products

PFAS: Uses, Occurrence, Messages

- In industrial and consumer products manufactured in U.S. and globally
- In manufacturing and processing
- Produced as intermediates and raw materials
- Occur as byproducts, as metabolites and via degradation

PFAS: BE CLEAR, SPECIFIC AND DESCRIPTIVE



Group Discussion on Webinar Content and Follow Up Items



Thank you



See you at the ITRC annual meeting PFAS Workgroup in
Boston March 26-28.