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An Overview of Production and Use of Per- and Polyfluoroalkyl Substances (PFASs)

Outline

- What are PFASs?
- How are PFASs produced and used?
- Take-home messages

What are PFASs?

EPA and 3M ANNOUNCE PHASE OUT OF PFOS

Release Date: 05/16/2000
Contact Information:

FOR RELEASE: TUESDAY, MAY 16, 2000

Following negotiations between EPA and 3M, the company today announced that it will voluntarily phase out and find substitutes for perfluorooctanyl sulfonate (PFOS) chemistry used to produce a range of products, including some of their Scotchgard lines. 3M data supplied to EPA indicated that these

PFOA Stewardship Program

In 2006, EPA invited eight major leading companies in the per- and polyfluoroalkyl substances (PFASs) industry to join in a global stewardship program with two goals:

- To commit to achieve, no later than 2010, a 95 percent reduction, measured from a year 2000 baseline, in both facility emissions to all media of perfluorooctanoic acid (PFOA), precursor chemicals that can break down to PFOA, and related higher homologue chemicals, and product content levels of these chemicals.
- To commit to working toward the elimination of these chemicals from emissions and products by 2015.

ANNEX XVII TO REACH – Conditions of restriction

Restrictions on the manufacture, placing on the market and use of cer substances, mixtures and articles

Entry 68
Perfluorooctanoic acid (PFOA) CAS No 335-67-1 EC No 206-397-9 and its salts.

Stockholm Convention on persistent organic pollutants (POPs)

2009 PFOS, its salts and POSF

2019 PFOA, its salts and PFOA-related compounds

https://pubs.acs.org/doi/abs/10.1021/acs.estlett.0c00255; https://engrxiv.org/exszc/

Five European Countries to Propose PFASs REACH Restriction; Request Comments

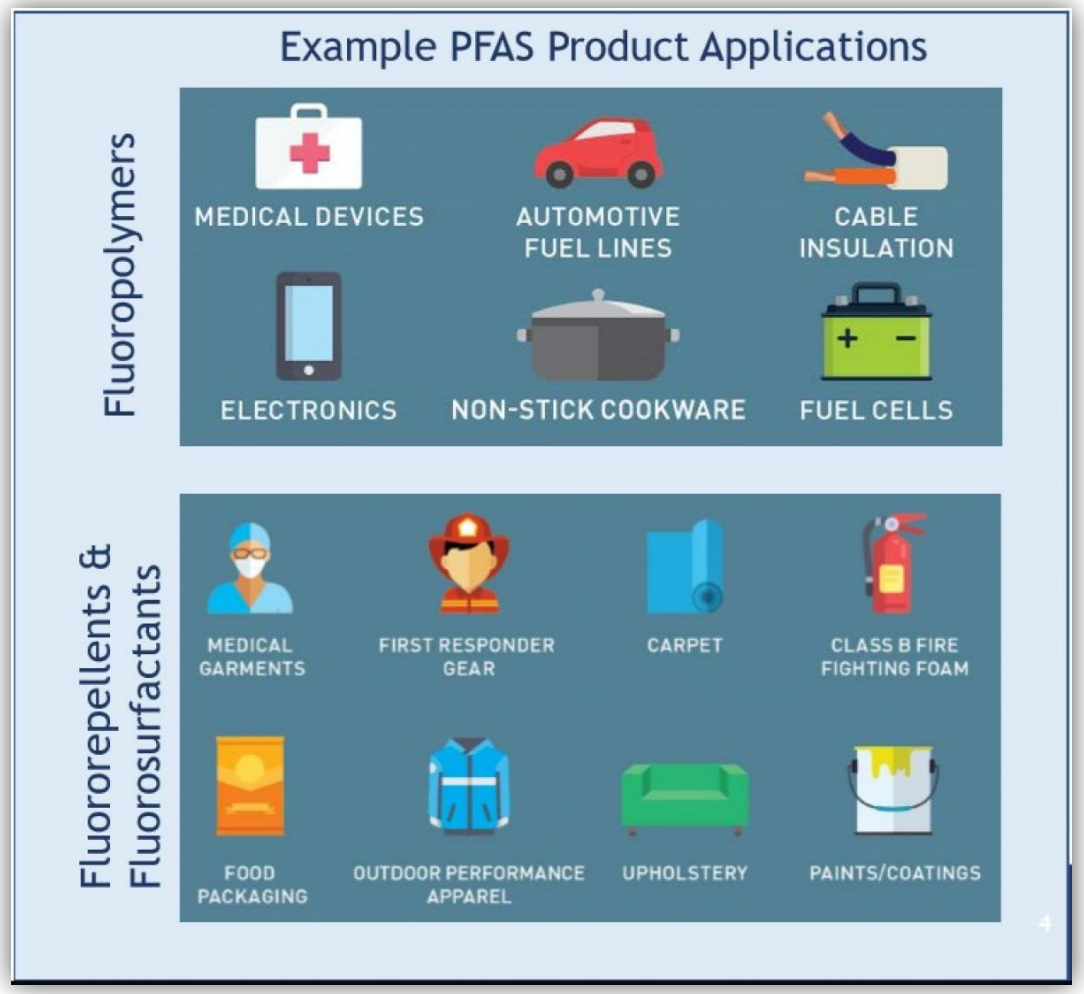
Thursday, May 21, 2020

Germany, Netherlands, Norway, Sweden, and Denmark plan to propose a joint REACH restriction to limit the manufacture and use of per- and polyfluoroalkyl substances (PFASs). As a preliminary step, the national authorities of these countries have issued a request for data on the products and mixtures containing PFASs currently being used and produced in the European Union, and products using alternatives to PFASs. The call for data is open until July 31, 2020. (An announcement about the call for data and the forthcoming PFAS restriction proposal can be found on ECHA's website.)

→ What are PFASs?

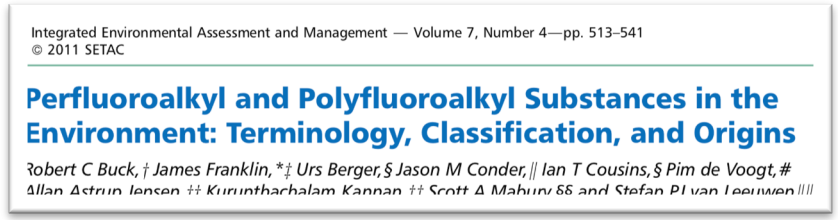
What are PFASs?

- A class of chemicals that have been widely **produced and used since the late 1940s**.



https://www.oaklodgewaterservices.org/surface-water/page/public-information-brief-pfas

What are PFASs?


Integrated Environmental Assessment and Management — Volume 7, Number 4—pp. 513–541

Perfluoroalkyl and Polyfluoroalkyl Substances 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 A Mabury, §§ and Stefan PJ van Leeuwen ‖‖

- **Buck et al. (2011)** – a milestone paper, providing an overview of PFASs detected in the environment, wildlife and humans, as well as recommendations on terminology

  → **PFASs = "**the **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 **C_nF_{2n+1}–**"

  → highlighting the variety of PFASs, e.g.
  "C_nF_{2n+1}–R" vs. "$C_nF_{2n+1}OC_mF_{2m+1}$–R"; perfluorinated vs. polyfluorinated; polymers vs. non-polymers; neutral vs. ionic (anionic, cationic, zwitterionic);

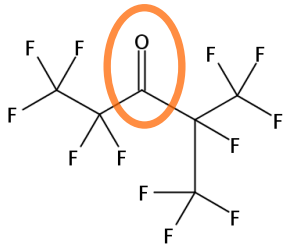
  → **The current common terminology covers only some of the PFASs.**

What are PFASs?

- In 2018, OECD published an updated PFAS List

  → Over 4,700 CAS numbers identified

  → **Many were not mentioned in Buck et al.**



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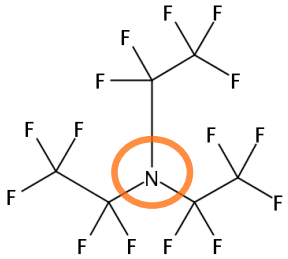

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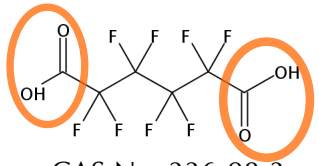

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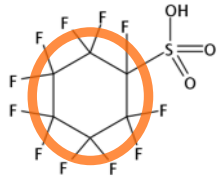

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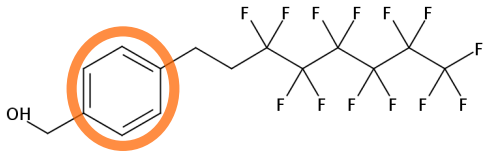

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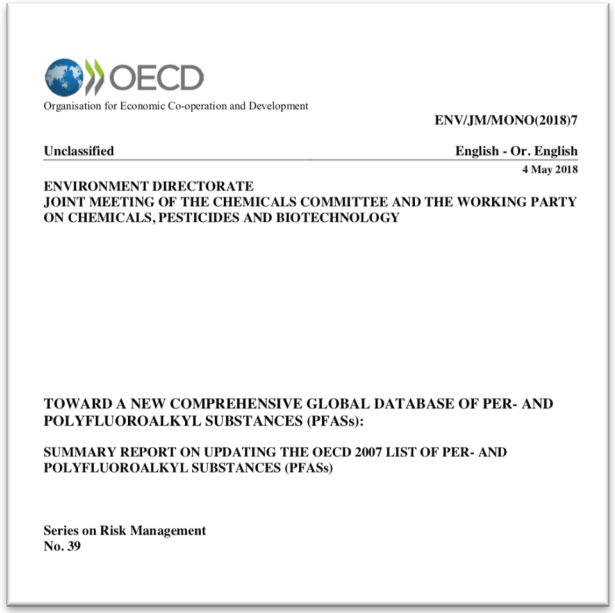


OECD

Organisation for Economic Co-operation and Development

ENV/JM/MONO(2018)7

Unclassified — English - Or. English

4 May 2018

ENVIRONMENT DIRECTORATE
JOINT MEETING OF THE CHEMICALS COMMITTEE AND THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY

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)

Series on Risk Management
No. 39

https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/

What are PFASs?

An **ongoing** project under the OECD/UNEP Global PFC Group

→ to have a more comprehensive overview of the PFAS universe

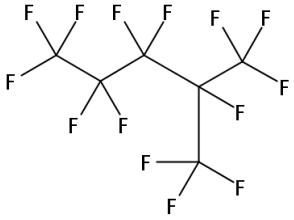
→ to reconcile the terminology of the PFAS universe, including a renewed look at the PFAS definition in Buck et al. (2011)

→ **Points to be revised (work in progress)**

> "the **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 $C_nF_{2n+1}-$"

Major Groups of PFASs

- **Perfluoroalkanes, perfluoroethers** and **perfluoroalkyl-*tert*-amines**



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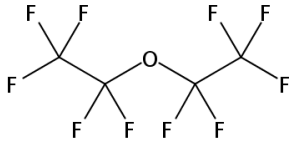

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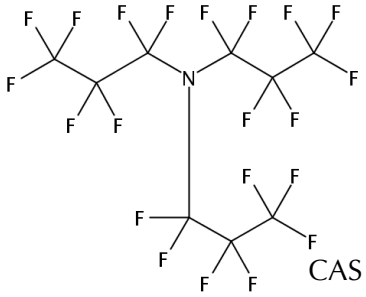

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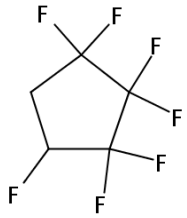
- **Certain hydrofluoro-carbons (HFCs), -ethers (HFEs)** and **-olefins (HFOs)**



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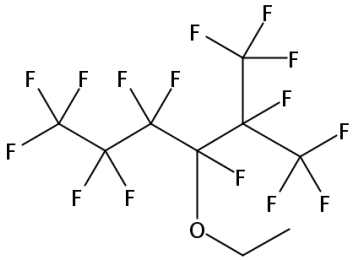

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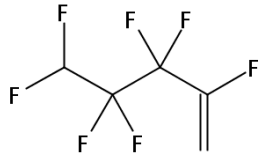
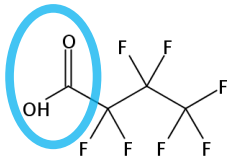


CAS No. 1547-26-8

- Perfluoroalkanes, HFCs, HFEs and HFOs have own common nomenclature systems using letters and numbers, e.g. HFC-134a: https://bit.ly/2M1Hp7l

Major Groups of PFASs

Perfluoroalkyl acids



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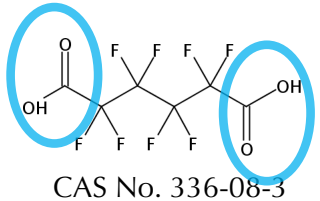

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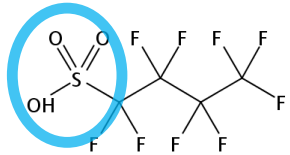

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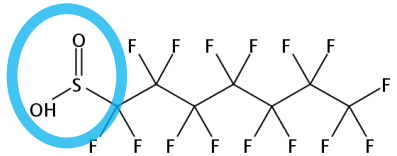

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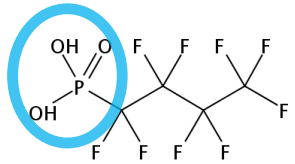

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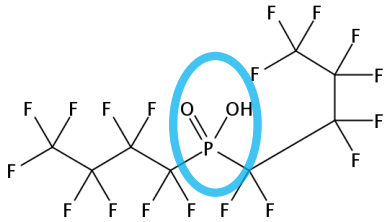

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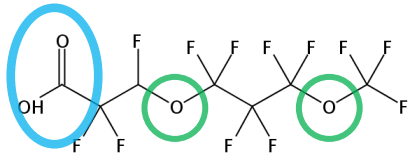
Per- and polyfluoroalkylether acids



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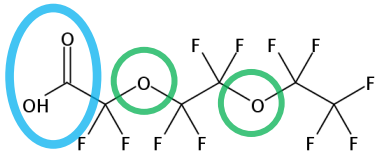

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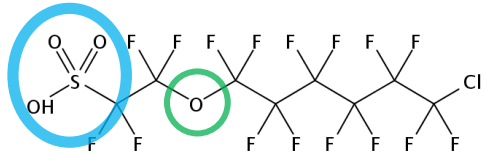
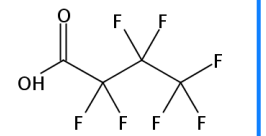


CAS No. 73606-19-6

Major Groups of PFASs

Perfluoroalkyl acids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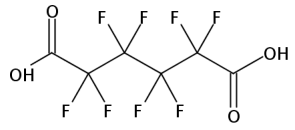
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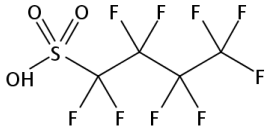
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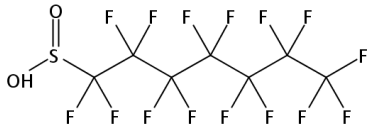
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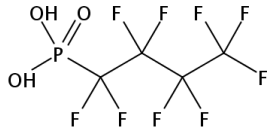
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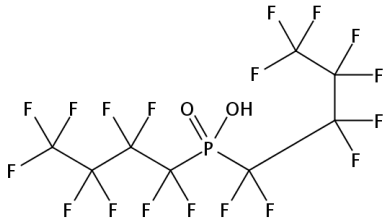
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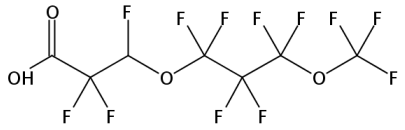
Per- and polyfluoroalkylether acids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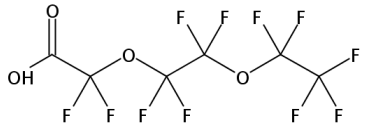
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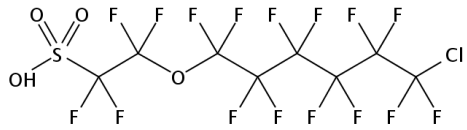

CAS No. 73606-19-6

A common terminology has been recommended by Buck et al. (2011).

Major Groups of PFASs

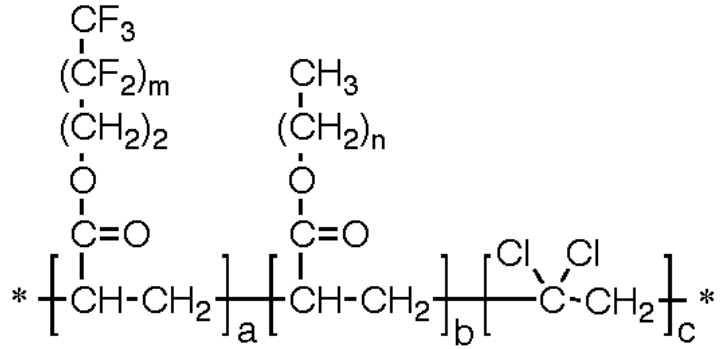
- **PACF/PASF/FT-based compounds → precursors to perfluoroalkyl acids**

perfluoroalkanoyl fluorides (PACFs)
$C_nF_{2n+1}CO_2F$ → **PACF-based substances** $C_nF_{2n+1}\mathbf{CO_2}$-R

perfluoroalkane sulfonyl fluorides (PASFs)
$C_nF_{2n+1}SO_2F$ → **PASF-based substances** $C_nF_{2n+1}\mathbf{SO_2}$-R

perfluoroalkyl iodides (PFAIs)
$C_nF_{2n+1}I$ → **n:2 fluorotelomer iodides (FTIs)** $C_nF_{2n+1}CH_2CH_2I$ → **n:2 fluorotelomer-based substances** $C_nF_{2n+1}\mathbf{CH_2CH_2}$-R

perfluoroalkylcarboxylic acids (PFCAs)
$C_nF_{2n+1}COOH$ → **n:1 fluorotelomer alcohols** $C_nF_{2n+1}CH_2OH$ → **n:1 fluorotelomer-substances** $C_nF_{2n+1}\mathbf{CH_2}$-R

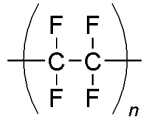
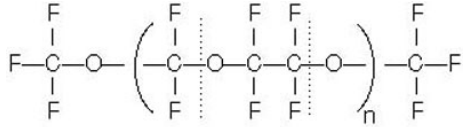


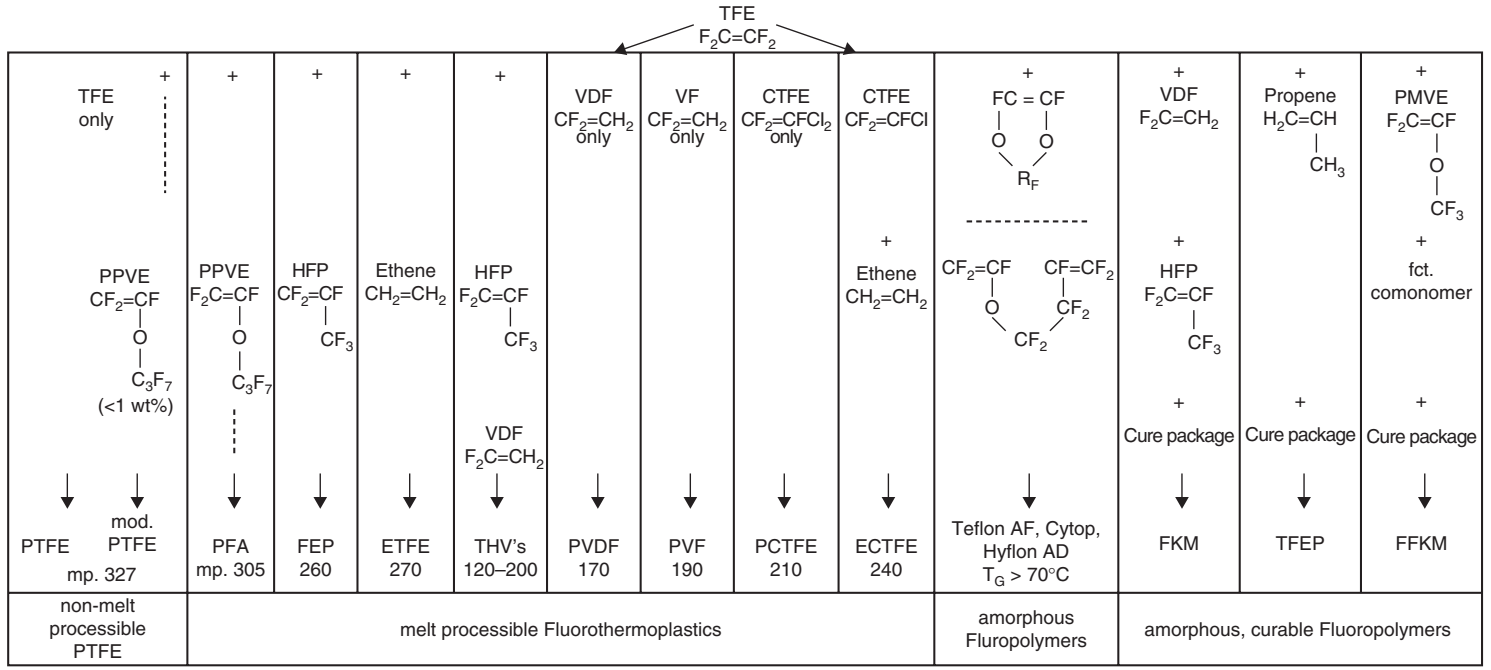
side-chain fluorinated polymers
e.g. (meth)acrylate, urethane or oxetane polymers

non-polymers
R = NH, $NHCH_2CH_2OH$, etc.

A common terminology for those with simple structures has been recommended in Buck et al. (2011), but not for those with more complex structures.

Major Groups of PFASs

- **Fluoropolymers**  **and perfluoropolyethers** 



Hintzer and Schwertfeger (2014), doi: 10.1002/9781118850220.ch21

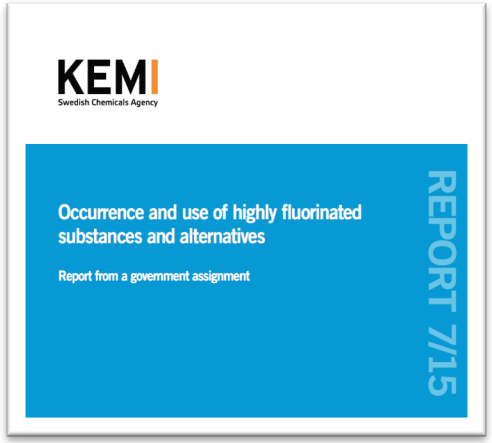
- The common chemical names (e.g. PTFE, PVDF, PFA) may refer to **a wide range of polymers with different structures, grades and properties**.

Identification of Individual PFASs on the Market

- **KEMI 2016 List**

  - focused on *all* highly fluorinated substances

  - about 2200 CAS numbers



- **OECD 2018 List**

  - focuses on PFASs with commercial sources and references

  - about 4800 CAS numbers (to date) with additional information

- **Online sources:**

  - Norman Network (https://www.norman-network.com/nds/SLE/);
  - US EPA Chemistry Dashboard (https://comptox.epa.gov/dashboard/chemical_lists/?search=pfas);
  - PubChem (https://pubchem.ncbi.nlm.nih.gov/classification/#hid=101)

Current Challenges in Identifying PFASs

- **Unclear description of many PFASs in the public domain**

  → Substances described only as "**reaction products**".

  e.g., CAS No. 88645-29-8 = "Ethene, 1,1,2,2-tetrafluoro-, oxidized, polymd., reduced, Me esters, reduced"

  → Substances described with **unclear terms**.

  e.g., "poly(difluoromethylene)", i.e. $–(CF_2)_n–$; "nonadecafluorodecenyl", i.e. $C_{10}F_{19}–$

  → Substances registered with only **trade names and general descriptions**.

  e.g., Sulflon S 233 (CAS No. 1891067-07-4) described as an amphoteric fluorosurfactant

- **The identities of many PFASs have been claimed as Confidential Business Information**.

  e.g., P120406 as "fluoroalkyl sulfonamide derivative" in the US EPA TSCA Inventory

How are PFASs Produced and Used?

How are PFASs Produced?

- **Electrochemical fluorination (ECF)**

  → e.g., $C_nH_{2n+1}COOH + (2n+2)HF \rightarrow C_nF_{2n+1}COF \rightarrow \ldots$

  → used for PFCAs, PFSAs, perfluoroalkyl-*tert*-amines, perfluoroalkanes, etc.

  → very aggressive process with many by-products (including branched isomers and cyclic analogues)

- **Telomerization**

  → e.g., $C_2F_5I + nCF_2CF_2 \rightarrow C_2F_5(CF_2CF_2)_nI$

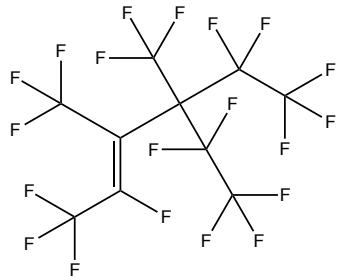
  $C_2F_5(CF_2CF_2)_nI + CH_2CH_2 \rightarrow C_2F_5(CF_2CF_2)_nCH_2CH_2I \rightarrow \ldots$

  → used for fluorotelomer-based compounds

  → may contain homologues as impurities

How are PFASs Produced?

- **Oligomerization**

  → e.g., 5 CF_2CF_2 → $C_{10}F_{20}$  → …

  $nCF_3CF\text{-}CF_2$ (HFPO) → $CF_3CF_2CF_2(CFCF_2O)_{n-2}CFCOF$ (Krytox® fluids) → …

  → used for perfluoroalkenes and derivatives, perfluoropolyethers, etc.

  → may contain homologues as impurities

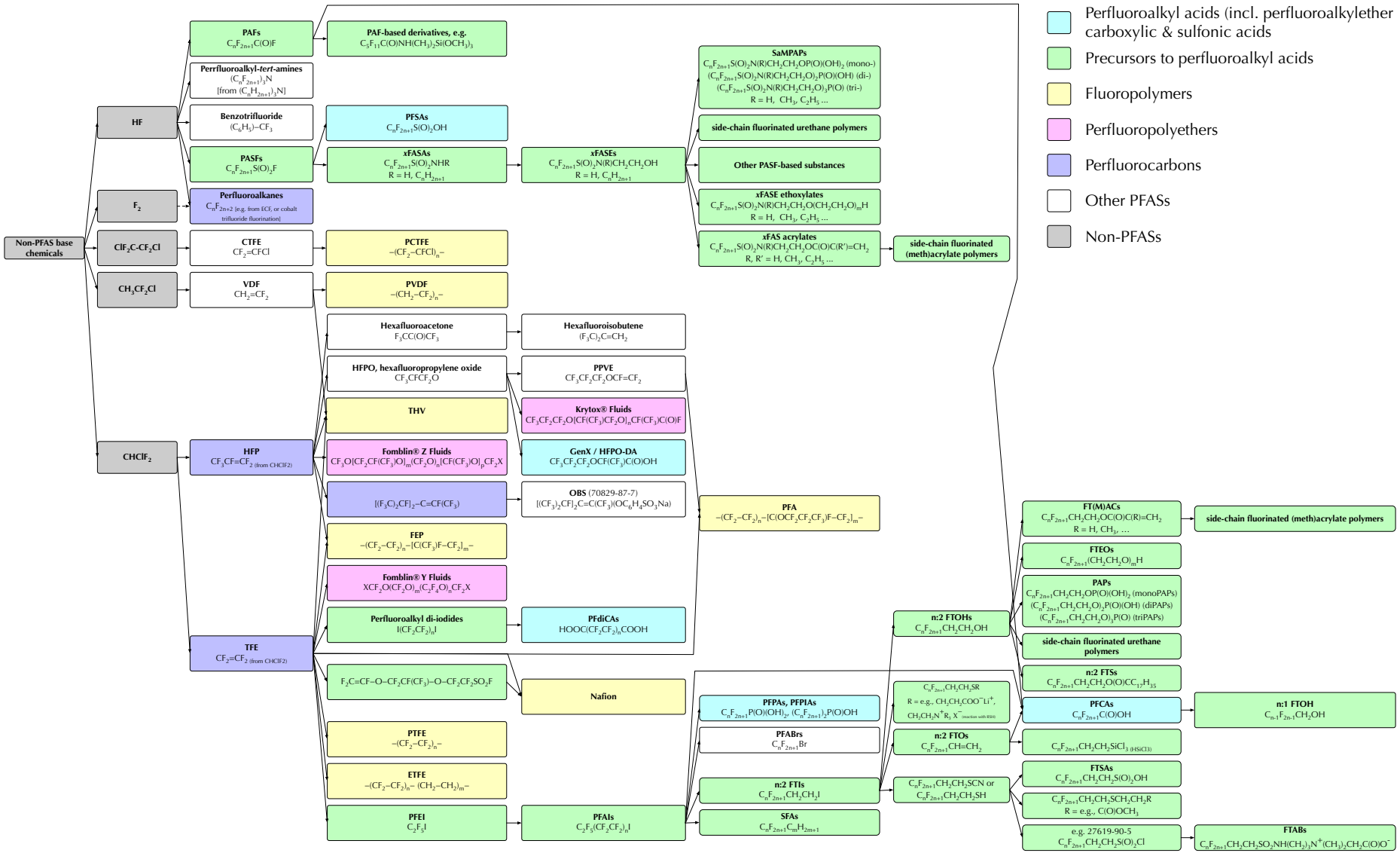
- **Polymerization**

  → used for fluoropolymers

  → suspension (granular) + emulsion polymerization (fine powder + aqueous dispersion)

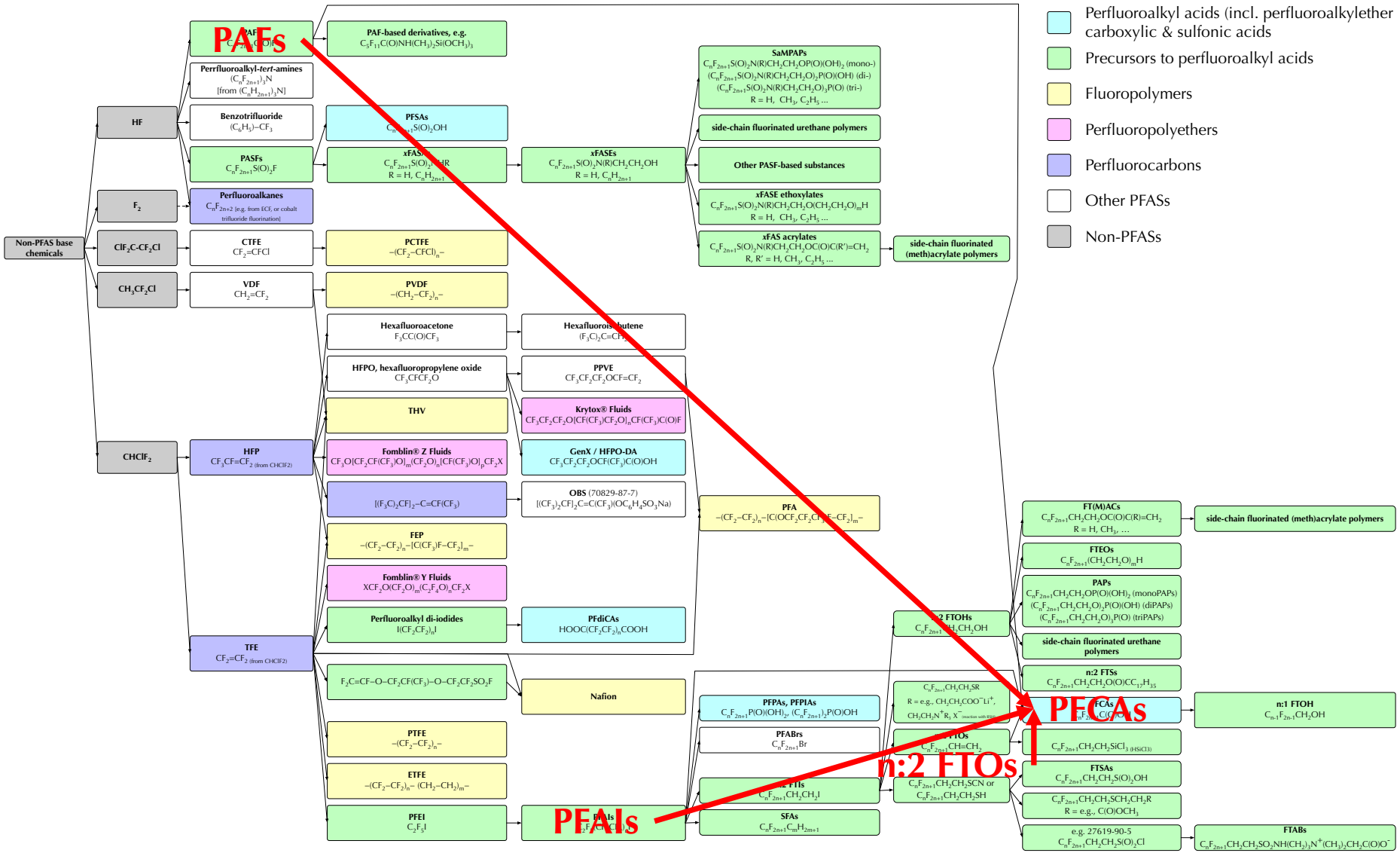
  → may contain homologues as impurities

How are PFASs Produced?



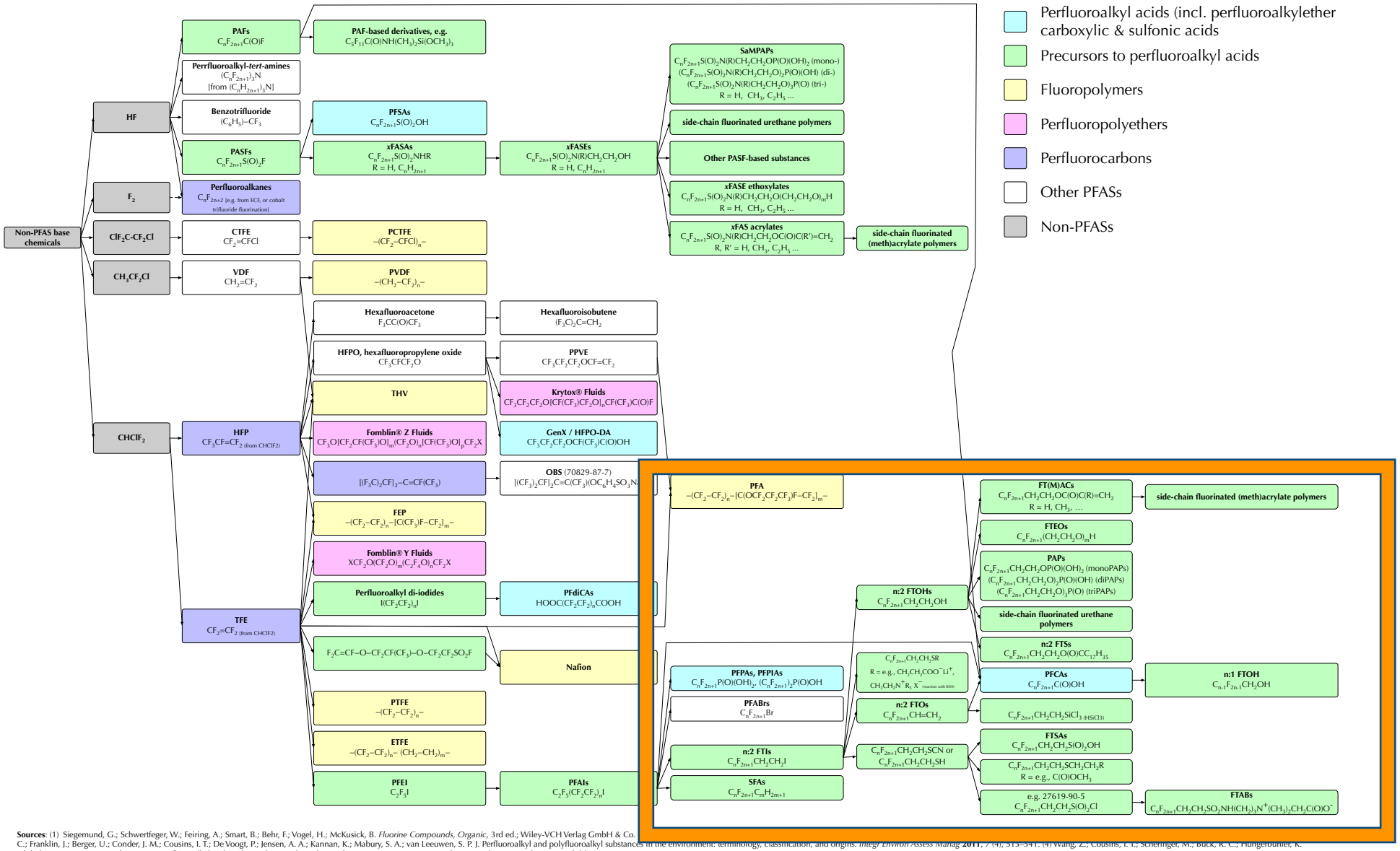
Sources: (1) Siegemund, G.; Schwertfeger, W.; Feiring, A.; Smart, B.; Behr, F.; Vogel, H.; McKusick, B. *Fluorine Compounds, Organic*, 3rd ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000; Vol. 33. (2) Banks, R. E.; Smart, B. E.; Tatlow, J. C. Organofluorine Chemistry: Principles and Commercial Applications. New York: Plenum, 1994. (3) Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; De Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integr Environ Assess Manag* **2011**, *7* (4), 513–541. (4) Wang, Z.; Cousins, I. T.; Scheringer, M.; Buck, R. C.; Hungerbühler, K. Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. *Environ Int* **2014**, *70*, 62–75.

How are PFASs Produced?



Sources: (1) Siegemund, G.; Schwertfeger, W.; Feiring, A.; Smart, B.; Behr, F.; Vogel, H.; McKusick, B. *Fluorine Compounds, Organic*, 3rd ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000; Vol. 33. (2) Banks, R. E.; Smart, B. E.; Tatlow, J. C. Organofluorine Chemistry: Principles and Commercial Applications. New York: Plenum, 1994. (3) Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; De Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integr Environ Assess Manag* **2011**, *7* (4), 513–541. (4) Wang, Z.; Cousins, I. T.; Scheringer, M.; Buck, R. C.; Hungerbühler, K. Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. *Environ Int* **2014**, *70*, 62–75.

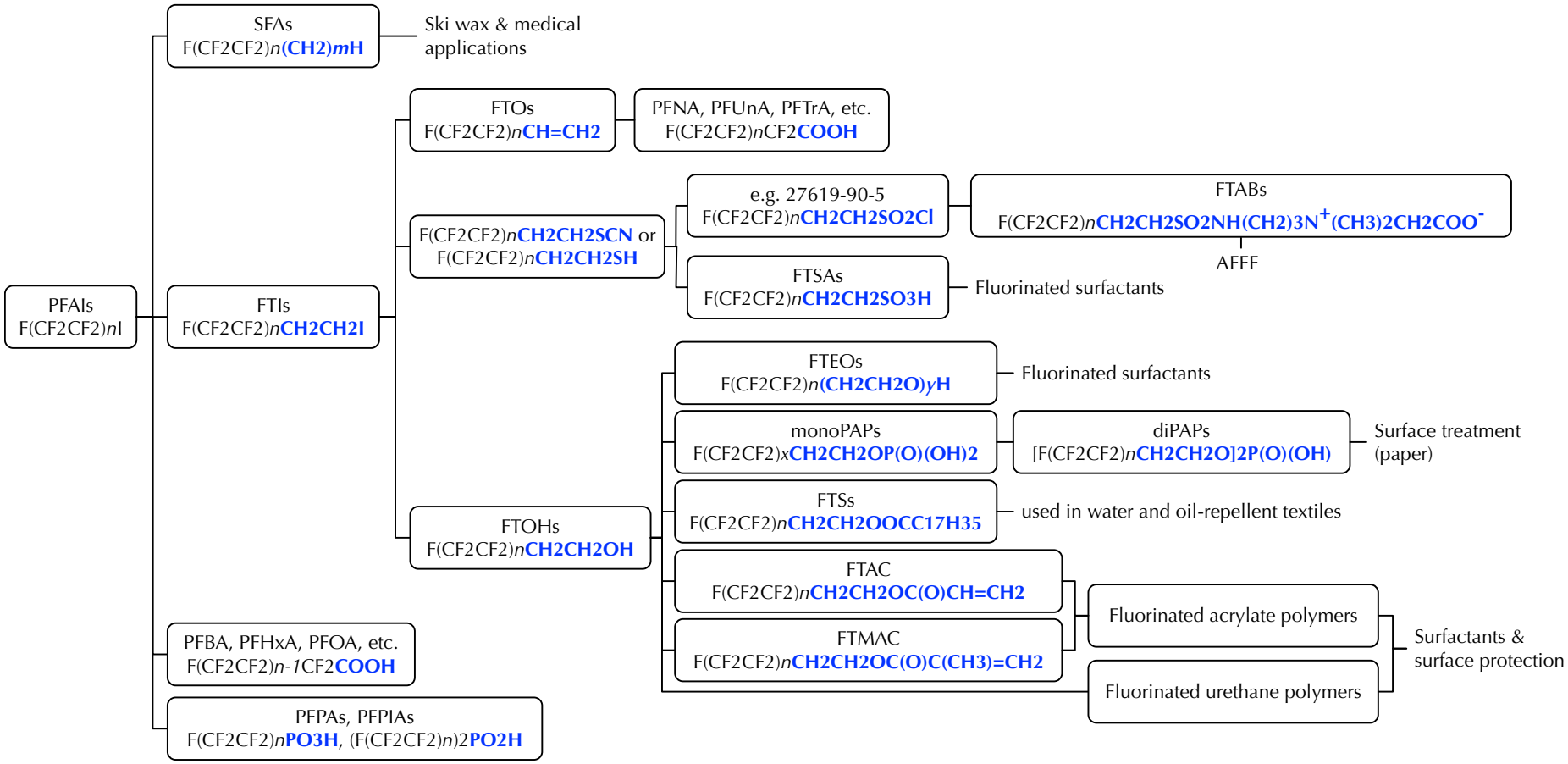
How are PFASs Produced?



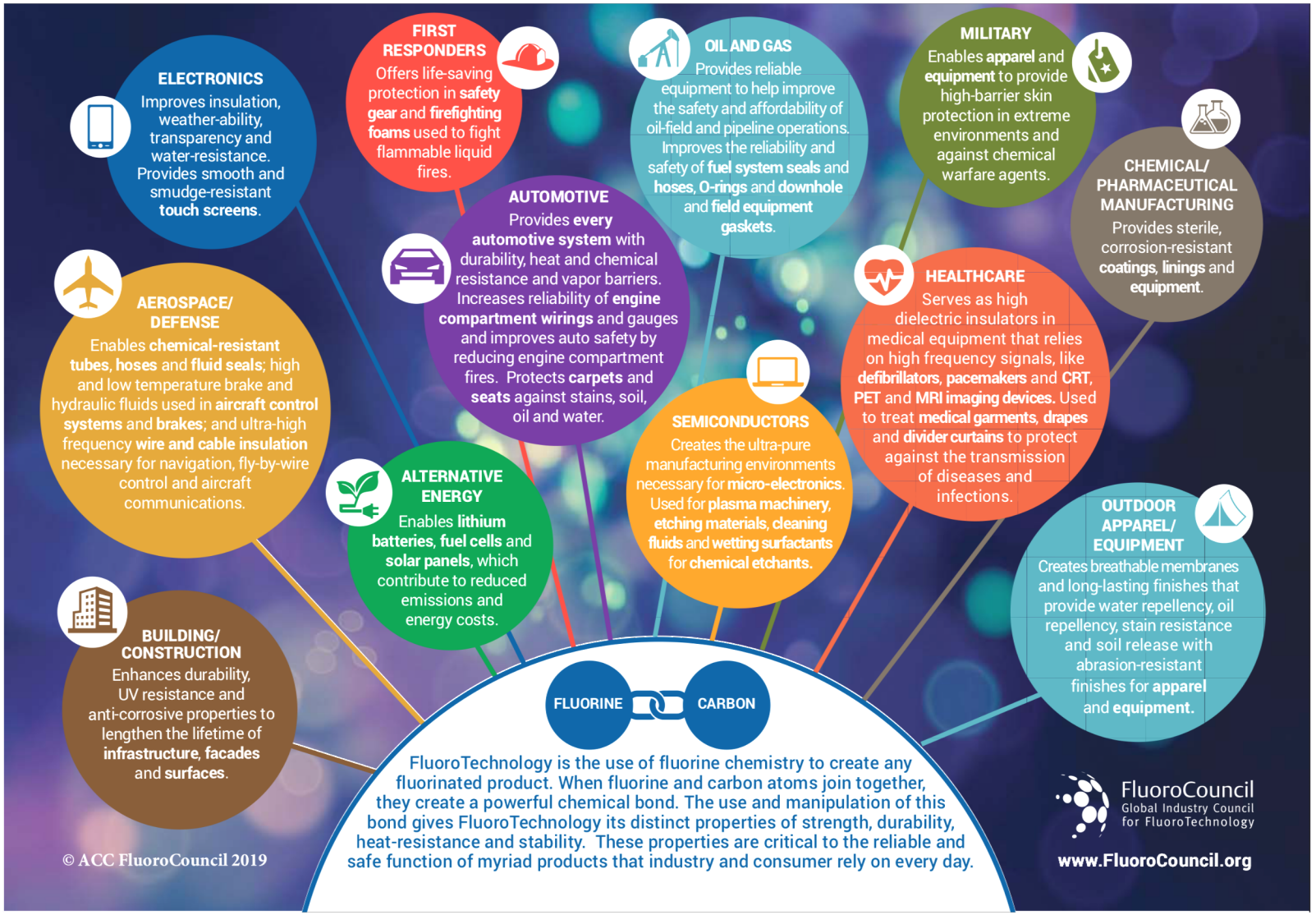
Sources: (1) Siegemund, G.; Schwertfeger, W.; Feiring, A.; Smart, B.; Behr, F.; Vogel, H.; McKusick, B. *Fluorine Compounds, Organic*, 3rd ed.; Wiley-VCH Verlag GmbH & Co. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; De Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integr Environ Assess Manag* **2011**, *7* (4), 513–541. (4) Wang, Z.; Cousins, I. T.; Scheringer, M.; Buck, R. C.; Hungerbühler, K. Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. *Environ Int* **2014**, *70*, 62–75.

How are PFASs Produced?

- Many PFAS-chemistries follow convention organic chemistry → very versatile



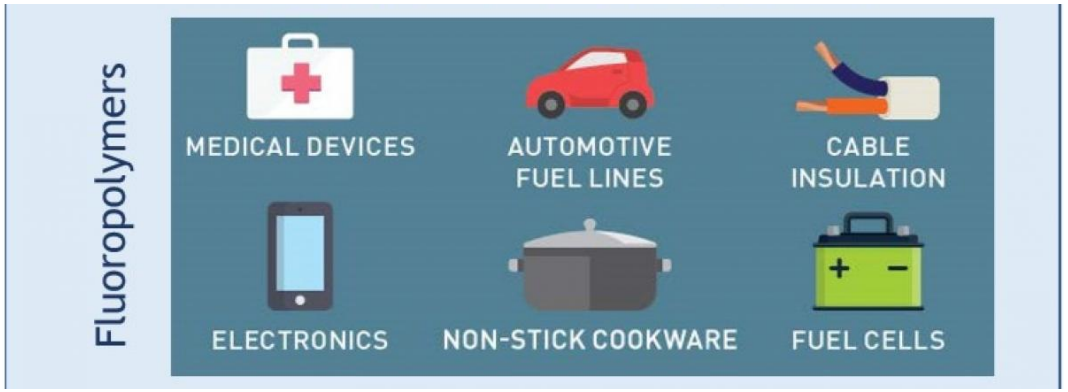
Major Uses of PFASs



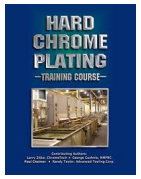
Aerospace
Alternative energy
Automotive
Building and construction
Chemicals and pharmaceutical
Electronics
First responders
Healthcare
Oil and gas
Outdoor apparel & equipment
Semiconductor, etc.
https://fluorocouncil.com/wp-content/uploads/2017/02/Fluoro-IG-compressed.pdf

Major Uses of PFASs

- **Major characteristics of PFASs, e.g.**
  - chemical and thermal stability, hydrophobic and oleophobic nature, good dielectric properties, etc.
- **PFASs have been and are used in a wide range of applications.**



PFAAs mainly as surfactants,
PACF-/PASF-/FT-based compounds as surfanctants or surface protectors (fluorepellents)



A new overview paper on the uses of PFASs is submitted to ESPI under Review

https://www.oaklodgewaterservices.org/surface-water/page/public-information-brief-pfas; https://engrxiv.org/2eqac/

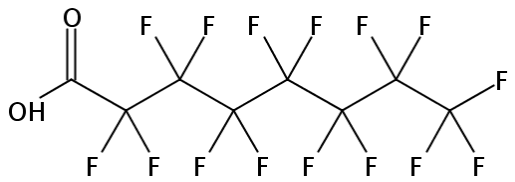
Current Global Trends of Production and Use

- There is **an ongoing industrial transition**, due to regulatory pressures

Developed Countries	Developing Countries
phase-out of production of long-chain PFCAs, PFSAs and their major precursors	**limited phase-out** of production of long-chain PFCAs, PFSAs and their major precursors, sometimes even **increased** production
some ongoing uses of long-chain PFASs in specific applications	ongoing uses of long-chain PFCAs, PFSAs and their major precursors with few limitations
transition to production and use of **novel and legacy** shorter-chain homologues or perfluoroalkylether-based substances (e.g., ADONA, HFPO-DA, etc.)	transition to production and use of **novel and legacy** shorter-chain homologues or perfluoroalkylether-based substances (e.g., F-53B)

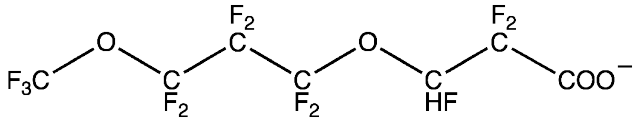
Current Global Trends of Production and Use

- **A proliferation of PFASs, e.g., as processing aids in the fluoropolymer production**

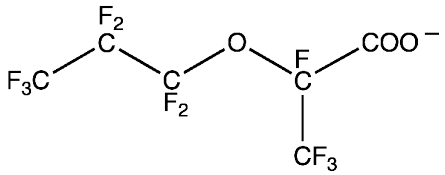


PFOA

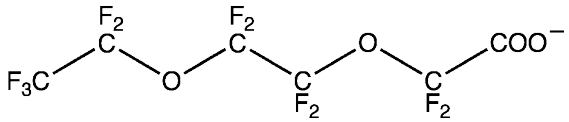
ADONA (CAS No. 958445-44-8)



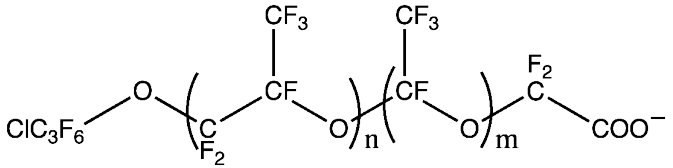
GenX (CAS No. 62037-80-3)



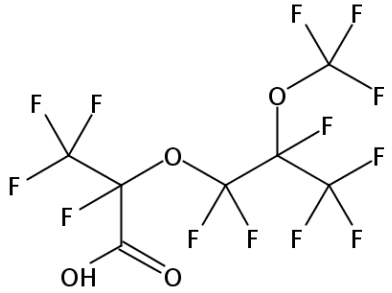
Asahi's product (CAS No. 908020-52-0)

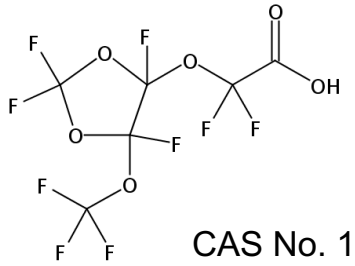


Solvay's product (CAS No. 329238-24-6)



Daikin's product (CAS No. 2479-73-4)





CAS No. 1190931-27-1

Current Challenges in Understanding PFAS Production and Use

- We know fairly well about the historical production and use of some fluoropolymers, long-chain PFCAs, PFSAs and some major precursors, including the volumes.

  → e.g. Wang et al. 2014a,b, 2016, 2017, 2020; Boucher et al. 2018; Glüge et al. 2020.

- However, for many other PFASs, **Limited to no** information reflect **in which time period, how, and in which amounts** they have been and are being produced and used.

- **Limited to no** information on **the occurrence and levels of production byproducts, unreacted residuals and degradation intermediates**.

Take-Home Messages

- **The PFAS universe is complex with thousands of compounds and different synthesis routes.** They have similarities in molecular structures, and also differences.
- Current work is ongoing to **revise the PFAS definition** and possibly **expand the common terminology** recommended by Buck et al. (2011).
- There is an ongoing industrial transition, both in developed and developing countries, on different paths though.
- For many PFASs, there is often **limited to no public information** on their production, uses and releases, sometimes even on their chemical identity. **Substantial resources have been invested to generate information that is already known by the industry** (e.g., identity, production, use).

→ The EU restriction may serve as an opportunity to reduce the complexity?

Acknowledgement

- Swiss Federal Office for the Environment (BAFU) for financial support
- My collaborators over the years: Konrad Hungerbühler, Martin Scheringer, Ian Cousins, Justin Boucher, Andreas Buser, Juliane Glüge, Xenia Trier, and many others!!

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Thank you for your attention!

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