



An Overview of the Problem with PFAS

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**Nordic Conference on PFAS Substitution, World Trade Center,
Stockholm, Sweden, 2 September 2024**

What are PFAS?

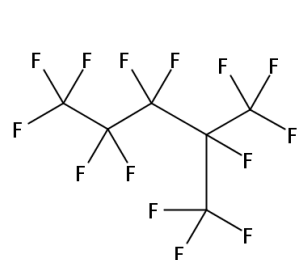
- **Buck et al. (2011)** – first class definition
 - **PFAS** = “the **highly fluorinated aliphatic substances** that contain **1 or more C atoms** on which all the H substituents ... have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety **$C_nF_{2n+1}-$** ” (has to contain at least **$-CF_3$**)
- **OECD:** broader definition
 - “...the fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom...” i.e. substances are PFAS that have **at least one $-CF_2-$ or $-CF_3$** moiety in their structure

Diversity of PFAS

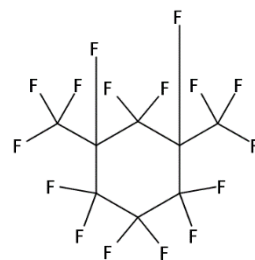
- Many thousands of **structurally diverse PFAS** in use in society
 - polymers & non-polymers; neutral, anionic, cationic & zwitterionic; solids, liquids & gases; reactive & inert; soluble & insoluble; volatile & involatile; mobile & immobile; bioaccumulative & non-bioaccumulative; highly toxic and relatively non-toxic
 - We don't know properties, toxicities etc. for most of them

Volatile neutral PFAS

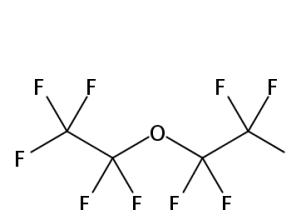
- Perfluoroalkanes (PFCs), perfluoroethers and perfluoroalkylamines



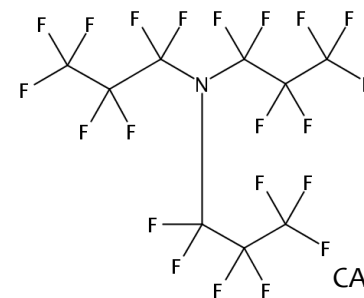
CAS No. 355-04-4



CAS No. 335-27-3

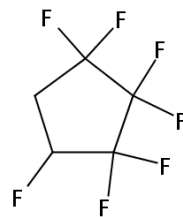


CAS No. 358-21-4

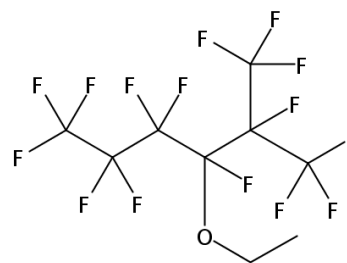


CAS No. 338-83-0

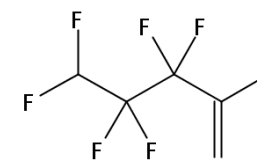
- Certain hydrofluoro-carbons (HFCs), -ethers (HFEs) and -olefins (HFOs)



CAS No. 15290-77-4



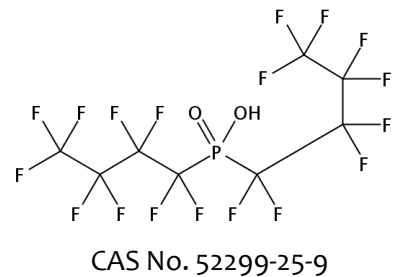
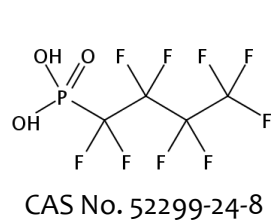
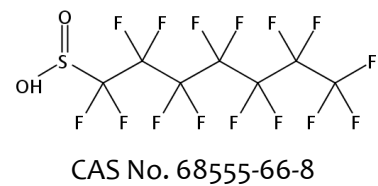
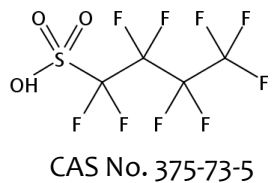
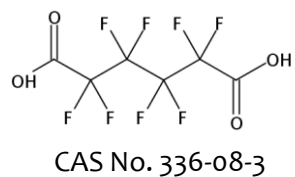
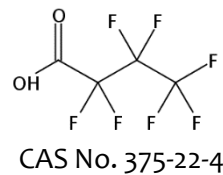
CAS No. 297730-93-9



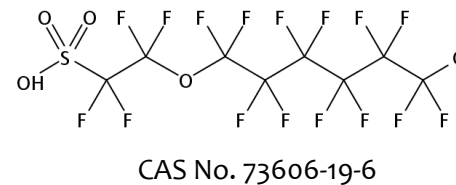
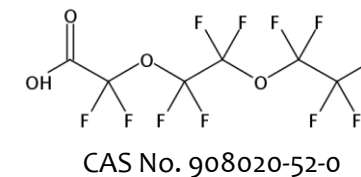
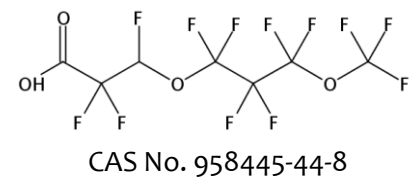
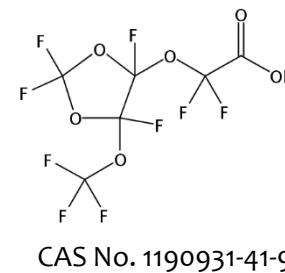
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Involatile anionic PFAS

- Per- and polyfluoroalkyl acids (PFAAs)

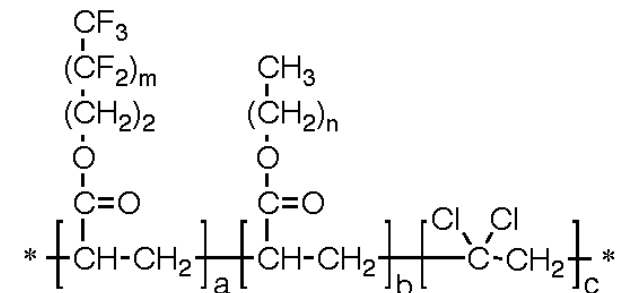


- Per- and polyfluoroalkylether acids



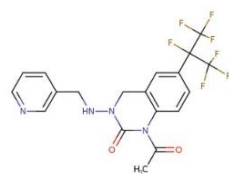
Fluorinated polymers

- Fluoropolymers (e.g. PTFE) (F in the backbone)
 - high molecular weight, stable, inert, insoluble, involatile, immobile, do not cross biological membranes, low leachables
- Side-chain fluorinated polymers (as used in textiles, carpets, food packaging)
 - non-fluorinated co-polymer backbone with fluorinated side chains
 - leachable PFAS, stable?

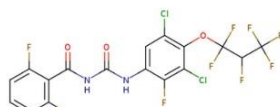


And many more: pesticides

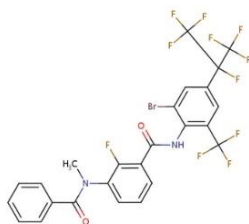
Highly Fluorinated



Pyrifluquinazon

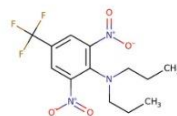


Noviflumuron

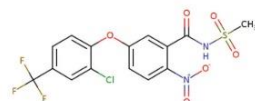


Broflanilide

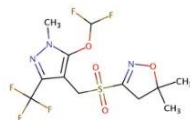
Highest Use



Trifluralin

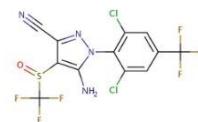


Fomesafen

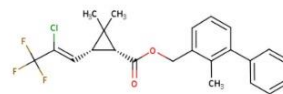


Pyroxasulfone

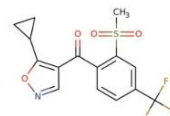
Known Water Contaminants



Fipronil

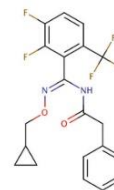


Bifenthrin

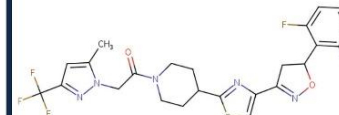


Isoxaflutole

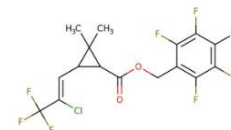
Fluorinated Aromatics



Cyflufenamid



Oxathiaprolin



Tefluthrin

"Inert" Ingredients



1,1,1,2-Tetrafluoroethane



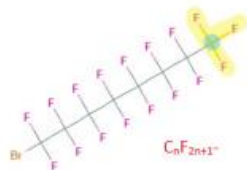
Polytetrafluoroethylene (PTFE)



Trans-1,3,3,3-tetrafluoroprop-1-ene

And many more: pharmaceuticals

A



Perflubron
CAS No. 423-55-2

B



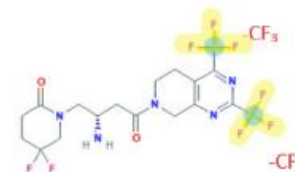
Enflurane
CAS No. 13838-16-9

C



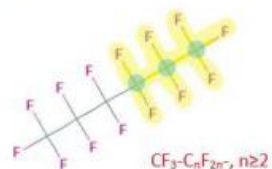
Alpelisib
CAS No. 1217486-61-7

D



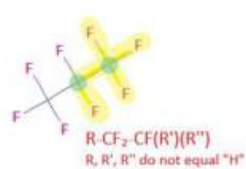
Gemigliptin
CAS No. 911637-19-9

E



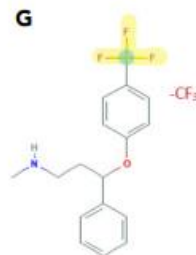
Perflexane
CAS No. 355-42-0

F



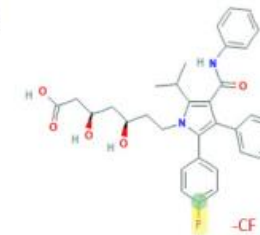
Perflutren
CAS No. 76-19-7

G



Fluoxetine (Prozac)
CAS No. 54910-89-3

H



Atorvastatin (Lipitor)
CAS No. 134523-00-5

Attempt to make comprehensive overview by OECD



So how many PFAS are there? It depends on how you count...

- **>7 million** on PubChem database
 - many only listed in patents
- ca. **14 000** in US EPA list
- ca. **10 000** in PFAS Restriction Proposal
- **1 670** with identified uses
 - Glüge et al. (2020) plus PFAS Restriction Proposal
- **531** are REACH registered (>1 tonne/a)

Global Production of PFAS

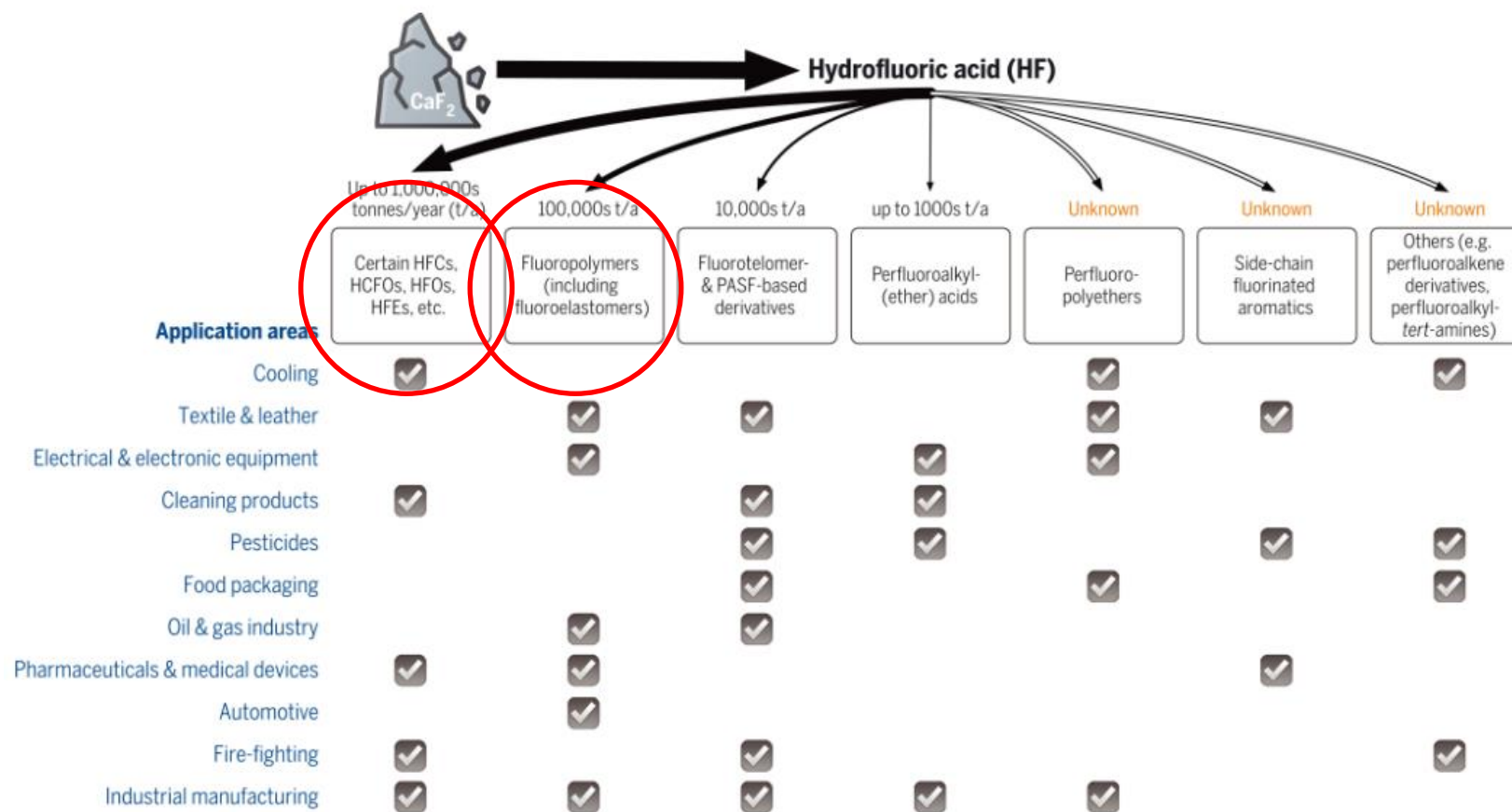
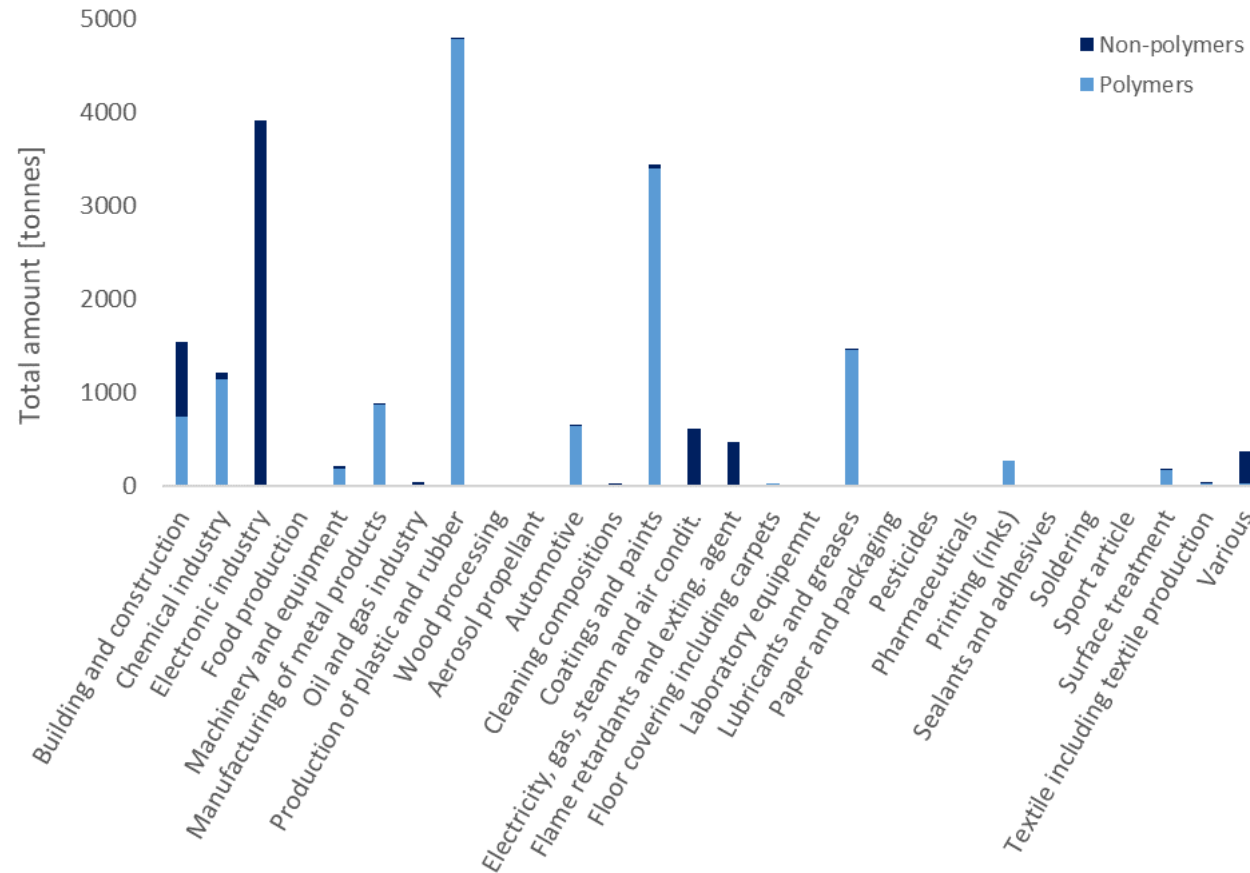


Fig. 1. Non-exhaustive summary of PFAS manufacturing, from production to consumer use.

Uses of PFAS?

(based on information in Substances in Preparations In Nordic countries (SPIN) database)



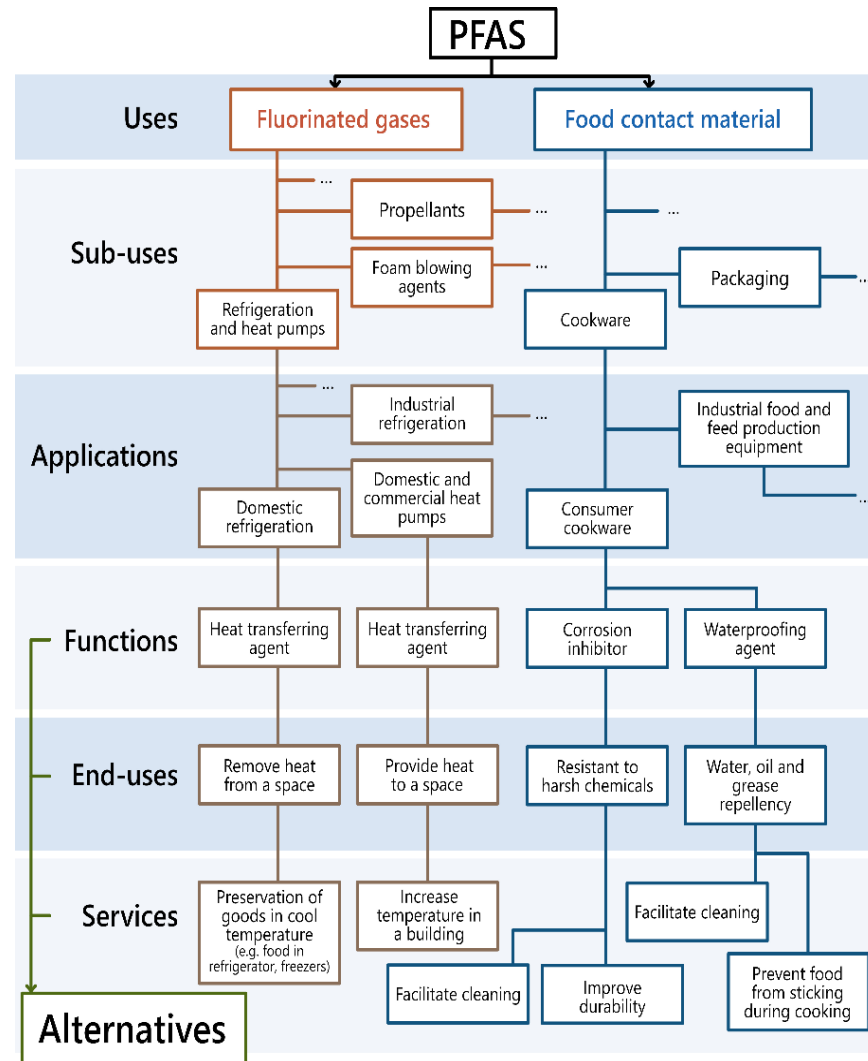
- More than 200 uses identified for more than 1400 PFAS
- Polymers dominate uses

Common features of PFAS that make them so useful

- Major characteristics of perfluoroalkyl moieties:
 - **high thermal and chemical stability** due to the strength of C-F bond
 - **hydrophobic** and **oleophobic** nature
- Especially useful as:
 - **Fluorosurfactants**
 - can lower the surface tension of water to 16 mN/m (half that compared to hydrocarbon surfactants)
 - **Surface protectors**
 - very low surface energies compared to hydrocarbon-based or silicone polymers, simultaneous water and oil/stain repellence

PFAS uses and alternatives database

- Database divided per use category of PFAS
- For each use category:
 - List of applications of PFAS along with the technical function, end use function and service function
 - List of PFAS substances identified as being used for each application
 - List of identified potential alternatives to PFAS for each application



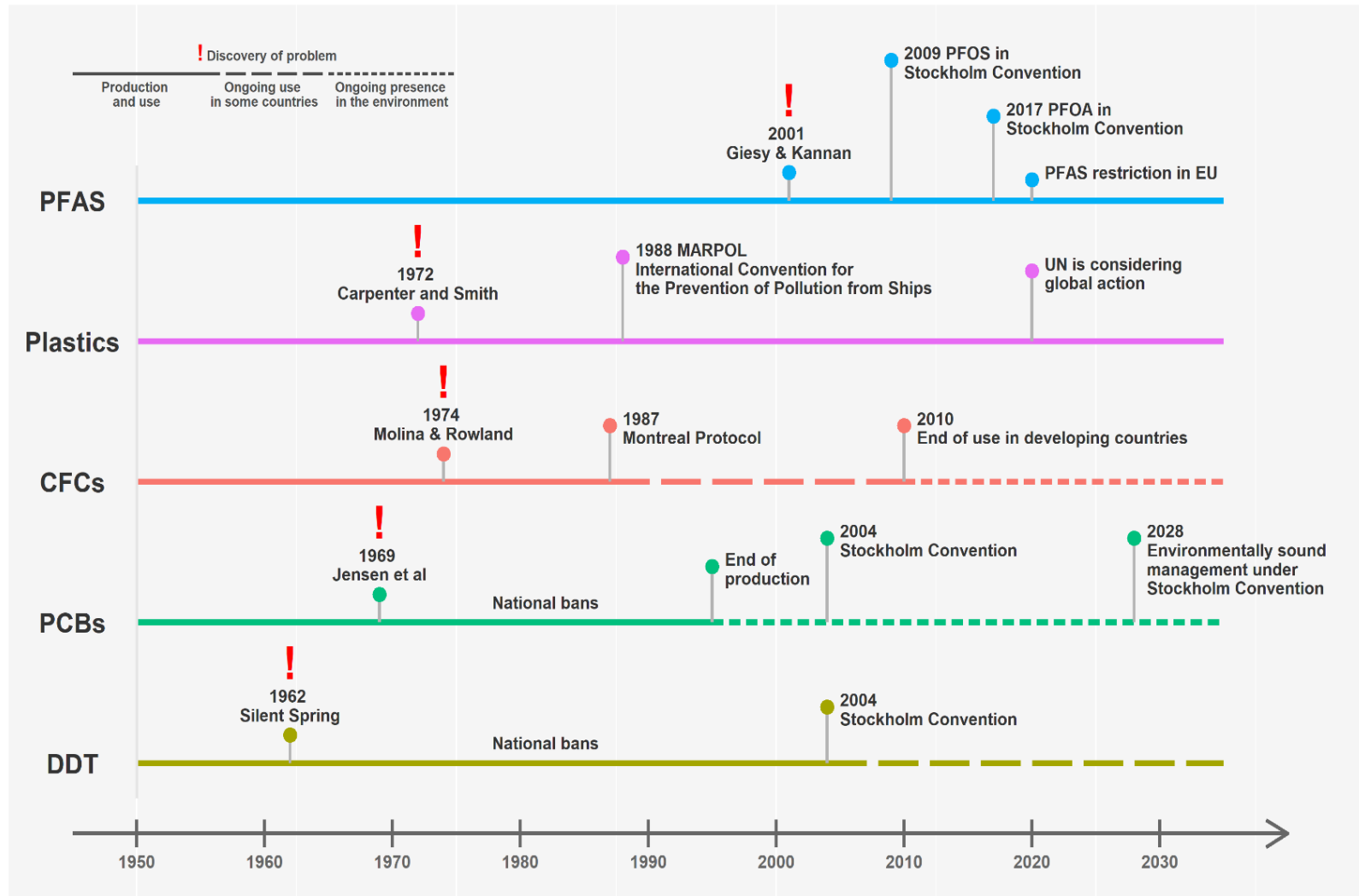
Madrid Statement

- Published in 2015
- Signed by 250 scientists from 38 countries
- Production and use of PFAS should be limited
- But are all PFAS problematic?
 - they have diverse properties, right?

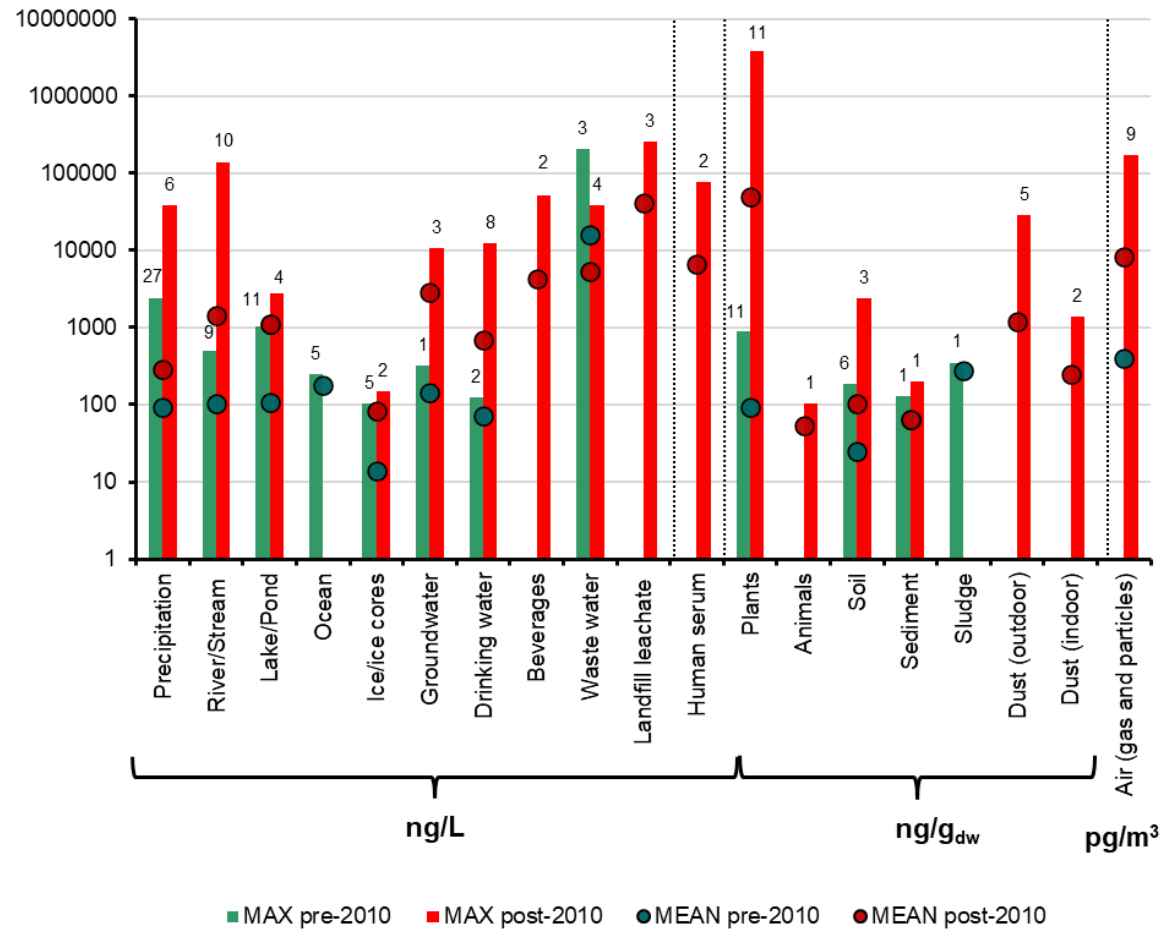
Are all PFAS of concern?

- **All PFAS are very persistent (vP)** (EU REACH)
 - they are either non-degradable or transform into stable terminal transformation products
 - they are all **extremely P** with no environmental degradation observed, due to C-F bonds
- Continual release of high P chemicals results in increasing levels and increasing probabilities of known and unknown effects. Exposure poorly reversible

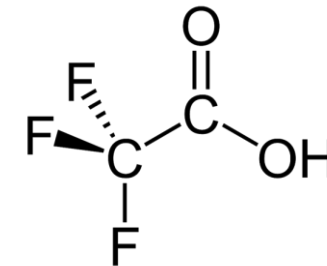
Problems with high persistence



TFA the “poster child” for the problem with high persistence



TFA concentrations in different media before 2010 (in green) and after 2010 (in red).



TFA – trifluoroacetic acid

Sources of TFA?

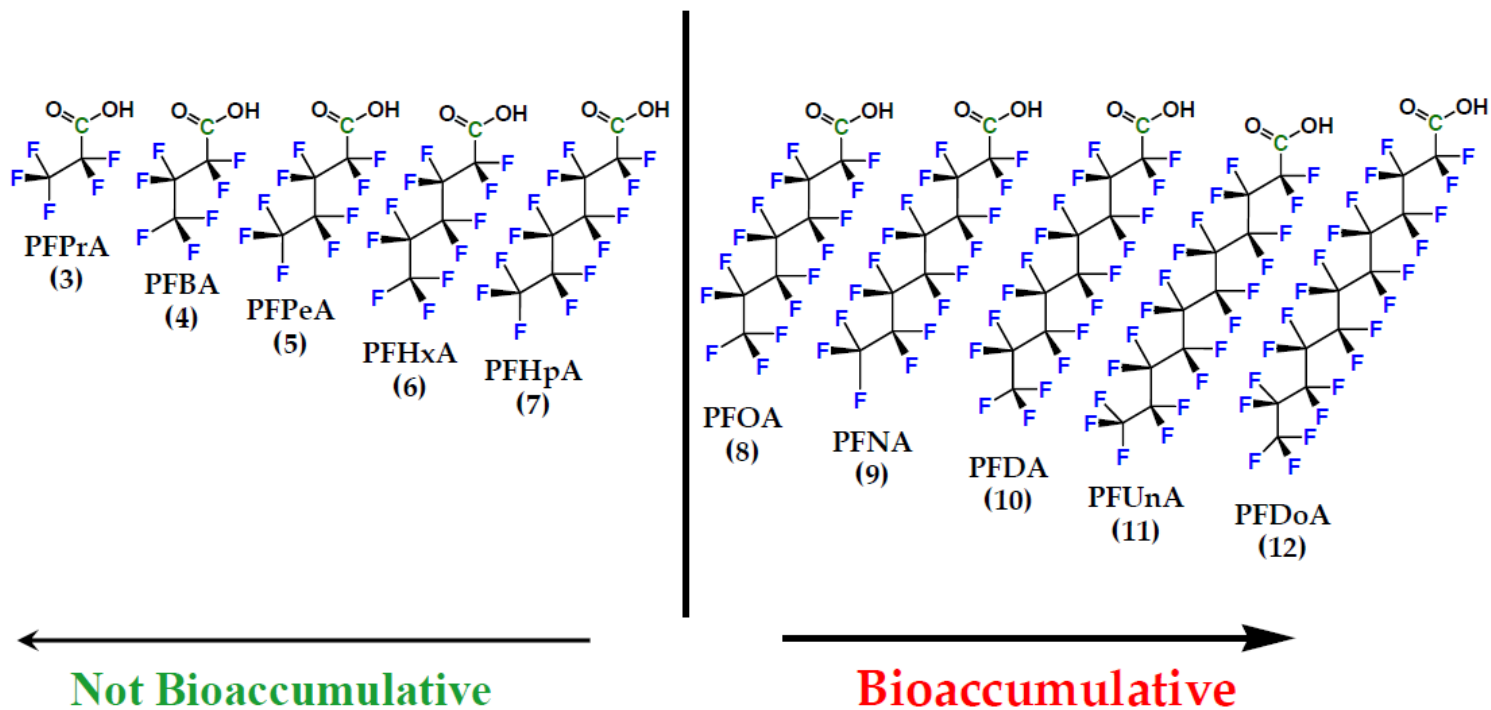
- Many “precursors”
 - refrigerants, pesticides, pharmaceuticals and other industrial chemicals
 - HFO-1234-yf, used as refrigerant, is a notable precursor
 - emissions of HFO-1234-yf projected to increase by factor of 7 between 2020 and 2050
- Destructive treatments of PFAS can also be a source of TFA (e.g. oxidation, incineration, electrolysis).
- Emissions hotspots include AFFF-contaminated sites, landfills and fluorochemical production facilities.

Are all PFAS of concern?

- Understand the toxicity (**T**) of about 4 PFAS well i.e. PFOS, PFHxS, PFOA, PFNA
 - i.e. increased cholesterol, **reduced vaccination efficiency in children**, reduced duration of breastfeeding, kidney and testicular **cancer**, decreased liver function, type 2 diabetes, osteoporosis, reduced birthweight, etc., etc.
 - less focus on ecotoxicology, but increasing
- PFAS with longer perfluoroalkyl chains are bioaccumulative (**B**)
- Some replacement PFAS are mobile (**M**) and toxic (**T**) (e.g. HFPO-DA/GenX)

Not all PFAS are bioaccumulative

Long-chain perfluoroalkyl acids are bioaccumulative



Bioaccumulation in humans

PFAS accumulation in humans

PFOA and PFOS in human serum

On average, serum concentrations of PFOA and PFOS in general populations from the US and European countries appear to be below 10 ng/mL (CDC & EFSA).

However, people living in areas with point sources and those who work with PFAS, have blood concentrations 100s to 1000s times higher than concentrations of those in the general population.



- Exposure from food, drinking water, dust and consumer products
- Significant fraction of organofluorine in human blood which is unexplained!

Mobility (**M**): a new regulatory paradigm

- Protects drinking water sources
- If chemicals **vP** and **vM**, or **P** and **M** and **T** then considered inherent hazards
 - New hazard class for CLP regulation, 20 April 2023.
- **M** in soil and water assessed by sorption to organic matter
 - organic carbon-water partition coefficient: K_{OC}
 - **M**: $\log K_{OC} < 4$, **vM**: $\log K_{OC} < 3$

Are fluoropolymers a problem?

- Fluoropolymers (e.g. PTFE)
 - high molecular weight, stable, inert, insoluble, involatile, immobile, do not cross biological membranes, low leachables
- Emissions during lifecycle
 - emissions of known and unknown PFAS during manufacturing
 - emissions of low molecular weight PFAS during incineration

Conclusions

- High persistence underlying driver of Nordic and global PFAS problems
 - driver for ubiquitous, long-lasting presence
- Continuous release will lead to accumulation somewhere in the environment until some known or unknown effect threshold is exceeded
- Solutions are:
 - Use of PFAS limited to so-called “essential uses”
 - Safe and Sustainable by Design (SSbD) principles to design/use less persistent and safer alternatives

Acknowledgements

Thanks to my research group, collaborators and funding from the European Union (ZeroPM) and FORMAS (grant number: 2020-01978).



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101036756.



<https://zeropm.eu/>

Reference list

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Slide 8: <https://www.sciencedirect.com/science/article/pii/S2589004222002905>

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Slide 10: <https://pubs.rsc.org/en/content/articlelanding/2020/em/d0em00291g> and
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Slide 14: <https://zeropm.eu/alternative-assessment-database/>

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Slide 21:

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Slide 24: Slide <https://setac.onlinelibrary.wiley.com/doi/10.1002/ieam.4035>,
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