The concept of essential use of Per- and Poly-fluoroalkyl Substances (PFAS)

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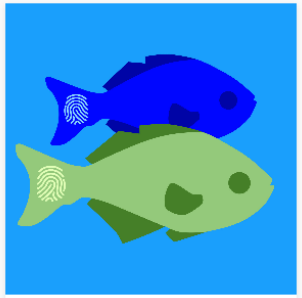

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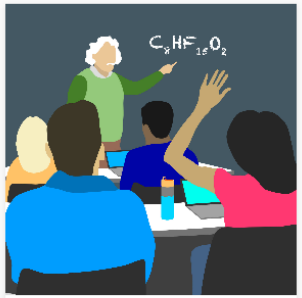

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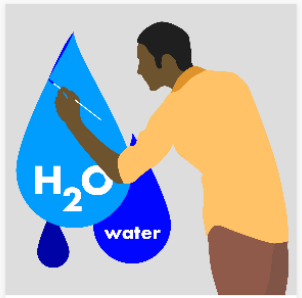

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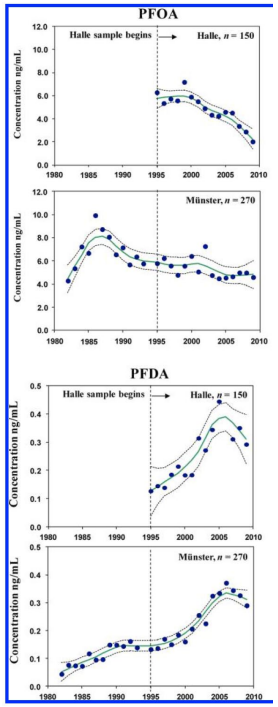
Concern about PFASs

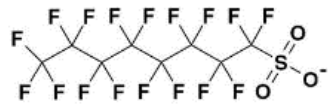
- Widespread human and environmental exposure
  - Particularly perfluorinated C_8 compounds – PFOS and PFOA (Yeung et al., 2013)

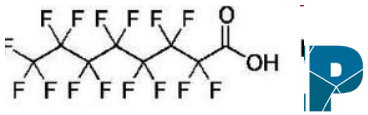


- Wide range of adverse effects (humans/animals)
  - Immunosuppression (DeWitt et al., 2008; Grandjean et al., 2013)
  - More PFOA, higher risk of being overweight (Haldersson et al., 2012)
  - Link [PFOA] in blood and insulin resistance (Timmermann et al., 2014)

- Regulatory action (PFOS withdrawal and PFOA action plan)

- Replacement with other fluorinated compounds (shorter, polyfluorinated; more complex molecules - precursors)





1000s of PFAS
100s produced *
10s monitored
2 targeted (EPA)

- Categories:

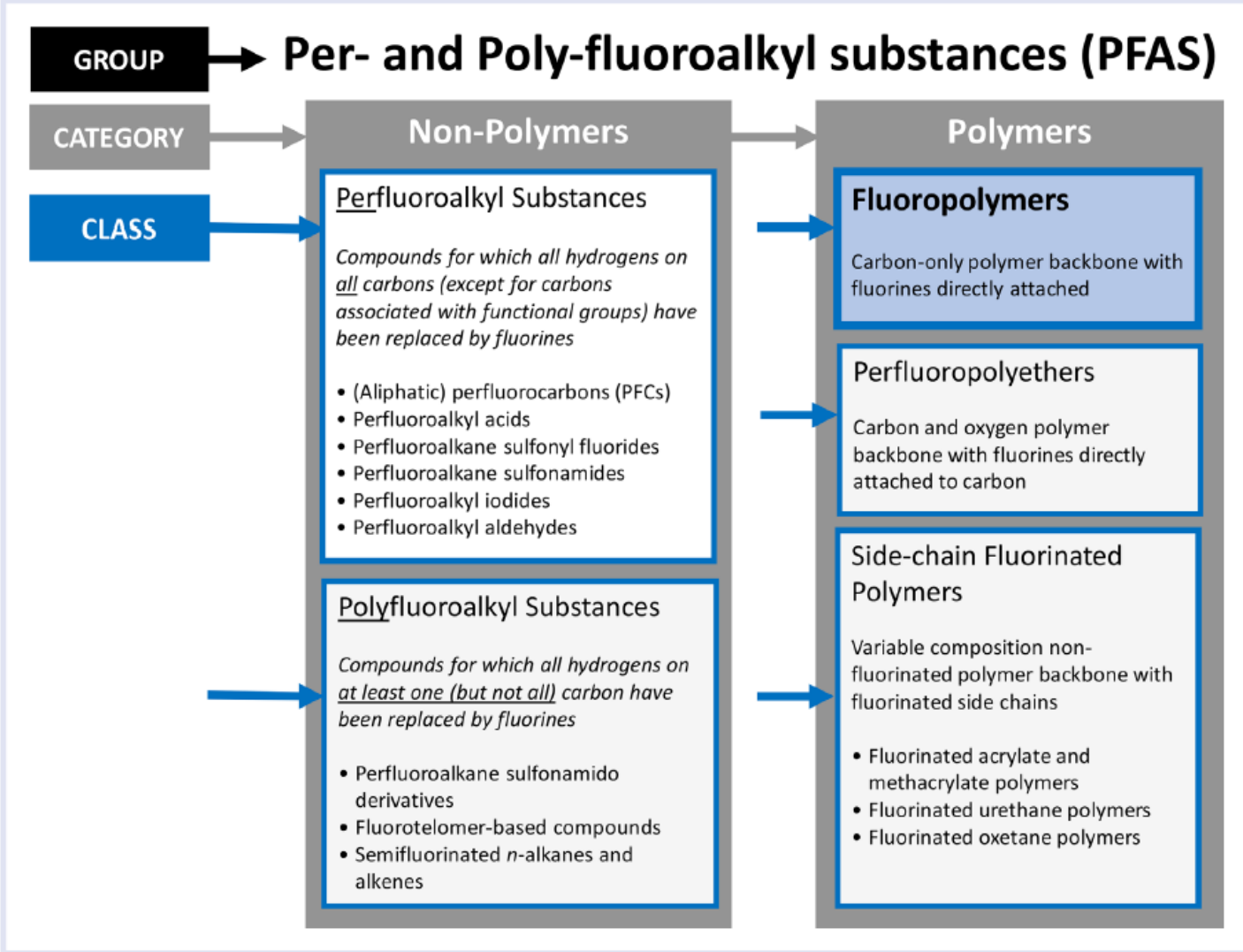


Figure 1. Per- and polyfluoroalkyl substances (PFAS).

The known unknowns are getting us

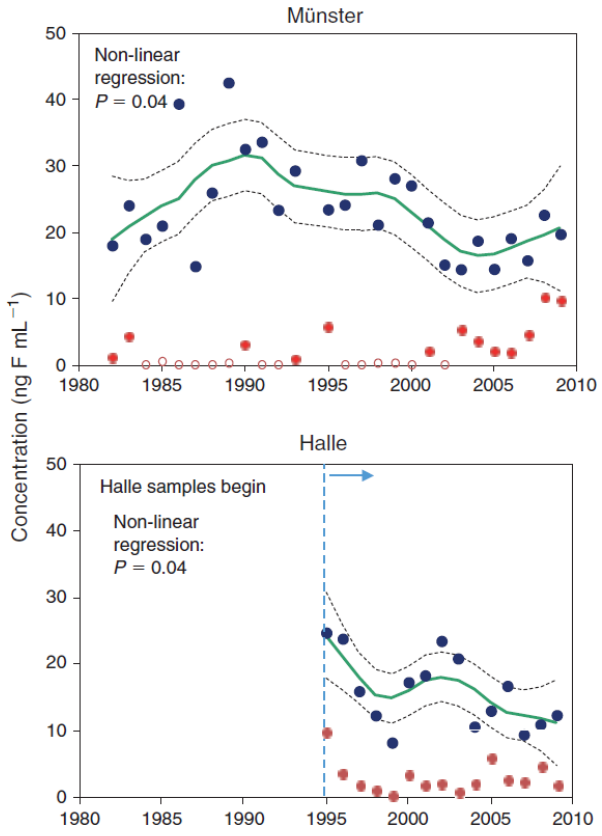


Fig. 3. Temporal trends of extractable organofluorine (EOF) and unidentified organofluorine concentrations (ng F mL^{-1}) in German plasma. (Blue dot indicates the mean value of EOF, dotted line indicates the 95 % confidence interval of the trend and green line indicates the trend generated using locally weighted regression smoother (LOESS); red dot indicates the mean value of unidentified organofluorine; open red dots indicates no unidentified organofluorine.)

Fig. 4. Composition and concentrations (ng F mL^{-1}) of extractable organofluorine (EOF) in German blood plasma samples (perfluorooctane sulfonate, PFOS; perfluoroalkyl sulfonate, PFSA; perfluorinated carboxylates, PFCAs; perfluorinated phosphinates, PFPiAs).

(Yeung and Mabury, 2016)

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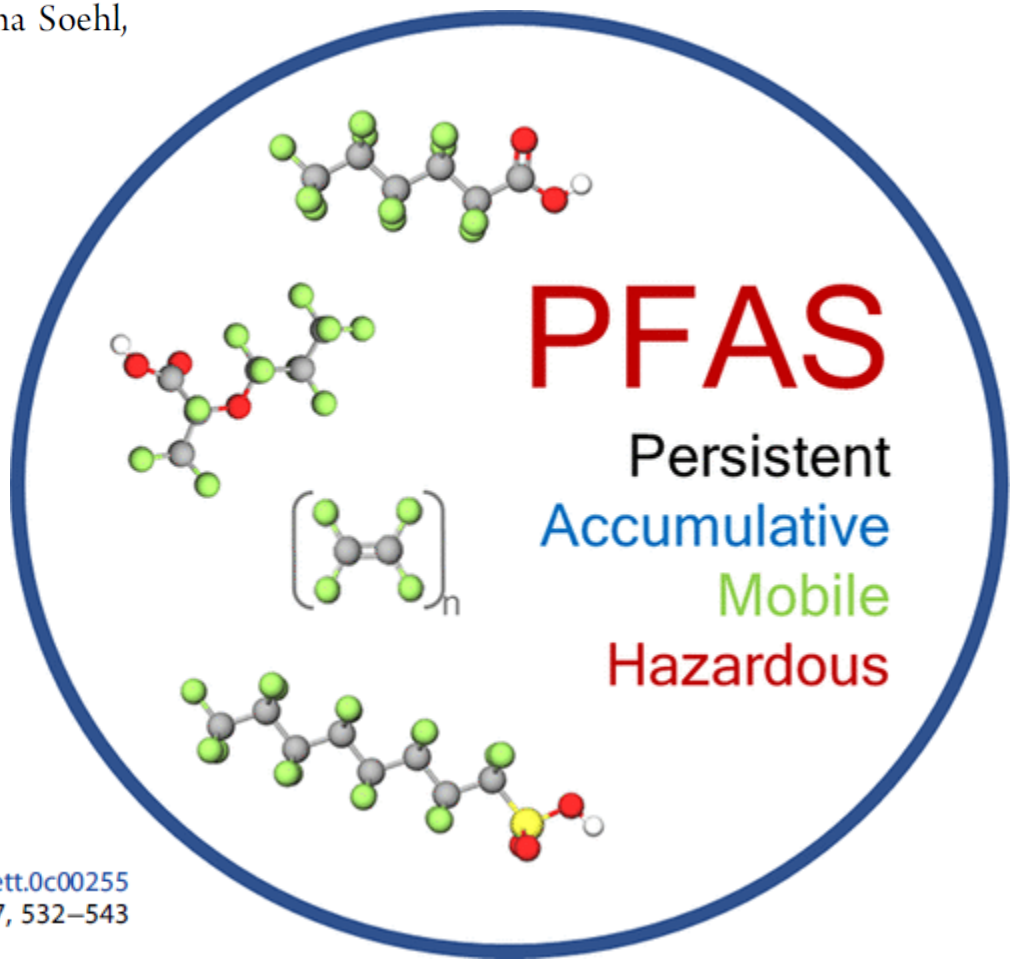
1 option – PFAS as a class

Scientific Basis for Managing PFAS as a Chemical Class

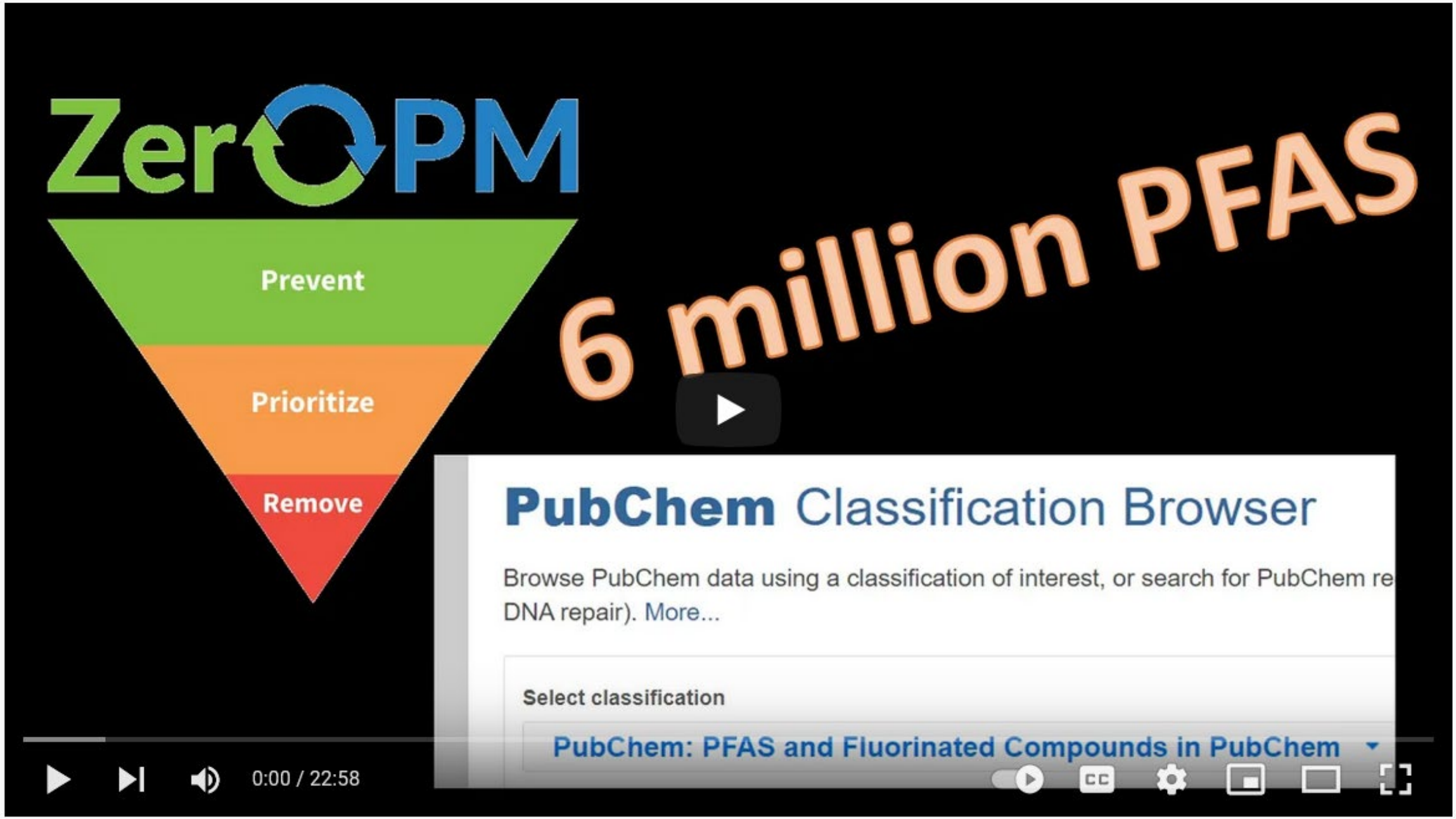
Carol F. Kwiatkowski,* David Q. Andrews, Linda S. Birnbaum, Thomas A. Bruton, Jamie C. DeWitt, Detlef R. U. Knappe, Maricel V. Maffini, Mark F. Miller, Katherine E. Pelch, Anna Reade, Anna Soehl, Xenia Trier, Marta Venier, Charlotte C. Wagner, Zhanyun Wang, and Arlene Blum

Box Key Messages

1. Per- and polyfluoroalkyl substances (PFAS) make up a class of extremely persistent chemicals, numbering in the thousands, that accumulate in the environment and living organisms and can be highly mobile, leading to global contamination.
2. The use of PFAS in numerous consumer and industrial applications has led to widespread human and environmental exposure from, for example, drinking water, food, and consumer products.
3. Toxicological and epidemiological studies have identified a broad range of adverse health outcomes associated with exposure to PFAS in people and animals.
4. We suggest a class-based approach to managing the human and environmental risks associated with all PFAS, including polymers.
5. We provide options for how governments and industry can apply the class-based approach, emphasizing the importance of eliminating non-essential uses of PFAS, and further developing safer alternatives and methods to remove all existing PFAS from the environment.



https://dx.doi.org/10.1021/acs.estlett.0c00255
Environ. Sci. Technol. Lett. 2020, 7, 532–543



#PFAS #PMT #Zeropollution

Navigating over 6 million PFAS! A walk through the PFAS tree with Emma Schymanski

Products that do or did contain PFAS

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Image source: www.sixclasses.org/videos/highly-fluorinated-chemicals.

PFAS are in over 60 different use categories

Are all of these uses essential?

Personal care products/cosmetics	Ski waxes	Fire-fighting foams	Apparel
Waterproof clothing	Easy care clothing	Food contact materials	Food production equipment
Medical devices	Pharmaceuticals	Laboratory supplies	Carpets and furniture
Cleaning products	Paint and lacquers	Pesticides	Sealants
These are only a few of the known use categories for PFAS.			

What is an essential use for a PFAS?

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CRITICAL REVIEW

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Cite this: DOI: 10.1039/c9em00163h

The concept of essential use for determining when uses of PFASs can be phased out

Ian T. Cousins, †*[a] Gretta Goldenman,[b] Dorte Herzke,[c] Rainer Lohmann,[d] Mark Miller,[e] Carla A. Ng,[f] Sharyle Patton,[g] Martin Scheringer,[h] Xenia Trier,[i] Lena Vierke,[j] Zhanyun Wang[k] and Jamie C. DeWitt[l]

Based on these definitions, how many use categories can we define for PFAS?

Based on the Montreal Protocol, which defined the concept of essential use for chlorofluorocarbons (CFCs).

- An essential use is a use necessary for health or safety or for the functioning of society.
- An essential use is a use for which there are no available technically and economically feasible alternatives.

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We had a gaping hole

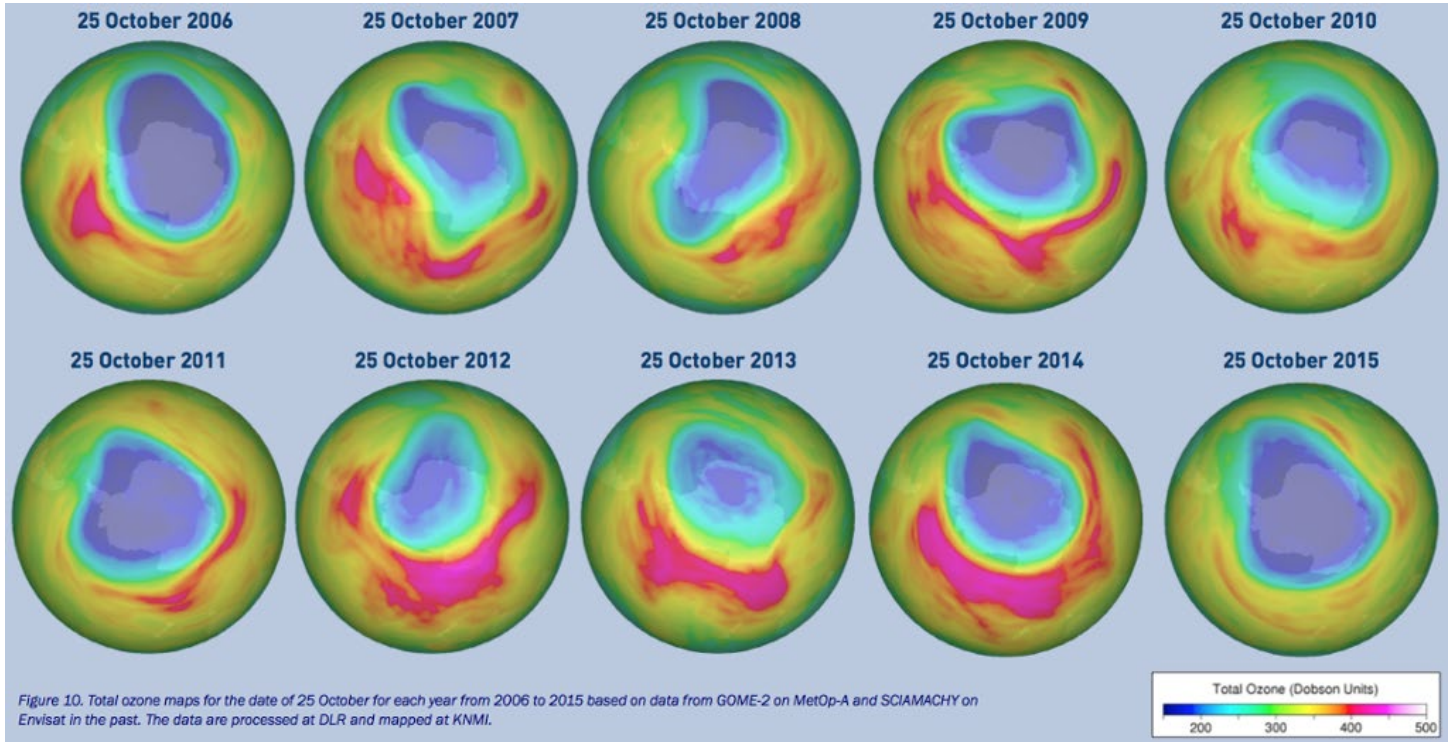


Figure 10. Total ozone maps for the date of 25 October for each year from 2006 to 2015 based on data from GOME-2 on MetOp-A and SCIAMACHY on Envisat in the past. The data are processed at DLR and mapped at KNMI.

Adopted on 15 September 1987, the Protocol is to date the only UN treaty ever that has been ratified every country on Earth - all 198 UN Member States.

Photograph: WMO

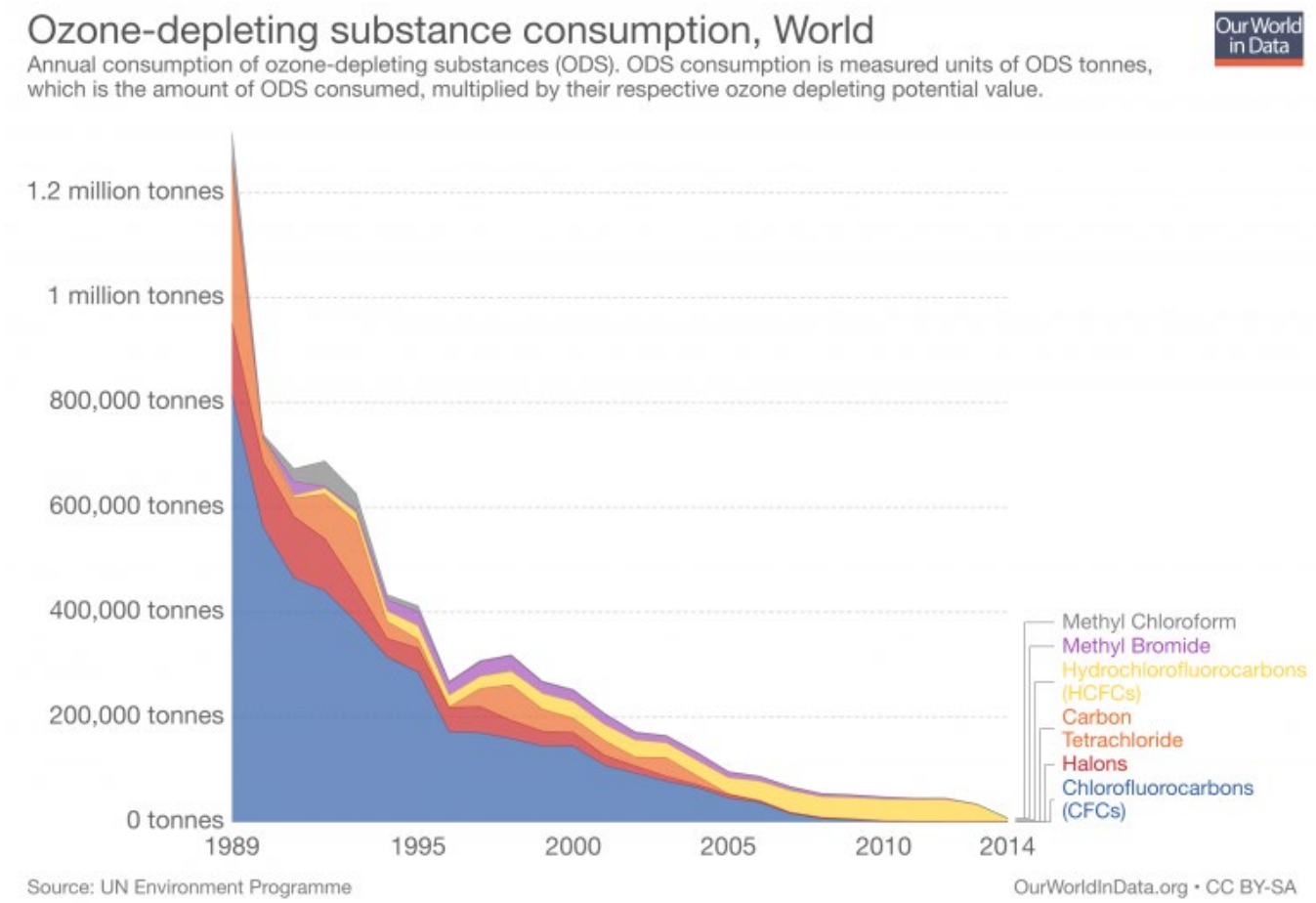
For background – ozone had gone missing

Sequential progress,

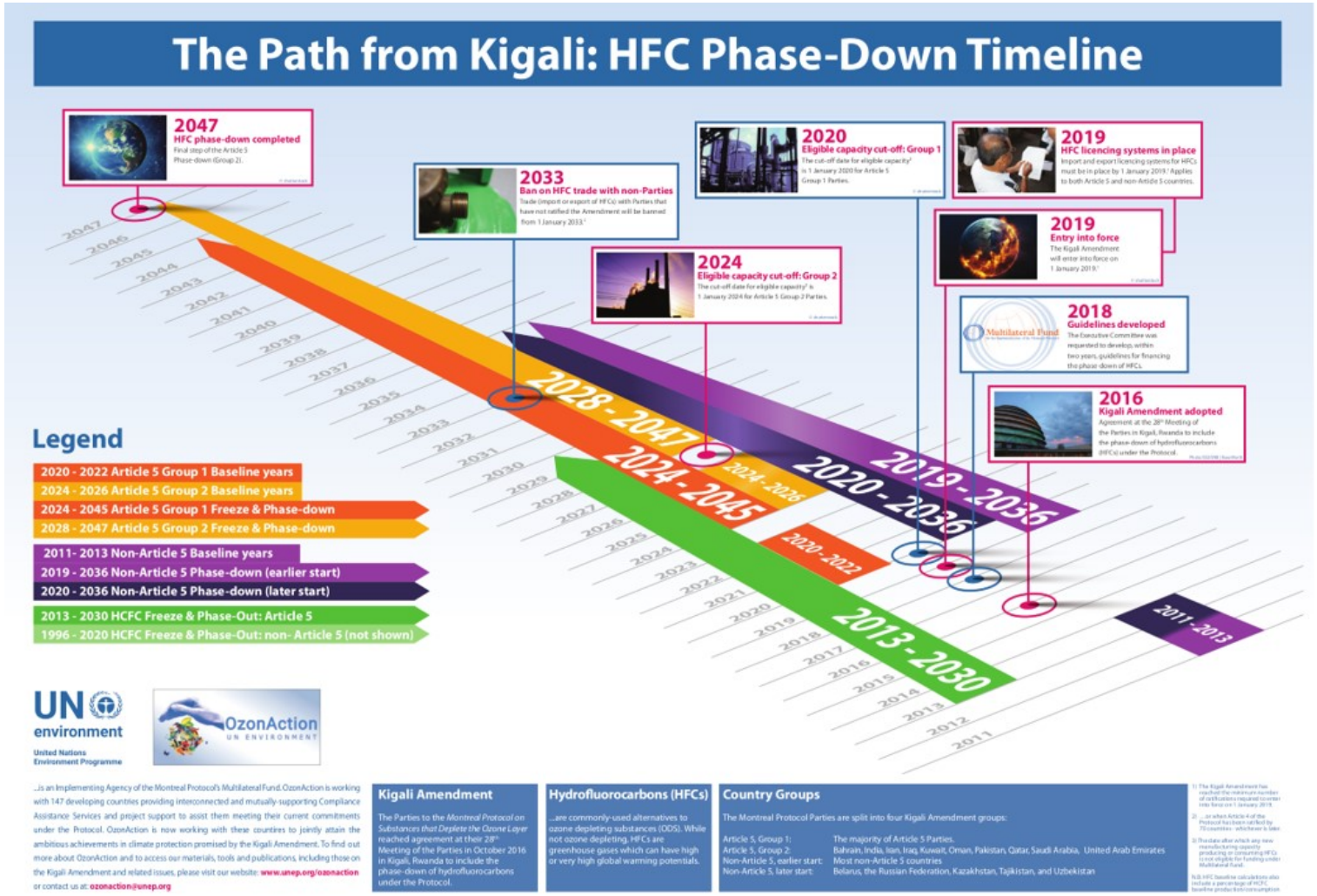
not simply regrettable substitutions:

- CFCs (MP)

- HCFCs (Montreal Amendment)
- HFCs (Kigali Amendment)



Leading the way



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Essential use concept for PFAS

Table 1 Three essentiality categories to aid the phase out of non-essential uses of chemicals of concern, exemplified with PFAS uses

Category	Definition	PFAS examples
(1) "Non-essential"	Uses that are not essential for health and safety, and the functioning of society. The use of substances is driven primarily by market opportunity	Dental floss, water-repellent surfer shorts, ski waxes
(2) "Substitutable"	Uses that have come to be regarded as essential because they perform important functions, but where alternatives to the substances have now been developed that have equivalent functionality and adequate performance, which makes those uses of the substances no longer essential	Most uses of AFFFs, certain water-resistant textiles
(3) "Essential"	Uses considered essential because they are necessary for health or safety or other highly important purposes and for which alternatives are not yet established[a]	Certain medical devices, occupational protective clothing

[a] This essentiality should not be considered permanent; rather, a constant pressure is needed to search for alternatives in order to move these uses into category 2 above.

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Table from: Cousins et al. 2019. Environmental Science: Processes & Impacts. DOI: 10.1039/c9em00163h

Table 2 Essentiality of PFASs in selected use categories

Use	Table 1 Category[a]
Personal care products including cosmetics	1
Ski waxes	1
Fire-fighting foams (commercial airports)	2
Fire-fighting foams (military)	2 or 3
Apparel (medical: long operations)	3
Apparel (protective clothing oil and gas industry)	3
Apparel (medical: short operations, everyday)	2
Apparel (military: occupational protection)	2 or 3
Waterproof jacket (general use)	2
Easy care clothing	1
Food contact materials	1, 2 or 3
Non-stick kitchenware (fluoropolymers)	1 or 2
Medical devices (fluoropolymers)	1, 2 or 3
Pharmaceuticals	2 or 3
Laboratory supplies, equipment and instrumentation	1, 2 or 3
Perfluorosulfonic membranes in fuel cells	2
Perfluorosulfonic membranes in chlor-alkali process	3

[a] Note that the categories in the above table represent the current evaluation and may change in the future.

Essential use concept for PFAS

"When considering chemical alternatives for PFASs, the focus should be on the service the product should deliver. The compound should therefore be evaluated for performance using the specifications required for the product as opposed to comparing directly to the PFAS being replaced…

Additionally, the potential for health hazard and potential for exposure…must be considered…"

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Table from: Cousins et al. 2019. Environmental Science: Processes & Impacts. DOI: 10.1039/c9em00163h

PFAS in personal care products and cosmetics such as hair products, powder, sun blocks, and skin creams.

PFAS do not appear to confer an essential function to these products and presence leads to direct human exposure to PFAS.

Decision of major retailers/brands to phase-out PFAS indicates that alternatives have been readily available.

Category 1 – non-essential

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PFAS in leisure clothing for water repellency.

PFAS in certain applications, such as polytetrafluoroethylene (PTFE) breathable membranes appear to be essential for water repellency.

Alternatives to PFAS are available (and on the market), including waxes, silicones, and hydrocarbons.

Category 2 – substitutable

PFAS in protective clothing for certain types of health care activities and for firefighter turn-out gear appears to be essential.

Category 3 – essential

However, R&D is warranted to identify safer alternatives to PFASs in these applications.

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Another consideration of PTFE

Non-stick cookware coated with PTFE.
PTFE is “inert” in products.

PTFE is not inert when being produced:

- Other PFAS are released during manufacture, including PFOA (i.e., in China) and GenX (a PFOA replacement used in manufacturing).
- What happens when product has reached end-of-life?

A lifecycle perspective is needed for the class of PFAS.

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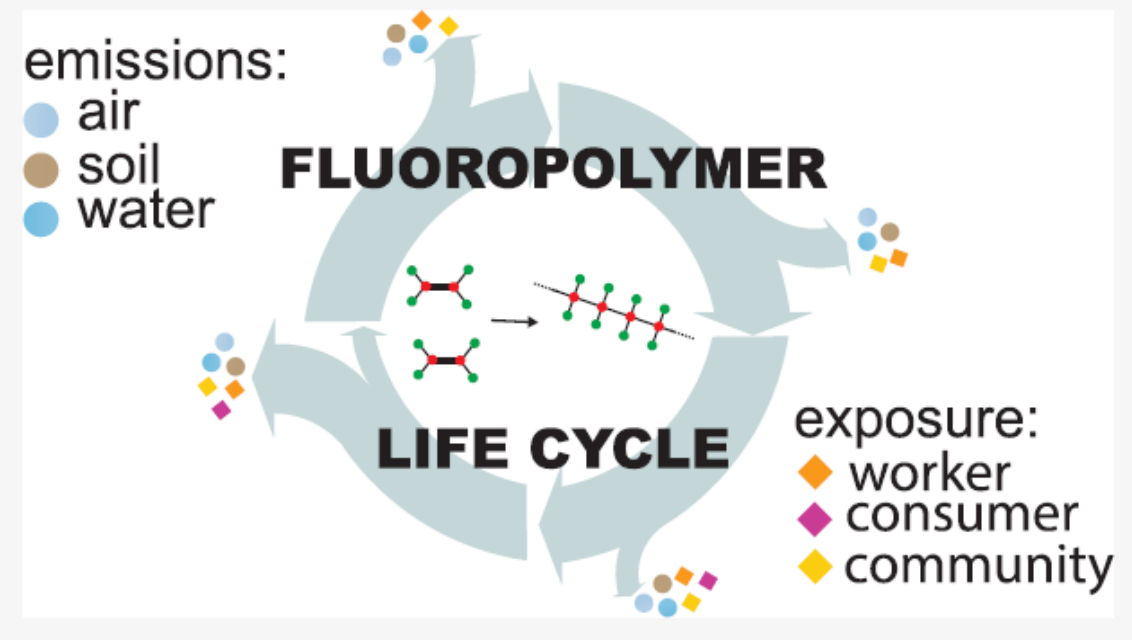
A closed loop process with zero discharge is a great step toward reducing the environmental and human health burden of PFAS…but is it feasible?

Questions of **essentiality** should also be considered, especially when the **lifecycle** of PFAS becomes part of the equation.
In general, production of **persistent chemicals** is always a bad idea.



Lohmann et al., 2020

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Finding essentiality feasible

3 aspects:

1) What is the function that the substance of concern in the use case,

2) Is function necessary for health and safety and critical for the functioning of society, and

3) If the function is necessary, whether there are viable alternatives for the chemical for this particular use.

(function could be “chemical function”, “end-use function”, and “service function”)

Non-essential:

- Aspect 2 is determined to be negative, or
- Aspects 2 and 3 are determined to be positive.
- 3-step procedure follows “functional substitution”.

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Cite this: *Environ. Sci.: Processes Impacts*, 2020, **22**, 2345

An overview of the uses of per- and polyfluoroalkyl substances (PFAS)†

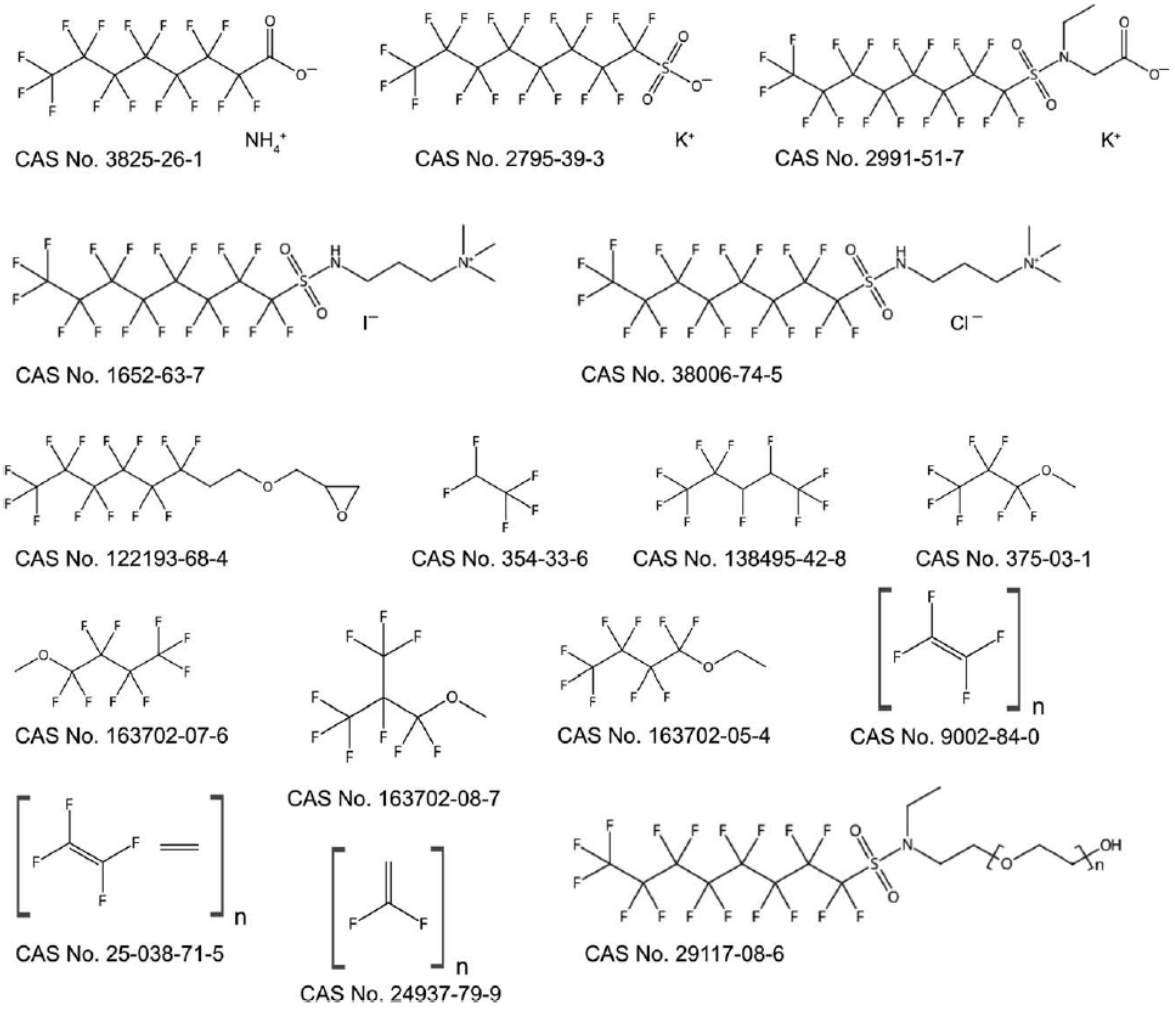
Juliane Glüge, *[a] Martin Scheringer, [a] Ian T. Cousins, [b] Jamie C. DeWitt, [c] Gretta Goldenman, [d] Dorte Herzke, [ef] Rainer Lohmann, [g] Carla A. Ng, [h] Xenia Trier [i] and Zhanyun Wang [j]

Industry branches	
Aerospace (7)	Mining (3)
Biotechnology (2)	Nuclear industry
Building and construction (5)	Oil & gas industry (7)
Chemical industry (8)	Pharmaceutical industry
Electroless plating	Photographic industry (2)
Electroplating (2)	Production of plastic and rubber (7)
Electronic industry (5)	Semiconductor industry (12)
Energy sector (10)	Textile production (2)
Food production industry	Watchmaking industry
Machinery and equipment	Wood industry (3)
Manufacture of metal products (6)	

Other use categories	
Aerosol propellants	Metallic and ceramic surfaces
Air conditioning	Music instruments (3)
Antifoaming agent	Optical devices (3)
Ammunition	Paper and packaging (2)
Apparel	Particle physics
Automotive (12)	Personal care products
Cleaning compositions (6)	Pesticides (2)
Coatings, paints and varnishes (3)	Pharmaceuticals (2)
Conservation of books and manuscripts	Pipes, pumps, fittings and liners
Cook- and bakingware	Plastic, rubber and resins (4)
Dispersions	Printing (4)
Electronic devices (7)	Refrigerant systems
Fingerprint development	Sealants and adhesives (2)
Fire-fighting foam (5)	Soldering (2)
Flame retardants	Soil remediation
Floor covering including carpets and floor polish (4)	Sport article (7)
Glass (3)	Stone, concrete and tile
Household applications	Textile and upholstery (2)
Laboratory supplies, equipment and instrumentation (4)	Tracing and tagging (5)
Leather (4)	Water and effluent treatment
Lubricants and greases (2)	Wire and cable insulation, gaskets and hoses
Medical utensils (14)	

The top 10 PFAS

Substance
Ammonium perfluorooctanoate
Potassium perfluorooctane sulfonate
Potassium *N*-ethyl perfluorooctane sulfonamidoacetate
1-Propanaminium, 3-[[(1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctyl)sulfonyl]amino]-*N*,*N*,*N*-trimethyl-, iodide (1 : 1)
1-Propanaminium, 3-[[(1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorooctyl)sulfonyl]amino]-*N*,*N*,*N*-trimethyl-, chloride
Oxirane, 2-[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy]methyl]-
1*H*-Pentafluoroethane
Pentane, 1,1,1,2,2,3,4,5,5,5-decafluoro-
Methyl perfluoropropyl ether
Methyl perfluorobutyl ether
Methyl perfluoroisobutyl ether
Ethyl perfluorobutyl ether
Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctyl)sulfonyl]amino]ethyl]-ω-hydroxy-
Polytetrafluoroethylene (PTFE)
Poly(vinylidene fluoride) (PVDF)
Ethylene tetrafluoroethylene copolymer (ETFE)



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What is the status of efforts to supplant the use of PFAS?

It depends

- Consumer pressure (textiles, cosmetics, furniture)
- Manufacturers' action (carpets)
- Legislation (food contact materials, AFFF)
- Litigation

https://pfascentral.org/pfas-free-products/

Where has essentiality caught on?

- EU:

In October 2020, the European Commission published the Chemicals Strategy for Sustainability. Among its many actions, it includes **phasing out the use of PFAS in the EU, unless their use is essential** and initiatives to reduce their emissions using all available legislative and non-legislative tools.

This article is more than **8 months old**

Maine bans toxic 'forever chemicals' under groundbreaking new law

State is the first to enact a broad ban of PFAS compounds, which are found in everything from cosmetics to cookware

Arguably, in several other states, too

- By piecemeal, though..
- Action on PFAS in cosmetics, carpets, food contact materials.
- Might be simply expanded to all consumer products where PFAS are deliberately added to the final product, rather than as part of the manufacturing process.

Thanks, again

- NIEHS, of course
- Global PFAS Science Pane;
- Partners/collaborators, grad students

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Thank you.

Questions?

Substitutions?

category	PFAS use essential	Substitutes available	Status
textiles	No *	yes	some progress
medical equipment	Yes	Maybe	Little
solar panels	unsure	unsure	Little
construction materials	Probably not	Probably yes	Little progress
household products	No	yes	some progress
firefighting	No *	yes	Major progress