The concept of essential use for determining when uses of per- and polyfluoroalkyl substances (PFAS) can be phased out

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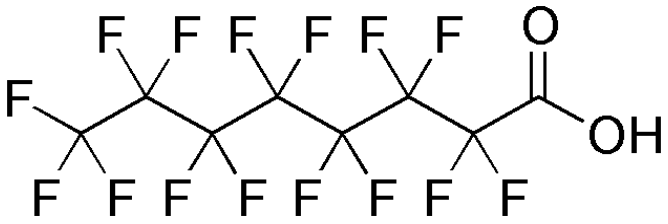
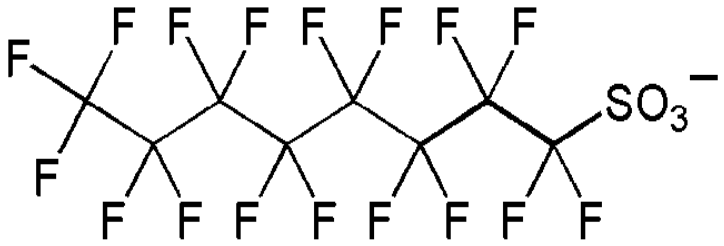
Svensk Förening för Toxikologi (SFT)
Seminar, 9th September, 2021

What are PFAS?



Perfluorooctanoic acid - PFOA
A perfluoroalkyl carboxylic acid (PFCA)



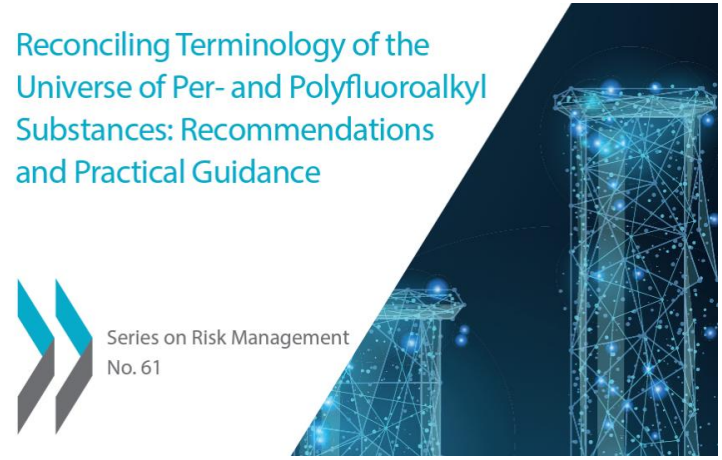
Perfluorooctane sulfonate - PFOS
A perfluoroalkane sulfonate (PFSA)

- PFCAs and PFSAs (and their precursors) – the focus of most research
- They come in a range of chain lengths. Long-chain PFCAs and PFSAs are persistent, bioaccumulative and toxic. PFOS & PFOA on Stockholm Convention.

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**highly fluorinated aliphatic substances** that contain **1 or more C atoms** on which all the H substituents … have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety **C_nF_{2n+1}–" (has to contain at least -CF_3)**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 planned (published recently)
  - "…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



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

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- Swedish Chemicals Agency (KEMI): 2060
- OECD: 4730
- US EPA dashboard: 9252
- CAS number searches (ChemSpider (http://www.chemspider.com/))
  - -CF_2- alone: 20 772 063 (**4 430 726 commercially available**, 16 341 337 not commercially available)
  - -CF_2CF_2-: 4 667 078 (**266 086 commercially available**, 4 400 992 not commercially available)
  - -$CF_2CF_2CF_2$-: 1 188 469 (**31 393 commercially available**, 1 157 076 not commercially available)
- Only 1 400 with identified uses…


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ROYAL SOCIETY OF CHEMISTRY

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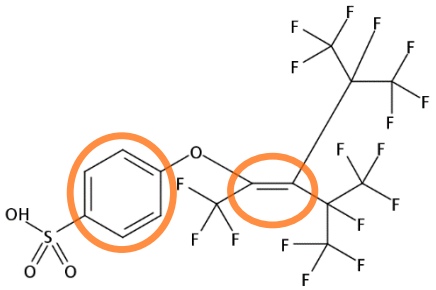
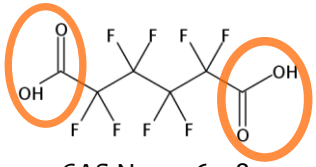
An overview of the uses of per- and polyfluoroalkyl substances (PFAS)†

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]

OECD 2018 Report – Expanding universe

- In 2018, OECD published an updated PFAS List
  → 4730 CAS numbers identified
  → **Many not covered by Buck et al. definition**





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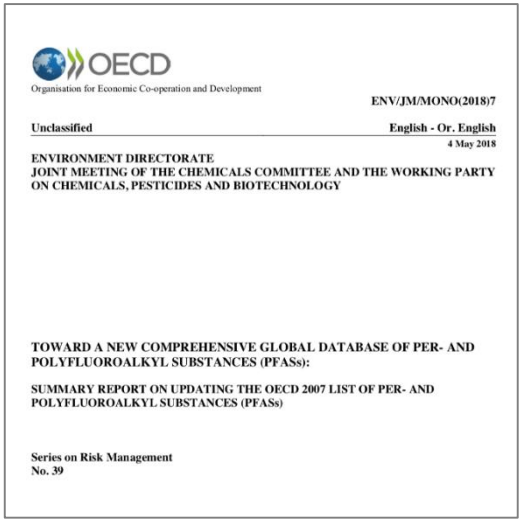
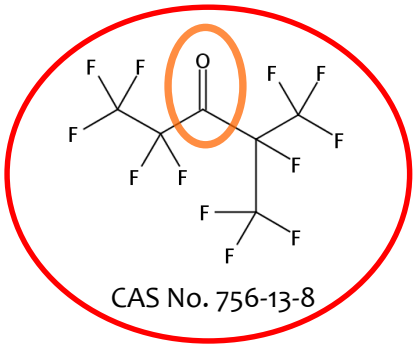
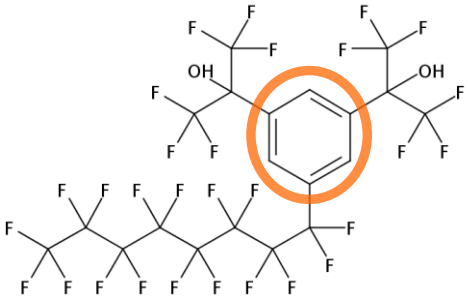


• Na CAS No. 70829-87-7



CAS No. 756-13-8



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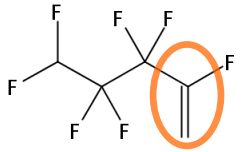

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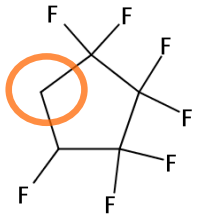
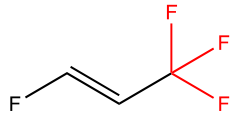
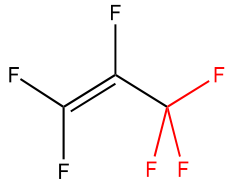


CAS No. 15290-77-4

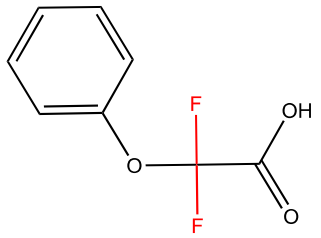
PFAS according to broader OECD definition (recently published)



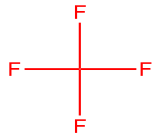
HFO-1234ze, CAS No. 29118-24-9



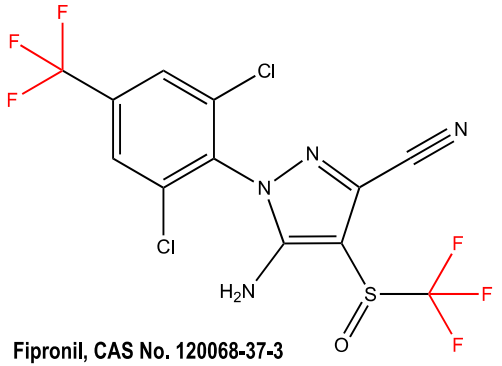
HFP, CAS No. 116-15-4



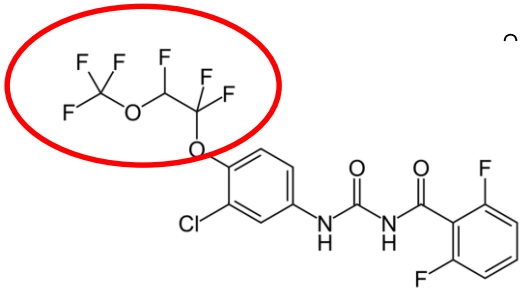
CAS No. 24210-45-5



CAS No. 75-73-0



Fipronil, CAS No. 120068-37-3



Novaluron, CAS No. 116714-46-6

Is the definition too broad for regulatory purposes?

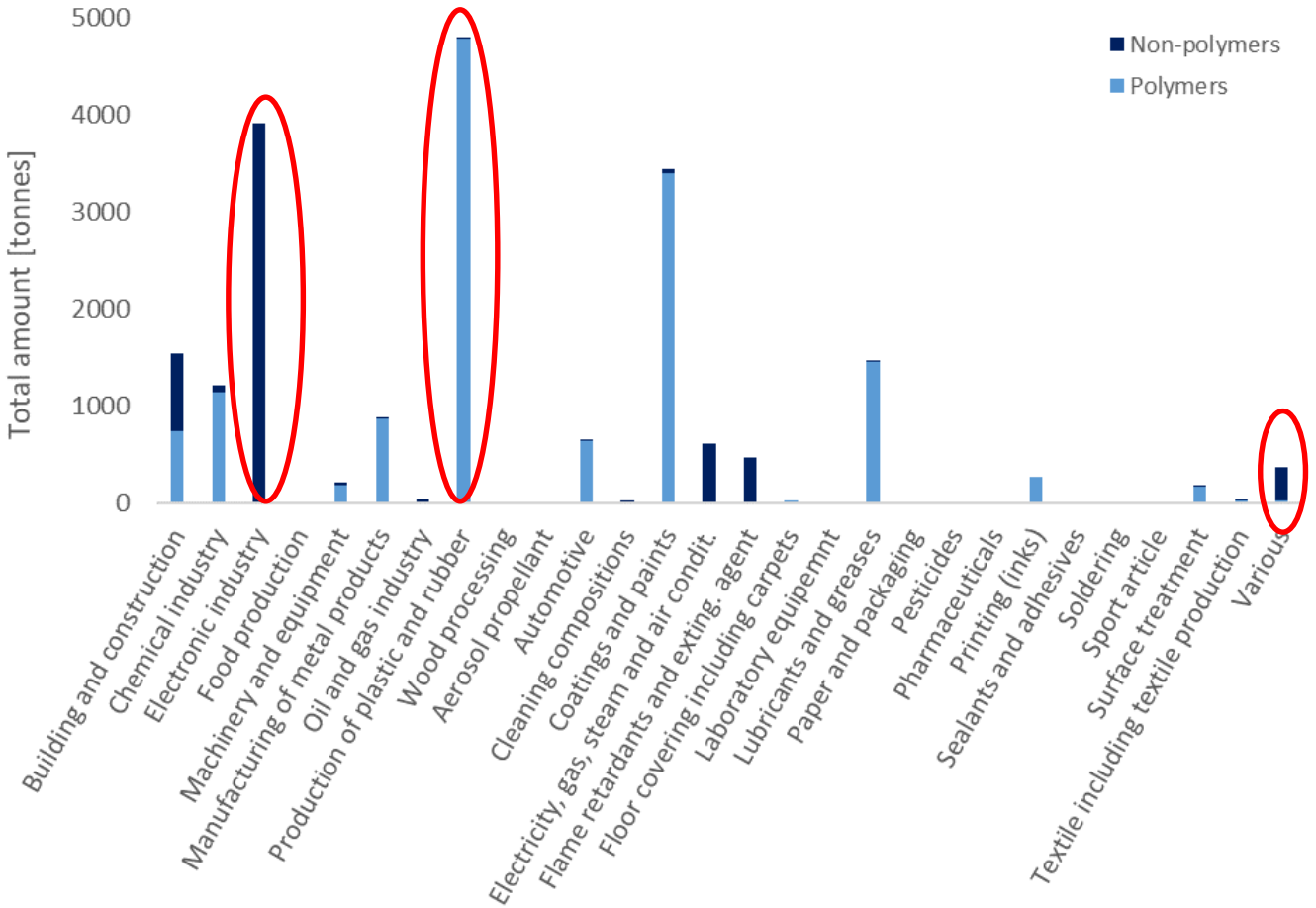
Diversity of PFAS

- 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

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

Uses of PFAS?



- More than 200 uses identified for more than 1400 PFAS

- Less well known uses:
  - ammunition,
  - climbing ropes,
  - guitar strings,
  - artificial turf,
  - soil remediation

Madrid Statement

Stockholm University

The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)

http://dx.doi.org/10.1289/ehp.1509934

Arlene Blum,[1,2] Simona A. Balan,[2] Martin Scheringer,[3,4] Xenia Trier,[5] Gretta Goldenman,[6] Ian T. Cousins,[7] Miriam Diamond,[8] Tony Fletcher,[9] Christopher Higgins,[10] Avery E. Lindeman,[2] Graham Peaslee,[11] Pim de Voogt,[12] Zhanyun Wang,[4] and Roland Weber[13]

May 2015

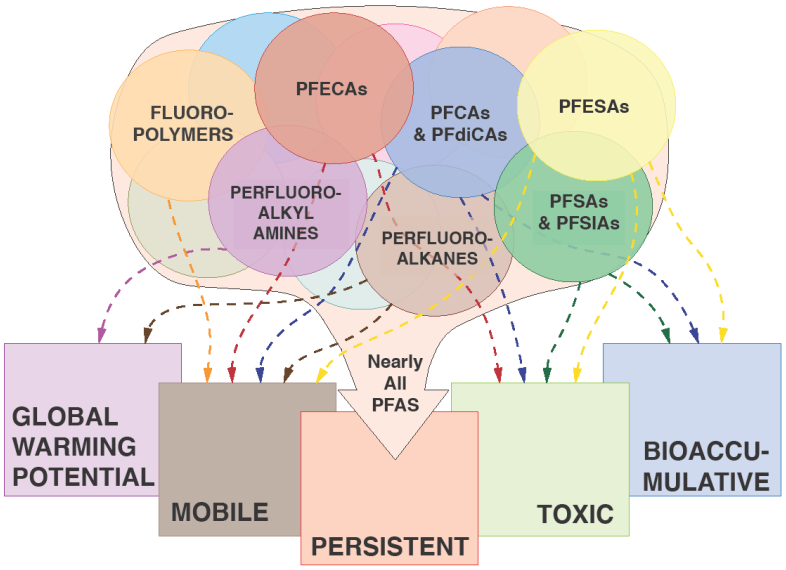
- Production and use of PFAS should be limited
- Based on concerns regarding high persistence and lack of knowledge on chemical structures, properties, uses, and toxicological profiles

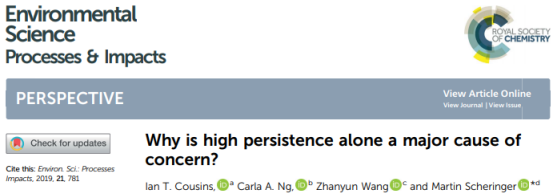
Are all PFAS of concern?

- **All PFAS are highly persistent** (EU REACH)
  - they are either non-degradable or transform ultimately into stable terminal transformation products
- Continual release of high P chemicals results in increasing levels and increasing probabilities of known and unknown effects. Exposure poorly reversible

PFAS Structural Sub-classes:

Potential Classification Options:

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Why is high persistence alone a major cause of concern?

Ian T. Cousins, Carla A. Ng, Zhanyun Wang and Martin Scheringer


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PERSPECTIVE

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The high persistence of PFAS is sufficient for their management as a chemical class

Ian T. Cousins, Jamie C. DeWitt, Juliane Glüge, Gretta Goldenman, Dorte Herzke, Rainer Lohmann, Carla A. Ng, Martin Scheringer and Zhanyun Wang

Phasing out uses of PFAS

- Impractical to ban all uses of PFAS in one step
  - Some applications may serve a critical role for which alternatives currently do not exist
  - However, if some uses of PFAS are found **not** to be **essential**, they could be eliminated without having to first find functional alternatives
- Montreal Protocol on Substances that Deplete the Ozone Layer
  - Introduced concept of essential uses or essentiality

Essentiality of PFAS?

- To critically evaluate the idea that uses of PFAS are essential in modern society, the essentiality of PFAS should be carefully tested against the available evidence for each of their uses
- Given the thousands of PFAS on the market and their many uses, this is a formidable task
- Adapt the definition of essentiality from the Montreal Protocol

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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]

Defining essentiality

Stockholm University

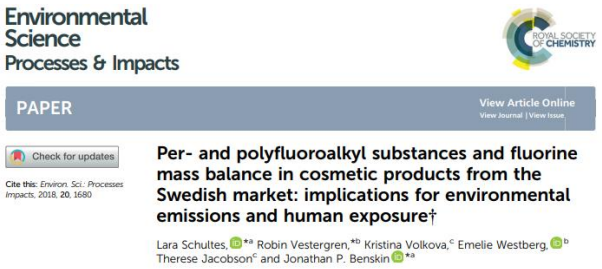
Category	Definition	PFAS examples
1 "Non-essential"	Uses that are not essential for health and safety, and the functioning of society. The use of substances is driven primarily by market opportunity.	Dental floss, water repellent surfer shorts, ski waxes
2 "Substitutable"	Uses that have come to be regarded as essential by society 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 by society because they are necessary for health or safety or other highly important purposes *and* for which alternatives are not yet established.*	Certain medical devices, occupational protective clothing.

* 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.

Application of Essentiality:

4 case studies

Cosmetics



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Per- and polyfluoroalkyl substances and fluorine mass balance in cosmetic products from the Swedish market: implications for environmental emissions and human exposure†

Lara Schultes, Robin Vestergren,*[b] Kristina Volkova,[c] Emelie Westberg, Therese Jacobson[c] and Jonathan P. Benskin*[a]

- PFAS found in hair products, mascara, foundations, face creams, sun blocks, skin creams, lip pencils
  - Technical function?
  - Potential human exposure (dermal/oral)

- Several major retailers/brands (L'Oréal, H&M, Lumene, The Body Shop, Isadora and Kicks) rapidly announced phase outs of PFAS
- Difficult to substitute 1:1, new formula needed
- Technical function of PFAS not essential: **Category 1**

Ski waxes

- Fluorinated waxes are favored by competitive skiers
- Waxes contain fluorinated alkanes, but also perfluoroalkyl carboxylates, including PFOA
- We don’t need to ski 5% faster. Non-essential, **Category 1**

FIS BANS SOME SKI WAXES

6TH DECEMBER 2019

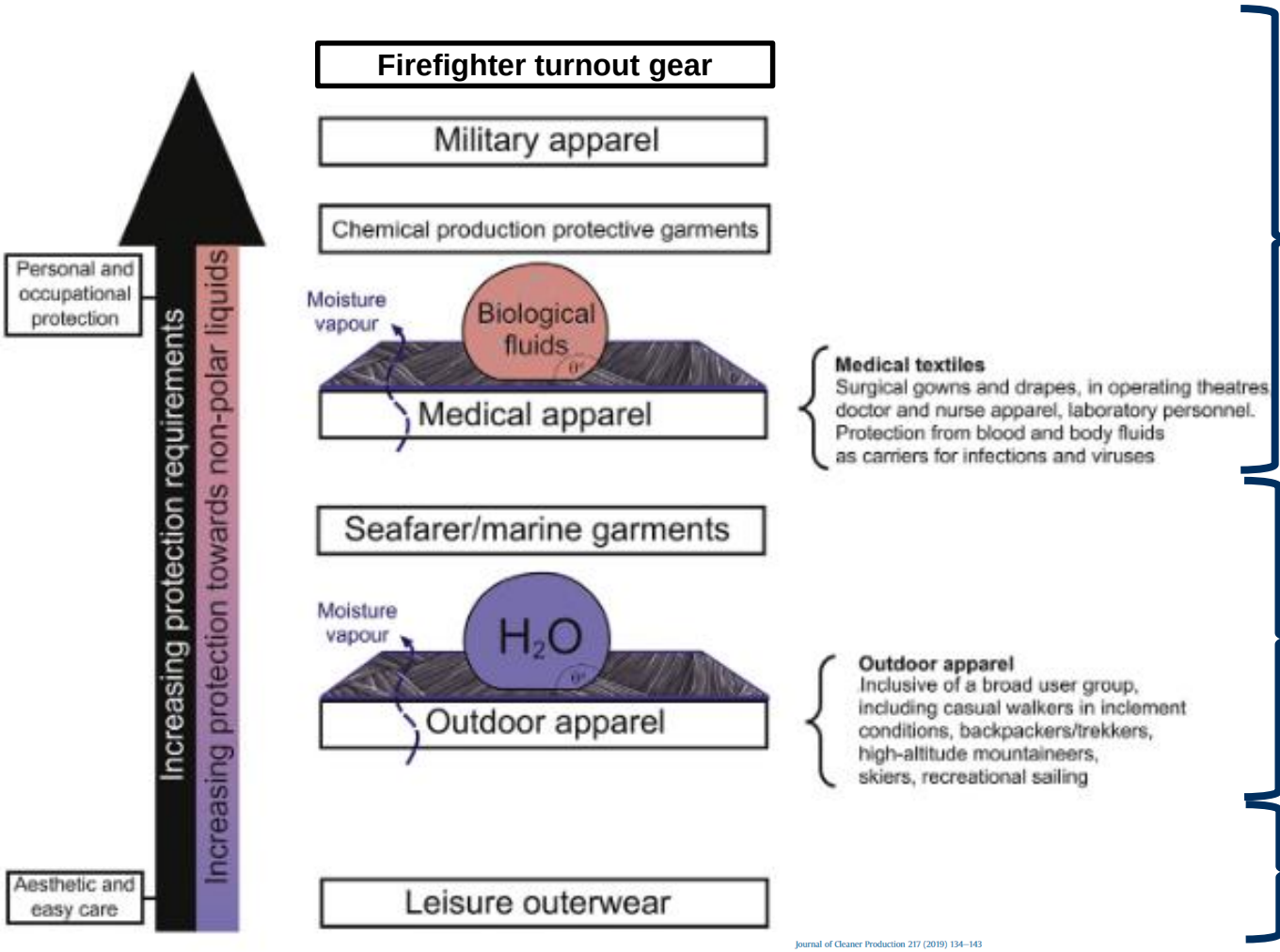
LAST MODIFIED ON FEBRUARY 19TH, 2020

Flourinated ski wax will not be able to be used by racers next season due to its impact on the environment and health.

AFFFs

- Extinguishing class B fuel fires
- Irreversible contamination of groundwater
- Fluorine-free class B foams (3F) available since early 2000s
  - meet the standard firefighting performance certifications
  - many commercial airports have phased out AFFFs
- Still some debate if AFFFs needed for certain scenarios
  - **Alternatives developed: Category 2**

Textiles



Journal of Cleaner Production 217 (2019) 134–143

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journal homepage: www.elsevier.com/locate/jclepro

Highly fluorinated chemicals in functional textiles can be replaced by re-evaluating liquid repellency and end-user requirements

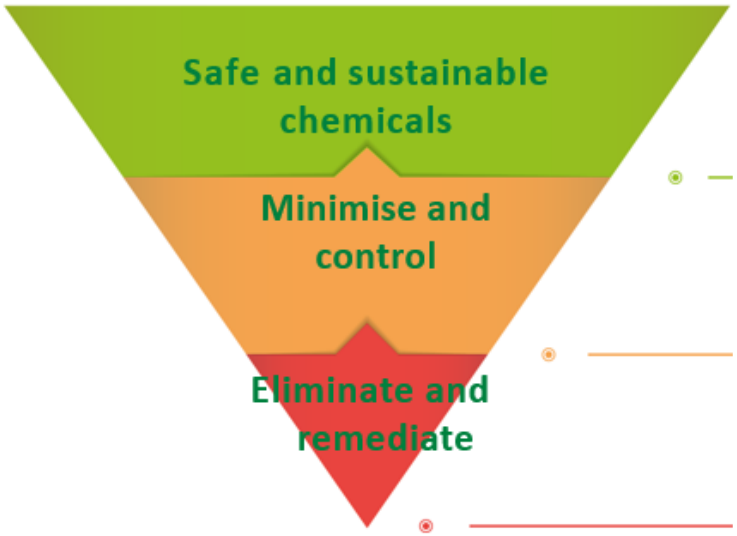
Steffen Schellenberger [a, 1], Philippa J. Hill [b, 1], Oscar Levenstam [c], Philip Gillgard [d], Ian T. Cousins [a, *], Mark Taylor [b], Richard S. Blackburn [b, **]

Conclusions/way forward

- Essential use concept can guide the phase-out of PFAS
  - Category 1 (non-essential uses) can be rapidly phased out
- Category 2 (substitutable uses) of PFAS
  - avoid regrettable solutions: chemical alternatives assessment (CAA)
  - US EPA's **Design for the Environment (DfE)**, Clean Production Action's **GreenScreen** and McDonough Braungart Design Chemistry **Cradle to Cradle™**
- Even when PFAS are considered category 3 (essential uses):
  - innovation should be encouraged to find safer alternatives
- Formidable task requiring technical knowledge!!

EU Chemicals Strategy, Oct. 2020

- "Essential use" concept incorporated
  - Broader than just PFAS
  - concept can speed up phase outs of non-essential uses of multiple classes of hazardous substances



Acknowledgements

- This work has been undertaken by the scientists collaborating as the Global PFAS Science Panel.

- We would like to thank the Tides Foundation for supporting our cooperation.

- This does not necessarily reflect the opinion or the policies of the German Environment Agency or the European Environment Agency.

Stockholm University

Thank you for your attention!

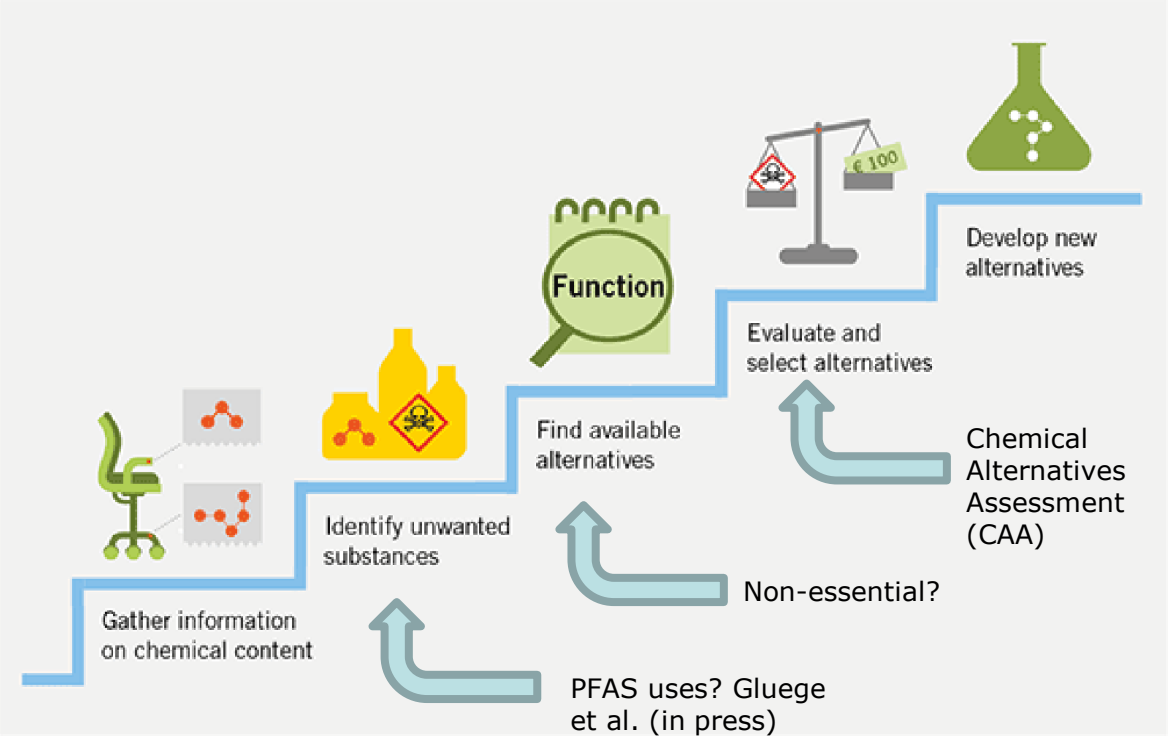
Bonus slides

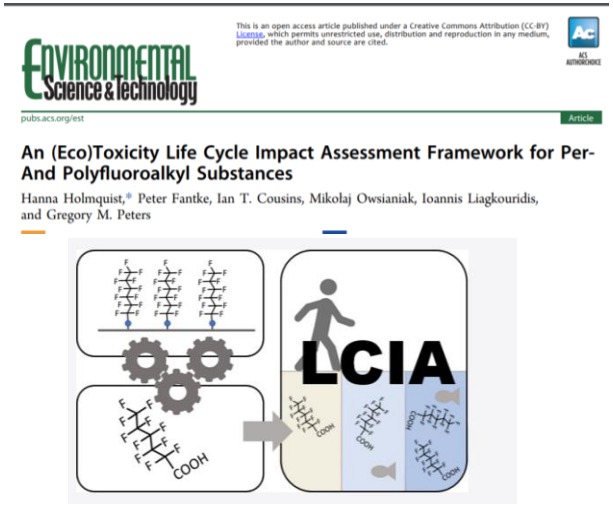
More examples

Use	Table 1 Category*
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 (paper and board)	1
Food production equipment (fluoropolymers)	1, 2 or 3
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

*Note that the categories in the above table represent the current evaluation and may change in the future.

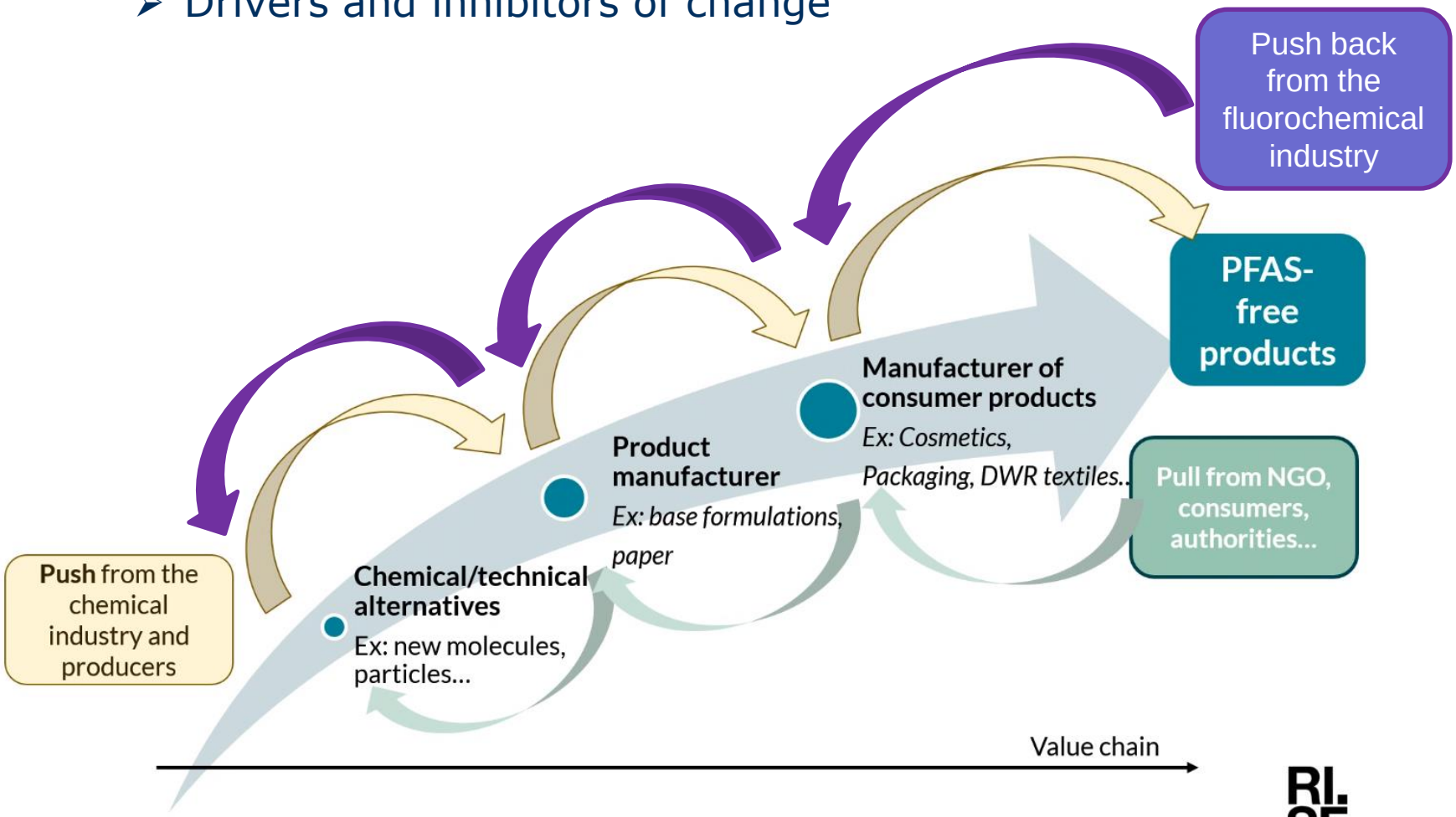
Chemical Substitution Model





Systemic Change Underway

- PFAS under global pressure
- Drivers and inhibitors of change



International Success Stories

- Banning of PFAS in paper and board used in food contact materials in Denmark
- Banning of fluorinated ski waxes in international competition
- Transition to Class B fluorine-free foams around the world
- Phasing out of PFAS in cosmetics by multiple retailers
- Fluorine-free durable water repellent outdoor equipment

- > 200 uses: The work is far from done!

Ongoing in the European Union

- Authorities of Denmark, Germany, Netherlands, Norway and Sweden are preparing a REACH restriction proposal for a wide range of PFAS
  - Unclear which PFAS included
  - Derogations granted according to essentiality
- Interested parties were invited to send in evidence and information on the use of PFAS by 31 July 2020
  - Gluege et al. was a key piece of evidence

PERSISTENT POLLUTANTS

PFAS restriction plan developing in EU

by *Cheryl Hogue*

MAY 16, 2020 | APPEARED IN **VOLUME 98, ISSUE 19**

Discussion points

- Scope of essentiality concept?
- Practical application
  - Criteria too vague? Essential for society?
  - Who decides?
  - Essential uses not essential chemicals or products!
- Lack of knowledge of uses of PFAS
- Chemical Alternative Assessment
  - Paralysis by analysis?
  - Who does it and how?