Ultrashort-Chain PFAS: The global threat of trifluoroacetic acid

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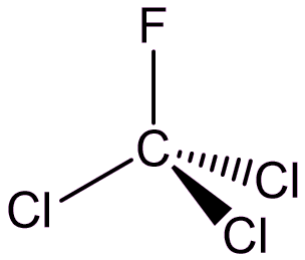
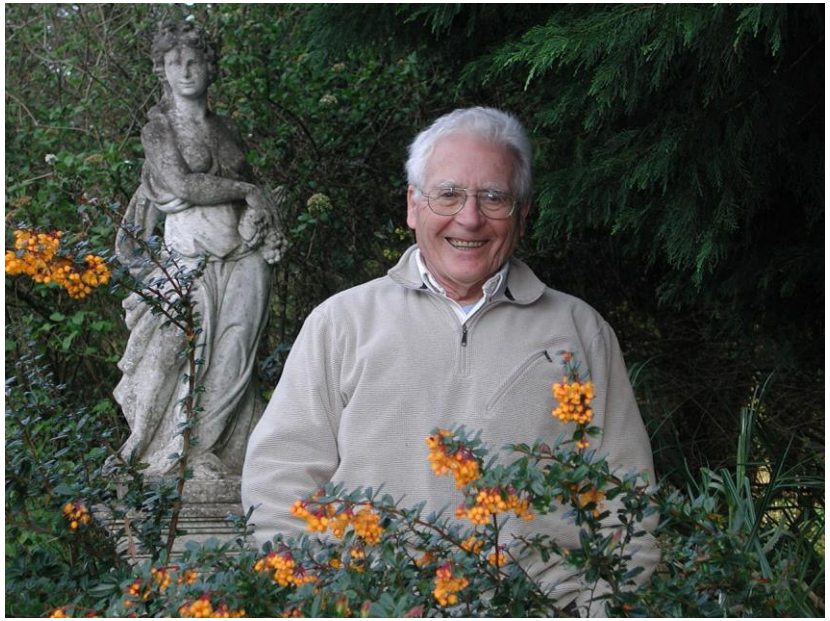
A precautionary tale….

James Lovelock (1919 – 2022)

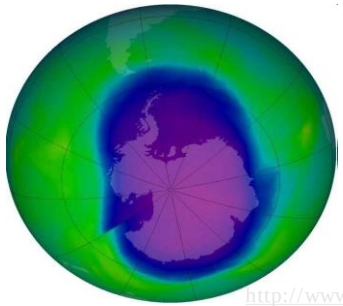




- **Invented the Electron Capture Detector (ECD)**
- **First to detect chlorofluorocarbons (CFCs) in the atmosphere**

- CFCs pose "no conceivable hazard"

Lovelock J (1988). The Ages of Gaia: A Biography of Our Living Earth



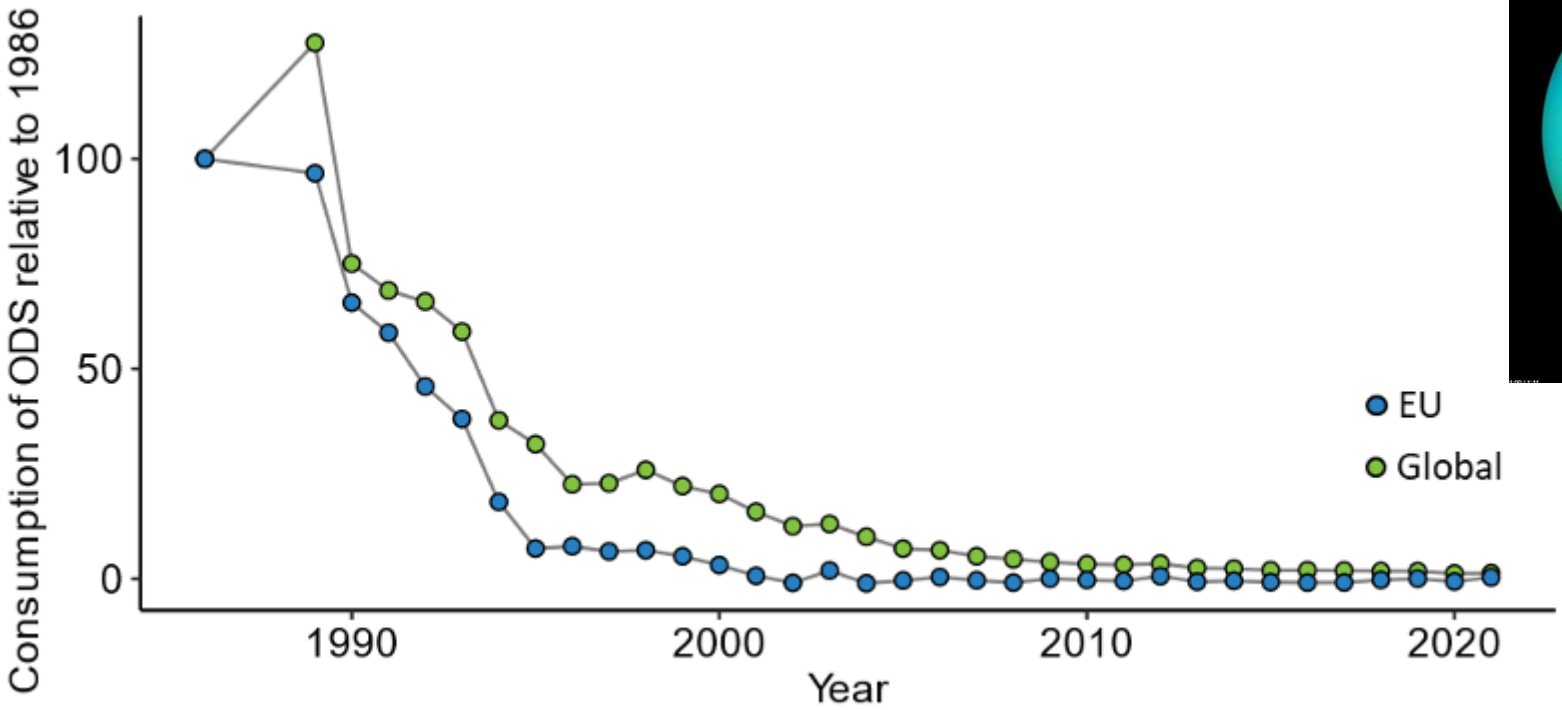
http://www.nasa.gov/vision/earth/environment/ozone_resource_page.html

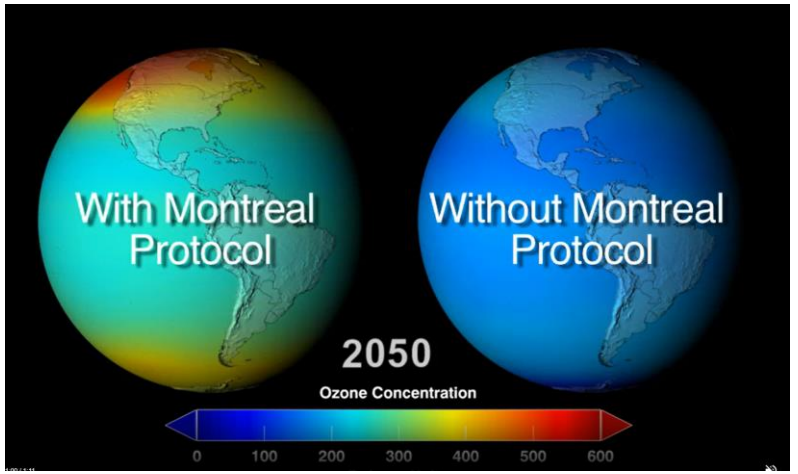
- CFCs pose "no conceivable toxic hazard"

Lovelock J (2000). Homage to Gaia: The Life of an Independent Scientist

https://en.wikipedia.org/wiki/James_Lovelock

The Montreal Protocol saved the planet. Without it there would be no photosynthesis





EU and global relative consumption of ozone depleting substances (ODS, like chlorofluorocarbons) since 1986, showing the reduction the consumption of ODS due to the Montreal Protocol.

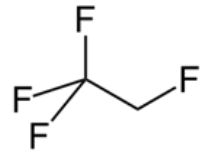
Chirsir, Palm *et al.* (2024 in press), ESEU, DOI: 10.26434/chemrxiv-2024-tn5t5

EEA (2023) EU and global consumption of controlled ozone-depleting substances — European Environment Agency. In: European Environmental Agency. 826

https://svs.gsfc.nasa.gov/cgi-bin/details.cgi?aid=10824

The history of the Montreal Protocol is a history of burden shifting via «drop in substitution»

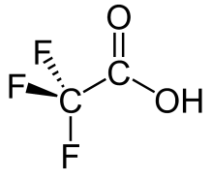
- 1st Gen: Chlorofluorocarbons (**CFCs**) – *Ozone depletion*
- 2nd Gen: Hydrochlorofluorocarbons (**HCFCs**)– less ozone depleting, but *green house gases*
- 3rd Gen: Saturated hydrofluorocarbons (**HFCs**) -> green house gases, *mild formation of TFA*



1,1,1,2-Tetrafluoroethane
(HFC-134a, Norflurane)

$h \cdot \upsilon$

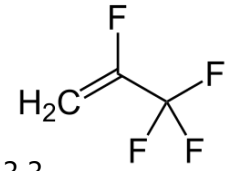
high global warming potential



Triflouroacetic acid (TFA) Yield between 7- 23%

Extremely persistent and mobile
Accumulates in the environment

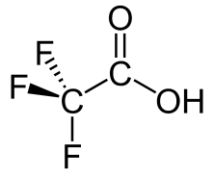
- 4th Gen: F-gases after Kigali amendment (2019): Unsaturated hydrofluoroolefins (**HFOs**), less global warming potential, ***increased formation of TFA***



2,3,3,3-
Tetrafluoropropene
(µHFC-1234yf)

$h \cdot \upsilon$

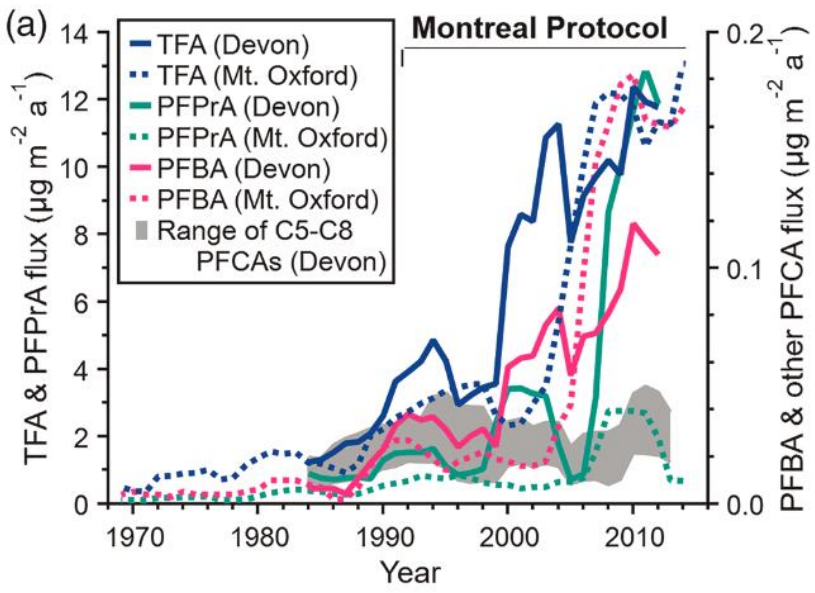
low global warming potential



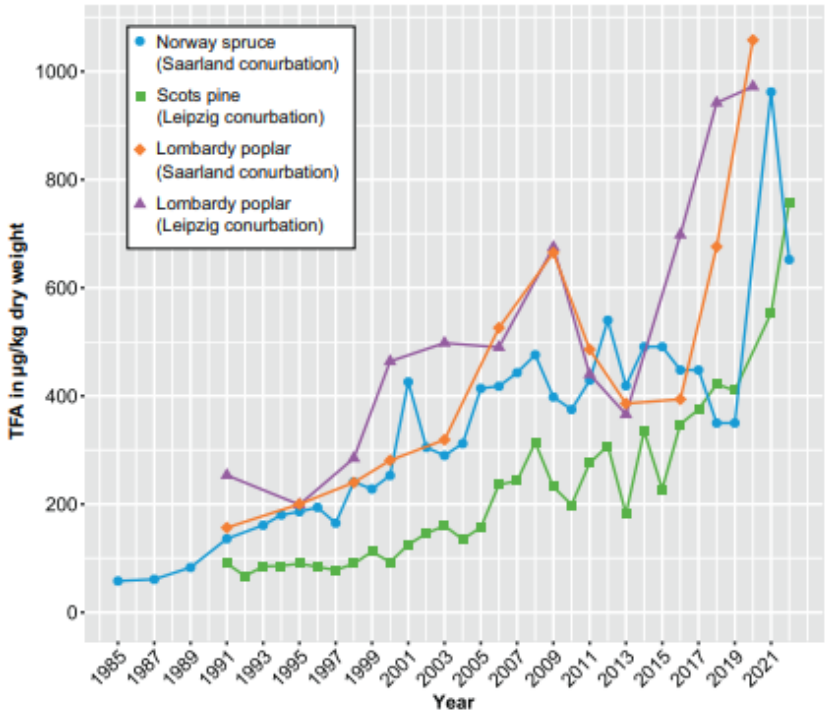
TFA Yield = 100% !

TFA is accumulating everywhere, largely coinciding with F-gas use following the Montreal Protocol

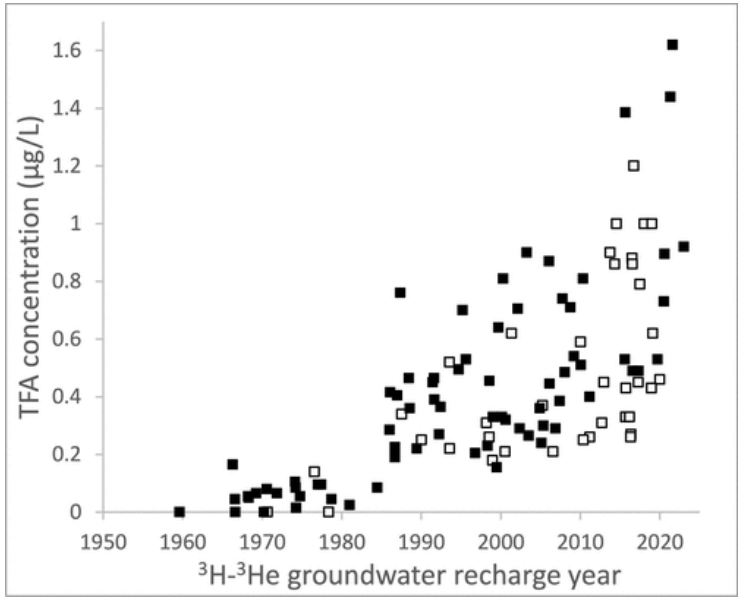
TFA accumulating in arctic ice cores



and in tree leafs



and in groundwater



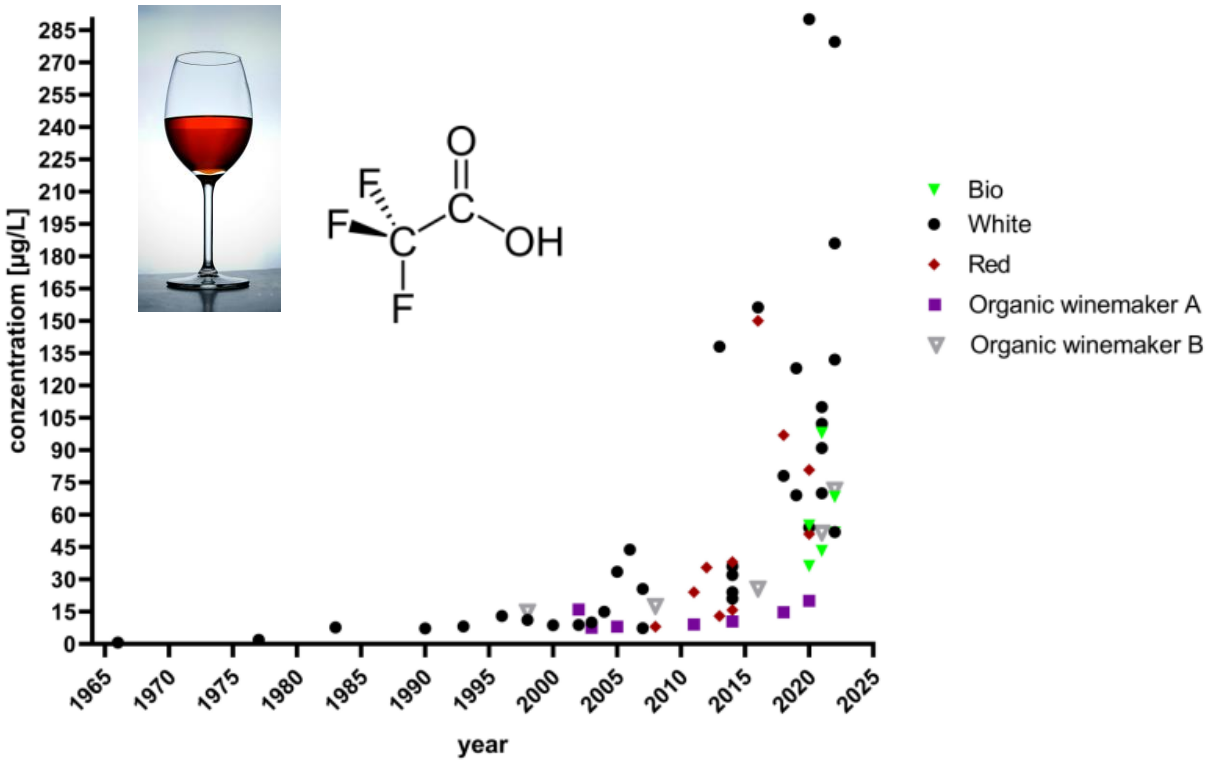
Pickard et al. Geophysical Research Letters (2020),47, e2020GL087535

Freeling and Björnsdotter, Current Opinion in Green and Sustainable Chemistry 2023, 41:100807

Albers and Sültenfuss, Environmental Science & Technology Letters 2024 11 (10), 1090-1095

TFA is increasing in what we all drink

…and in wine



Drinking water (median)[1,2]

- Germany: 1.5 µg/L
- 19 countries: 0.23 µg/L

Tea (median): 2.4 µg/L[2]

Beer (median) 6.1 µg/L[2]

Orange juice (mean 34 µg/L)[3]

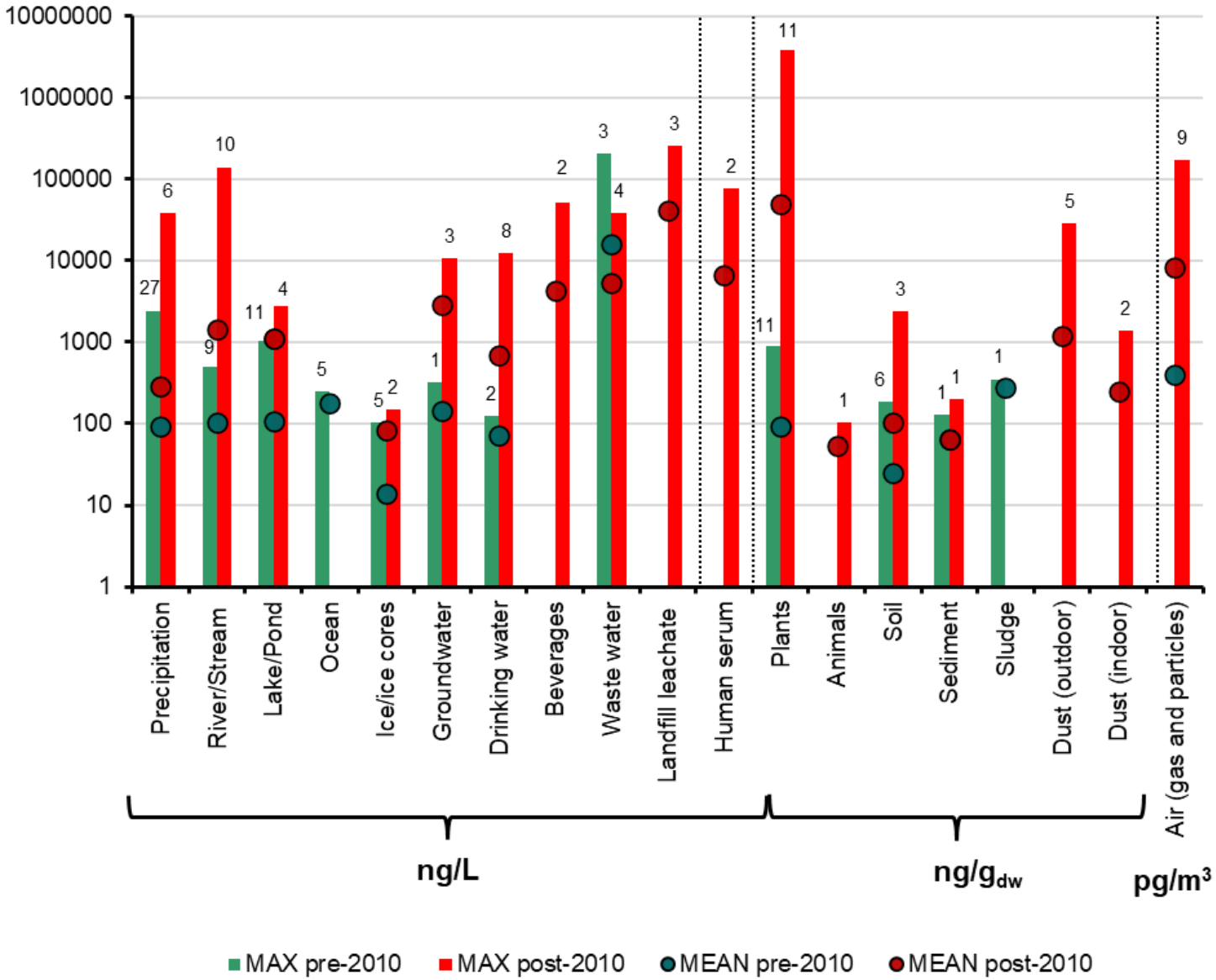
Apple juice (mean 6.2 µg/L)[3]

Unpublished data: Michael Müller. Uni. Freiburg
michael.mueller@pharmazie.uni-freiburg.de (used with permission)

Wine image: Sai Balaji Varma Gadhiraju

1. Neuwald et al. *Environmental Science & Technology* **2022** *56* (10), 6380-6390
2. Scheurer & Nödler. *Food Chemistry*, *351*, 129304.
3. Van Hees et al. https://cdnmedia.eurofins.com/european-east/media/uxcnaa2c/eurofins_tfa_tfms_juice_24_final.pdf

TFA is accumulating everywhere it can be measured



Chinese blood 97% detection
Median 8.5 µg/L
Similar to levels of the sum of all long-chain, bioaccumulative PFAS

USA blood serum 74% detection
Median 6.0 µg/L
Twice the levels of the sum of all long-chain, bioaccumulative PFAS

What levels of TFA will be in the blood of future generations? What will the impact of this be

Duan et al. (2020) Environ Int 134:105295.
Zheng et al. (2023) ES&T 2023, 57, 15782-15793
Arp et al. ES&T 2024, 58, 45, 19925-19935

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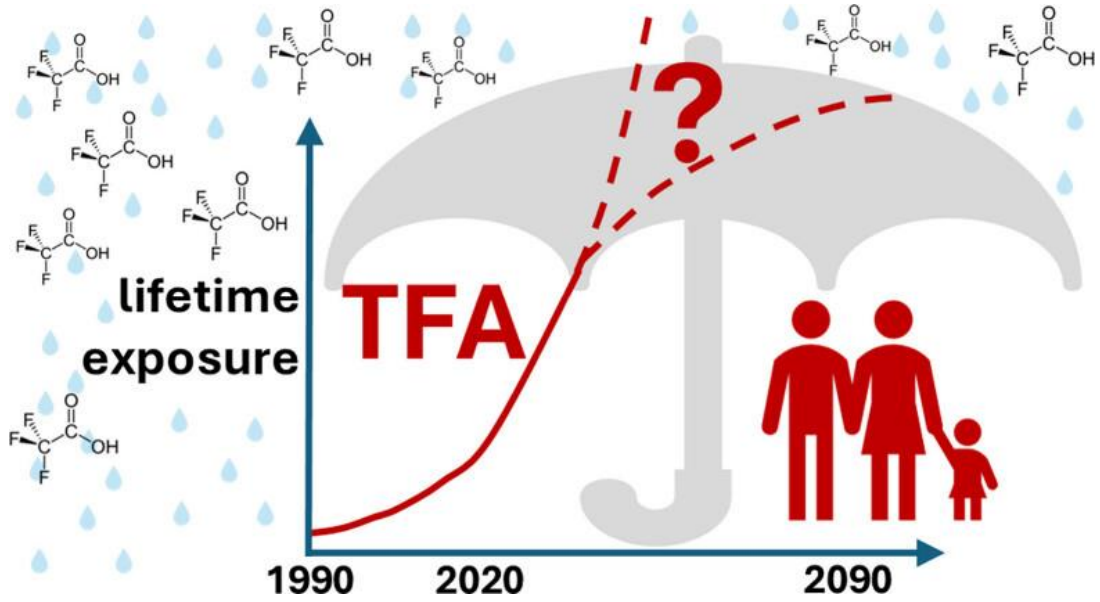
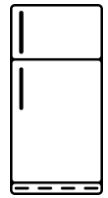
- Increasing Sources
- Irreversible Effects
- Solutions to a Global Threat

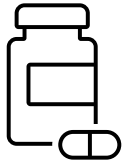


Increasing Sources

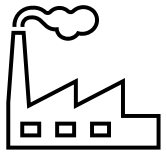
Agricultural chemicals



Refrigerants and blowing agents

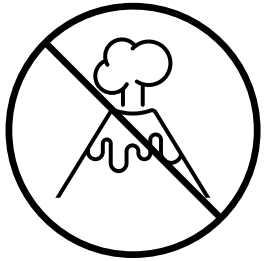


Pharmaceuticals



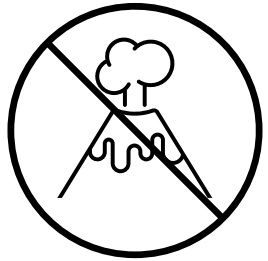
PFAS production and products

PFAS remediation



No natural sources

No evidence that TFA is of natural origin

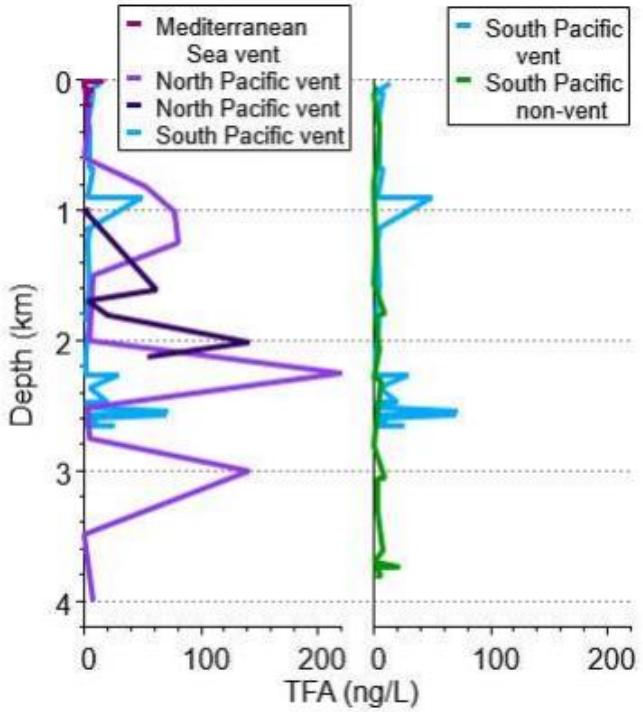


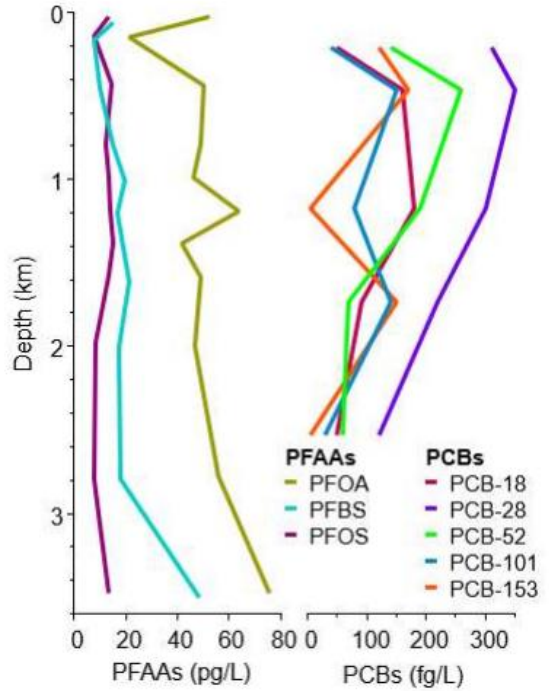
No natural sources

Hypothesis (2001-2005) of a **natural origin** of TFA in the deep oceans[1,2]

Hypothesis **no longer supported**[3]

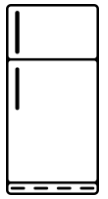
- No TFA gradients by deep sea vents
- TFA, PFAS and other synthetic substances in deep sea via
  - ❑ oceanic currents
  - ❑ sinking of dense water formed on continental shelfs
  - ❑ Marine snow deposition
- Inconsistent with time trends in rain/ice cores



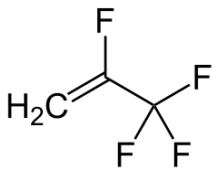


1) *Frank et al. Environmental Science & Technology* 2002 *36* (1), 12-15
2) Scott et al. *Environmental Science & Technology* 2005 *39* (17), 6555-6560
3) *Joudan et al. Environ. Sci.: Processes Impacts*, 2021,23, 1641-1649

F-gases used as refrigerants and blowing agents

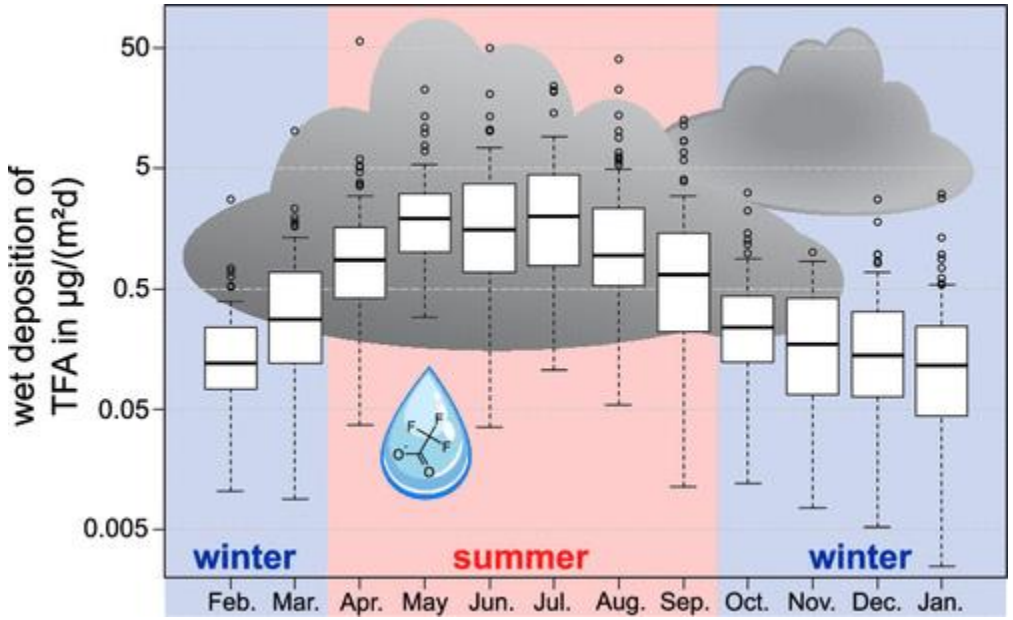


EU-28



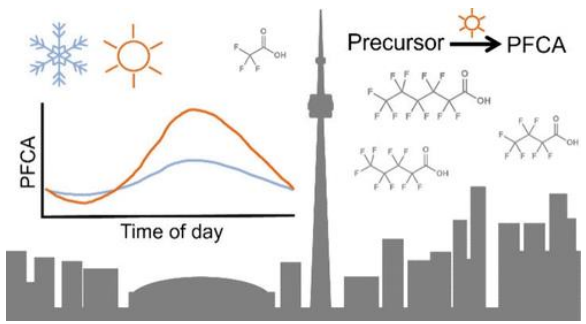
Substance	2000	2010	2020	2030	2040	2050	Total TFA sum (2000-2050)	Share of total sum
HFC-134a	3,895	7,595	6,351	1,756	1,084	836	202,781	14.7 %
u-HFC-1234yf	0	0	6,902	37,432	45,469	47,650	1,125,699	81.3 %

Behringer et al. UBA Texte | 73/2021



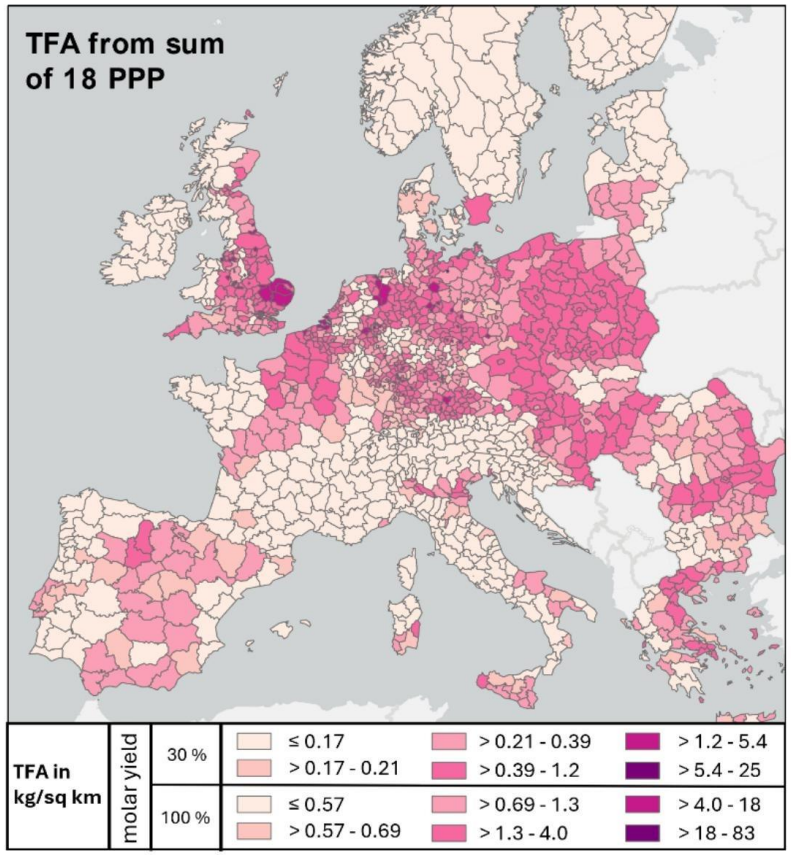
Freeling et al. *Environmental Science & Technology* **2020** *54* (18), 11210-11219

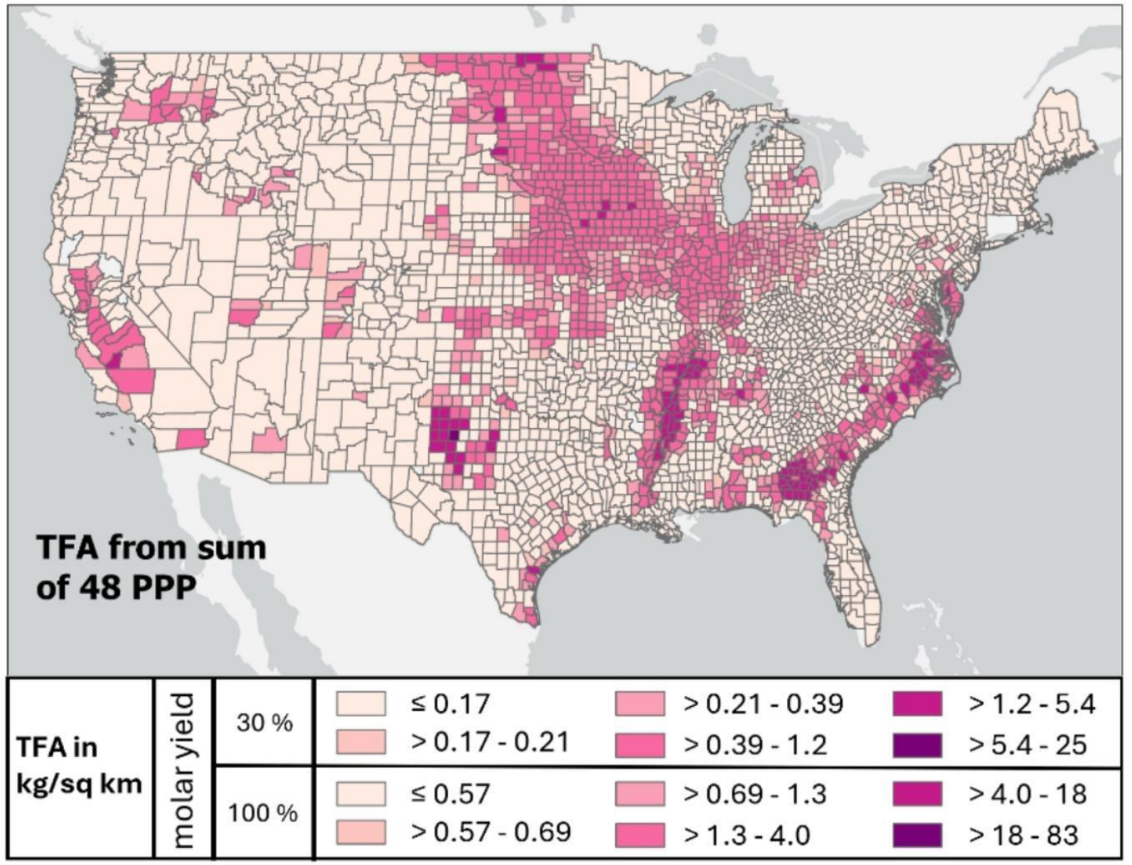
- 2020 rain concentrations in increase by a factor 5 by 2040
- This accumulates in the environment
- atmospheric TFA is formed from volatile precursors ((F-gases and others)



Young et al. *Environmental Science & Technology Letters* **2024** *11* (12), 1348-1354

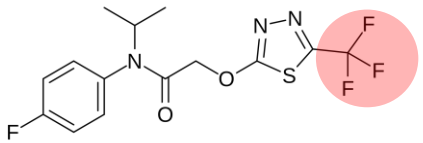
Pesticide/Herbicide precursors lead to TFA hotspots in agricultural areas



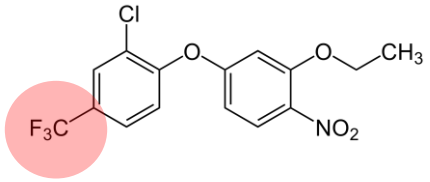


Major precursors:

flufenacet

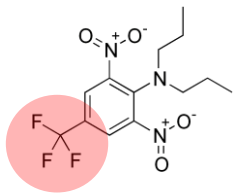


oxyfluorfen

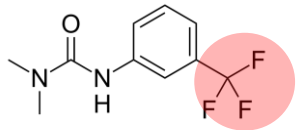


Major precursors

trifluralin

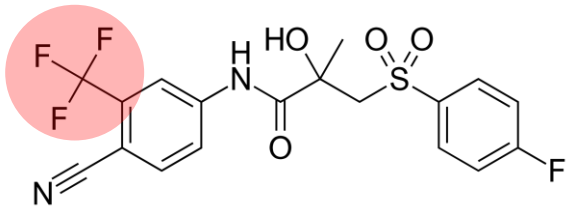


fluometuron

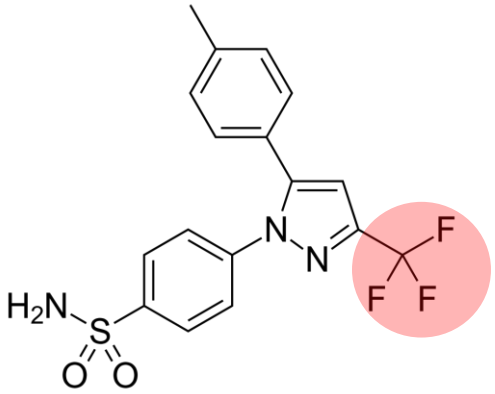


Joerss et al. (2024) *Environment International*, *193*, 109061.

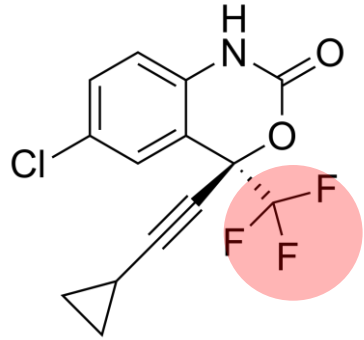
Pharmaceuticals



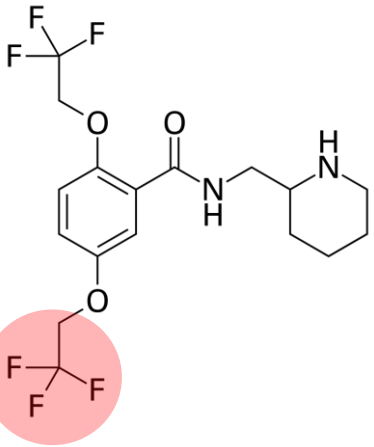
Bicalutamide – since 1995
(prostate cancer treatment)



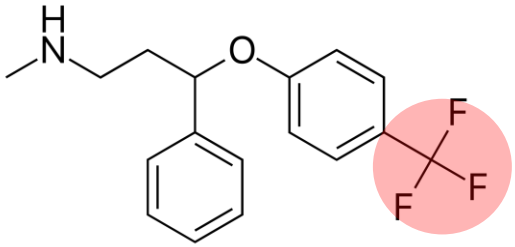
Celecoxib – since 1999
(Non-steroidal anti-inflammatory)



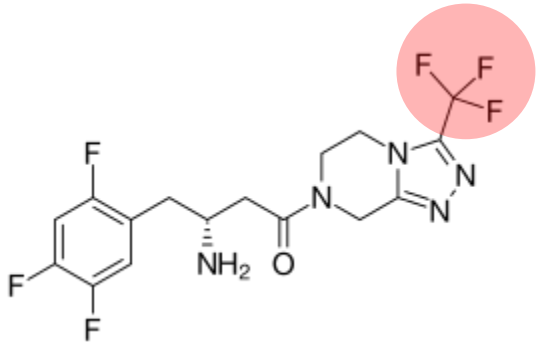
Efavirenz – since 1998
(HIV/AIDS treatment)



Flecainide – since 1985
(fast heart-rate treatment)



Fluoxetine (Prozac) - since1986
(Anti-depressant)

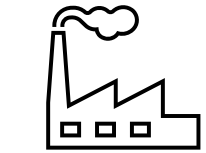


Sitagliptin – since 2006
(Anti-diabetic)

Sludge/biosolid

Agricultural chemicals

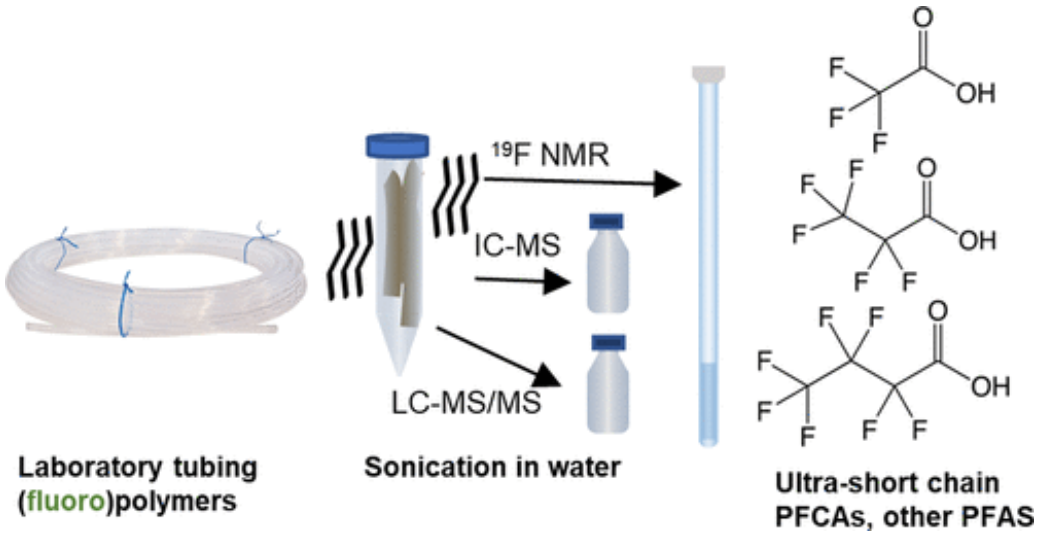
Release from PFAS production and products



PFAS production and products

Richard Hurd

- EU production of TFA 100 – 1000 tonnes/year
- TFA releases during F-gas, Fluoropolymer and PFAS production (e.g. 7500 µg/L in river Arias near a PFAS production facility)[1]



- Fluoropolymers *and plastics* leach TFA
- 126 +/- 96 µg/kg TFA leach from FEP tubing
- 1 to 7 µg/kg TFA leach from PVC tubing

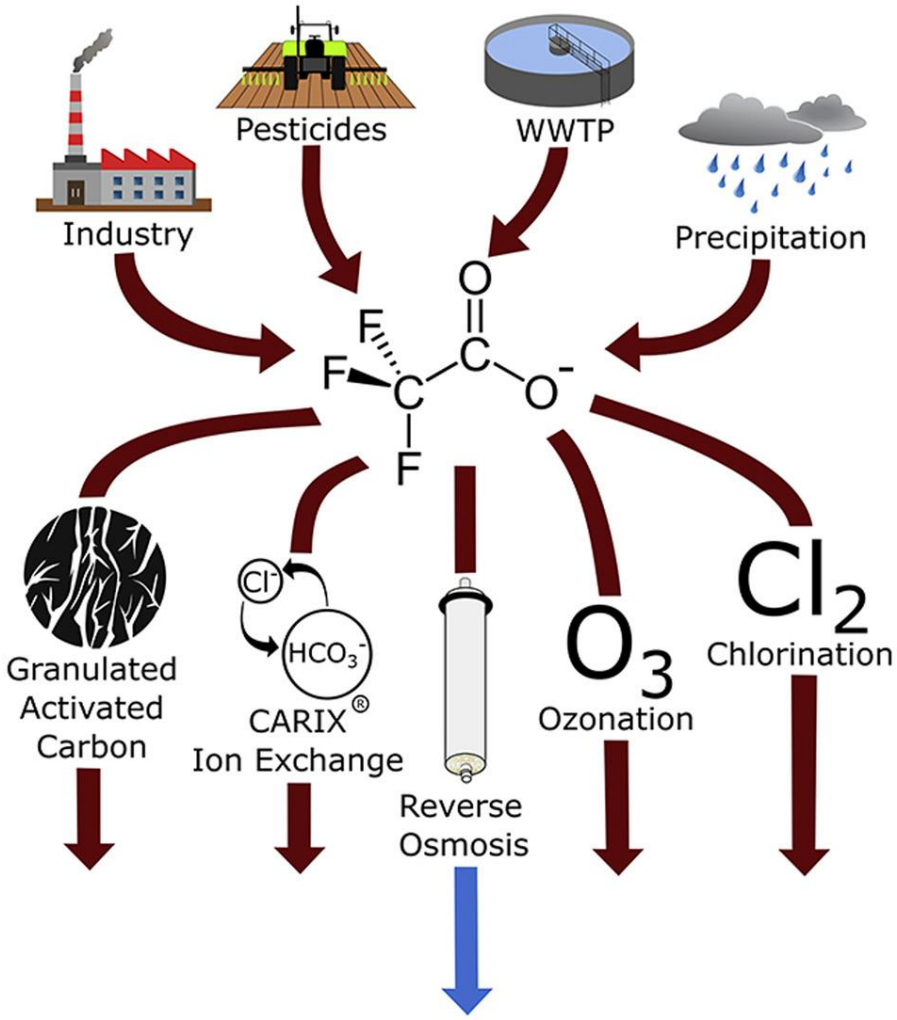
[1]https://www.generations-futures.fr/wp-content/uploads/2024/02/rapport-salindres-pfas.pdf

Joudan et al. Environ. Sci. Technol. Lett. 2024, 11, 3, 237-242

Water treatment ineffective at removing TFA, ….or can form TFA

PFAS remediation

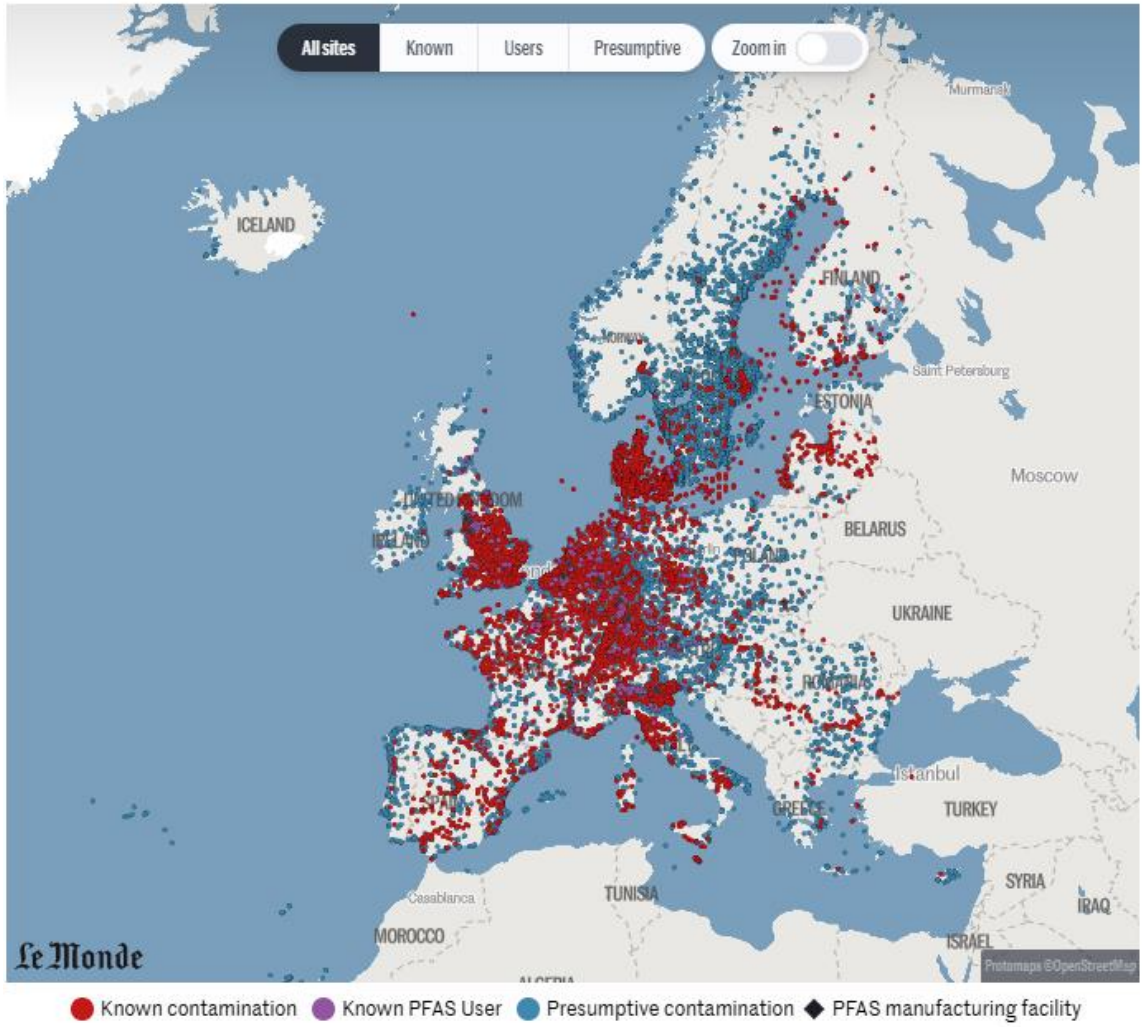
- Sorption techniques (activated carbon, ion exchange resins) -> **do not filter TFA**
- **Enhanced degradation techniques** (ozonation, chlorination, photolysis, electrolysis, incineration, pyrolysos etc.) **can lead to TFA formation from precursors** (along with other PFAS, F-gases)
- **Reverse osmosis** only technique that works for TFA, but requires an expensive destruction step for brines



Scheurer et al. (2017). *Water research*, *126*, 460-471.

The absurd costs of TFA remediation…

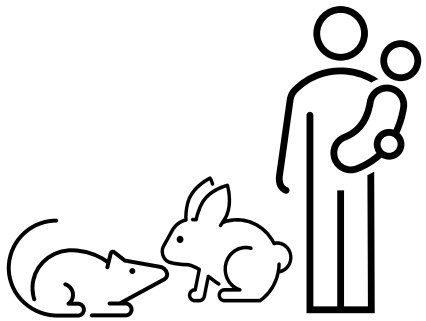
- Recent collaboration with *Forever Pollution Project* and Prof. Ali Ling
- Cost to remediate emerging ultra-short chain PFAS like TFA in Europe **100 billion EUR/y** (ca 100 billion USD/y) for water and soil
- Combination of reverse osmosis and super critical water oxidation for brines
- Would make drinking water more expensive and no longer mineral….
- Still be exposed to TFA…the wine will still be contaminated..



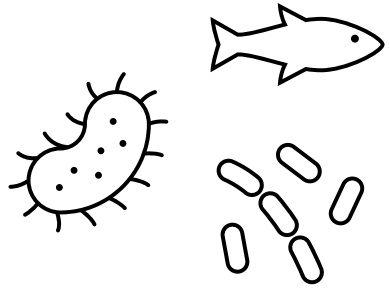
Source: Forever Pollution Project

https://foreverpollution.eu/lobbying/

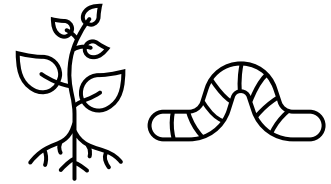
Irreversible effects



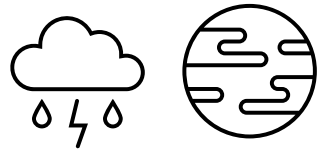
mammals



Aquatic algae / microbes



Soils / terrestrial ecosystems



Planetary boundaries

Toxicity to Mammals

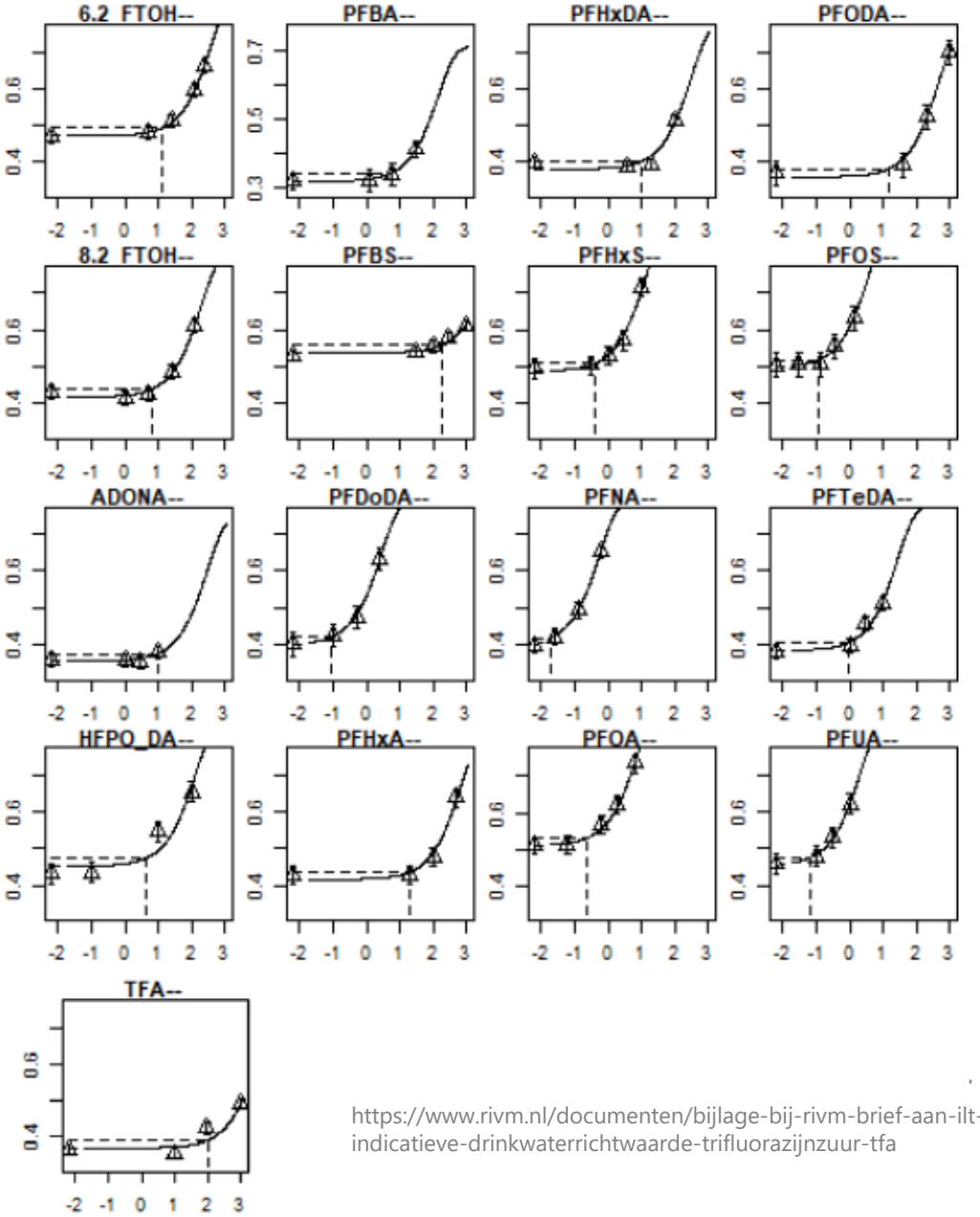
RIVM (2022)
Chronic rat toxicity (feeding)
Dose response: Male liver weight vs dose
Relevant potency factor: TFA is 0.002 x toxic as PFOA

*Corresponds to a **water threshold value of 2.2 µg/L***
Exceeded in an increasing number of areas

ECHA REACH Dossier (2024)
Han Wistar Rabbits
embryo-fetal developmental toxicity <180 mg/kg/day

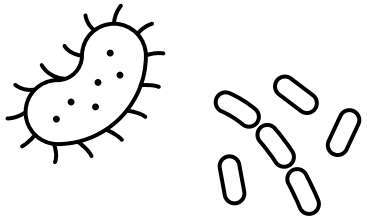
multiple folded retina and absent aqueous/vitreous humor were above the … historical control data range

Rategory 1B: Presumed human reproductive toxicant



https://www.rivm.nl/documenten/bijlage-bij-rivm-brief-aan-ilt-indicatieve-drinkwaterrichtwaarde-trifluorazijnzuur-tfa

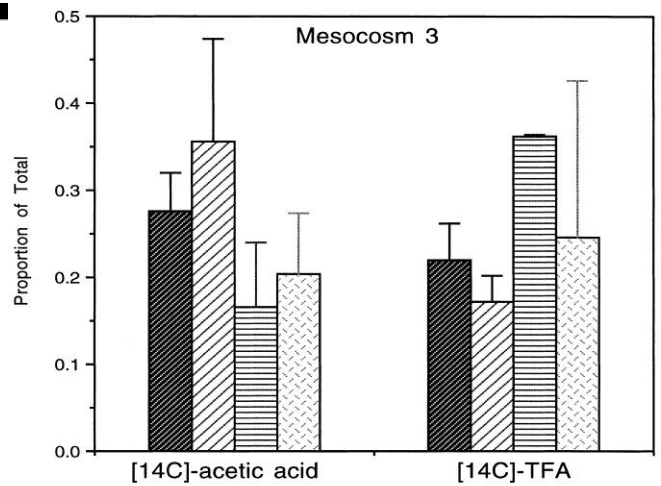
TFA able to become part of the lipids and biomolecules inside microbes …. no follow-up since 1999

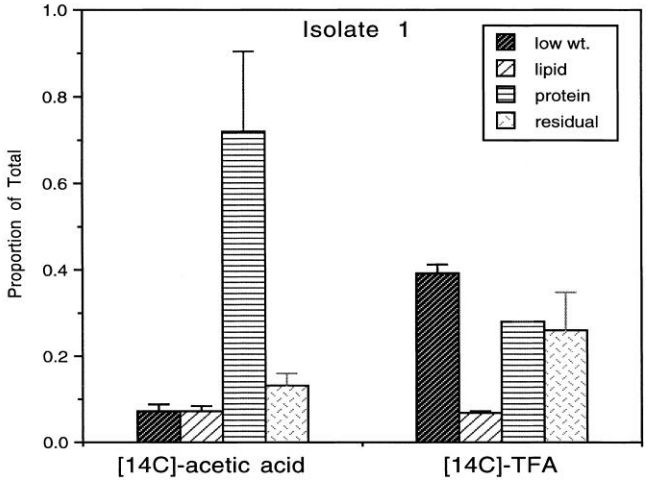


Trifluoroacetate, an Atmospheric Breakdown Product of Hydrofluorocarbon Refrigerants: Biomolecular Fate in Aquatic Organisms

LAUREL J. STANDLEY* AND
THOMAS L. BOTT

Stroud Water Research Center, Academy of Natural Sciences of Philadelphia, 970 Spencer Road, Avondale, Pennsylvania 19311





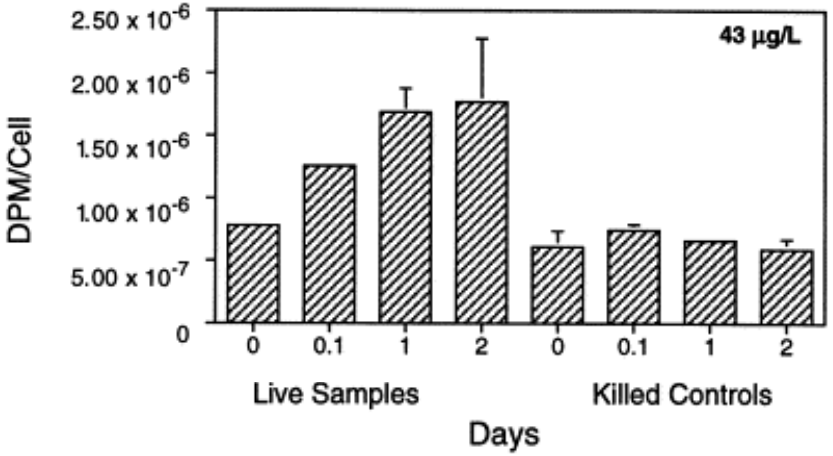
ELSEVIER

Water Research
Volume 33, Issue 6, April 1999, Pages 1538-1544

Research Note

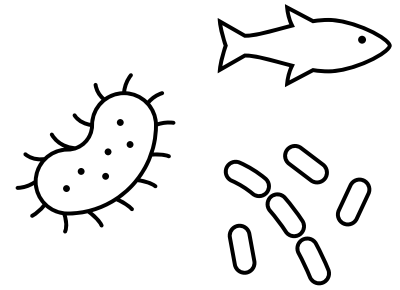
Incorporation of trifluoroacetate, a hydrofluorocarbon decomposition byproduct, by freshwater benthic microbial communities

Thomas L. Bott, Laurel J. Standley



If TFA covalently bonded with lipids, membranes, biomolecules, etc. they would ultimately be degraded to TFA… again

Toxicity to aquatic ecosystems



Aquatic algae / microbes

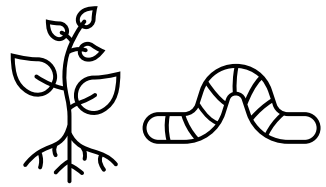
Aquatic toxicity of TFA

- No observable effect concentration (NOEC) of **120 µg/L** for *Raphidocelis subcapitata* – (Solvay data reported in Berends et al. 1999, USEEP ECOTOX). Used to derive a PNEC of **0.12 to 12 µg/L**
- Ignored as an outlier in some reports, but appears reproducible
- ECHA REACH uses a **ErC10 of 5600 µg/L** based on an algae growth study, PNEC of 560 µg/L

- Aquatic Concentrations exceeded in TFA hotspots and an increasing number of freshwater environments
- All aquatic toxicity data for TFA is days to months, not years/lifetimes: reason to treat data with precaution

Berends, A. G.; Boutonnet, J. C.; De Rooij, C. G.; Thompson, R.S. Toxicity of Trifluoroacetate to Aquatic Organisms. Environ. Toxicol.Chem. 1999, 18 (5), 1053−1059.

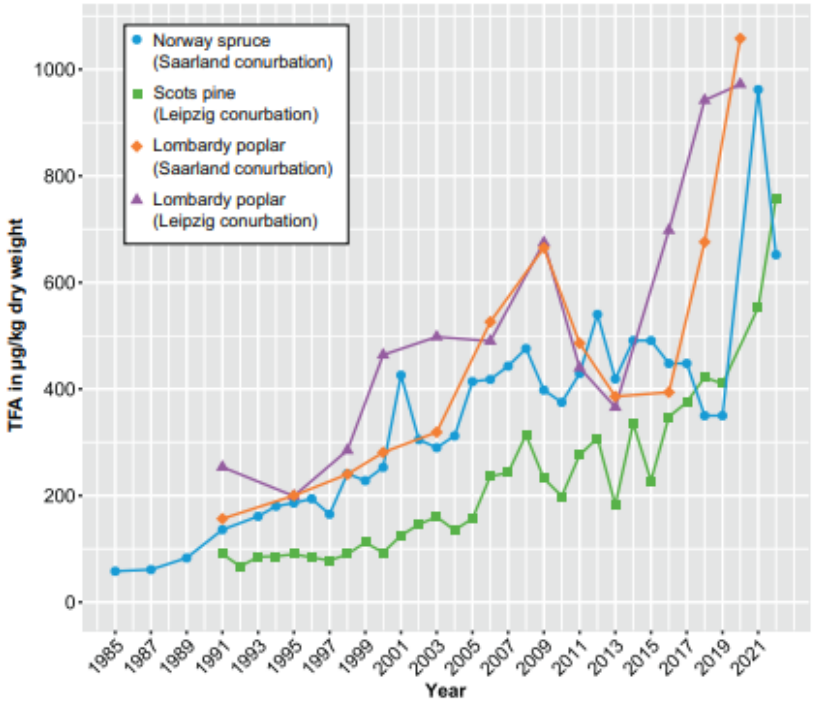
Toxicity to soil and terrestrial systems



Soils / terrestrial ecosystems

- ECHA REACH dossier: long term No observable effect concentration (NOEC) **0.83 mg/kg soil** (plant shoot growth)
- TFA readily bioaccumulates in plants/shoots from soil
- Effects on the soil pH, microbial respiration, bacterial abundance and litter decomposition were reported at TFA concentrations in soil in hotspots **(0.0013–2.4 mg/kg$_{dw}$)**, above this problems related to TFA acidity can occur.

- **Soil concentrations at TFA hotspots already exceed these concentrations**
- **Little long exposure studies on terrestrial systems**



TFA increasing in tree leaves

Chen et al. *Environ. Sci. Technol.* **2018**, *52* (15), 8263− 8271
Freeling and Björnsdotter, Current Opinion in Green and Sustainable Chemistry 2023, 41:100807

Planetary Boundary Threat of TFA

Disturbances to the «homeostasis» or of earth processes. Exceed this, Earth would leave the Holocene where humans evolved.

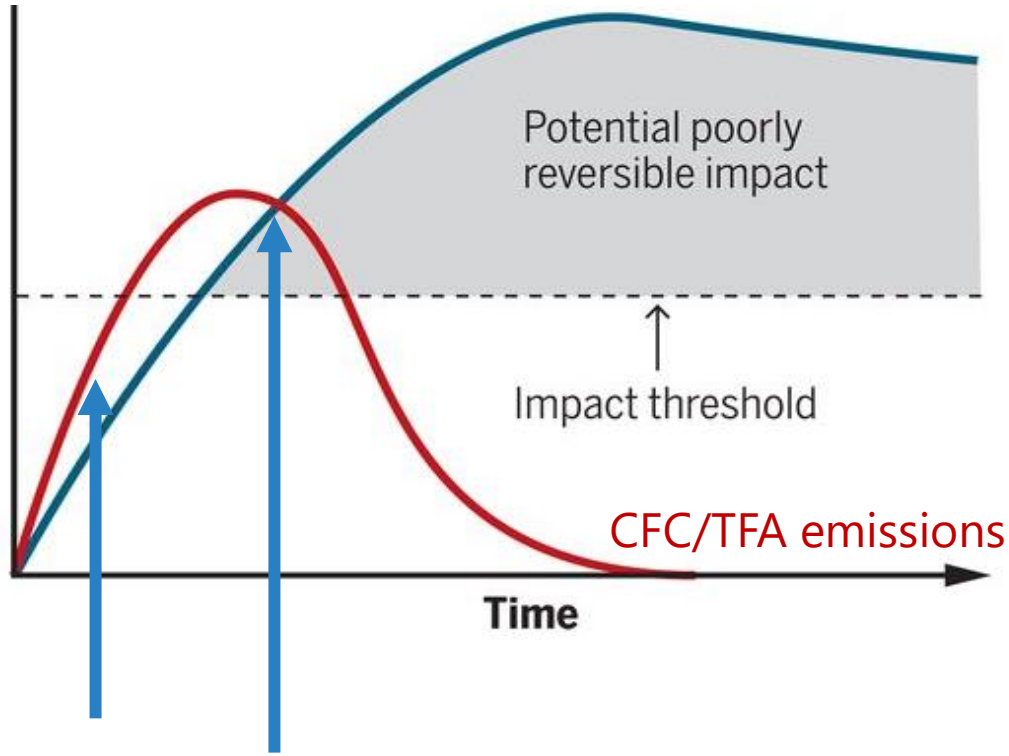
Conditions for novel entities:[1,2]

Condition 1: pollution disrupts a vital earth system process of which we are ignorant.
TRUE: impacts at hotspots occur now, ignorant of impacts from life-long intergeneration exposure (ignorant)

Condition 2: disruptive effect is not discovered until …manifested at a global scale
TRUE: TFA increases globally

Condition 3: impacts are poorly reversible because level of global pollution cannot be readly reduced
TRUE: TFA is already diluted, stock piles of sources exist. Most TFA we emit will exist in water for the future of earth

Planetary boundaries

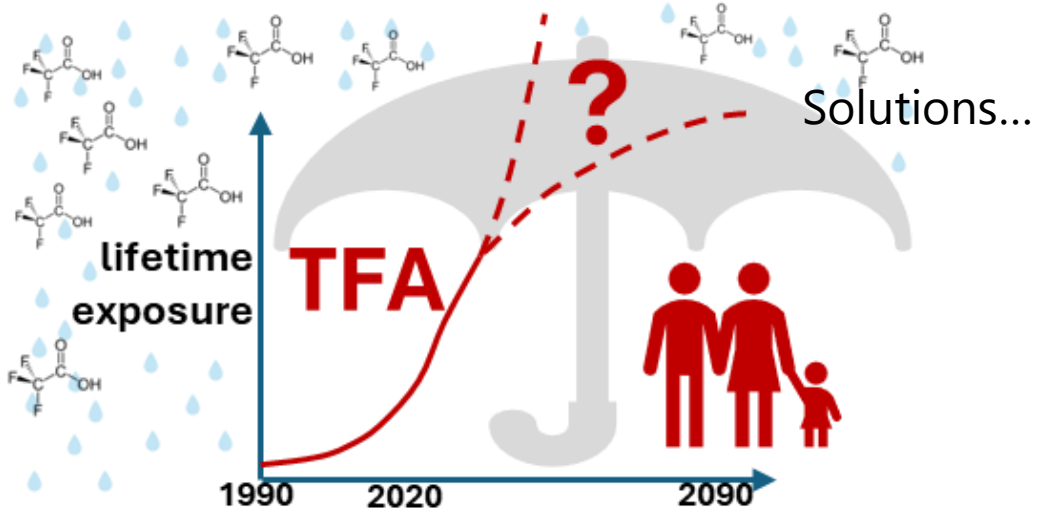


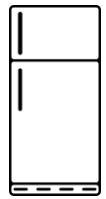
Not a threat
CFCs - Lovelock (1988)
TFAs – Boutonnet (1999)

Planetary boundary threat realized and exceed
CFC – ozone depletion -> Montreal Protocol
TFA – ?????

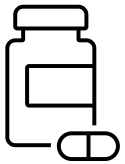
1. Persson et al. *Environ. Sci. Technol.* **2013**, *47* (22), 12619− 12622
2. MacLeod et al. *Science* 373,61-65(2021)

Solutions to a Global Threat

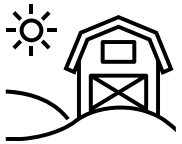




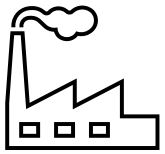
Refrigerants and blowing agents



Pharmaceuticals



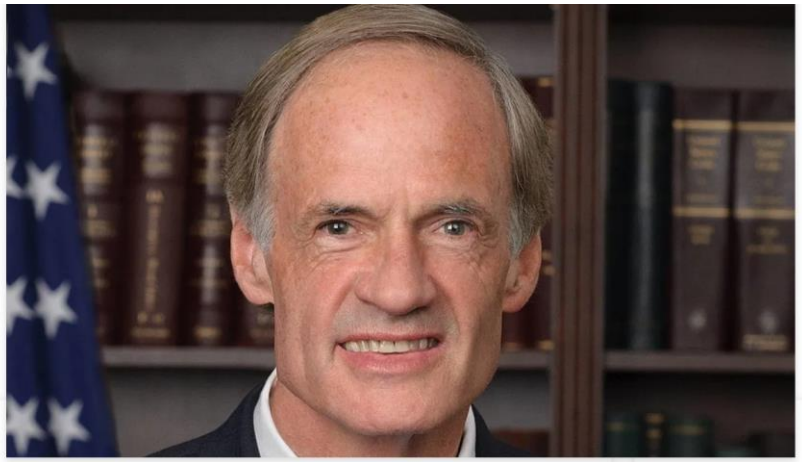
Agricultural chemicals



PFAS production and products

TFA is a PFAS, regulate it like a PFAS

- PFAS (Per- and polyfluoroalkyl substances)
- OECD definition of PFAS includes TFA, as does scientific consensus
- TFA considered PFAS by EU, 23 US states
- Broad scientific consensus (see statement below)
- USEPA draft definition does not, certain regions try to explicitly exclude TFA in the PFAS definition



Tom Carper, U.S. Senator from Delaware; image from United States Senate, Public domain, via Wikimedia Commons

U.S. Senate Committee Proposes Bill That Excludes F-Gases and TFA from Definition of PFAS

Stakeholders can provide feedback on the bill through July 3.

Newsletter

May 7, 2024

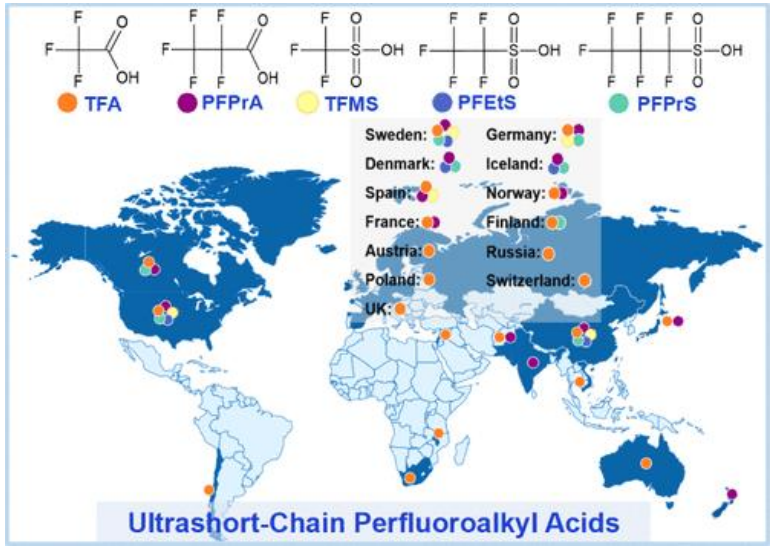
Scientists' Statement on Defining PFAS

The undersigned are scientists with expertise in per- and polyfluoroalkyl substances ("PFAS"). We study the use and health & environmental effects of PFAS, and support reducing the adverse impacts of PFAS, the "forever chemicals". Here, we address the necessity for government agencies and legislatures to adopt complete PFAS definitions grounded in science without political interference.

PFAS are used in consumer and industrial applications as surfactants and to impart oil, water, and stain resistance. There are thousands of PFAS chemicals and all well-studied PFAS show human health harms ranging from immune system dysfunction to increased risk of certain cancers.[1] All PFAS are distinguished by the presence of at least one fully fluorinated carbon atom. The carbon-fluorine bond is the strongest single bond in organic chemistry[2], giving all PFAS the shared trait of persistence, leading to their accumulation in our bodies and ecosystems. The health and environmental risks of PFAS coupled with their extreme environmental persistence[3] requires a class-based approach[4] and a definition that reflects that.

The following are science-based definitions:

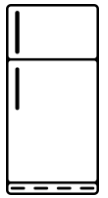
- The "at least one fully fluorinated carbon" definition that has been used by 23 US states, the Department of Defense, and Congress.[5]
- The nearly identical 2021 OECD definition that was crafted by a panel of international PFAS experts, including those representing the chemical industry and US EPA.[6]



Zhi et al. *Environmental Science & Technology* **2024** *58* (49), 21393-21410
DOI: 10.1021/acs.est.4c04453

https://drive.google.com/file/d/1YLB2zvWG5Ez6VeMqqbw77LpVEj0JTj1H/view

Solution to F-gases used as refrigerants



Refrigerants and blowing agents

Fifth generation of F-gases in the Montreal Protocol can be free of TFA precursors

	CO_2	Ammonia	Propane	Isobutane	Others
Domestic refrigeration				X	
Stand-alone refrigeration systems in commercial stores	x	x	X	x	x
Multipack centralized refrigeration systems in commercial stores	X	x	x		
Industrial refrigeration	x	X			
Transport refrigeration of goods	x		x		x
Ultra-low and low temperature freezers		x	x		x

Environmental Science Processes & Impacts

ROYAL SOCIETY OF CHEMISTRY

CRITICAL REVIEW

View Article Online
View Journal | View Issue

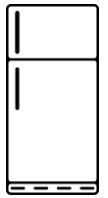
Check for updates

Cite this: *Environ. Sci.: Processes Impacts*, 2024, **26**, 1955

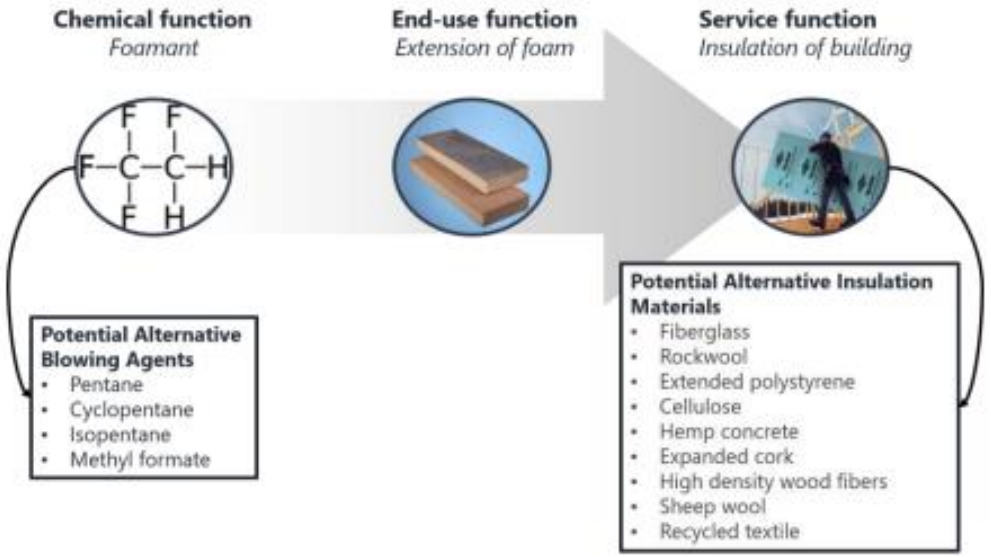
Finding non-fluorinated alternatives to fluorinated gases used as refrigerants†

Juliane Glüge, ‡*[a] Katharina Breuer, ‡[b] Armin Hafner,[c] Christian Vering,[b] Dirk Müller,[b] Ian T. Cousins,[d] Rainer Lohmann,[e] Gretta Goldenman[f] and Martin Scheringer[a]

Solution to F-gases used as blowing agents



Refrigerants and blowing agents



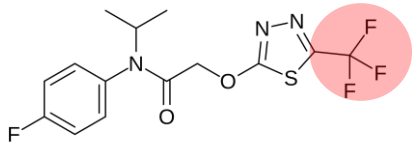
- Alternative chemicals to use to make polyurethane and XPS foam than (e.g. pentane, methyl formate)

- Alternatives to polyurethane and XPS foam for many functions.

PhD thesis defence - Romain Figuiére
Event by Department of Environmental Science | Stockholm University

Pesticides and Pharmaceuticals

- TFA precursor Flufanecet to be non-renewed in Europe (draft decision)
- more of this!



Brussels, XXX
PLAN/2024/2430 Rev. 0
[…](2024) XXX draft

COMMISSION IMPLEMENTING REGULATION (EU) …/...

of XXX

concerning the non-renewal of the approval of the active substance flufenacet, in accordance with Regulation (EC) No 1107/2009 of the European Parliament and of the Council, and amending Commission Implementing Regulation (EU) No 540/2011 and Commission Implementing Regulation (EU) 2015/408

PERSISTENT POLLUTANTS

Are fluorinated drugs PFAS?

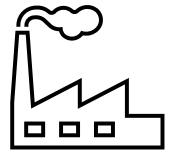
Proposed regulations in the European Union present an uncertain future for pharmaceuticals and agrochemicals—and motivation to design greener ones

BRIANNA BARBU, C&EN STAFF

- Biodegradable, non-fluorinated drugs an active area of «green pharmacy» innovation
- Evaluate switching to PFAS free alternatives when recommending medications

https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2024.8997
Barbu (2024). https://pubs.acs.org/doi/pdf/10.1021/cen-10226-feature1

Phase out and restrict PFAS (including fluoropolymers)
- particularly in products where they are not essential/alternatives available



PFAS production

and products

California LEGISLATIVE INFORMATION

California Senate Bill 903, USA

Existing law prohibits PFAS in certain food packaging.

Existing law, commencing January 1, 2025, prohibits PFAS in any new, not previously used, textile articles and in any cosmetics.

This bill would, beginning January 1, 2032, prohibit a person from distributing, selling, or offering for sale a product that contains intentionally added PFAS.

https://leginfo.legislature.ca.gov/faces/billTextClient.xhtml?bill_id=202320240SB903

ECHA EUROPEAN CHEMICALS AGENCY

Next steps for PFAS restriction proposal

The European Chemicals Agency (ECHA) outlines how its two scientific committees will progress in evaluating the proposal to restrict per- and polyfluoroalkyl substances (PFAS) in Europe.

Helsinki, 13 March 2024 – Following the screening of a large number of comments received during the consultation, ECHA is clarifying the next steps for the proposal to restrict PFAS under REACH, the EU's chemicals regulation.

https://echa.europa.eu/de/-/next-steps-for-pfas-restriction-proposal

Provide tools for industry to find where and in what it is using PFAS

PFAS production and products

https://pfas.chemsec.org/

The rap battle against PFAS

https://www.youtube.com/watch?v=1q06fUMT_U4

ZeroPM alternative assessment database

- Find alternative for PFAS based on chemical function, end-use function, and function as a service

PFAS production and products

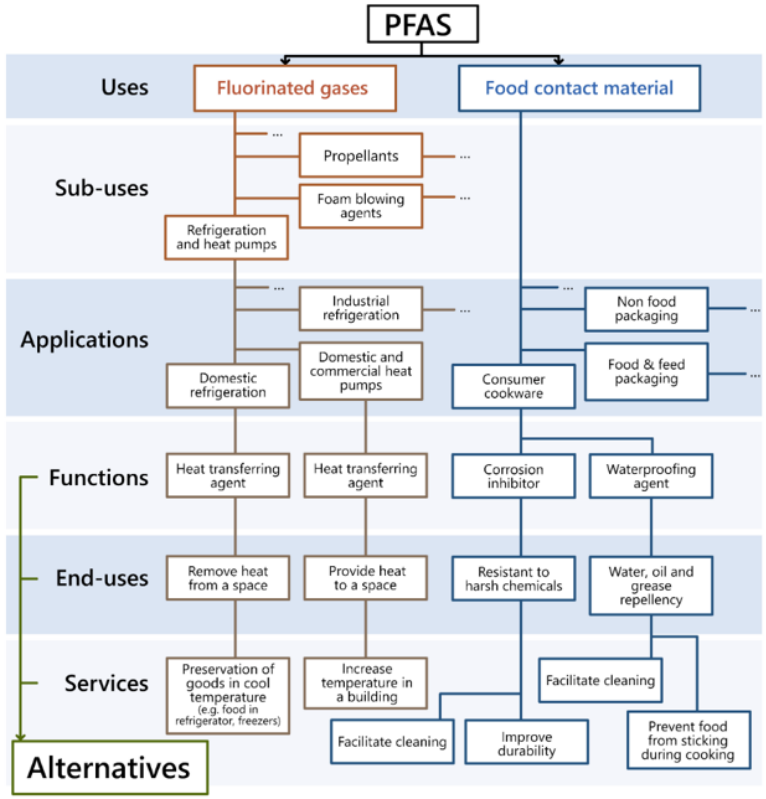


Figure: General structure of the ZeroPM alternatives database for PFAS – Examples of fluorinated gases and food contact material

ZEROPM ALTERNATIVE ASSESSMENT DATABASE

https://zeropm.eu/alternative-assessment-database/

Effective labelling

PFAS production and products

How do PFAS labels affect consumer intentions?

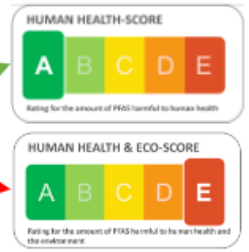
N = 450

- Prelim data (subject to updates!)
- No effect of framing on WTB (eco, health or eco-health).
- Big effects of rating (Control vs. A; Control vs. E).

Contrasts and Estimates (H_{1a})

Rating Label	β	*SE*	*z*	*p*
Control vs A Rating	-0.558	0.057	-9.845	< .001***
Control vs E Rating	1.832	0.059	30.830	< .001***
A Rating vs E Rating	2.390	0.083	28.845	< .001***

Note: The table provides estimate pairwise comparisons for all contrasts (β), along with the



29% of Europeans **have previously heard of the term PFAS**, also known as 'forever chemicals'

When given the definition of PFAS, also known as 'forever chemicals'...

81% of citizens are concerned about the potential **health effects when exposed to PFAS**

16% Disagree

While **84%** of citizens are concerned about **the effects of PFAS on the environment**

13% Disagree

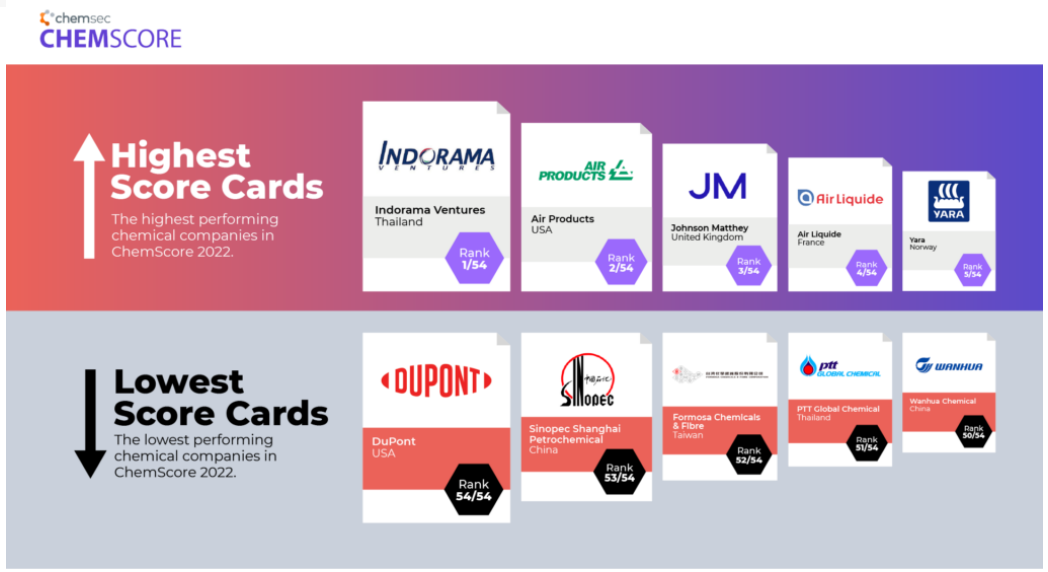
Source: Special Eurobarometer 550 – "Attitudes of Europeans to the environment" Fieldwork: March-April 2024
* The figures show the top-3 most frequently cited items out of 8 options
** The figures show the top-3 most frequently cited items out of 5 options

Ellise Suffill, ZeroPM pieces #17 - Expert & non-expert perceptions on PFAS & essentiality in everyday products. https://zenodo.org/records/10628255

Invest in the growing market for PFAS and TFA free alternatives

SUSTAINABLE FINANCE

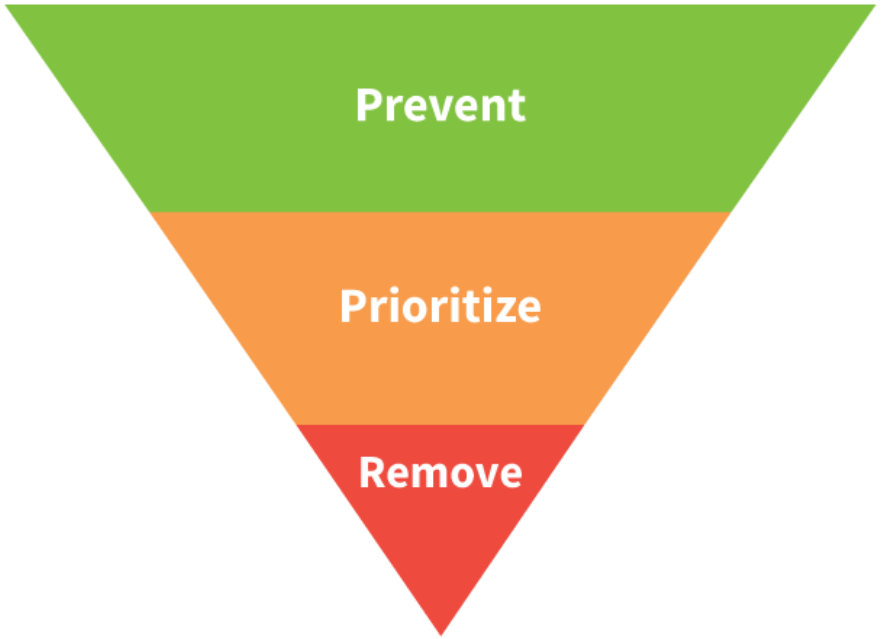
Investors with $8 trillion call for phase-out of dangerous "forever chemicals"



PFAS production and products

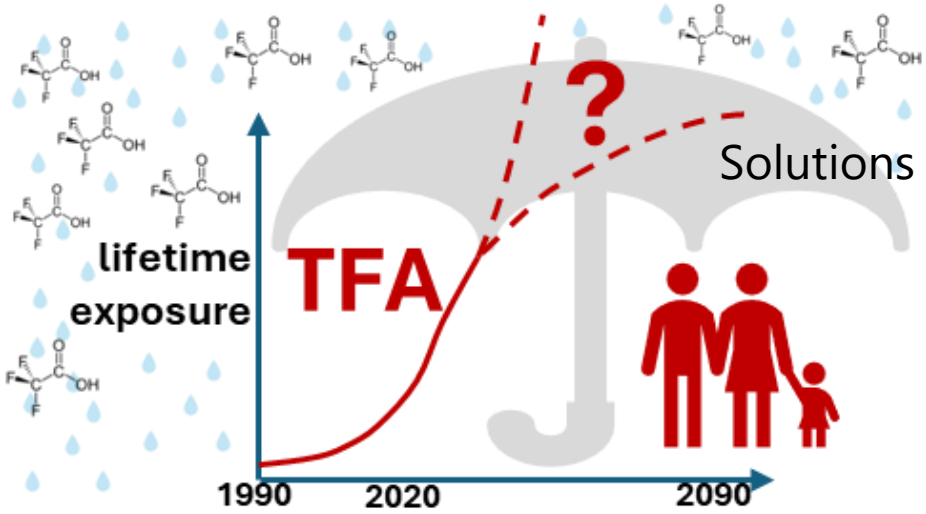
https://marketplace.chemsec.org/
https://chemscore.chemsec.org/
https://pfas.chemsec.org/

We have the tools now to transition away from TFA, to stabilize exposure



All you need is love and:

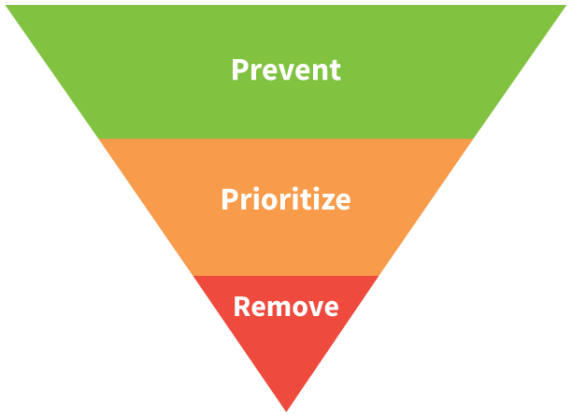
- Transition to PFAS and TFA free alternatives, start with TFA precursors produced in greatest volume
- Classify and label TFA as a PFAS, and integrate in PFAS reduction strategy (national and business)
- Remove TFA from active emission sources (industry effluent), ideally via the polluter pays principle



Acknowledgements

https://pubs.acs.org/doi/10.1021/acs.est.4c06189

ZerOPM



2021-2026

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Contact: hans.peter.arp@ngi.no

https://zeropm.eu/