ZerOPM

ICCE 2025 BELGRADE

Trifluoroacetic Acid (TFA) as a Planetary Boundary Threat

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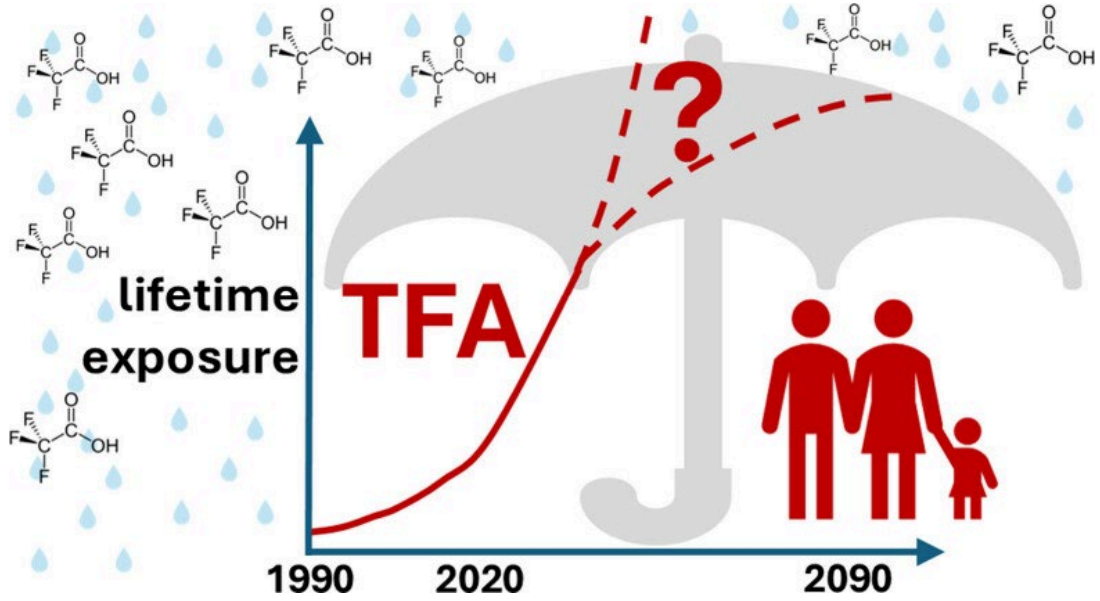
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101036756.

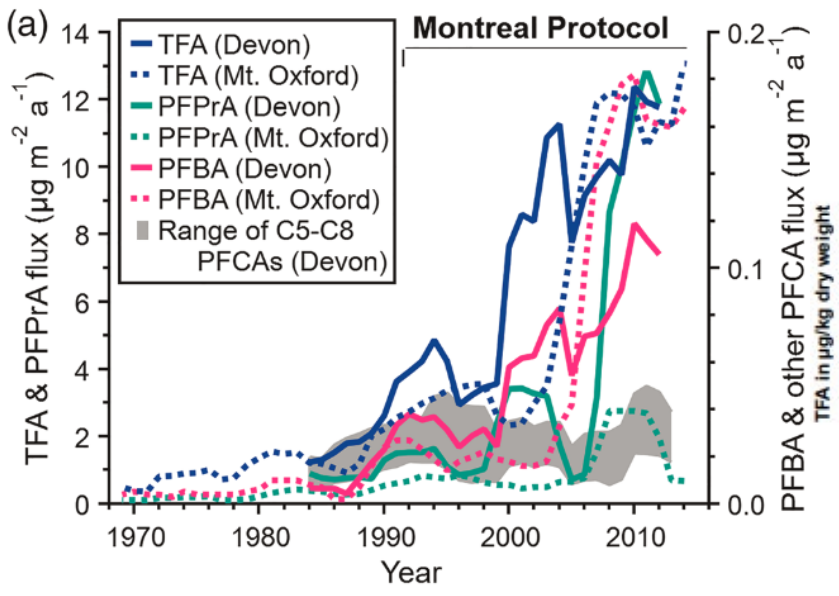
Contents

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

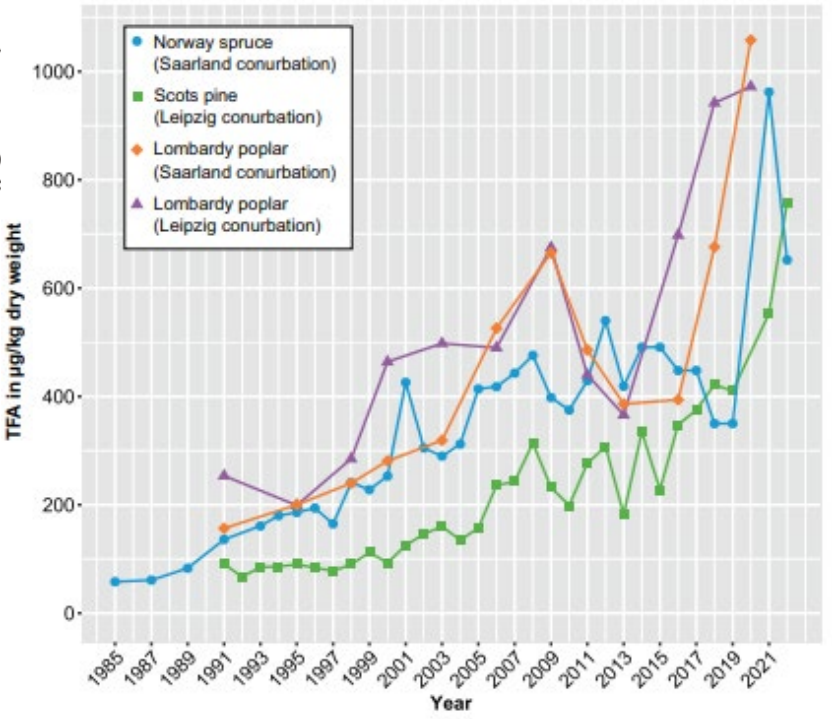


TFA is accumulating everywhere, largely coinciding with F-gas use following the Montreal Protocol and TFA use in many pesticides and other products

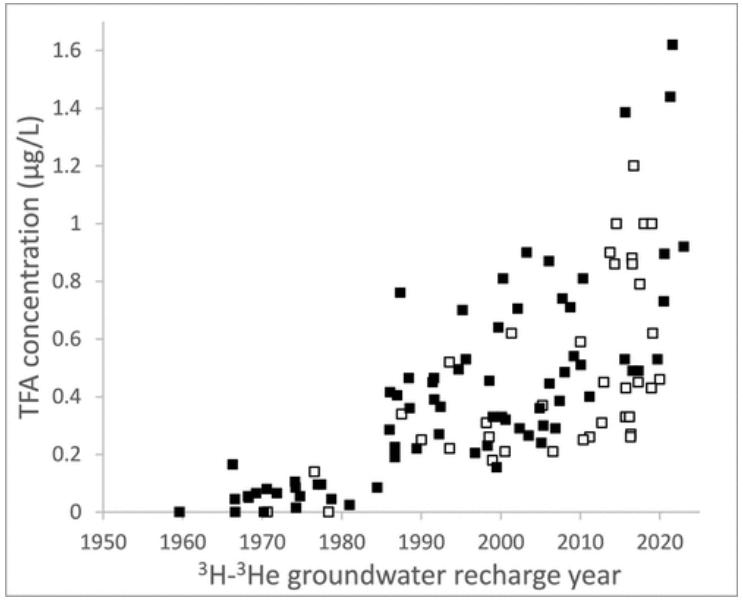
TFA accumulating in arctic ice cores

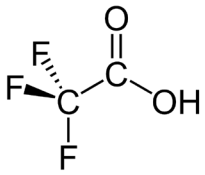


and in tree leaves



and in groundwater





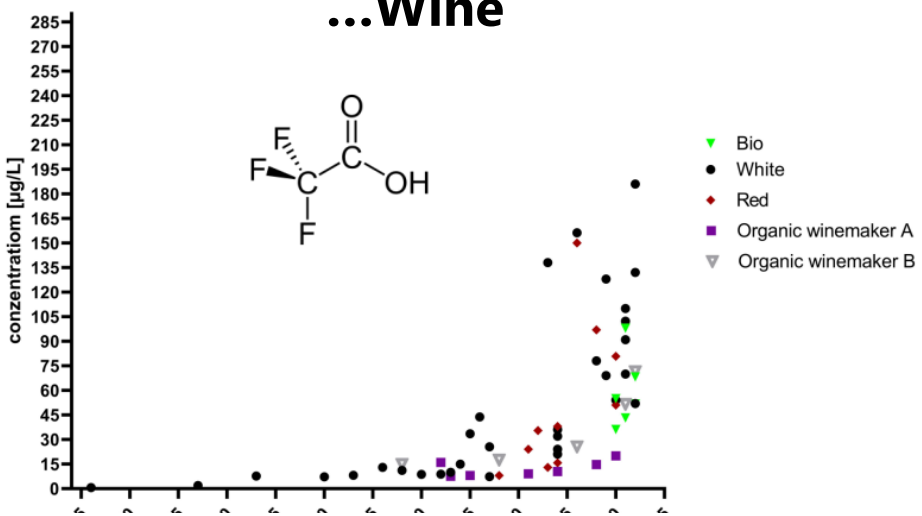
Pickard et al. Geophysical Research Letters (2020),47, e2020GL087535

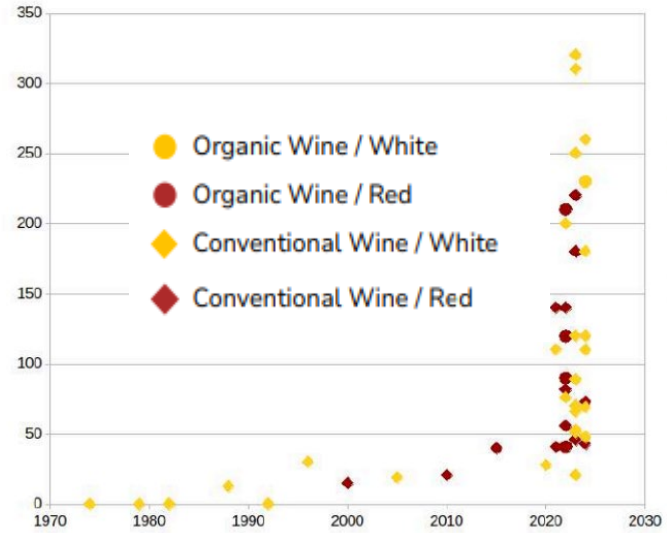
Freeling and Björnsdotter, Current Opinion in Green and Sustainable Chemistry 2023, 41:100807

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

TFA is increasing in all that we drink

…Wine





Up to 300 µg/L

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

Wine image: Sai Balaji Varma Gadhiraju

PAN Europe: Message from the Bottle – The Rapid Rise of TFA Contamination Across the EU

Drinking water (median)[1,2]

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

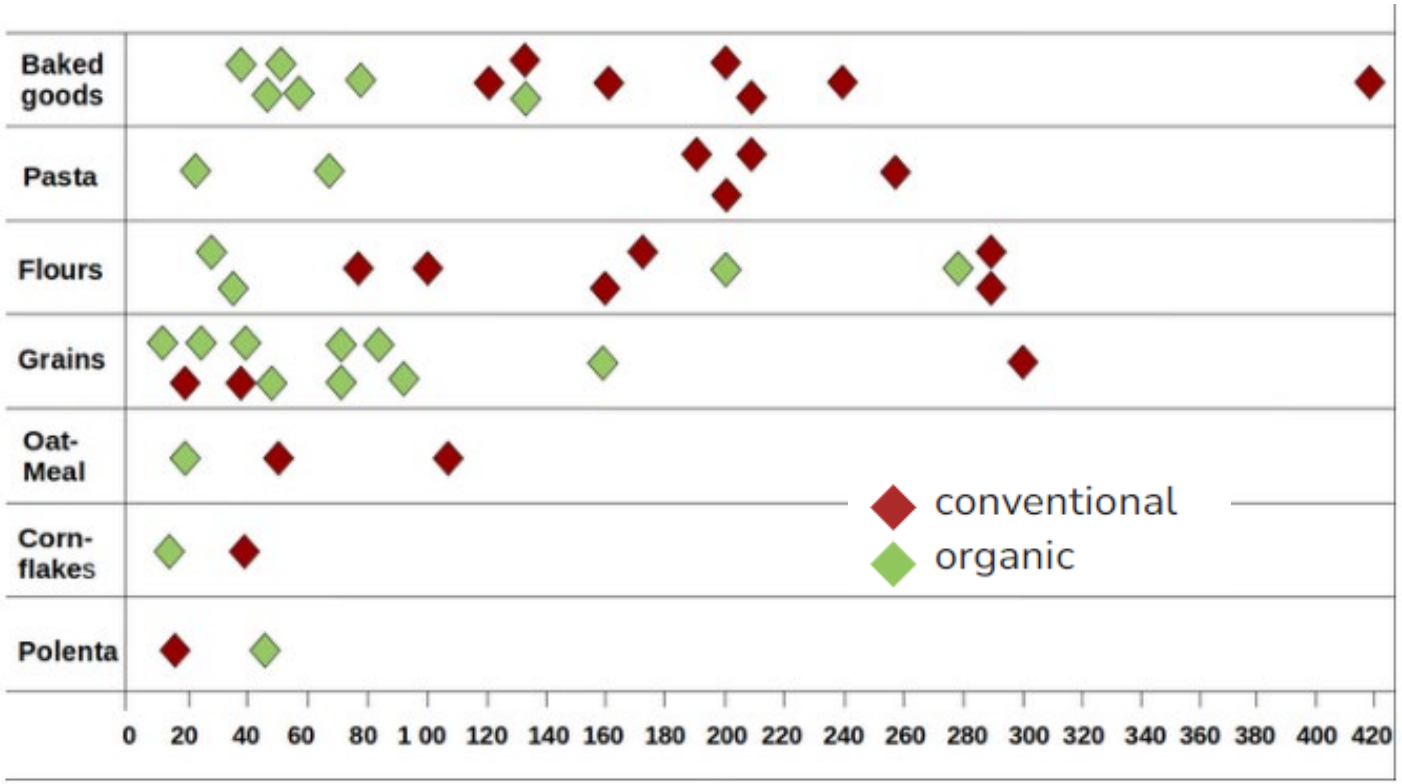
Tee (median): 2.4 µg/L[2]

Beer (median) 6.1 µg/L[2]

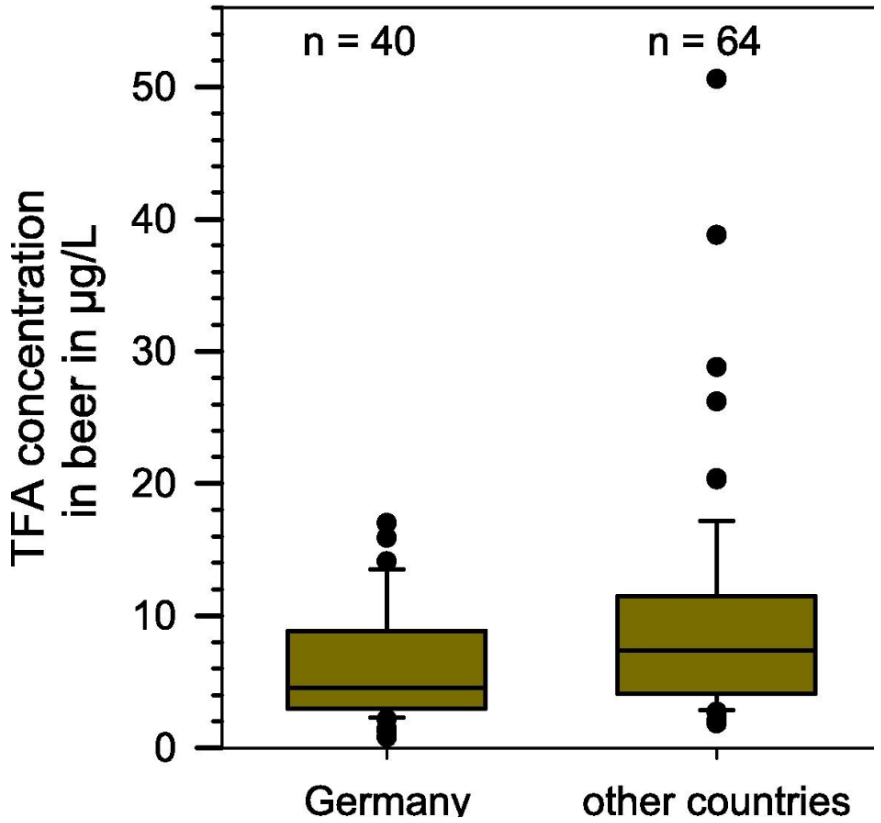
Orange juice (mean 34 µg/L)[3]

Apple juice (mean 6.2 µg/L)[3]

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

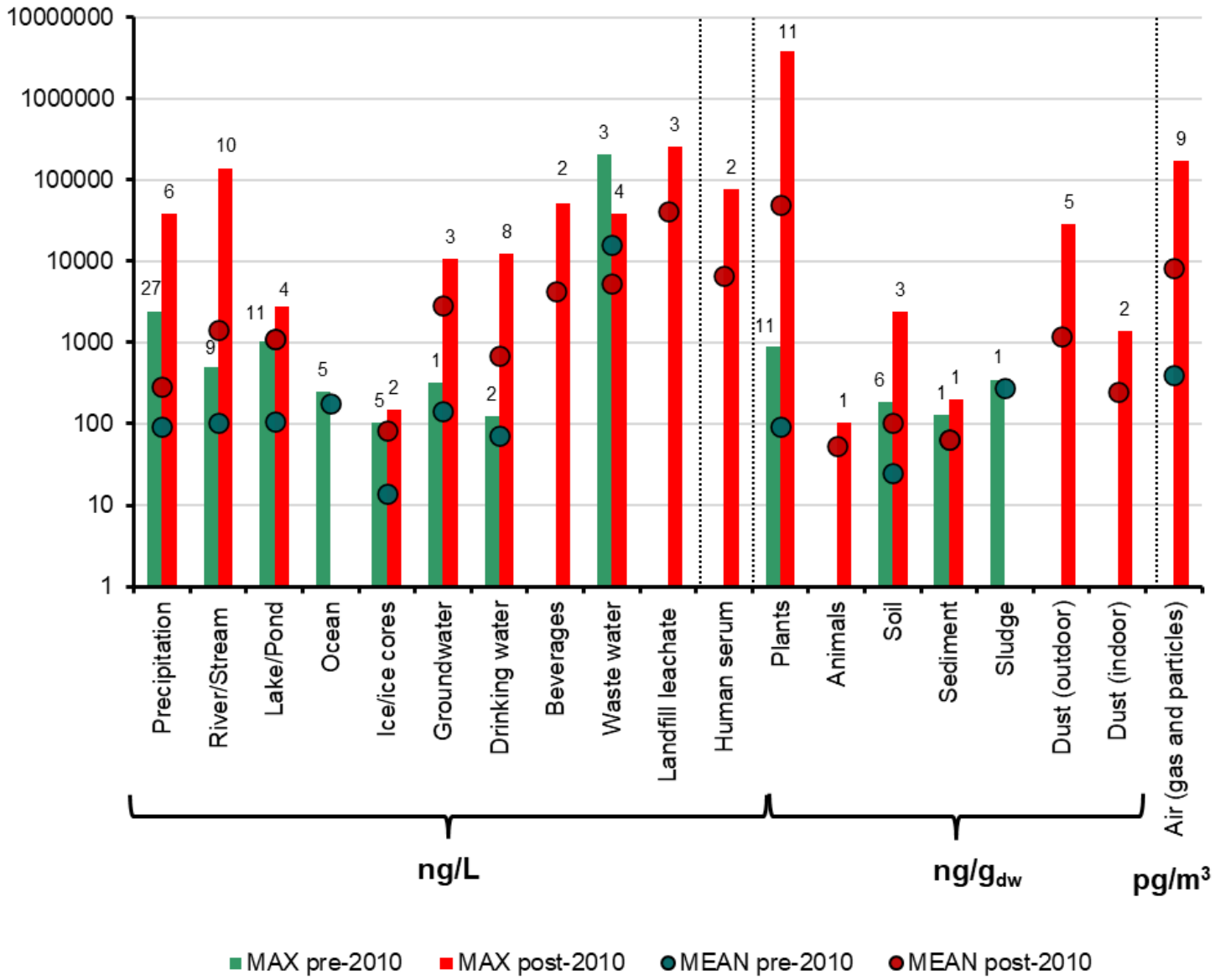


µg/kg dw



Scheurer und Nödler Food Chemistry 351 (2021) 129304

TFA is accummulating everywhere it can be measured



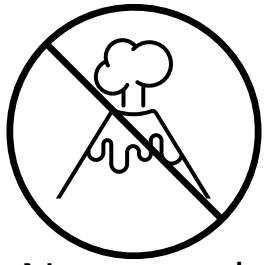
Chinese blood 97% detection
Median 8.5 µg/L
Similar to levels of the sum of all long-chain, bioaccumulative PFAS

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

No evidence that TFA is of natural origin

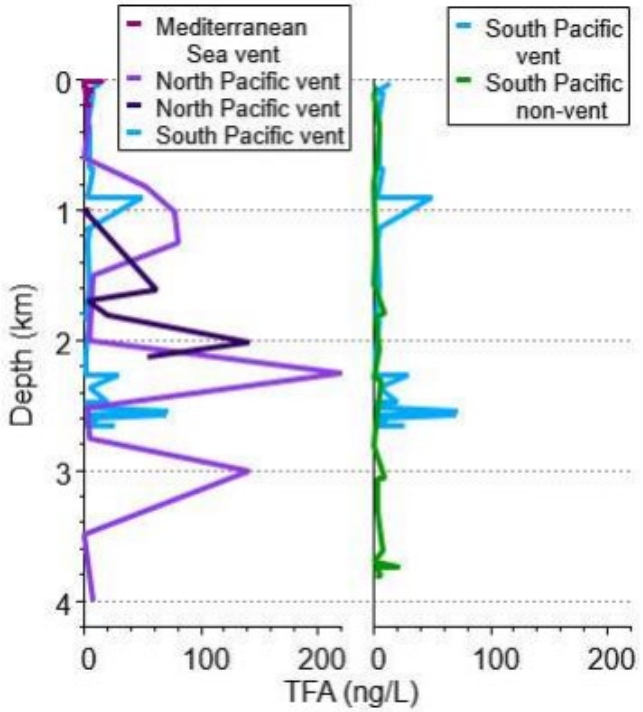


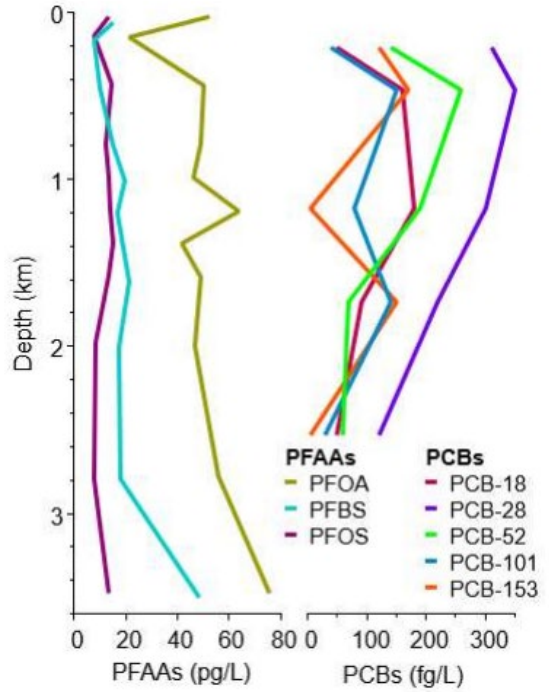
No natural sources

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

Hypothesis **no longer supported**[3]

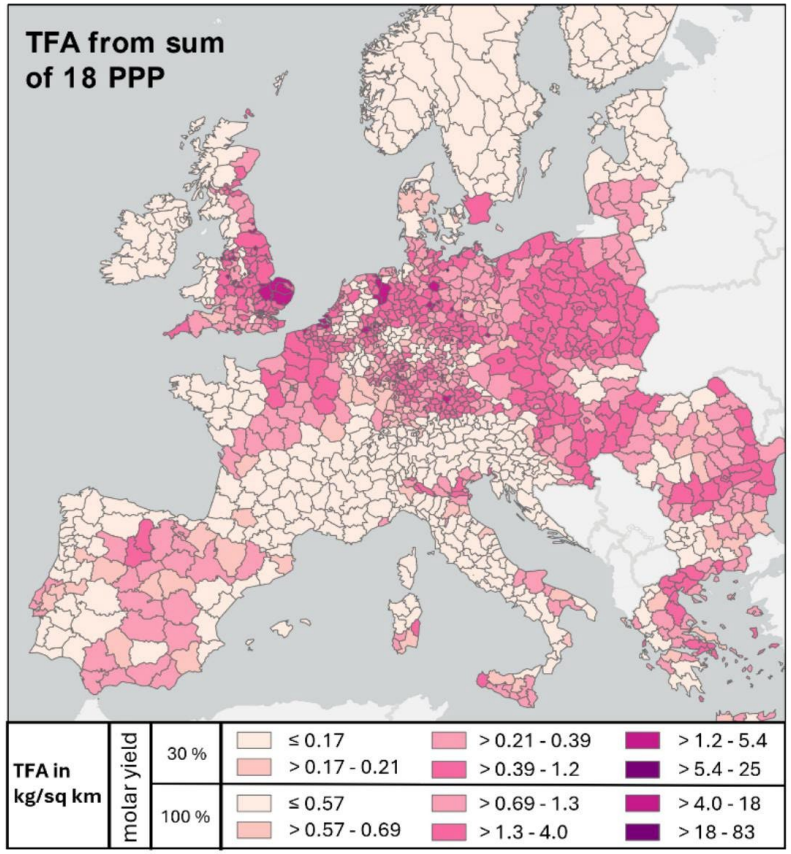
- No TFA gradients by deep sea vents
- TFA, PFAS and other synthetic substances in deep sea via
  - ❑ oceanic currents
  - ❑ sinking of dense water formed on continental shelfs
  - ❑ Marine snow deposition
- Inconsistent with time trends in rain/ice cores

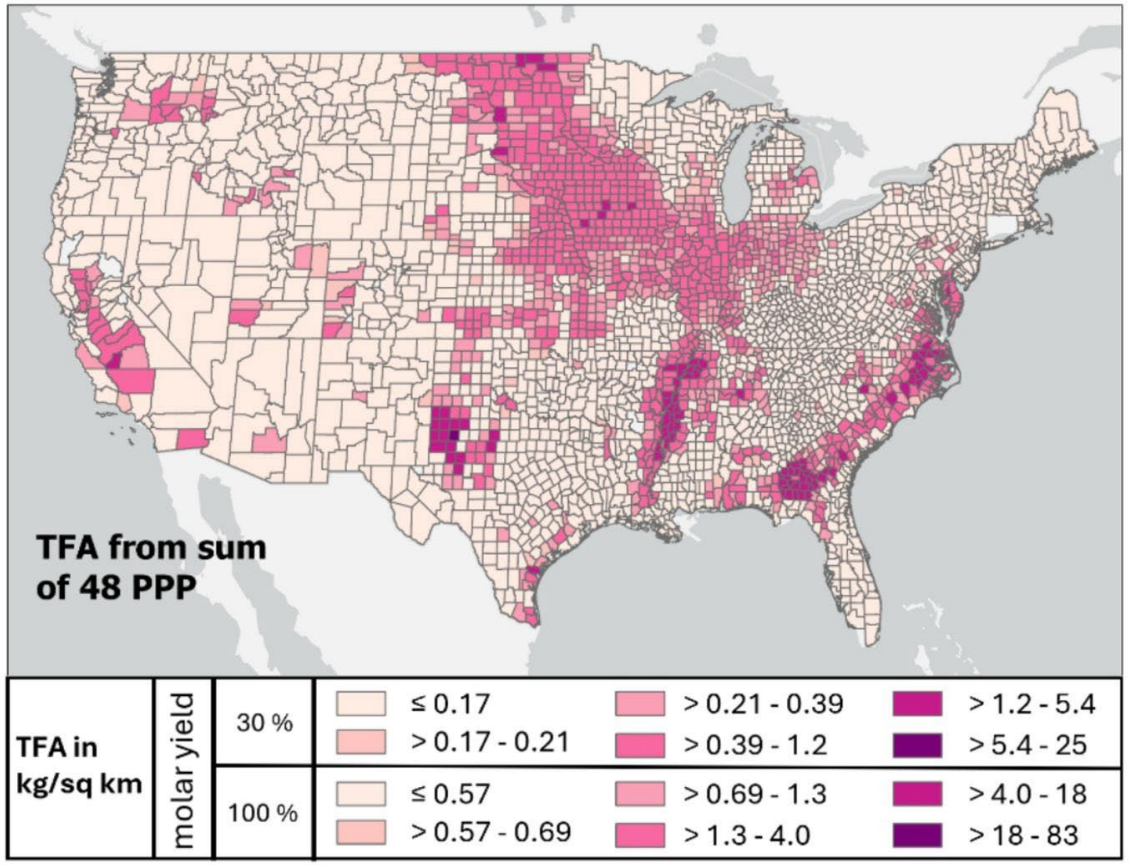




1) *Frank et al. Environmental Science & Technology* 2002 *36* (1), 12-15
2) Scott et al. *Environmental Science & Technology* 2005 *39* (17), 6555-6560
3) *Joudan et al. Environ. Sci.: Processes Impacts*, 2021,23, 1641-1649

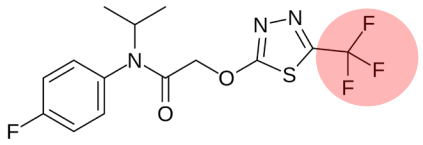
Pesticide/Herbicide precursors lead to TFA hotspots in agricultural areas



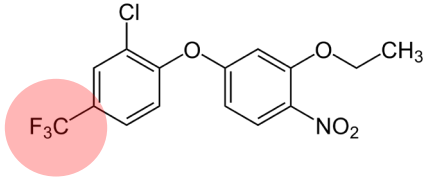


Major precursors:

flufenacet

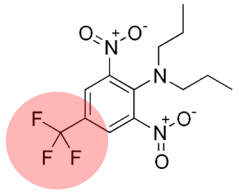


oxyfluorfen

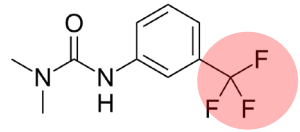


Major precursors

trifluralin

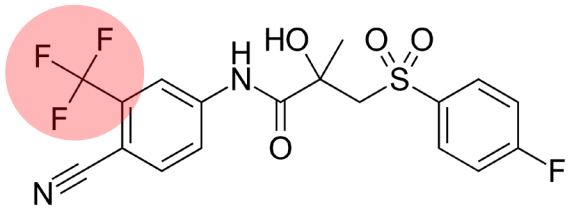


fluometuron

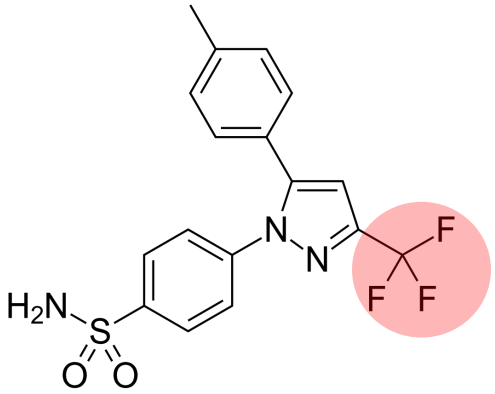


Joerss et al. (2024) *Environment International*, *193*, 109061.

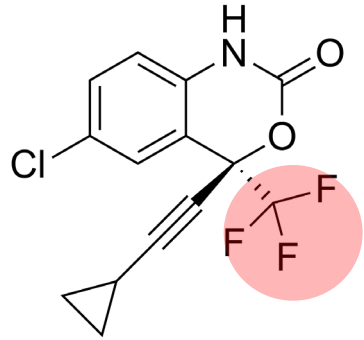
Pharmaceuticals



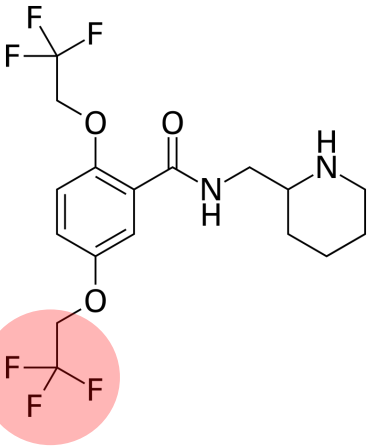
Bicalutamide – since 1995
(prostate cancer treatment)



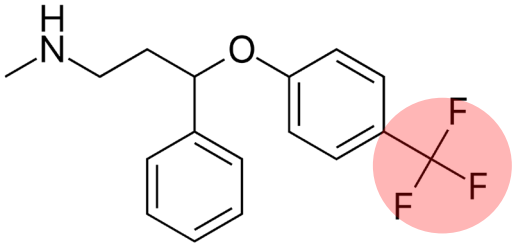
Celecoxib – since 1999
(Non-steroidal anti-inflammatory)



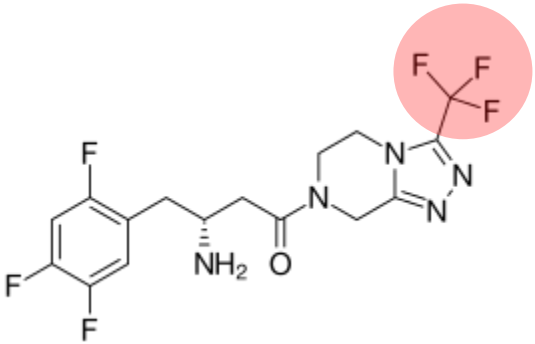
Efavirenz – since 1998
(HIV/AIDS treatment)



Flecainide – since 1985
(fast heart-rate treatment)

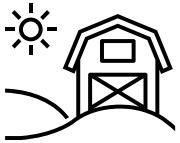


Fluoxetine (Prozac) - since1986
(Anti-depressant)



Sitagliptin – since 2006
(Anti-diabetic)

Sludge/biosolid

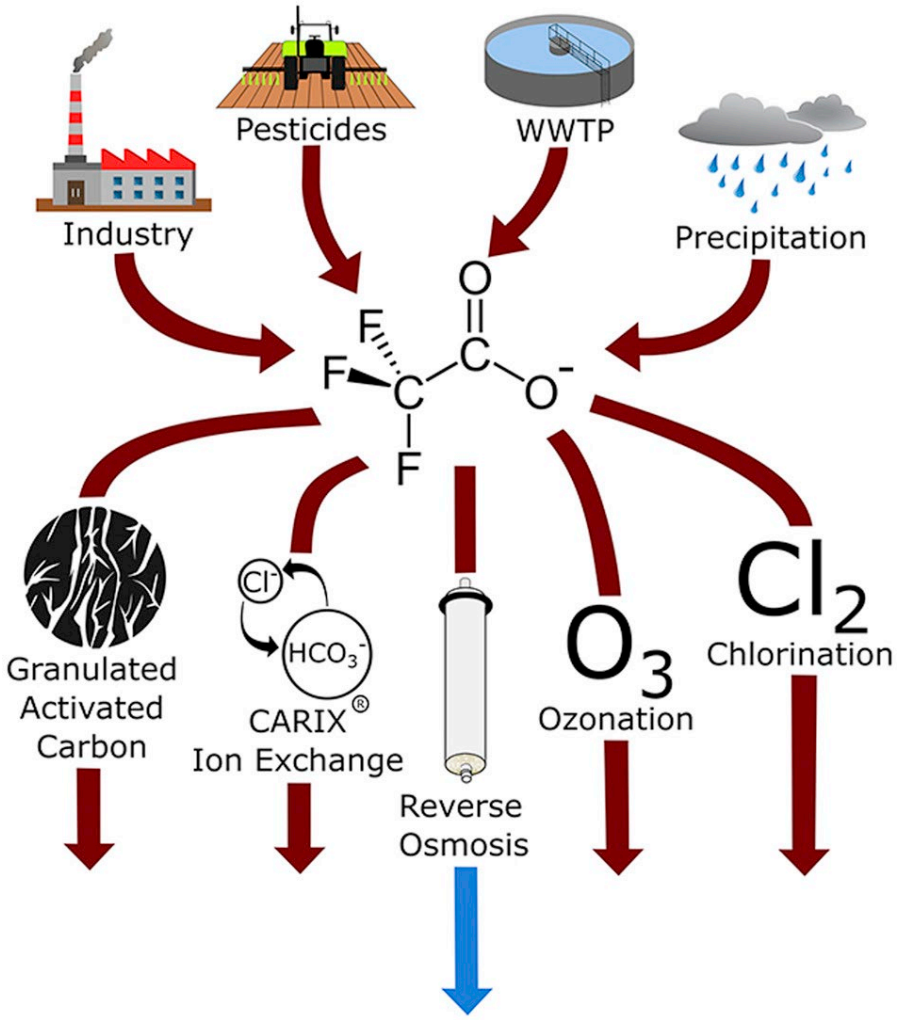


Agricultural chemicals

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

PFAS remediation

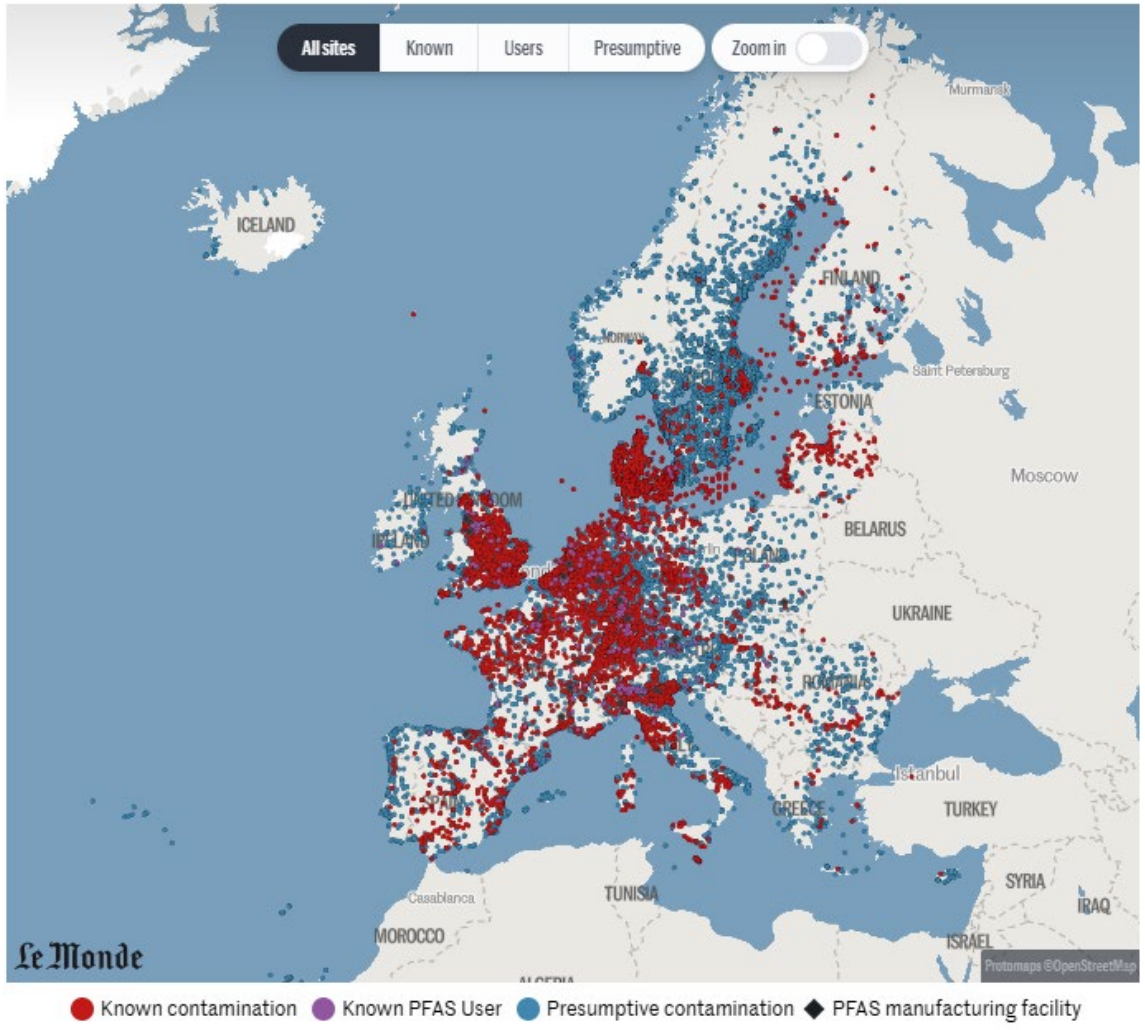
- **Enhanced degradation techniques** (ozonation, chlorination, photolysis, electrolysis, incineration, pyrolysos etc.) **can lead to TFA formation from precursors** (along with other PFAS, F-gases)
- Sorption techniques (activated carbon, ion exchange resins) -> **do not filter TFA**
- **Reverse osmosis** 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..

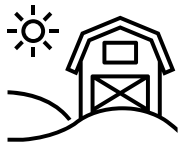


Source: Forever Pollution Project

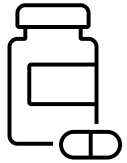
https://foreverpollution.eu/lobbying/

TFA from Multiple Sources Accumulates in Multiple recipients

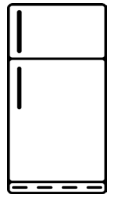
Increasing sources



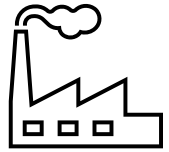
TFA precursor pesticides



TFA precursor Pharmaceuticals

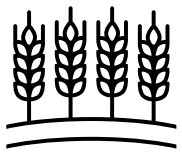


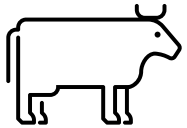
TFA precursor Refrigerants and blowing agents

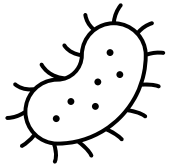


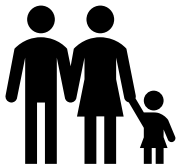
Other PFAS production

recipients of irreversible accumulation









Toxicity to Mammals

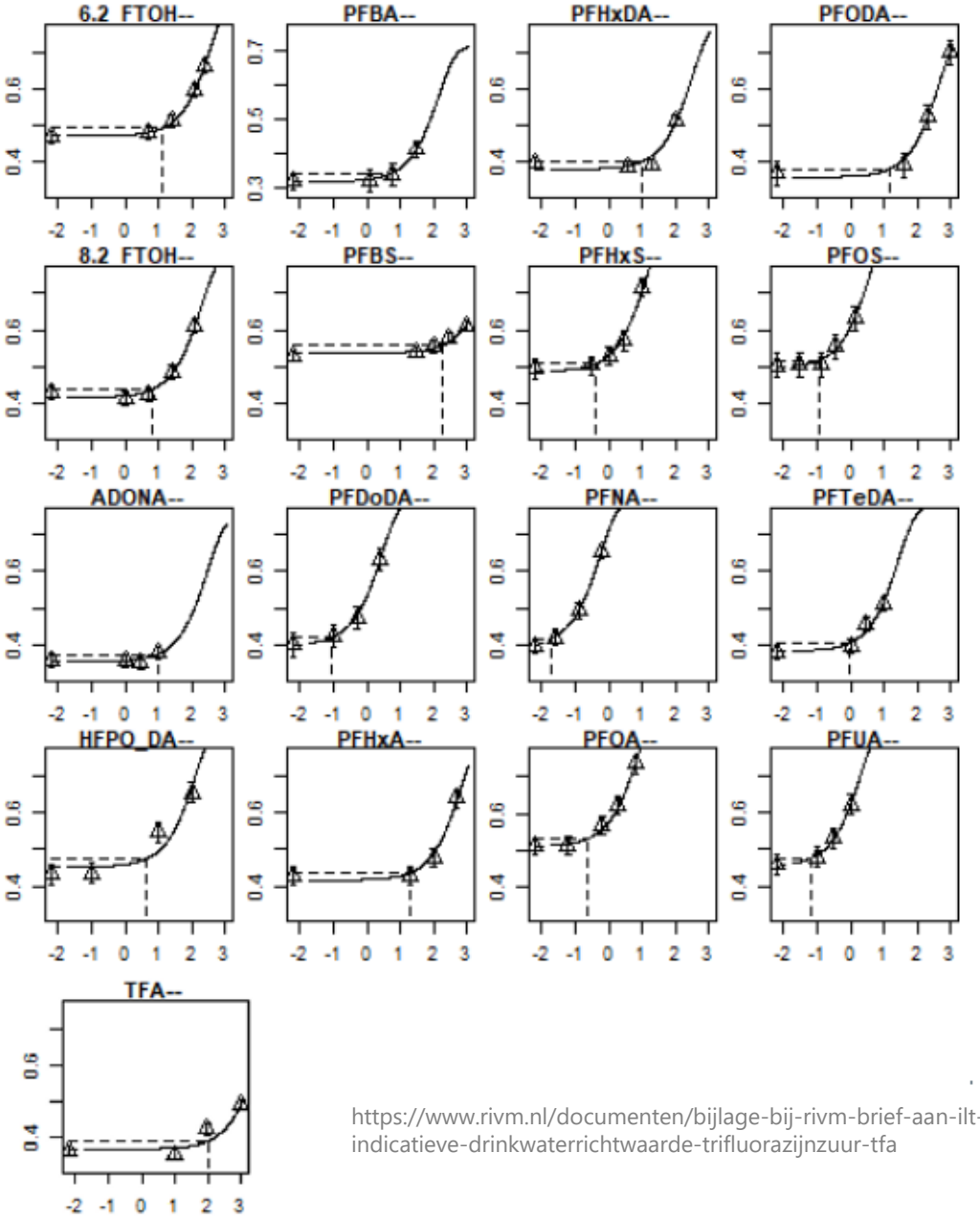
RIVM (2022)
Chronic rat toxicity (feeding)
Dose response: Male liver weight vs dose
Relevant potency factor: TFA is 0.002 x toxic as PFOA

*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

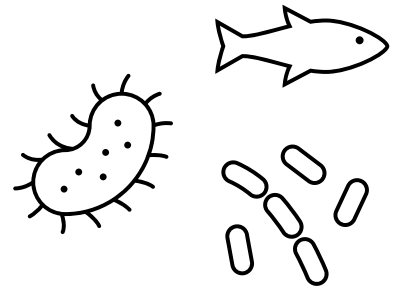
multiple folded retina and absent aqueous/vitreous humor were above the … historical control data range

Rategory 1B: Presumed human reproductive toxicant



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

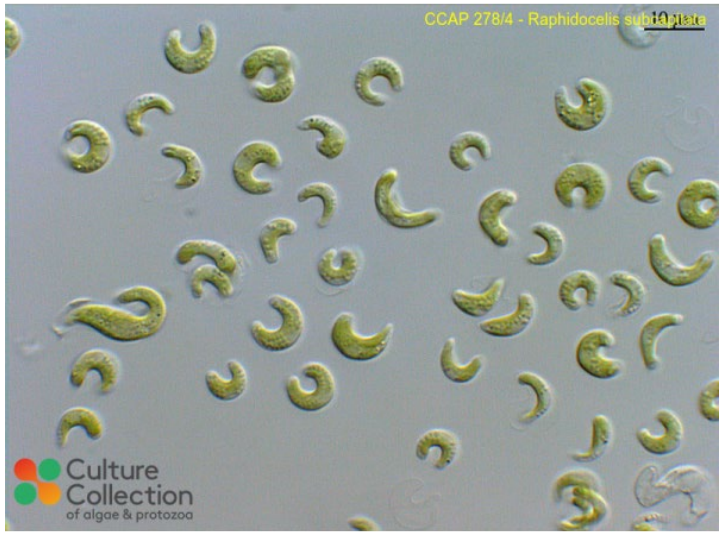
Toxicity to aquatic ecosystems



Aquatic algae / microbes

Aquatic toxicity of TFA

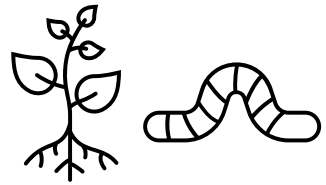
- No observable effect concentration (NOEC) of **120 µg/L** for *Raphidocelis subcapitata* – (Solvay data reported in Berends et al. 1999, USEEP ECOTOX). Used to derive a PNEC of **0.12 to 12 µg/L**
- Ignored as an outlier in some reports, but appears reproducible



- 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.

Jan Kopřiva

- **Soil concentrations at TFA hotspots already exceed these concentrations which decrease soil quality**
- **Little long exposure studies on terrestrial and agricultural systems**

TFA affecting soil health

Chen et al. *Environ. Sci. Technol.* **2018**, *52* (15), 8263− 8271

Planetary Boundary Threat of TFA

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

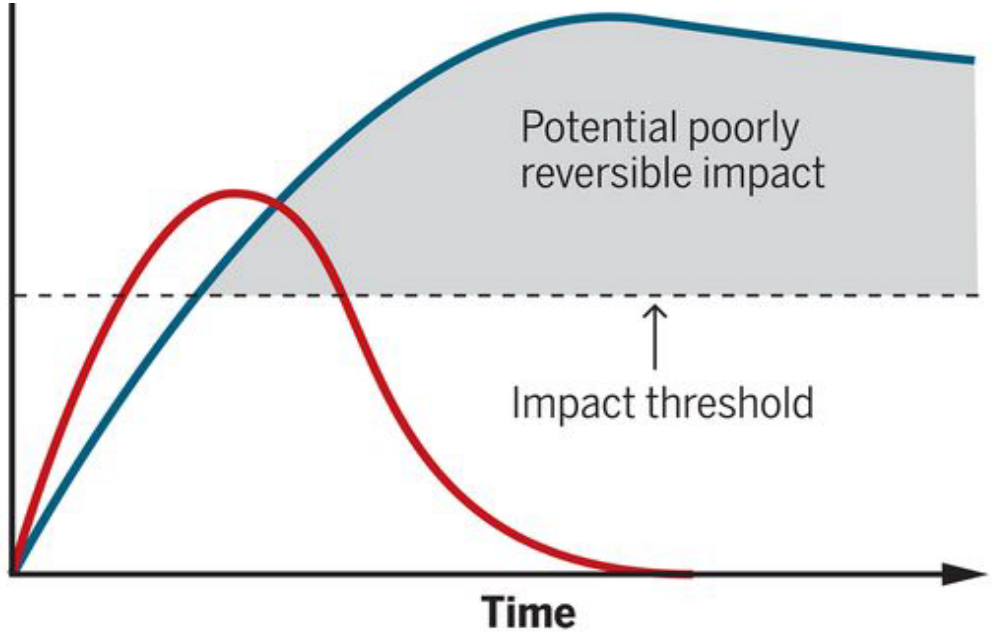
Conditions for novel entities:[1,2]

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

Impacts persiste even after phase-out. What will the severity be?

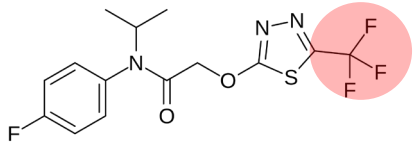


TFA emissions

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

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?

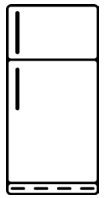
Proposed regulations in the European Union present an uncertain future for pharmaceuticals and agrochemicals—and motivation to design greener ones

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

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

Refrigeration

Indoor Climate

Miscellaneous

	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

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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]

Effective Communication and Labelling

How do PFAS labels affect consumer intentions?

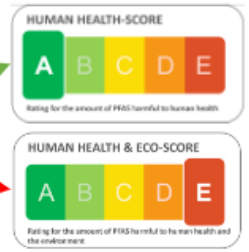
N = 450

- 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

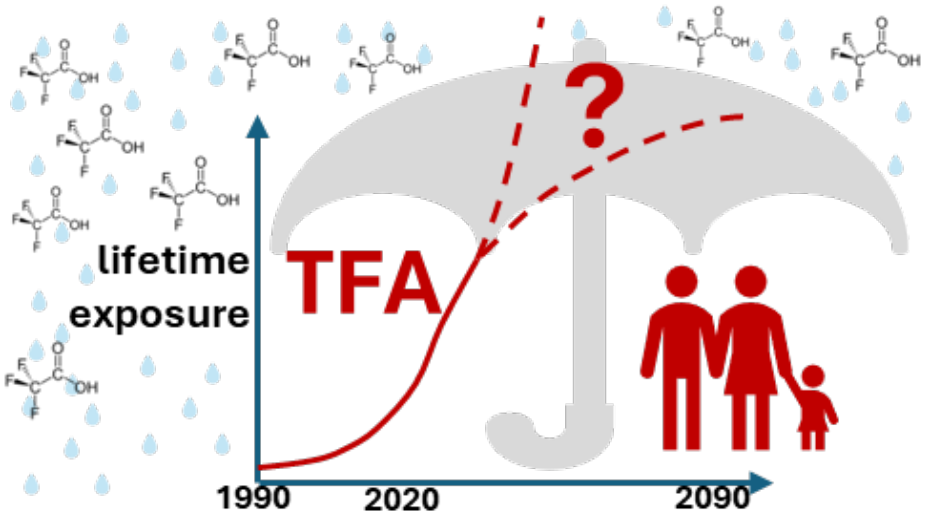
While **84%** of citizens are concerned about **the effects of PFAS on the environment**

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

Solutions to a global threat:



- Transition to alternative technologies that do not involve precursors to TFA
- Better understand the exposure irreversible impacts of TFA on soil, plants, microbes and humans
- Safely dispose existing stockpiles and hotspots of TFA-precursors

Acknowledgements

https://zeropm.eu/removal-workshop/

Submission Deadline: September 30, 2025

2021-2026

Thanks to funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101036756

https://zeropm.eu/