



Roundtable on PFAS pesticides and water contamination in the EU

When? 19 March 2025 at 12:00 CET Where? European Parliament, Brussels

The global threat from the increasing accumulation of trifluoroacetic acid

Hans Peter H. Arp

Norwegian Geotechnical Institute (NGI) & Norwegian University of Science and Technology (NTNU)

Contact: hans.peter.arp@ngi.no



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

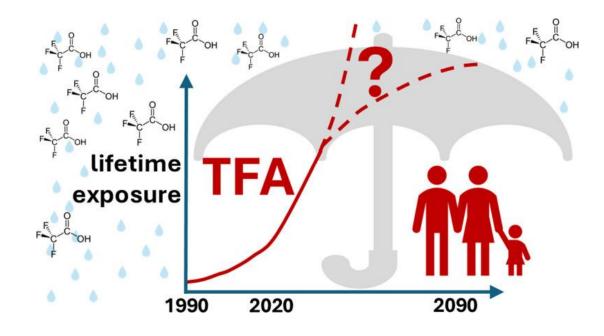
Contents

Increasing Sources

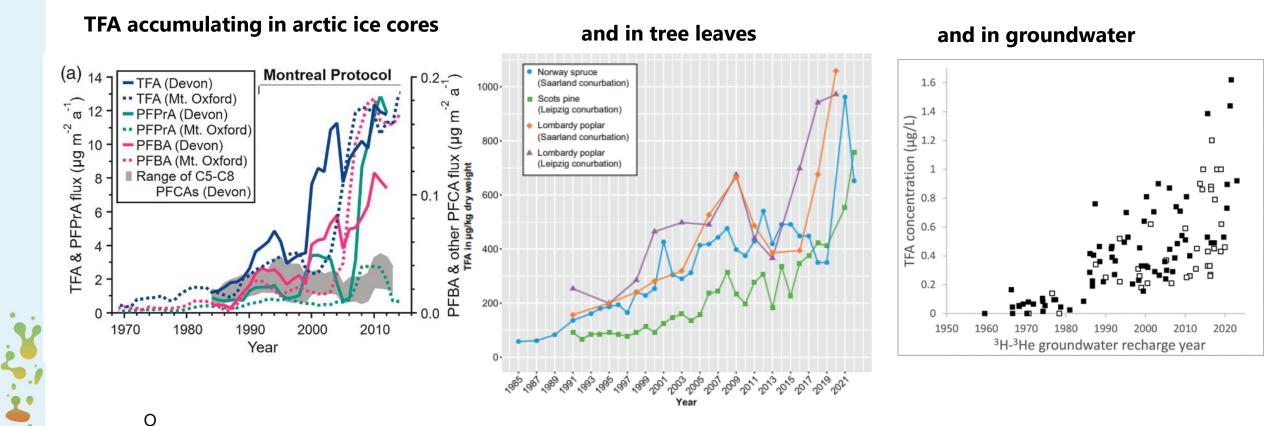




Solutions to a Global Threat



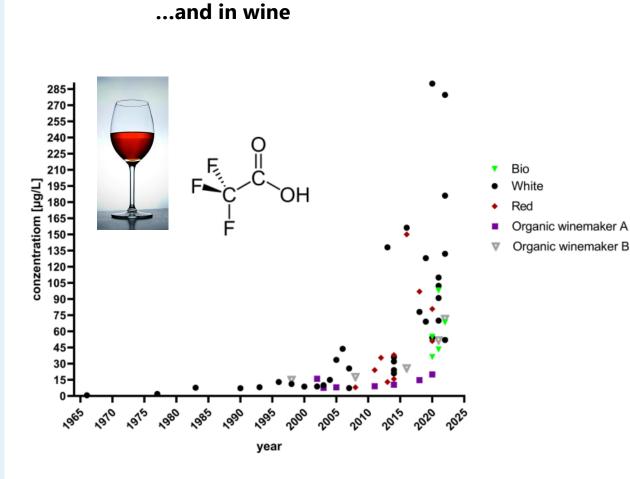
TFA is accumulating everywhere, largely coinciding with F-gas use following the Montreal Protocol and TFA use in many pesticides and other products



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 what we drink



Drinking water (median)^{1,2}

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

Tea (median): 2.4 µg/L²

Beer (median) 6.1 µg/L²

Orange juice (mean 34 µg/L)³

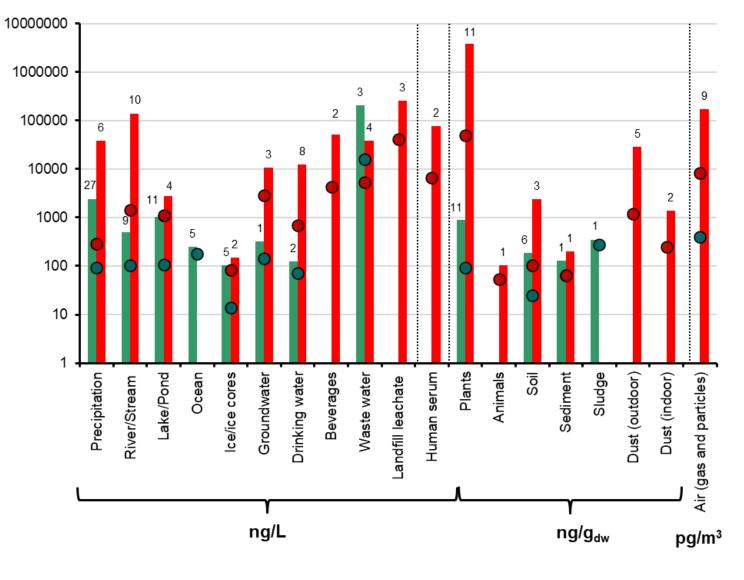
Apple juice (mean 6.2 µg/L)³

- 1. Neuwald et al. Environmental Science & Technology 2022 56 (10), 6380-6390
- 2. Scheurer & Nödler. Food Chemistry, 351, 129304.

 Van Hees et al. <u>https://cdnmedia.eurofins.com/european-</u> east/media/uxcnaa2c/eurofins tfa tfms juice 24 final.pdf

Unpublished data: Michael Müller.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

TFA is accumulating everywhere it can be measured





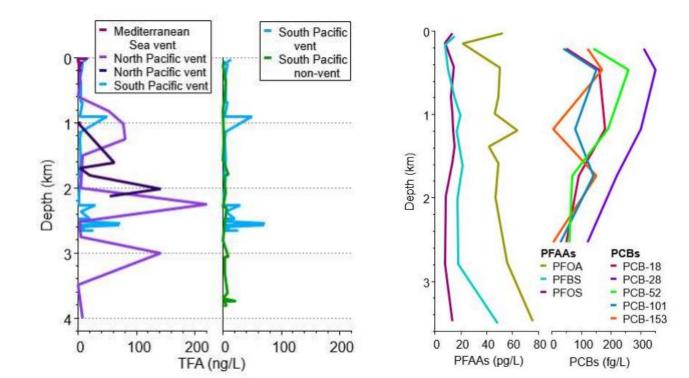
Chinese blood 97% detection Median 8.5 µg/L Similar to levels of the sum of all long-chain, bioaccumulative PFAS



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



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

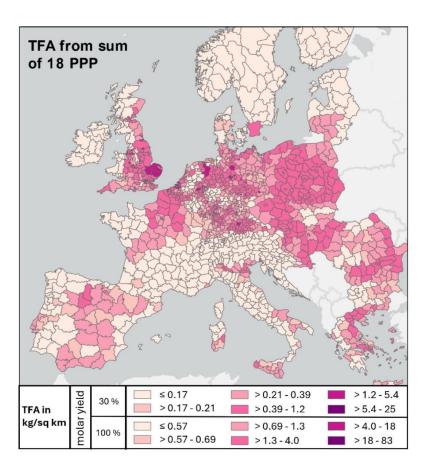
- 1) Frank et al. Environmental Science & Technology 2002 36 (1), 12-15
- 2) Scott et al. Environmental Science & Technology 2005 39 (17), 6555-6560
- 3) Joudan et al. Environ. Sci.: Processes Impacts, 2021,23, 1641-1649

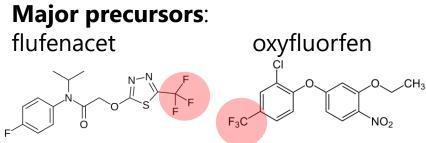
No evidence that TFA is of natural origin



Pesticide/Herbicide precursors lead to TFA hotspots in agricultural areas







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

Active substance	Current period of (re)approval
Beflubutamid	01/12/2007 - 31/10/2026
Cyflufenamid	01/04/2010 - 31/03/2024
Cyflumetofen	01/06/2013 - 31/10/2025
Diflufenican	01/01/2009 - 31/12/2023
Flazasulfuron	01/08/2017 - 31/07/2032
Flonicamid	01/09/2010 - 30/11/2026
Fluazifop-P	01/01/2012 - 31/12/2023
Fluazinam	01/03/2009 - 29/02/2024
Flubendiamide	01/09/2014 - 31/08/2024
Flufenacet	01/01/2004 - 15/06/2025
Flumetralin	11/12/2015 - 11/12/2023
Fluometuron	01/06/2011 - 31/08/2024
Fluopicolide	01/06/2010 - 31/08/2026
Fluopyram	01/02/2014 - 31/01/2024
Flurochloridone	01/06/2011 - 31/03/2026
Flutianil	14/04/2019 - 14/04/2029
Flutolanil	01/03/2009 - 29/02/2024
Gamma-Cyhalothrin	01/04/2015 - 31/03/2025
Isoxaflutole	01/08/2019 - 31/07/2034
Lambda-Cyhalothrin	01/01/2002 - 31/03/2024
Mefentrifluconazole	20/03/2019 - 20/03/2029
Metaflumizone	01/01/2015 - 31/12/2024
Oxathiapiprolin	03/03/2017 - 03/03/2027
Oxyfluorfen	01/01/2012 - 31/12/2024
Penoxsulam	01/08/2010 - 31/05/2026
Penthiopyrad	01/05/2014 - 31/05/2025
Picolinafen	01/11/2016 - 30/06/2031
Prosulfuron	01/05/2017 - 31/07/2024
Pyridalyl	01/07/2014 - 30/06/2024
Pyroxsulam	01/05/2014 - 30/04/2025
Sulfoxaflor	18/08/2015 - 18/08/2025
Tau-Fluvalinate	01/06/2011 - 31/08/2024
Tefluthrin	01/01/2012 - 31/12/2024
Tembotrione	01/05/2014 - 31/07/2024
Tetraconazole	01/01/2010 - 31/12/2023
Trifloxystrobin	01/08/2018 - 31/07/2033
Tritosulfuron	01/12/2008 - 30/11/2023

https://www.pan-europe.info/sites/pan-

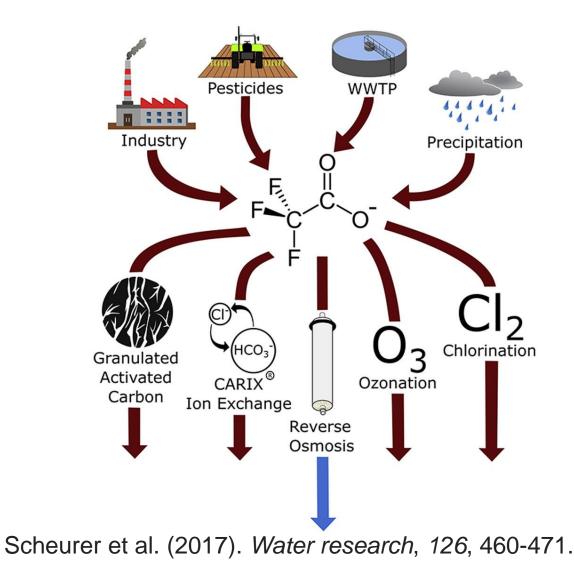
europe.info/files/public/resources/reports/PFAS%20Pesticides%20report%20November%202023.pdf

Water treatment ineffective at removing TFA,or can form TFA



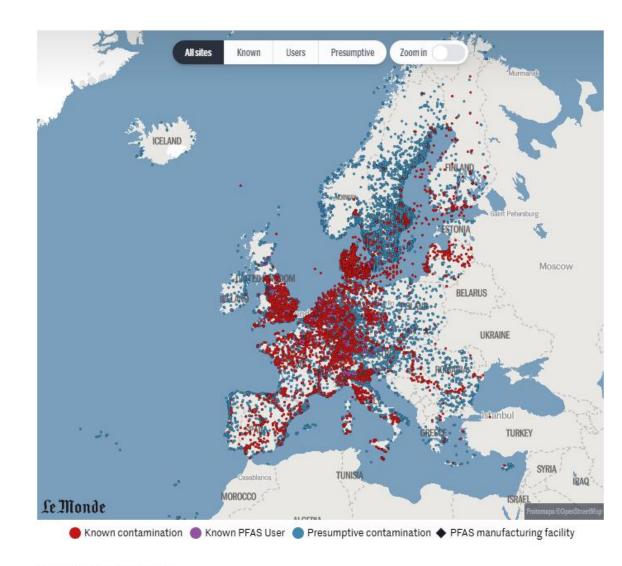
- Enhanced degradation techniques

 (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

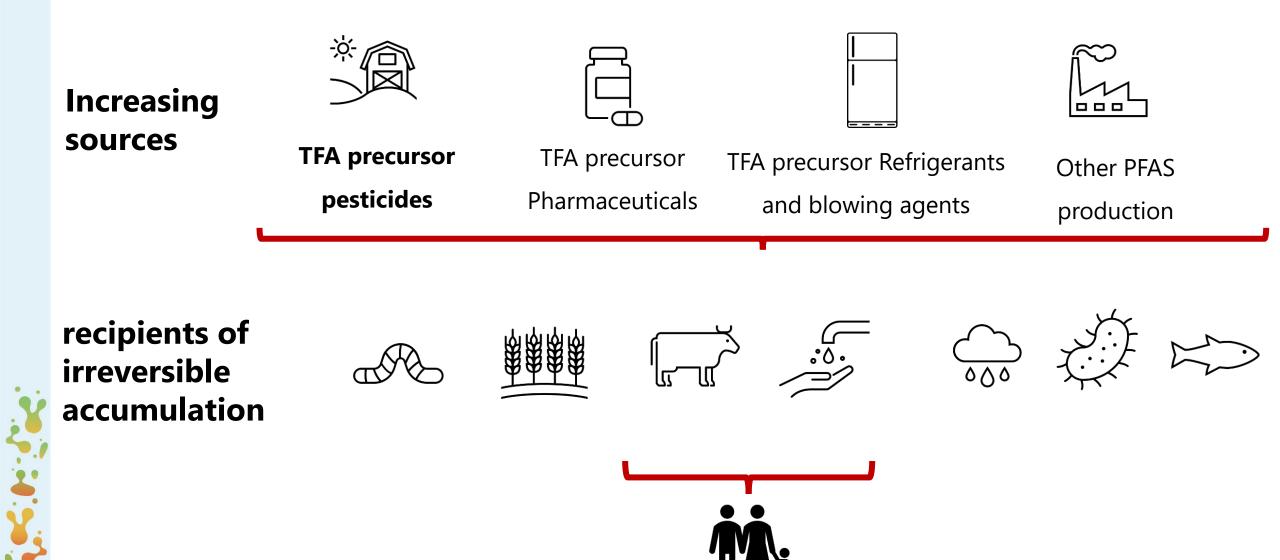


The absurd costs of TFA remediation...

- 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..



TFA from Multiple Sources Accumulates in Multiple recipients



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

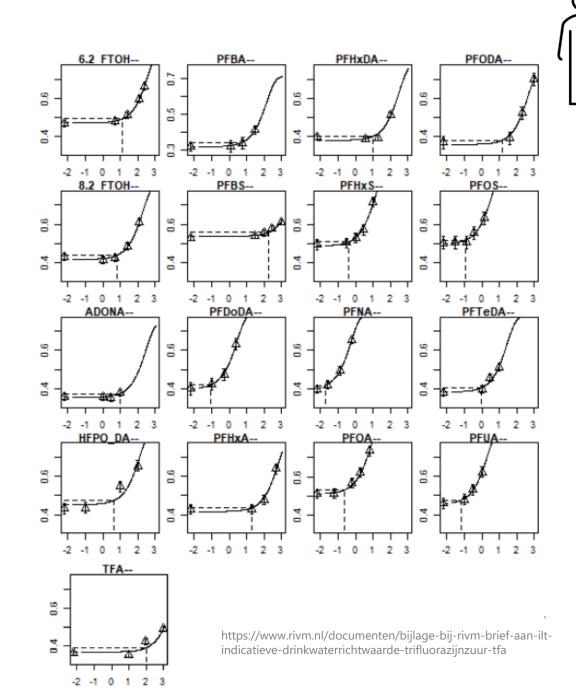
ECHA REACH Dossier (2024) Han Wistar Rabbits



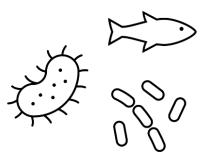
embryo-fetal developmental toxicity <180 mg/kg/day

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

Rategory 1B: Presumed human reproductive toxicant



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



Jan Kopřiva

TFA affecting soil health

Planetary Boundary Threat of TFA

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

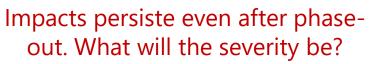
Conditions for novel entities:^{1,2}

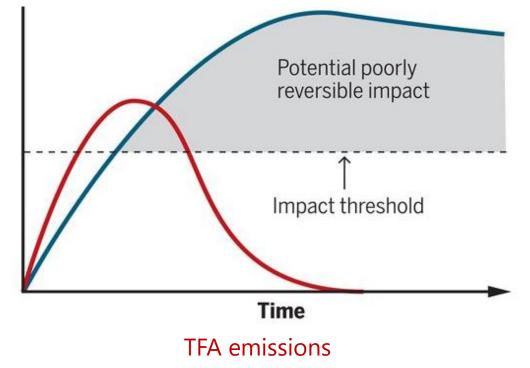
Condition 1: pollution disrupts a vital earth system process of which we are ignorant. **TRUE: impacts at hotspots occur now, ignorant** of impacts from life-long intergeneration exposure (ignorant)

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

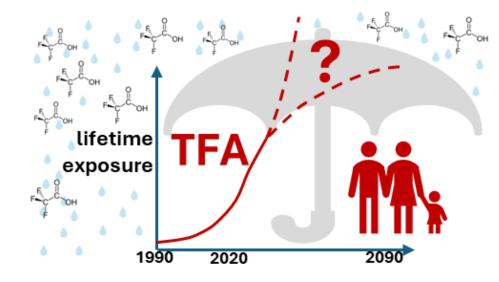




1. Persson et al. Environ. Sci. Technol. 2013, 47 (22), 12619-12622

2. MacLeod et al. Science 373,61-65(2021)

Solutions to a global threat:



- Transition to PFAS free pesticides before irreversible impacts occur
- Better understand the irreversible impacts of TFA on soil, plants, microbes and humans
- Safely dispose existing stockpiles of PFAS pesticides

Acknowledgements



Prioritize

Remove



2021-2026

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





This article is licensed under <u>CC-BY 4.0</u> (C) Perspective

pubs.acs.org/est

The Global Threat from the Irreversible Accumulation of Trifluoroacetic Acid (TFA)

Hans Peter H. Arp,**[§] Andrea Gredelj,[§] Juliane Glüge, Martin Scheringer, and Ian T. Cousins



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

Contact: hans.peter.arp@ngi.no