

TFA- sources and occurrence

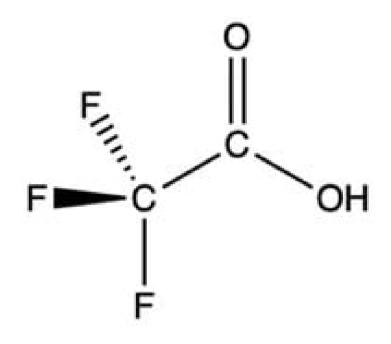
Leo Yeung Örebro Universitet

Trifluoroacetic acid

- Perfluoroacetic acid
- CAS number 76–05-1; MW = 114.02 g/mol
- the shortest chain of all PFCAs with just two carbons
- a strong organic acid (p K_a of app. 0.23 -0.43)
- high volatility (relatively high vapor pressure (11 kPa at 20°C, 3 pa for 8:2 FTOH, 5.2 to 40.7 pa for PFOA 25-45°C))

Barton et al., 2008 J. Chem. Eng. Data; Keith et al., 2016 Journal of Toxicology and Environmental Health, Part B





Per- and polyfluoroalkyl substances (PFAS)?

The working definition of a PFAS used by EPA's Office of Pollution Prevention and Toxics (OPPT), which administers TSCA (Toxic Substances Control Act):

"a structure that contains the unit R-CF₂-CF(R')(R"), where R, R', and R" do not equal "H" and the carbon-carbon bond is saturated (note: branching, heteroatoms, and cyclic structures are included)"

TFA, with just one fluorinated carbon, is not considered a PFAS per the U.S. Environmental Protection Agency (EPA) definition due to it containing only one –CF3 group in the molecule



Per- and polyfluoroalkyl substances (PFAS)

PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/CI/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group $(-CF_3)$ or a perfluorinated methylene group $(-CF_2-)$ is a PFAS".

The "noted exceptions" refer to a carbon atom with a H/Cl/Br/I atom attached to it.

Organisation for Economic Co-operation and Development (OECD). 2021. Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance.



Regulations

- not currently regulated by the U.S. EPA
- The Ministry of the Environment and Gender Equality in Denmark has a quality requirements for consumer taps of to be < 9 µg/L
- German Federal Environment Agency (Umweltbundesamt, UBA) recommends TFA concentrations in drinking water to be < 60 µg/L
- National Institute for Public Health and the Environment (RIVM) has derived the indicative drinking water guideline vale of 2.2 $\mu g/L$



Uses of TFA

- Ion-pair reagent for separation of small ionizable compounds in chromatography
- Solvent for polymers and polymer processes \bullet
 - electrospinning solvent
 - an efficient promoter for several polymerization reactions \bullet
- Re-arrangement of chemical structure ullet
 - a common catalyst for most acid-catalyst rearrangements
- Synthesis of trifluoromethyl (CF3-) building blocks and trifluoromethyl (CF3-) \bullet substituted compounds
 - Pesticides, pharmaceuticals ullet



Lopez and Salazar 2013, J. Fluorine Chemistry

Sources of TFA

Natural sources

- ...detected in the ocean in the range of 200 ng/L, even detected in remote locations, such as the Southern Oceans, the concentrations of TFA do not vary with depth
- Sampling in various parts of the Arctic, Atlantic, and Pacific oceans revealed that • levels in deep (>1000 m) waters of the Atlantic were close to 160 ng/L this depth was older than 1,000 yr
 - hydrothermal vent
- Nielsen et al. reported very low concentrations (below MDL of 2 ng/L) of TFA in • ancient, pre-industrial (>2000 years old) freshwater samples from Greenland and Denmark, suggesting no significant natural sources.
- Berg et al. used 15,000-year-old groundwater as a method blank for their • measurement of TFA in rainwater and surface waters and did not observe TFA above the detection limit of 5 ng/L



Sources of TFA

CRITICAL REVIEW

Check for updates

Insufficient evidence for the existence of natural trifluoroacetic acid

Cite this: Environ. Sci.: Processes Impacts, 2021, 23, 1641

Shira Joudan, 🔘 a Amila O. De Silva 🔘 b and Cora J. Young 🔘 *a

Berg et al. used 15,000-year-old groundwater as a method blank for their measurement of TFA in rainwater and surface waters and did not observe TFA above the detection limit of 5 ng/L



View Article Online View Journal | View Issue

Sources of TFA

Anthropogenic sources

- Direct source \bullet
- Indirect source \bullet
 - atmospheric photodegradation of hydrofluorocarbon (HFCs) \bullet and hydrofluoroolefin (HFO)
 - atmospheric degradation of fluorotelomer alcohols (FTOHs)
 - thermolysis of fluoropolymers
 - degradation of pesticides and pharmaceuticals containing the -CF3 moiety



TFA on the news...

LES DÉCODEURS · PFAS

Record levels of 'forever chemicals' found in one French village's water

By Stéphane Horel

Published on February 7, 2024, at 3:00 pm (Paris), updated on February 17, 2024, at 10:16 am

Ō 10 min read Lire en français



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INVESTIGATION | Unprecedented analyses are revealing spectacular levels of trifluoroacetic acid (TFA) in <u>streams</u> around a PFAS production plant in Salindres, in southern France, as well as in the village's drinking water.

https://www.lemonde.fr/en/lesdecodeurs/article/2024/02/07/record-levels-of-forever-chemicalsfound-in-one-french-village-s-water-supply_6502237_8.html



The logo of Belgian chemical group Solvay is Photo Purchase Licensing Rights

Sept 24 (Reuters) - Belgian chemicals group Solvay announced on Tuesday plans to enter into talks with labour unions to cease production at its Salindres site in France.

"The envisaged discontinuation o said in a statement.

The group expects to eliminate these positions between early 2025 and October 2025.

The Salindres site is responsible for producing trifluoroacetic acid (TFA) and its fluorinated derivatives. Both are organic compounds classified as PFAS according to the <u>OECD</u> definition.

https://www.reuters.com/ 2024-09-24/

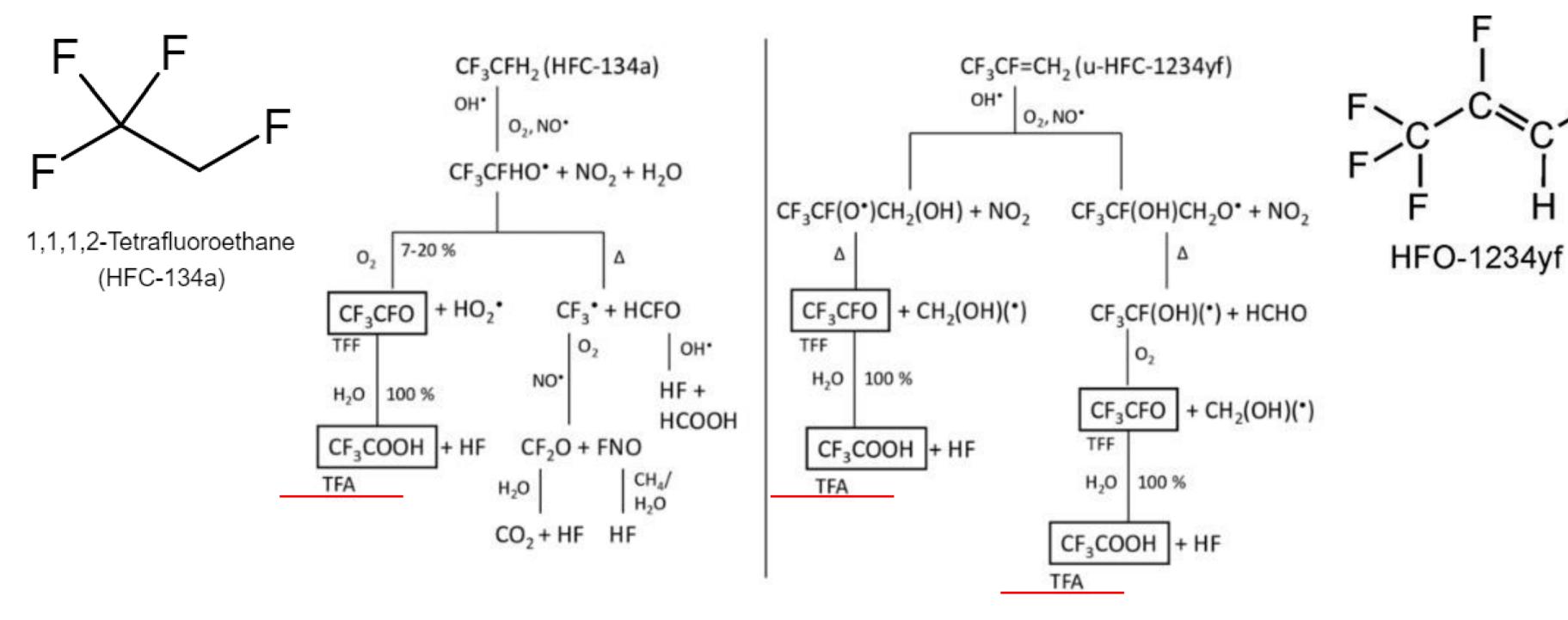


The logo of Belgian chemical group Solvay is seen at its headquarters in Brussels, Belgium, July 29, 2015. REUTERS/Francois Lenoir/File

"The envisaged discontinuation of these activities would result in the elimination of 68 positions," Solvay

https://www.reuters.com/markets/europe/solvay-cut-68-jobs-salindres-site-2025-

Atmospheric photodegradation of hydrofluorocarbon (HFCs) and hydrofluoroolefin (HFO)



Persistent degradation products of halogenated refrigerants and blowing agents in the environment: type, environmental concentrations, and fate with particular regard to new halogenated substitutes with low global warming potential. Texte | 73/2021, Umweltbundesamt



Atmospheric photodegradation of hydrofluorocarbon (HFCs) and hydrofluoroolefin (HFO)



A two-year measurement campaign of TFA at 8 monitoring sites in Germany showed that TFA levels in precipitation are already several times higher than they were 25 years ago and are expected to rise even further.

Phase down of HFCs – the Kigali Amendment ...gradual reduction by 80-85 per cent by the late 2040s...

 $CO_2 + HF HF$

Persistent degradation products of halogenated refrigerants and blowing agents in the environment: type, environmental concentrations, and fate with particular regard to new halogenated substitutes with low global warming potential. Texte | 73/2021, Umweltbundesamt



Degradation of Fluorotelomer Alcohols

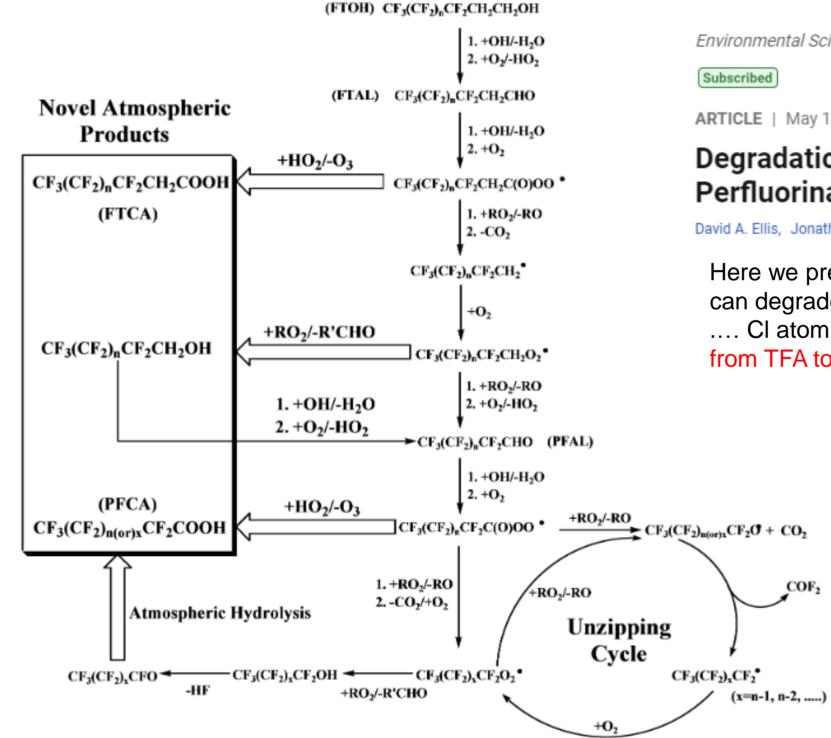


FIGURE 1. OH-initiated oxidation pathways for telomer alcohols, where n = 2, 4, or 6, leading to formation of PFCAs. R and R' are nonspecific alkyl species in the smog chamber, similar species of which would play an identical role. x is an integer less than n. Significant previously unreported reactions are indicated with large arrows.

Environmental Science & Technology > Vol 38/Issue 12 > Article

ARTICLE | May 12, 2004

Degradation of Fluorotelomer Alcohols: A Likely Atmospheric Source of Perfluorinated Carboxylic Acids

David A. Ellis, Jonathan W. Martin, Amila O. De Silva, Scott A. Mabury, Michael D. Hurley, Mads P. Sulbaek Andersen, and Timothy J. Wallington

Here we present smog chamber studies that indicate fluorotelomer alcohols (FTOHs) can degrade in the atmosphere to yield a homologous series of PFCAs CI atom initiated oxidation of 8:2 FTOH yielded the entire suite of PFCAs ranging from TFA to PFOA (in addition to PFNA)....





Biodegradation of Fluorotelomer compounds



Chemosphere Volume 254, September 2020, 126894

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|-------------|
| Chemosphere |
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Fluorochemicals biodegradation as a potential source of trifluoroacetic acid (TFA) to the environment

soil solution microbial growth inoculum landfill soil microbial culture Microbial culture generation

Mei Sun °, Jia'nan Cui °, Junyu Guo ° 📯 🖾 , Zihan Zhai ° ^b, Peng Zuo °, Jianbo Zhang ° 📯 🖾



Science of The Total Environment Volume 760, 15 March 2021, 143356



Formation of perfluorocarboxylic acids (PFCAs) during the exposure of earthworms to 6:2 fluorotelomer sulfonic acid (6:2 FTSA)

<u>Shuyan Zhao ° ∧ ⊠</u>, <u>Tianqi Liu °, Lingyan Zhu ^b,</u> <u>Liping Yang ^b, Yvlu Zong °,</u> Huanting Zhao °, <u>Longhui Hu °, Jingjing Zhan °</u>6:2 FTOH was terminally transformed to 5:3 polyfluorinated acid (5:3 FTCA; 12.5 mol%), perfluorohexanoic acid (PFHxA; 2.0 mol%), perfluoropentanoic acid (PFPeA; 1.6 mol%), perfluorobutyric acid (PFBA; 1.7 mol%), and TFA (2.3 mol%) by day 32 in the landfill soil microbial culture system

...4:2 FTOH could remove multiple –CF2 groups by microorganisms and produce PFPeA (2.6 mol%), PFBA (17.4 mol%), TFA (7.8 mol%).

....6:2 FTSA could be biodegraded by microorganisms in soil to trifluoroacetic acid (TFA), perfluoropropionic acid (PFPrA), perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA) and perfluorohexanoic acid (PFHxA)....



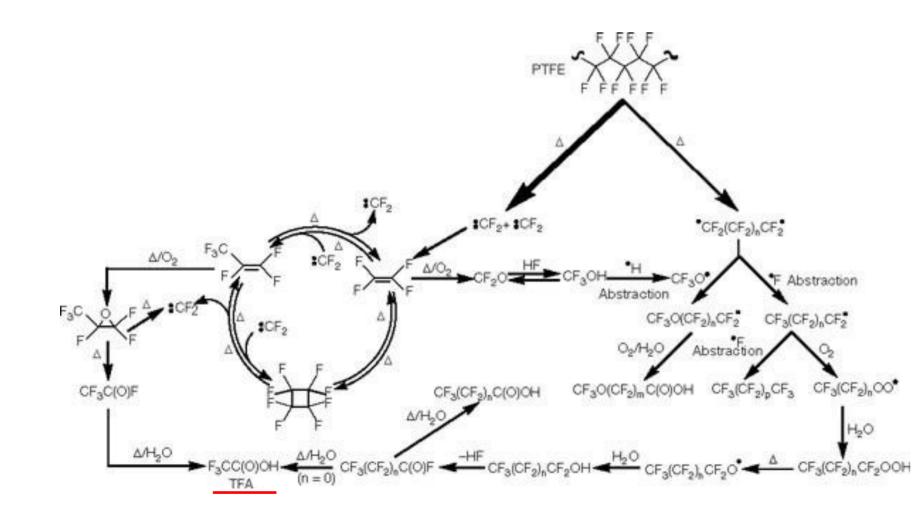
Thermolysis of fluoropolymers

Letter | Published: 19 July 2001

Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment

David A. Ellis, Scott A. Mabury [™], Jonathan W. Martin & Derek C. G. Muir

Nature 412, 321–324 (2001) Cite this article

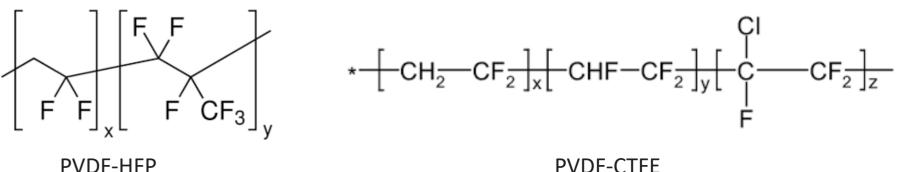




The contribution of fluoropolymer thermolysis to trifluoroacetic acid (TFA) in environmental media

Jia'nan Cui ª, Junyu Guo ª, Zihan Zhai ª ʰ, Jianbo Zhang ª Ӓ 🖾

Average TFA yields of PTFE, PVDF-HFP and PVDF-CTFE were 1.2%, 0.9% and 0.3%, respectively.





Chemosphere Volume 222, May 2019, Pages 637-644



PVDF-CTFE



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Thermolys

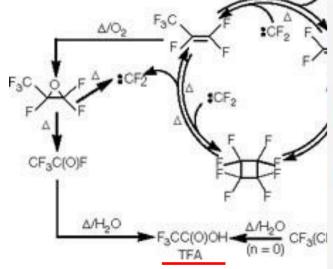
Letter | Published: 19 July 2001

Thermolysis of flue halogenated organ

<u>David A. Ellis, Scott A. Mabury</u>⊠, <u>Jc</u>

Nature 412, 321–324 (2001) Cite





Swedish project first to measure PFAS in flue gases from waste incineration

IVL Swedish Environmental Research Institute, together with three energy and waste companies, will test new methods for measuring the environmentally hazardous substance PFAS at Swedish waste incineration plants. This is the first time the methods have been tested on a large scale. The research project is be supported by the US Environmental Protection Agency and the Swedish Environmental Protection Agency.

Our offer \vee About I



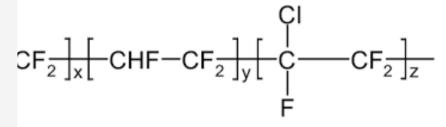




opolymer cetic acid (TFA) in

g° A ⊠

• F-CTFE were 1.2%, **0.9% and 0.3%**,



PVDF-CTFE

Degradation of pesticides and pharmaceuticals containing the -CF3 moiety



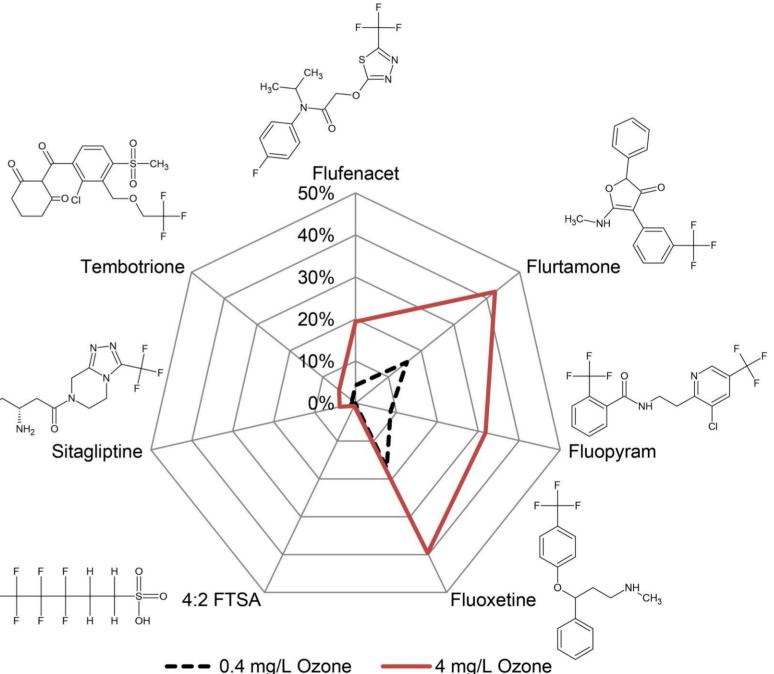
Water Research Volume 126, 1 December 2017, Pages 460-471

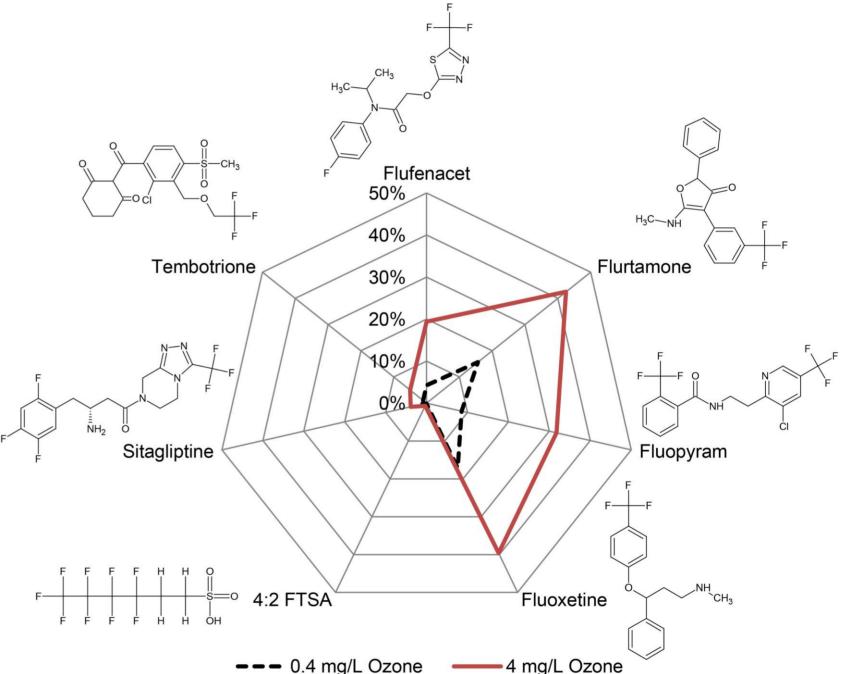


Small, mobile, persistent: Trifluoroacetate in the water cycle – Overlooked sources, pathways, and consequences for drinking water supply

Marco Scheurer a 😤 🖾 , Karsten Nödler a, Finnian Freeling a, Joachim Janda a, Oliver Happel a, Marcel Riegel °, Uwe Müller °, Florian Rüdiger Storck °, Michael Fleig °, Frank Thomas Lange °, Andrea Brunsch^b, Heinz-Jürgen Brauch^a

...Biological degradation and ozonation batch experiments with chemicals of different classes (flurtamone, fluopyram, tembotrione, flufenacet, fluoxetine, sitagliptine and 4:2 fluorotelomer sulfonate)





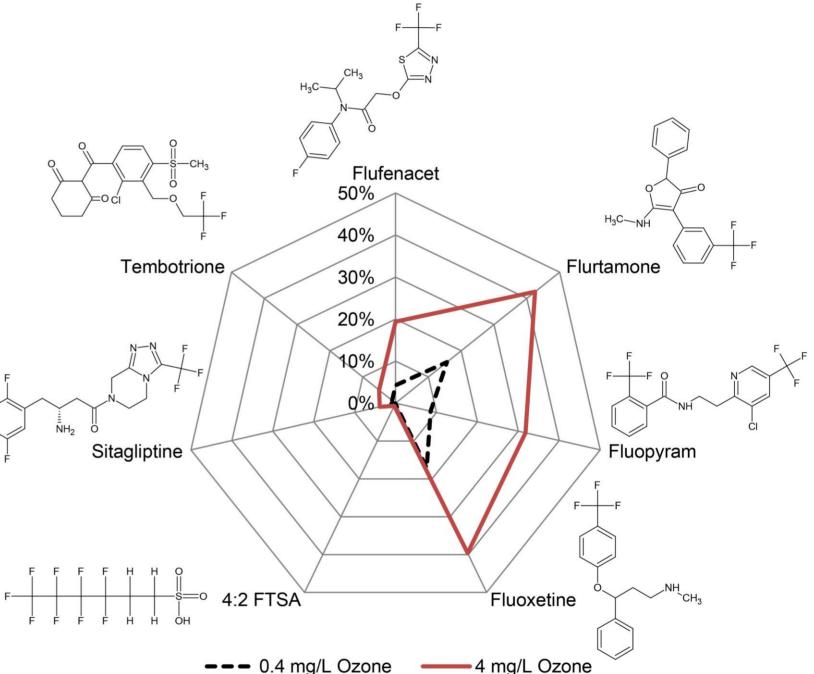


Fig. TFA formation from selected potential precursor compounds upon ozonation at two ozone dosages. Percentage of formation calculated on a molar base.



Degradation of pesticides and pharmaceuticals containing the -CF3 moiety

Applied Microbiology and Biotechnology (2021) 105:9359–9369 https://doi.org/10.1007/s00253-021-11675-3

ENVIRONMENTAL BIOTECHNOLOGY

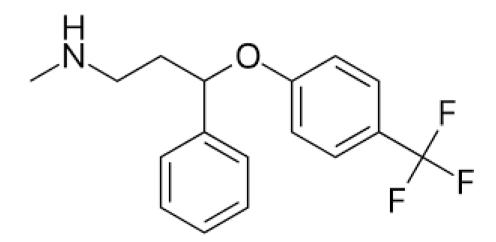


Bacterial degradation of the anti-depressant drug fluoxetine produces trifluoroacetic acid and fluoride ion

Mohd Faheem Khan¹ · Cormac D. Murphy¹

In this paper, we demonstrate that common environmental bacteria can use FLX as a sole carbon and energy source......The final products of the degradation pathway were trifluoroacetate and fluoride ion...





Fluoxetine

Elevated TFA levels in subjects with history of taking fluoxetine

20 sera samples purchased commercially

 10 samples subjects had recorded of using Fluoxetine

 10 samples subject did not report or known use of any fluorinated pharmaceuticals

| Sample code | PFAS (ng F/mL) | TFA (ng F/mL) | Seproxetine and Fluoxetine (ng F/mL) |
|----------------|----------------|---------------|--|
| MH23-015 : 237 | 4.2 | 12.7 | 0.4 |
| MH23-015 : 236 | 1.8 | 14.9 | 0.2 |
| MH23-015 : 235 | 3.7 | 14.2 | 0.3 |
| MH23-015 : 234 | 1.4 | 22.5 | |
| MH23-015 : 233 | 5.0 | 13.2 | 0.4 |
| MH23-015 : 232 | 3.4 | 9.9 | 0.3 |
| MH23-015 : 231 | 2.4 | 12.9 | 1.3 |
| MH23-015 : 230 | 1.7 | 19.5 | 0.1 |
| MH23-015 : 229 | 4.5 | 8.8 | 0.4 |
| MH23-015 : 228 | 1.1 | 14.6 | |
| MH23-015 : 227 | 1.6 | 3.3 | |
| MH23-015 : 226 | 1.6 | 2.8 | |
| MH23-015 : 225 | 1.2 | 6.2 | |
| MH23-015 : 224 | 2.2 | | |
| MH23-015 : 223 | 2.1 | | |
| MH23-015 : 222 | 1.1 | 4.4 | |
| MH23-015 : 221 | 84.4 | | |
| MH23-015 : 220 | 2.9 | 4.3 | |
| MH23-015 : 219 | 5.4 | 3.9 | |
| MH23-015 : 218 | 184.7 | | |

Known and unknown PFAS in human blood in a Norwegian cohort and possible sources of exposure – collaboration with National Institute of Public Health and Örebro University funded by Nordic Council of Ministers



Occurrence in the Environment

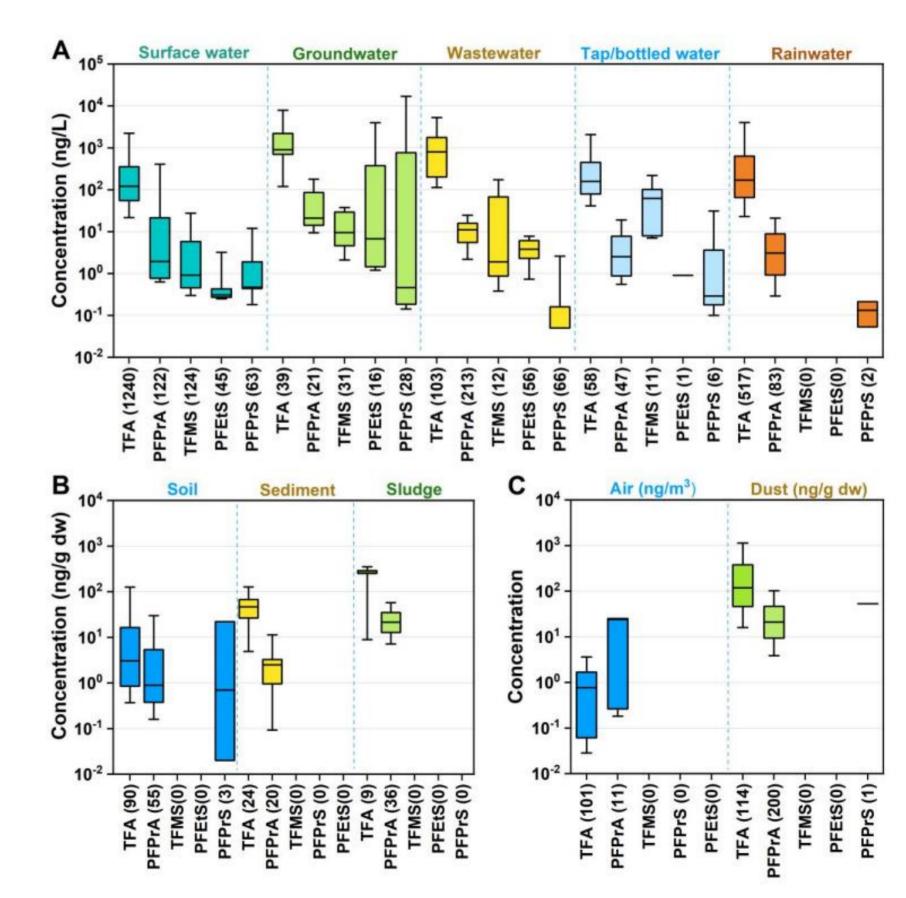
Environmental Occurrence and Biotic Concentrations of Ultrashort-Chain Perfluoroalkyl Acids: Overlooked Global Organofluorine Contaminants

Yue Zhi,1* Xiongwei Lu,1 Gabriel Munoz,2 Leo W. Y. Yeung,3 Amila O. De Silva,4 Shilai Hao,5 Huan He,6

Yonghui Jia,1 Christopher P. Higgins,5 Chuhui Zhang5*

- TFA has been detected in different environmental samples including human blood
- Aquatic samples range from 0,01 to 510000 (rainwater) ng/L
- Solid samples ranged from 0,04 to 2400 (soil) ng/g dw

Figure. The box represents the data ranging from 25 to 75%, and the line inside the box shows the median concentration. Whiskers denote the 10th and 90th percentiles of the data. Numbers in parentheses represent the number of samples. Data was obtained from published papers (1990-2024).





Occurrence in the Environment

In Sweden,

Groundwater:

- TFA was found in 90 percent of the sample < TFA with a median level of 190 ng/L and a maximum level of 2700 ng/L
- TFA: 130 5400 ng/L (Agricultural area)

Drinking water:

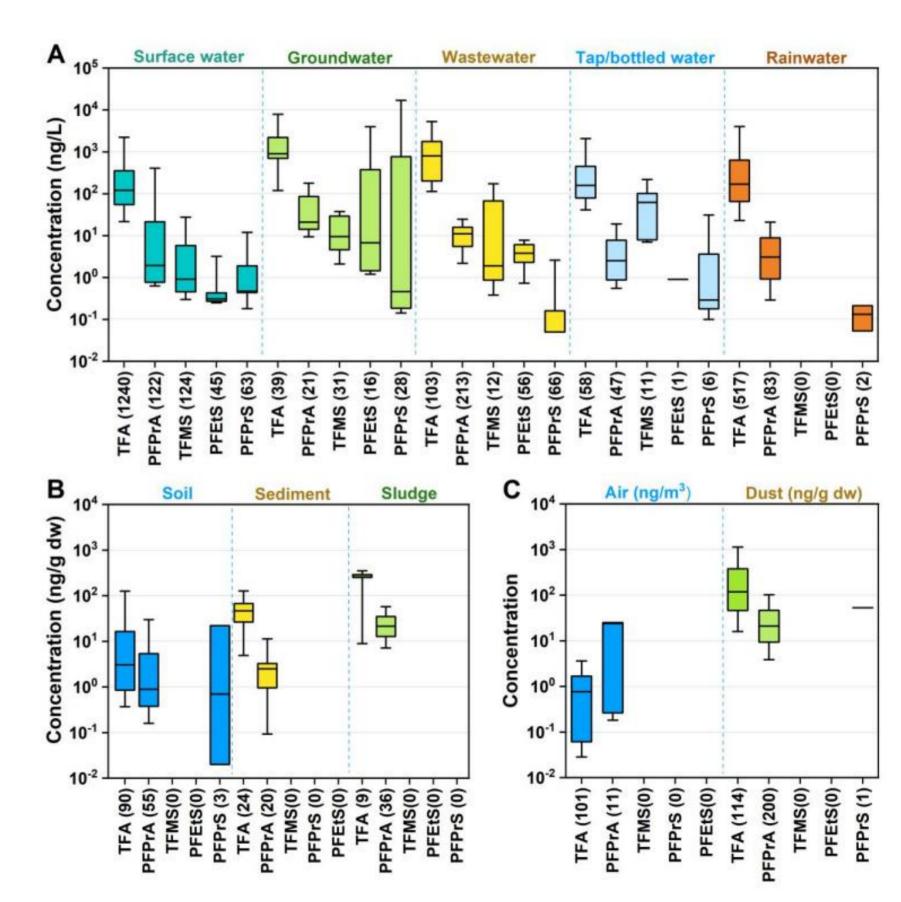
TFA was present in all ranging from 70-720 ng/L (280 ± 160 ng/L)

Effluent for irrigation: 846 - 1390 ng/L

Surface water:

- 30 ng/L to 820 ng/L
- 890 2400 ng/L (Agricultural area)

https://www.sgu.se/globalassets/grundvatten/miljoovervakning/pm_pfas_gv-2023.pdf Boström, G., Tröger, R., Jonsson, O. & Gönczi, M. CKB rapport 2024:1. SLU Björnsdotter et al. 2022 Environ Sci Technol. https://cdnmedia.eurofins.com/europeaneast/media/2867434/eurofins_ultrashort_pfas_drink_water_23.pdf Nationell miljöövervakning 2022, Golovko et al. urn:nbn:se:naturvardsverket:diva-10292

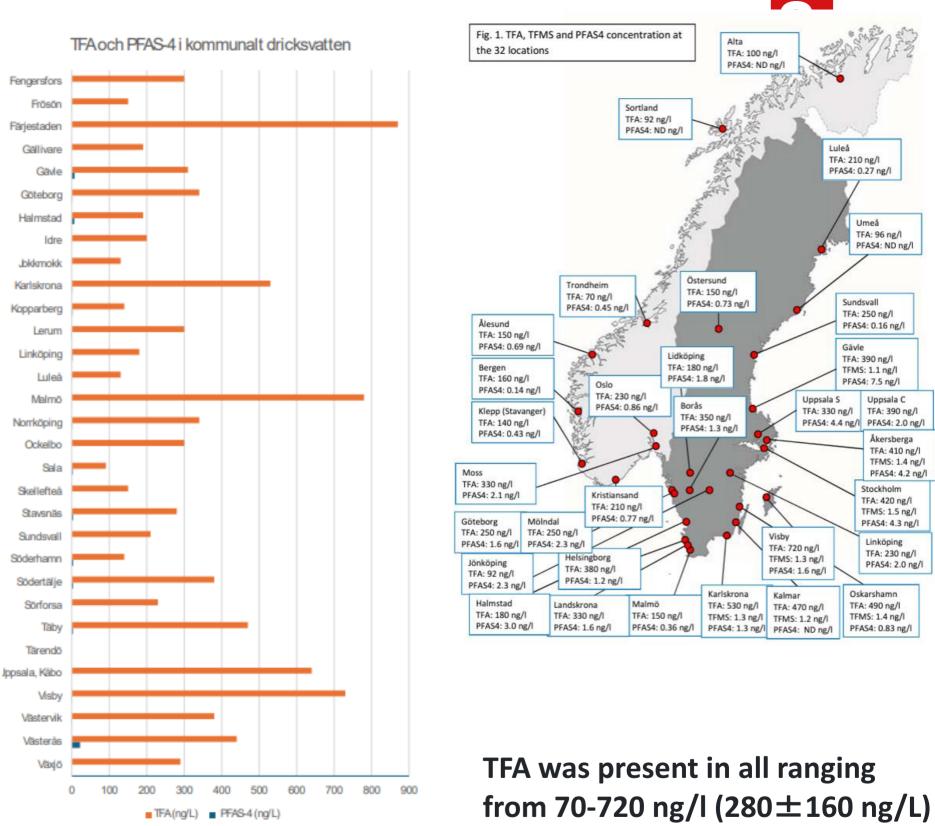




TFA levels in drinking water

| | | TFA concentration ng/L | | | |
|---------|--------------|------------------------|--|--|--|
| Sweden | Lidköping | 148 | | | |
| | Örebro | 295, 305, 316 | | | |
| | Malmö | 208 | | | |
| | Karlshamn | 241 | | | |
| Norway | Oslo | 199 | | | |
| | Bergen | 94.6 | | | |
| | Longyearbyen | 69 | | | |
| | Ny Ålesund | 90 | | | |
| Denmark | Copenhagen | 68.3 | | | |
| | | | | | |

- The Ministry of the Environment and Gender Equality in Denmark has a quality requirements for consumer taps of to be $< 9 \mu g/L$
- German Federal Environment Agency (Umweltbundesamt, UBA) recommends TFA concentrations in drinking water to be < 60 µg/L
- National Institute for Public Health and the Environment (RIVM) has derived the indicative drinking water guideline vale of 2.2 µg/L



Nature conserve society

https://cdn.naturskyddsforeningen.se/uplo ads/2024/10/Analysrapport-pfas-2024.pdf

https://www.eurofins.se/tjaenster/miljoeoch-vatten/nyheter-miljo/eurofins-studyultrashort-pfas-in-swedish-and-norwegiandrinking-water/



Ultra-Short-Chain Perfluoroalkyl Acids Including Trifluoromethane Sulfonic Acid in Water Connected to Known and Suspected Point Sources in Sweden

Maria K. Björnsdotter,*[®] Leo W. Y. Yeung, Anna Kärrman, and Ingrid Ericson Jogsten

Man-Technology-Environment Research Centre (MTM), Örebro University, 701 82 Örebro, Sweden

Fire fighting training sites^a: <34 – 14 000 ng/L Landfill leachate: 1200 – 4400 ng/L 1000 – 1200 ng/L Landfill storm water: <34 – 500 ng/L Landfill leachate from hazardous waste: <34 - 2700 ng/L Hazardous waste management facility^b:

^a(outflowing water from a rock shelter representing a combination of groundwater, storm water, and surface water from the nearby areas) ^bsurface water near the hazardous waste management facility

Banks et al. 1998 Process Sad. Environmen. Prot. Jackson et al. 2011, Environ. Sci. Technol.



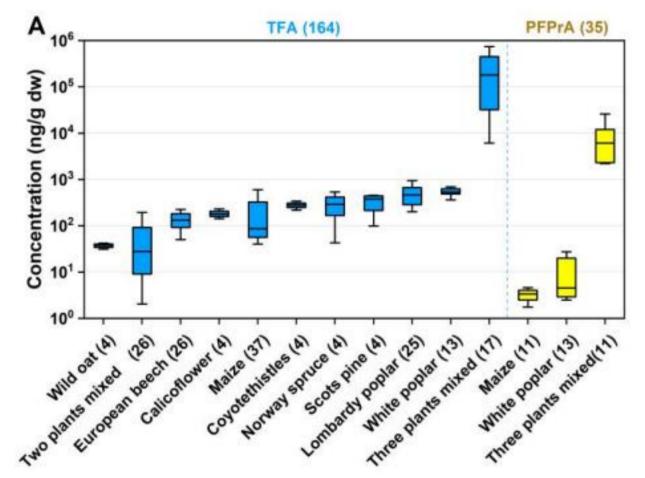
pubs.acs.org/est

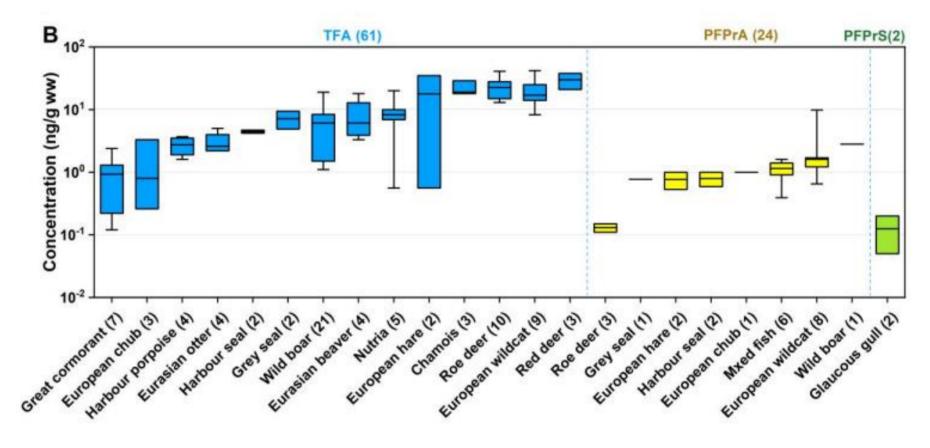




Heptafluoropropane (HFC-227ea) and perfluoro-2-methyl-3-pentanone are used in fire suppression systems.

Occurrence in the Environment





Field measurements of plant bioconcentration factors (Log BAFs) have been reported, with mean Log BAFs for TFA as 3.2 in willow, 1.8-4.1 in maize, 2.4 in poplar, and 4.4 in pyramidalis (Thuja?).



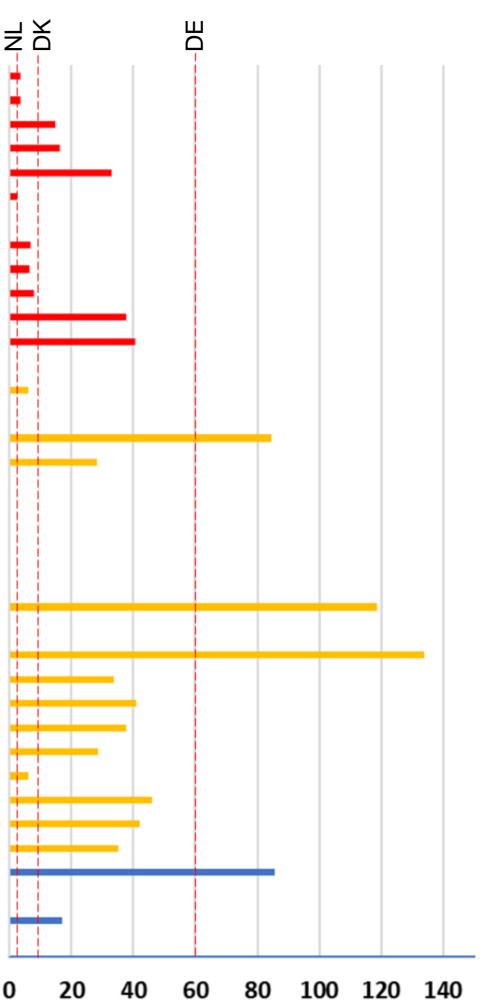
TFA in Beverages 2.0 n = 40 n = 64 n = 22 n = 55 50 TFA concentration in tap water in μg/L 1.5 TFA concentration in beer in µg/L 40 30 1.0 20 0.5 10 0 0.0 Germany other countries other countries Germany 14 -\$ Ig/L 2 nfusion 10 2 atio Der ent in tea an con -0 TFA -0 Terrain Contraction Contracti 10

Apple drink concentrate Apple drink concentrate Apple ECO juice concentrate Apple ECO juice concentrate Apple ECO juice concentrate Apple juice Apple juice Apple juice Apple juice Apple juice Apple juice concentrate Apple juice concentrate Blood orange juice with pulp Fresh Orange Fresh Orange Fresh Orange Fresh Orange Fresh Orange ECO Fresh Orange ECO Fresh Orange ECO Orange ECO juice concentrate Orange ECO juice concentrate Orange ECO juice concentrate Orange ECO juice with pulp Orange juice concentrate Orange juice with pulp Orange juice with pulp Orange juice without pulp Orange, Apple, Passion concentrate Pear drink concentrate Tomato juice Lemon drink concentrate

Scheurer and Nödler 2021 Food Chem

https://www.eurofins.se/tjaenster/livsmedel/nyheter-food-feed/high-levels-of-ultrashort-pfas-tfa-and-tfms-in-juice-and-fruit-puree/

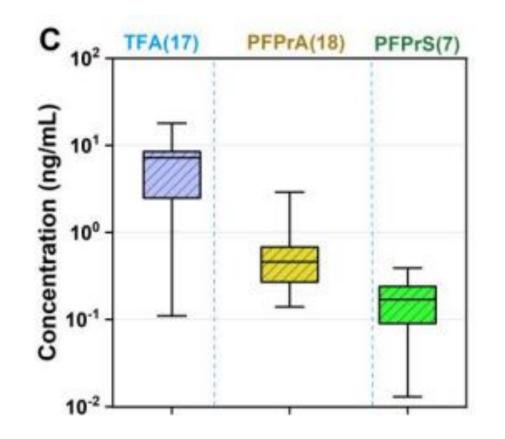
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TFA concentration µg/L



Occurrence in human serum



- In Sweden, 148 whole blood samples from the general Swedish • population and found TFA: 62%
- US (Indiana): TFA detection frequency: 74%, median level: 6.0 ng/mL. China: serum samples TFA (8.5 ng/mL). Norway (Oslo): TFA detection frequence: 100%, median 6.75 ng/mL
- range 2.7 16 ng/mL

In Indiana, US, TFA was the only PFAA for which serum concentrations significantly correlated with both dust and water levels (Spearman 752 correlation coefficients (r) = 0.40, p < 0.001 and r = 0.28, p = 0.01, respectively);

Pharmacokinetics

There is little or no available data on the absorption, disposition, and elimination of TFA. In healthy human volunteers the half-life for renal excretion of TFA administered intravenously is 16 hr (Holaday and Cummah, 1976). In patients receiving halothane anesthesia the resultant metabolically-formed TFA had a half-life in the blood of 52-60 hr (Dallmeier and Henschler, 1977).



Holaday, D.A. and Cunnah, R. 1976. Distribution and elimination of trifluoroacetic acid in man. Paper presented at the Annual Meeting American Society of Anesthesiologists. [As cited in: Holaday, D.A. (1977); Absorption, biotransformation, and storage of halothane. Environ. Health Perspectives 21, 165-169.]

Results - PFAS data

All 215 sera data Among 65 PFAS studied, PFOA, PFNA, PFDA, PFHxS, PFHpS, PFOS and TFA were detected in all samples

Other PFAS did not show any detection in any samples are not listed here

| ng/mL | min | max | median | average | SD | detection frequency |
|----------|-------|--------|--------|---------|-------|---------------------|
| PFHpA | 0.020 | 0.099 | | | | 51 |
| PFOA | 0.179 | 3.986 | 0.747 | 0.835 | 0.452 | 100 |
| PFNA | 0.078 | 1.408 | 0.295 | 0.347 | 0.206 | 100 |
| PFDA | 0.030 | 0.512 | 0.115 | 0.137 | 0.089 | 100 |
| PFUnDA | 0.013 | 0.578 | 0.105 | 0.136 | 0.108 | 99 |
| PFDoDA | 0.018 | 0.068 | | | | 27 |
| PFTrDA | 0.008 | 0.192 | | | | 72 |
| PFTDA | 0.020 | 0.033 | | | | 6 |
| PFBS | 0.014 | 0.034 | | | | 8 |
| PFHxS | 0.262 | 2.721 | 0.839 | 0.903 | 0.409 | 100 |
| PFHpS | 0.010 | 0.367 | 0.061 | 0.081 | 0.064 | 100 |
| L-PFOS | 0.301 | 8.360 | 1.653 | 2.093 | 1.611 | 100 |
| BrPFOS | 0.167 | 5.131 | 0.890 | 1.250 | 0.949 | 100 |
| 6:2 FTSA | 0.010 | 0.120 | | | | 2 |
| 8:2 FTSA | 0.010 | 0.080 | | | | 46 |
| TFA | 2.693 | 16.021 | 6.750 | 6.913 | 2.342 | 100 |
| PFPrA | 0.185 | 0.592 | | | | 22 |
| FOSAA | 0.022 | 0.054 | | | | 4 |
| MeFOSAA | 0.010 | 0.215 | | | | 22 |
| EtFOSAA | 0.022 | 0.030 | | | | 1 |
| PFOSA | 0.010 | 0.058 | 0.016 | 0.019 | 0.008 | 80 |



EOF data

| Total number of samples analyzed | | | 215 | | | |
|----------------------------------|--------------------------------------|-----|-----|---------|---------|----|
| Number of sample above LOQ | | • | 164 | | | |
| Max | | | 32 | | _ | |
| Min | | 7,6 | | ng F/mL | | |
| | Median | | 4,6 | ng F/ml | _ | |
| | | min | max | median | average | SD |
| % | quantifiable PFAS to EOF | 19 | 120 | 62 | 61 | 20 |
| % | quantifiable PFAS without TFA to EOF | 5 | 95 | 29 | 32 | 16 |

| Total number of samples analyzed | | | 215 | | | |
|----------------------------------|--------------------------------------|------|-----|---------|---------|----|
| Number of sample above LOQ | | | 164 | | | |
| Max | | | 32 | ng F/ml | - | |
| | Min | | 7,6 | ng F/ml | _ | |
| | Median | 14,6 | | ng F/ml | _ | |
| | | min | max | median | average | SD |
| % | quantifiable PFAS to EOF | 19 | 120 | 62 | 61 | 20 |
| % | quantifiable PFAS without TFA to EOF | 5 | 95 | 29 | 32 | 16 |

When EOF data are below method detection limit, value of method detection limit is used for calculating the proportion of PFAS to EOF



Concluding remarks

- TFA is everywhere •
- Removal of TFA is difficult though it can be removed by using ion exchange resin, activated carbon (new) or reverse osmosis
- Numerous sources of TFA to the environment via direct/indirect routes •
 - The report from 73/2021 projects a large additional share to the • amounts of TFA or trifluoroacetate in the atmosphere, especially through the emissions of the refrigerant u-HFC-1234yf from mobile and stationary air conditioning.
- The German Chemical Agency proposed to classify TFA as toxic to \bullet reproduction based on a recent study from Bayer on the reproductive toxicity of TFA in rabbits, which found severe fetal malformations.
- A German standard method to measure TFA will be available in the \bullet beginning of 2025.



TEXTE 73/2021

Final report

Persistent degradation products of halogenated refrigerants and blowing agents in the environment: type, environmental concentrations, and fate with particular regard to new halogenated substitutes with low global warming potential

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Toxicity data

Acute toxicity tests, no effects of NaTFA on water fleas (*Daphnia magna*) and zebra fish (Danio rério) were found at a concentration of 1,200 mg/L.

A 7-d study with duckweed (*Lemna gibba* G3) revealed a NOEC of 300 mg/L

...on the basis of the combined results of the laboratory tests and a previously reported semi-field study, we can consider a TFA concentration of 0.10 mg/L as safe for the aquatic ecosystem.

Long-term "derived no-effect level" / oral / Systemic effects of 0.042 mg/kg bw per day based on the 90-day rat study was established by ECHA (uncertainty factor (UF) 200 for the extrapolation from subchronic to chronic); observation: both mean absolute and relative liver weights were increased

minimal to moderate diffuse centrilobular hepatocellular hypertrophy an increased incidence of hepatocellular necrotic foci in males



Bayer 2014; Berends et al. 1999, Environ. Toxicol. Chem.

Guideline values in drinking water

- The Ministry of the Environment and Gender Equality in Denmark has a quality requirements for consumer taps of to be $< 9 \mu g/L$
- German Federal Environment Agency (Umweltbundesamt, UBA) recommends TFA concentrations in drinking water to be < 60 µg/L
- National Institute for Public Health and the Environment (RIVM) has derived the indicative drinking water guideline vale of 2.2 $\mu g/L$

