TFA – Analys och Förekomst

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Testing for Life

Background

What are PFAS chemicals?

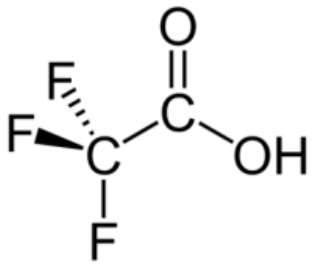
OECD, 2021: “…the fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom…”

PFAS = Any substance with a -CF2 - or -CF3 moiety in their structure

”Forever chemicals” – very persistent (vP)

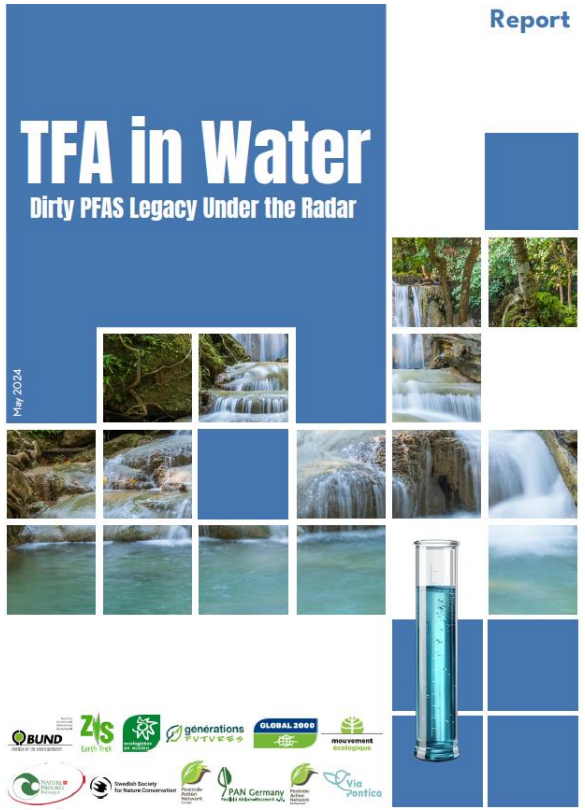
Non-degradable or transformed into stable products in the environment

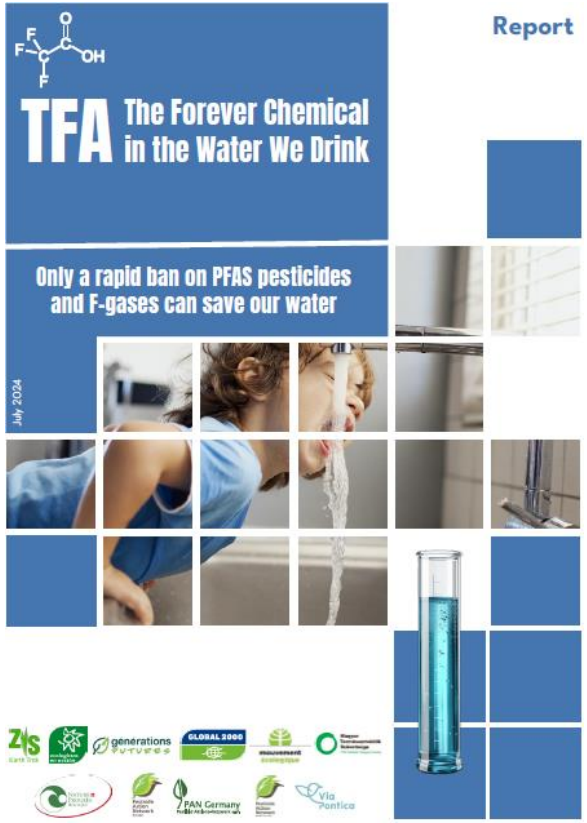
PFAS substances do not occur naturally, all PFAS are produced by humans.



TFA – trifluoroacetic acid

Increased awareness of ultrashort TFA





- TFA detected in all waters 50-2500+ ng/l
- Proposition from Germany to ECHA, reproduction toxicity of TFA. ECHA proposal published in May 2025.

Ultrashort PFAS – Background

Emerging environmental contaminants

- Widespread occurrence in drinking water, ground- & surface waters
- Accumulation in plants
- Included in PFAS definition (OECD, 2021)

Ultrashort PFAS: 1-3 carbon atoms

- TFA (trifluoroacetic acid) most studied, TFMS (triflic acid), PFEtS, PFPrA, PFPrS

Sources

- Breakdown of “modern” freons in the atmosphere → precipitation
- TFMS additive in Li- battery electrolytes
- 35-40 pesticides approved in the EU may degrade to TFA
- Certain pharmaceuticals (ie Prozac) may degrade to TFA

Drinking water guideline values

- TFA: NL 2 200 ng/l, DK 9 000 ng/l, IT 10 000 ng/l, DE 60 000 ng/l
- Drinking Water Directive PFAS total 500 ng/L
- TFA to be included in EQS directive (surface waters)

Analysis

Analysis TFA and Ultrashort PFAS - Water

Analytical development of TFA and ultrashort

- Active field since (late) 1990's
- Montreal protocol – introduction of "new" refridgerants (HCFC, HFC, HFO, HCFO) e.g. HFO-1234yf, HCFOs-1233zd, HCFC-124)
- UNEP EEAP reporting (TFA, PFPrA, PFBA) to parties of the protocol
- Scientific reports on TFA in ice cores. Natural occurence?
- TFA can be analysed using both Gas (GC) and Liquid (LC) methods with different detectors
- Subsequent development of analysis of further matrices, food, biota, soil etc
- Development of improved, more sensitive, instruments
- Rapid development in all aspects

Analysis TFA and Ultrashort PFAS - Water

Björnsdotter et al, 2020

Table 2 Summary of analytical methods and method performance for quantification of ultra-short-chain PFAAs in water samples

Sample preparation	Separation-detection technique	Quantification	Sample matrix	Sample volume (mL)	Instrument run time (min)	Analytes	Extraction efficiency (%) based on matrix spike	LOD/LOQ (ng/L)	Reference (publication year)
Sample volume reduction to 50 mL by rotary evaporation at 55 °C. Derivatization and salting-out LLE with ethyl acetate. Removal of water and evaporation to dryness at 30 °C. Re-dissolution in benzene/toluene followed by volume reduction to 2 mL.	GC-MSD (SIM)	Internal standard calibration using ^{13}C-labeled trichloroacetic acid	Rain ($n = 2$) Snow ($n = 3$) Groundwater ($n = 2$) Surface water ($n = 4$) Subsurface water ($n = 3$) Drinking water ($n = 3$)	500–1000	40	TFA PFPrA	89 ± 7	0.1–1[a]/–	Scott and Alaee [31] (1998)[e], Scott et al. [16] (2000)[f], Scott et al. [19] (2002)[e], Scott et al. [15] (2005), Scott et al. [18] (2005), Scott et al. [32] (2006)[e], Scott et al. [17] (2006)
Extraction by anion-exchange SR Empore disk, derivatization. Surface water samples with salinity > 500 µS were cleaned up by LLE prior to extraction.	GC-ECD	External standard calibration	Rain ($n = 2$) Tap water ($n = 2$) Surface water ($n = 6$)	400	30	TFA	Rain 97 ± 4 Tap water 105 ± 0.3 Surface water 102 ± 4	32/36	Wujcik et al. [33] (1998)
WAX-SPE	Ion-exchange HPLC-MS/MS	Internal standard calibration using ^{13}C-PFBA and ^{13}C-PFOS	Rain ($n = 4$)	100	30	TFA PFPrA PFEtS PFPrS	76 ± 9 105 ± 1 105 ± 3 105 ± 4	–/0.5[b] –/0.1[b] –/0.1[b] –/0.5[b]	Taniyasu et al. [20] (2008)
WAX-SPE	SFC-MS/MS	–	Rain ($n = 2$) Surface water ($n = 2$)	200	8	TFA PFPrA PFEtS PFPrS	79 ± 10 84 ± 8 93 ± 7 85 ± 4	–/0.2–0.5[b]	Yeung et al. [34] (2017)
WAX-SPE after adjusting the pH to 3.8–4.0	RP-LC-ESI-MS/MS	Internal standard calibration using ^{13}C-TFA	Spring water ($n = 1$) Tap water ($n = 21$) Groundwater ($n = 42$) Surface water ($n = 43$)	50	20	TFA PFPrA	Tap water 97 ± 0.7 Groundwater 99 ± 4 Surface water 101 ± 1 Tap water 95 ± 2 Groundwater 83 ± 2 Surface water 104 ± 5	5.5/26[c] 0.9/4.3[c]	Janda et al. [11] (2018)
Direct injection	SFC-MS/MS	Internal standard calibration using ^{13}C-PFBA	Surface water Groundwater Landfill leachate	0.25	11	TFA	81 ± 0.4	34[d]/–	Björnsdotter et al. [35] (2019), Björnsdotter et al. [28] (2019)

- GC methods require derivatization (typically)
- LC (UPLC) – pre-conc-entration/clean-up with SPE
- Increasing number of “direct injection” LC applications
- Mass spectrometry detection (MS or MS/MS)
- LOD/LOQ <1-36 ng/l
- TFA, PFPrA, PFEtS, PFPrS, (TFMS/PFMeS)

Analysis TFA and Ultrashort PFAS

TFA and ultrashort PFAS – Observations and analytical capacity

- TFA is everywhere – easy to contaminate
- TFA has relatively low sensitivity
- Direct injection simplifies handling and risk of contamination
- TFA/ultrashort have their own production line (incl equipment)
- TFA has a “standard” LOQ of 50 ng/l, 1-3 ng/l for others
- Both LC and GC are being used at commercial labs
- Accreditation
- Use bottles supplied by the lab
- Detects of TFA in ~98-99% of water samples
- Food/biota matrices require extraction (acid methanol, EURL method). LOQ 1-10 µg/kg
- Ultrashort PFAS incl TFA are difficult to analyse together with “regular” PFAS due to small molecular size, high polarity and charge – “mixed mode” (RP/ion-exchange) columns typically used
- PFPrS can many times be included with “regular” PFAS
- TFA becoming integrated into PFAS and “PFAS pesticides” issues

Commission notice on PFAS methods in DWD

C/2024/4910

Commission Notice

Technical guidelines regarding methods of analysis for monitoring of per- and polyfluoroalkyl substances (PFAS) in water intended for human consumption

(C/2024/4910)

Sum of PFAS (PFAS20 (21,22))

The methods of analysis should meet the general and specific requirements regarding the parameter *'PFAS'* as set out in Annex III to the Directive. The recommended methods of analysis for the parameter *'Sum of PFAS'* are:

— EN 17892:2024 part A	(LC-MS, direct injection method)
— EN 17892:2024 part B	(LC-MS, SPE enrichment method)

PFAS Total

Currently, the methods recommended in these guidelines as proxies for measuring the *'PFAS Total'* parameter are neither standardised nor harmonised; the recommendations cover the principles of analysis but do not provide guidance on preparing the sample:

1. TOP assay (total oxidisable precursor assay)
2. EOF-CIC (combustion ion chromatography (CIC) after extraction of fluorine (EOF))
3. LC-HRMS suspect and non-target analysis (liquid chromatography high resolution mass spectrometry)

The Commission recommends the following approach for reporting analytical results of *'PFAS Total'*:

Step 1:	Determine the analytical result for *'PFAS Total'* ([PFAS Total]) by using one of the three recommended proxy methods of analysis, indicating which method has been used ([PFAS $Total_{TOP}$], [PFAS $Total_{EOF\text{-}CIC\ PFOAeq}$] or [PFAS $Total_{HRMS}$]).
Step 2:	Determine the analytical result for the substance TFA ([TFA]) using a targeted method of analysis. The targeted method should comply with the requirements set out in Annex III to the Directive, in particular with the requirements in Part B for the *'PFAS Total'* parameter.
Step 3:	The analytical report includes the reporting of [PFAS Total], [TFA] and [PFAS Total] – [TFA], indicating which proxy method and targeted method have been used.
Step 4:	If [PFAS Total] – [TFA] < 0, it is recommended to mark the reported analytical results in step 3 as inconclusive.

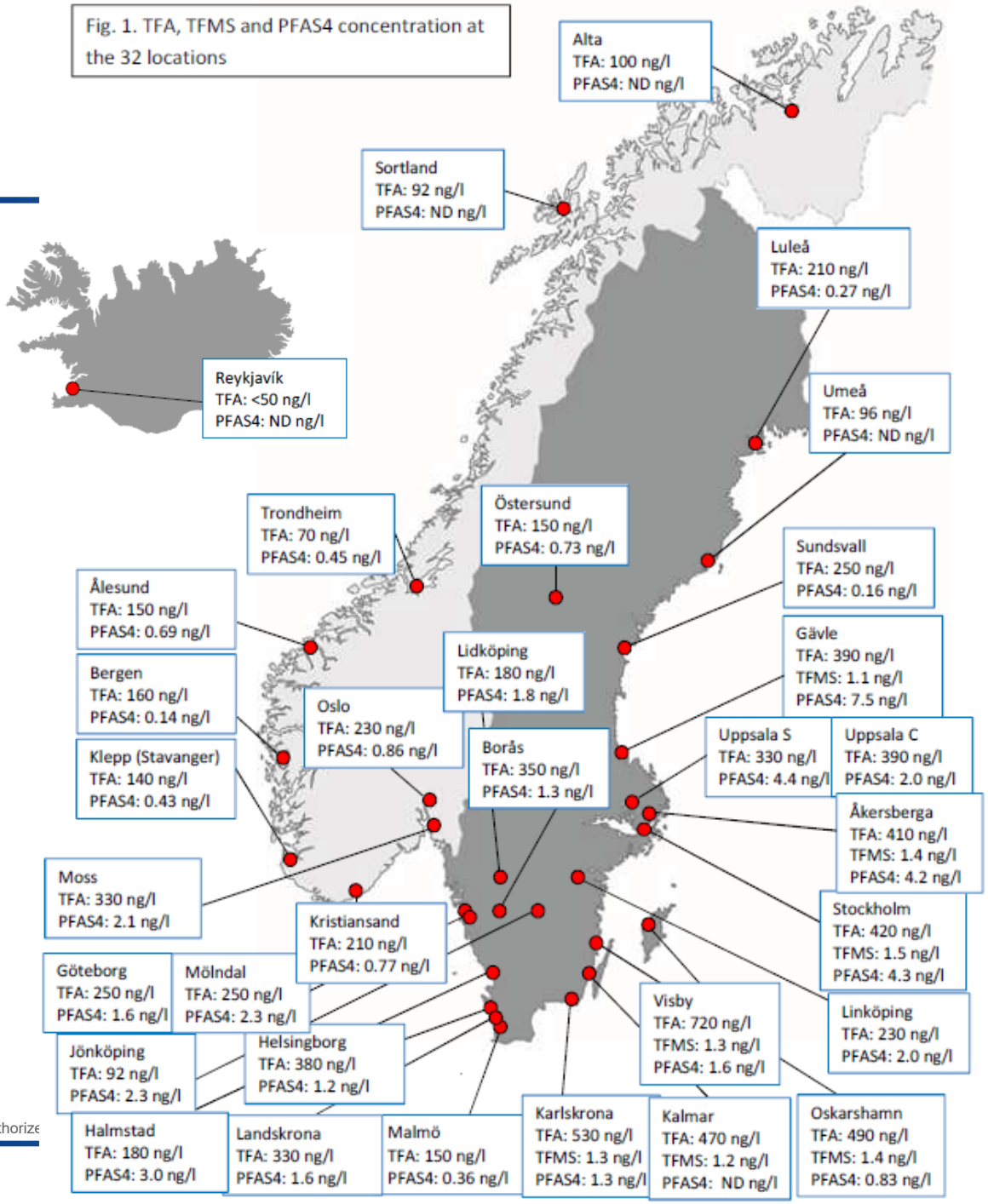
- Sum of PFAS = PFAS 20/21/22: New EN standard
- PFAS total – Three methods
  - TOP, EOF and LC-HRMS (called proxys)
  - None of the three methods is ”optimal” for ultrashort PFAS (incl TFA)
  - Will this cause negative “inconclusive” values?
- Evaluation of PFAS total requires a separate TFA analysis

TFA – Environmental Prescence

Eurofins Study 2023: Ultrashort PFAS in drinking water

Sweden & Norway (+Iceland)

- TFA is everywhere 70-720 ng/l (Trondheim - Visby)
- TFA corresponds to 99% of identified PFAS
- Icleand TFA: ND, PFAS4: ND
- Groundwater sources has a tendency of lower concentration (not stat significant)
- Infiltrated groundwater maximum TFA on average
- TFMS is detected in 6 places
- Three localities add up to >500 ng/l, limit value for PFAS tot according to DWD if TFA had been included
- Guideline values for TFA in DE (60 000 ng/l), IT (10 000 ng/l), DK (9 000 ng/l) and NL (2 200 ng/l)



Ultrashort PFAS in drinking water - Europe

Denmark

- TFA not detected in most places
- PFAS4 below LOQ in 5 out of 6 locations
- Very limited PFAS22
- Groundwater = lower concentrations
- Effect of purification in waterworks unknown

Germany/Austria

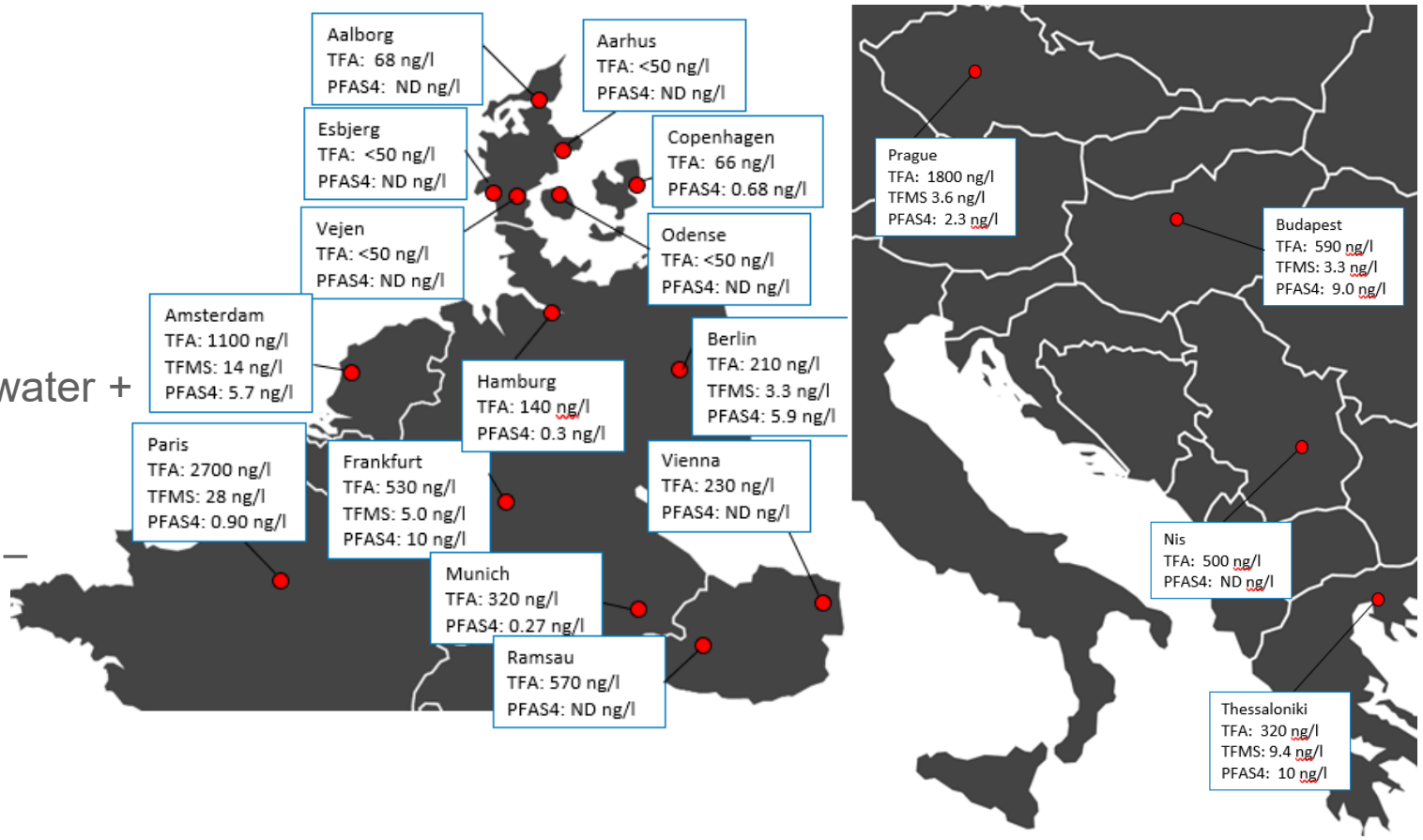
- Highest in DE, Frankfurt, infiltrated surface water + "existing" groundwater
- Ramsau, AU: 570 ng/l
- Remaining cities, groundwater/spring water – generally lower levels

France (Paris)

- Surface water from the River Avre

Eastern Europe

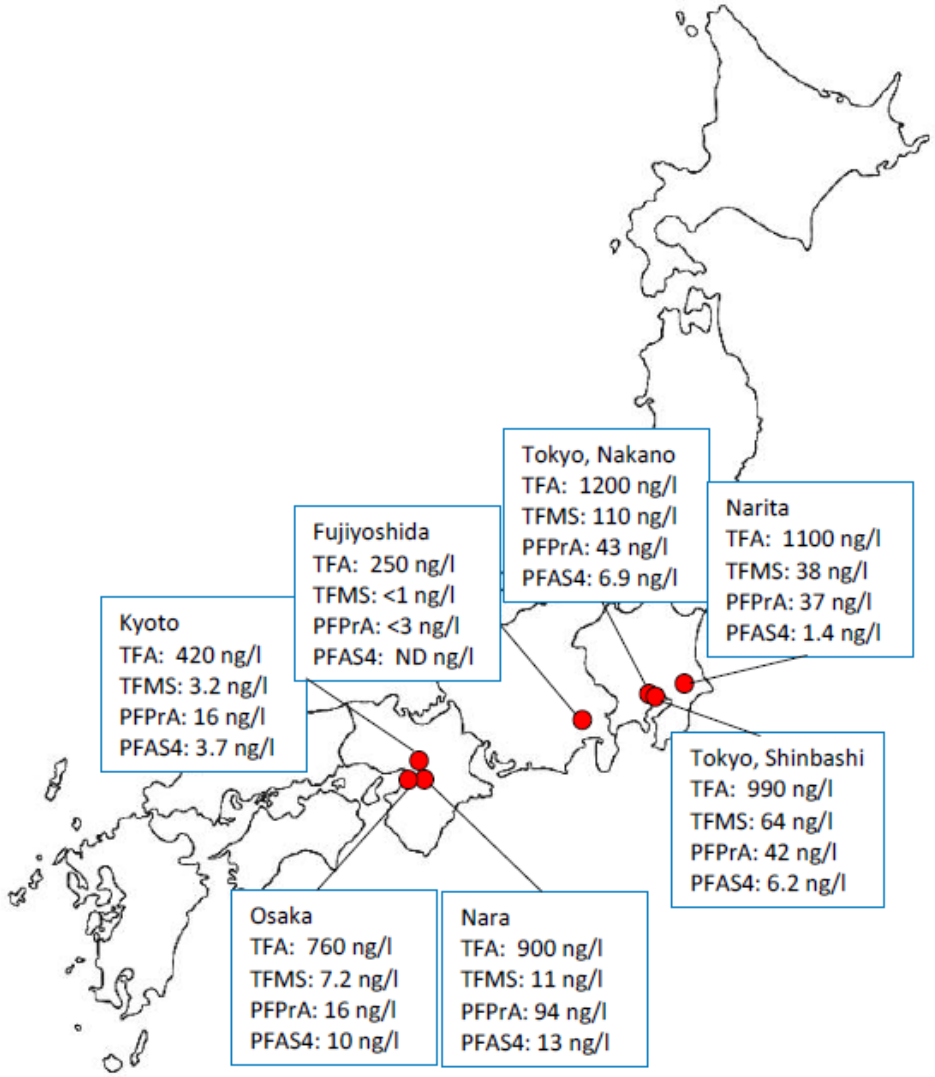
- TFA highest in Prague, 1800 ng/l
- PFAS4 – ND to 10 ng/l
- Sources unknown



Ultrashort PFAS in drinking water - Japan

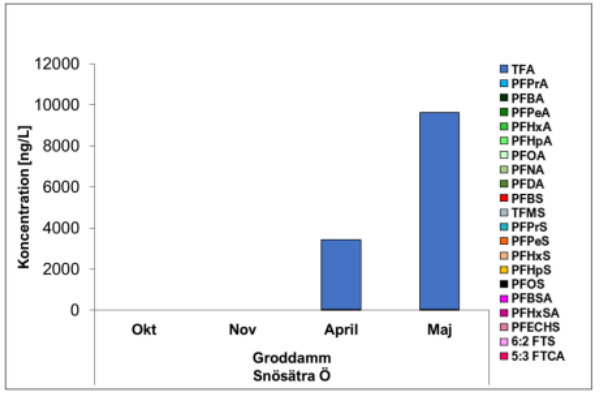
Japan

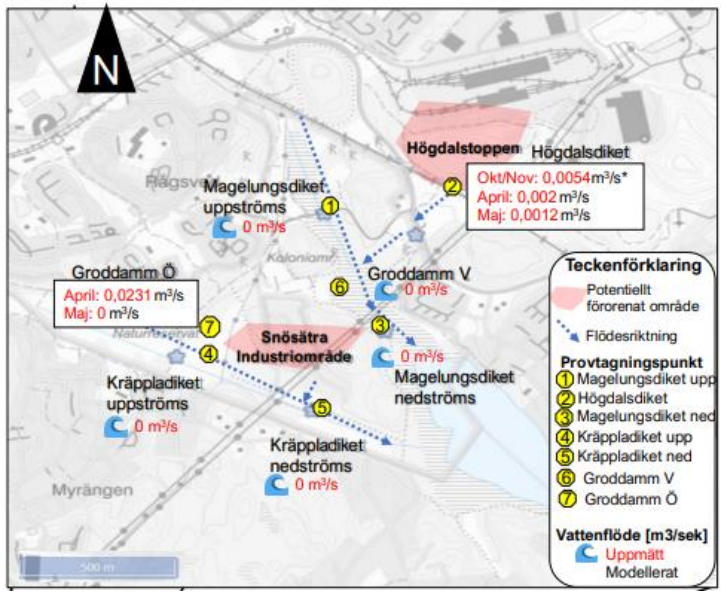
- TFA 250-1200 ng/l
- PFPrA: one ND, six bewteen 16-94 ng/l
    - Higher than Europe
- PFAS4: ND-13 ng/l
- Tokyo: surface water from 3 rivers
- Osaka: Yodo river system
- Kyoto: Lake Biwa + 2 rivers

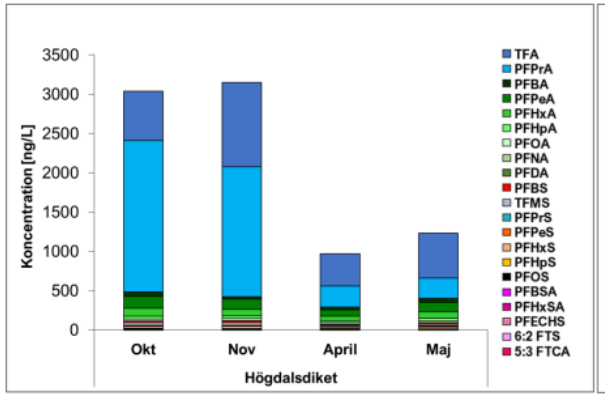


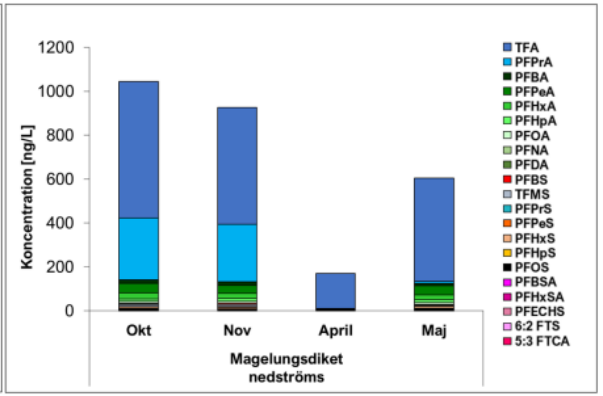
PFAS Mass Balance in Three Stockholm Lakes

- Study commissioned by City of Stockholm,
- PFAS mass balances for lakes Flaten, Magelungen, and Drevviken (2022-23)
- Identify and rank PFAS transport pathways, sources, and assess seasonal variations.
- Sampling at 16 inflow/outflow points, flows, analysis of 49 PFAS
- 20 PFAS detected; concentrations ranged 260–9600 ng/l
- Ultrashort PFAS dominated, especially TFA (>90% of PFAS content)
- PFPrA high at Högdals- and Magelugnsdiket
- PFOS >EQS (0.65 ng/l) and PFAS4 >4 ng/l in all samples
- Atmospheric deposition significant for ultrashort PFAS
- Further investigations needed: detailed studies of Högdalsdiket and Snösätra runoff





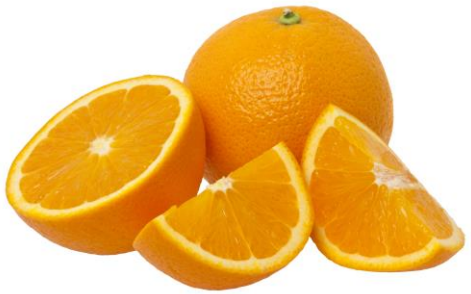




Filipovic…van Hees, Karlsson et al, 2025

Eurofins Study – Juice and Puree

Orange juice: mean **34 000** ng/l



Fresh Oranges: <**2 500** to **84 000** ng/l

Smoothies/Squeezable fruit smoothies for children: <**2 500** to **30 000** ng/l

Apple juice, mean = **6 200** ng/l

All samples with detected levels exceeds **NL** water guideline value **2 200** ng/l, most **DK** value **9 000** ng/l, one **DE** value **60 000** ng/l.

Study done in cooperation with Örebro University

TFA & Pesticides in Wine – PAN/Global 2000 Report

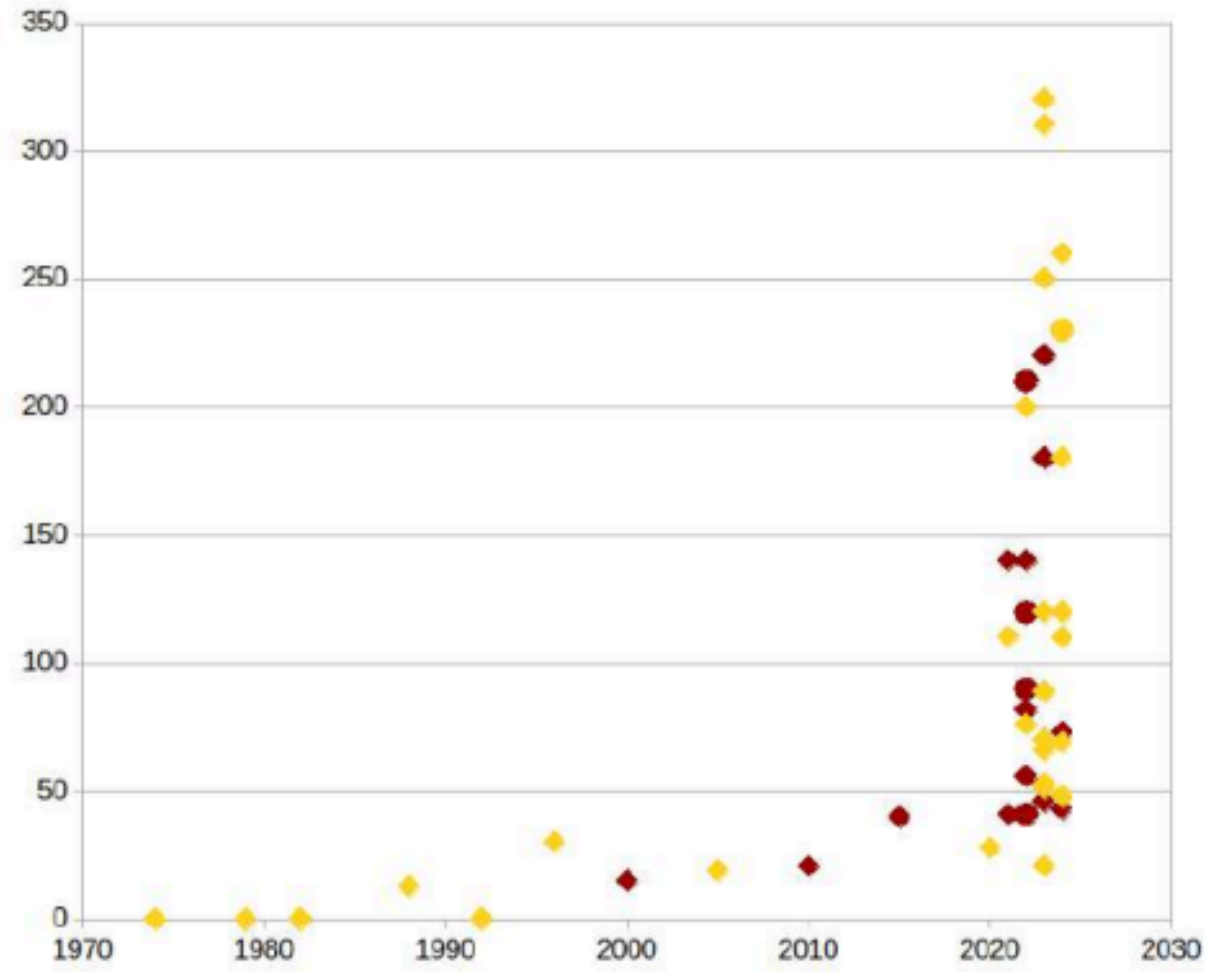


Figure 2b: TFA Levels in 49 Wine Samples from 1974 to 2024 [µg/L].

Diamonds represent conventional wines, circles represent organic wines. Red symbols indicate red wine; yellow symbols indicate white wine.

- Organic Wine / White
- Organic Wine / Red
- Conventional Wine / White
- Conventional Wine / Red

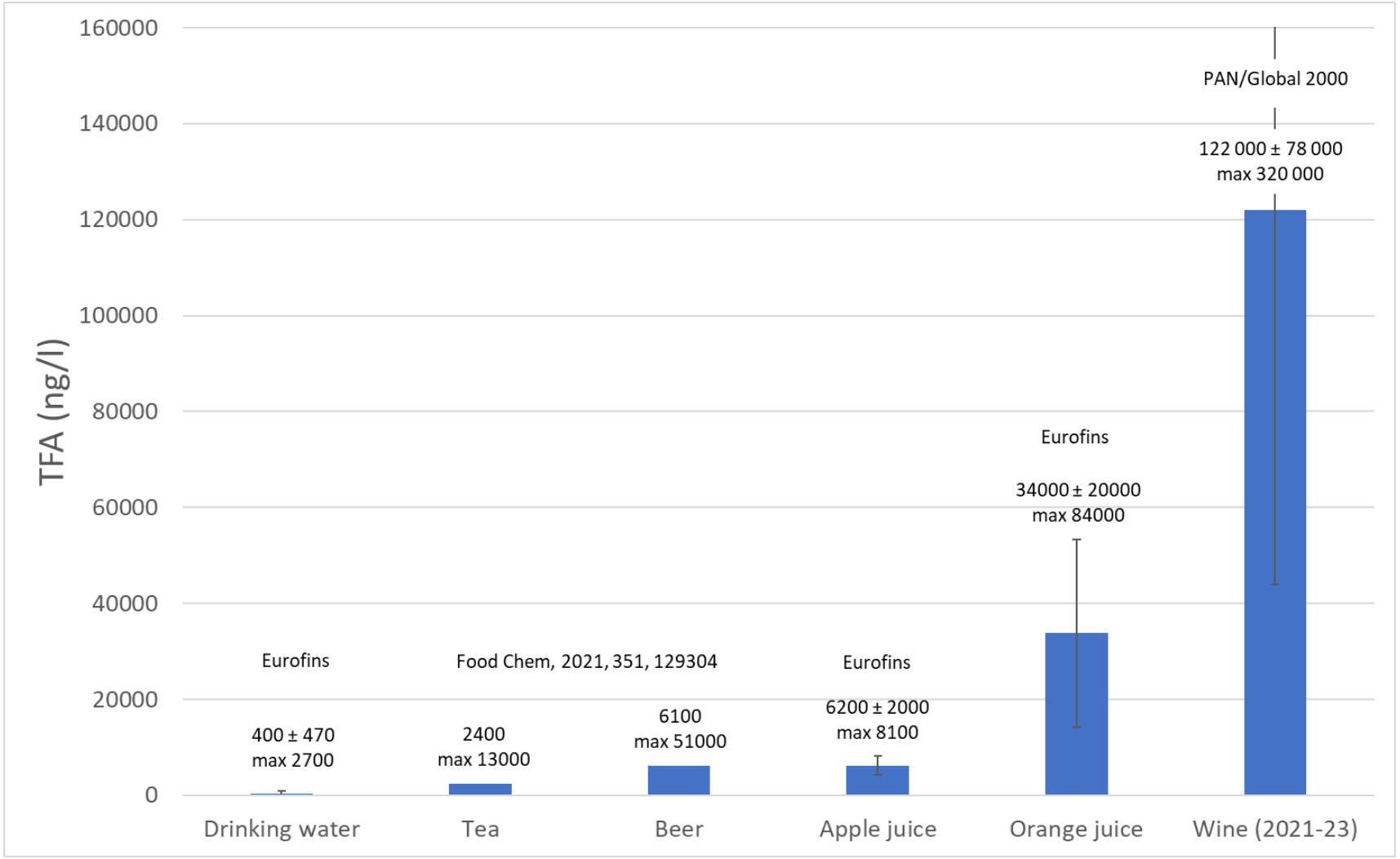
- Samples in the time period 1974-2015
- Big variation within and between EU countries
- All tested wines have levels of TFA

Overview – TFA in Beverages and Drinking Water

- Mean ± std dev
- 300x more TFA in wine than drinking water on average
- Large variation. Std dev can be 50% of mean or larger

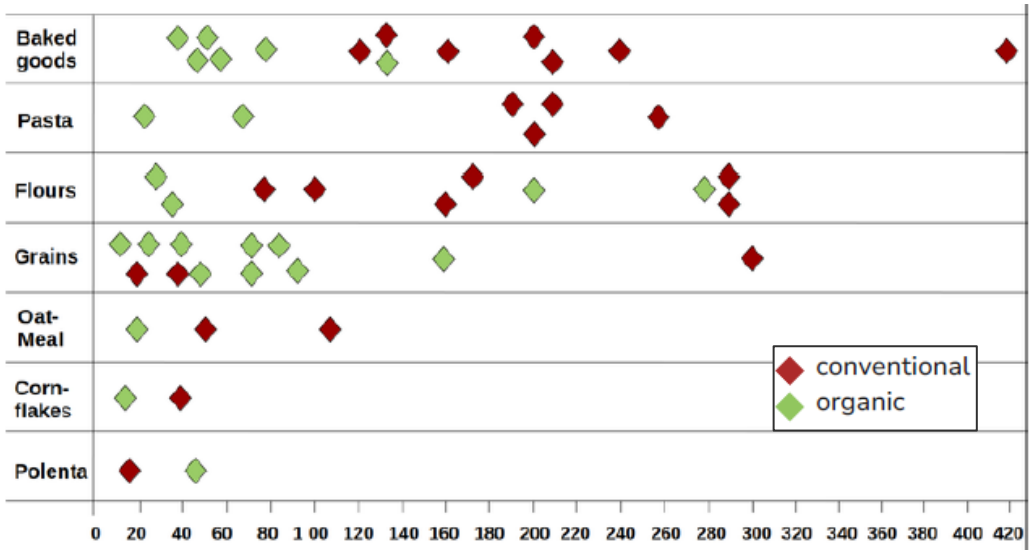
Drinking water guideline values

- TFA: NL 2 200 ng/l, DK 9 000 ng/l, DE 60 000 ng/l.
- Drinking Water Directive PFAS total 500 ng/L.



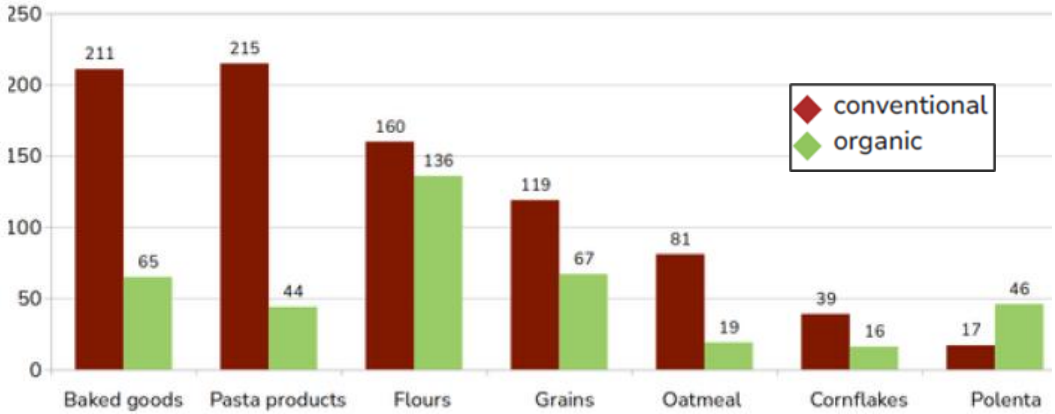
TFA in Cereal Products – PAN/Global 2000/AK Report

TFA in organic and conventional food



- Overall average 120 µg/kg (13-420)
- Conventional 3.5x higher, statistically significant

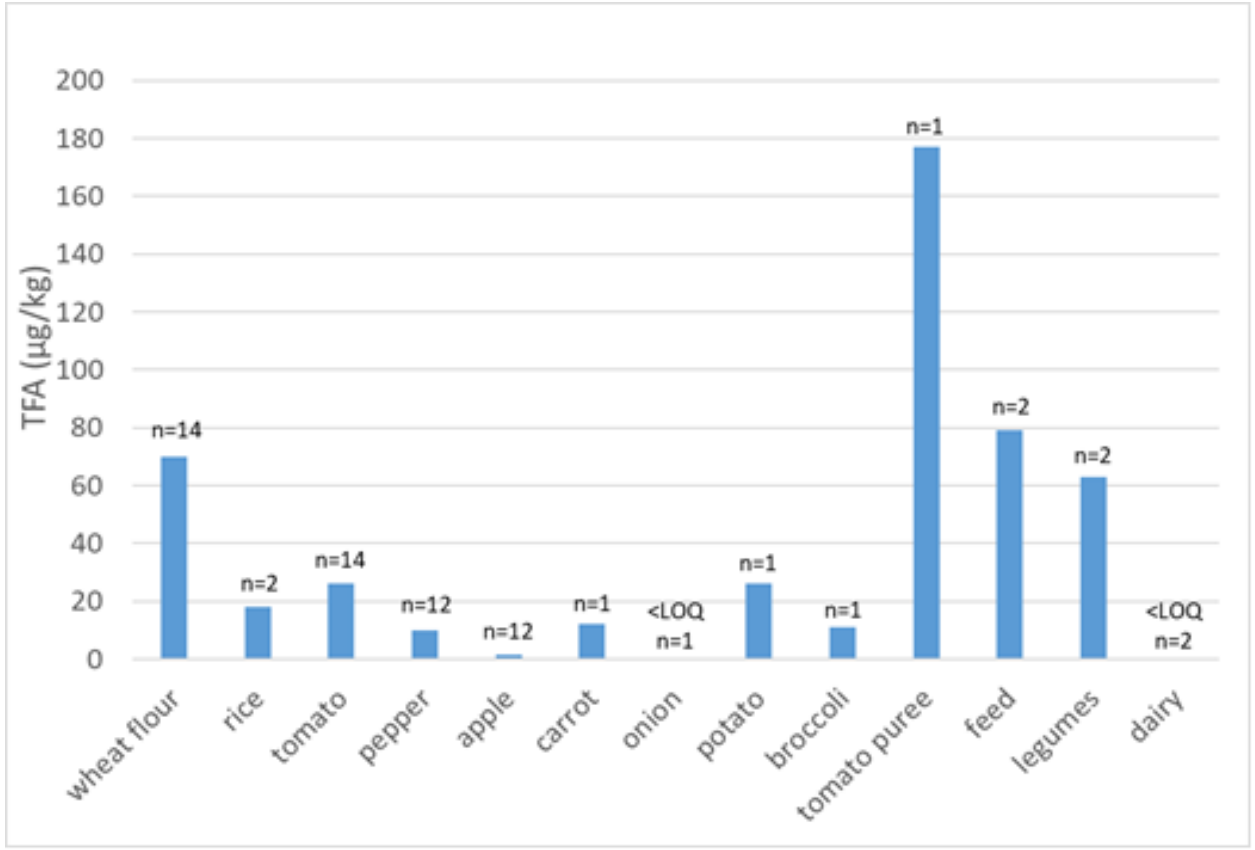
Mean values of TFA for different foods



- Highest TFA seen for conventional bakery products
- Organic lower for 6 out of 7 categories

TFA in vegetables, fruit and flour - Eurofins

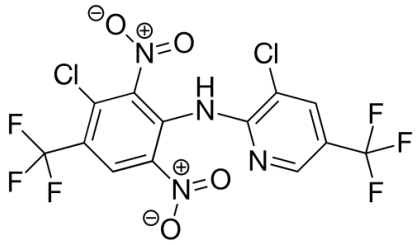
Average and single concentrations TFA



- Range of vegetable foods (+milk and yogurt)
- Average values shown for foodstuffs with replicates
- TFA range <LOQ (=10) to 210 µg/kg
- Highest ave. for wheat flour, feed, legumes
- Lower average value for fluor than in PAN (2025) – 70 vs ~150 µg/kg. Swedish wheat flour 26 µg/kg
- Similar levels between organic and conventional produce
- Tomato plants ~85 µg/kg, potato 480 µg/kg

Research Project – Fluazinam/TFA in Potato Farming

- "Lysimeter experiments for table potatoes with different control measures against potato leaf mold and brown rot"
- The Rural Economy and Agricultural Society (Hushållningssällskapet)
  - Objective: to study the use of fluazinam - enrichment of fluazinam and its degradation products (TFA) in water and soil, and the extent to which they are taken up into potatoes (plant/potato)
  - Field trial for potato farming +/- fluazinam (and other "PFAS pesticides"), and without pesticides, 4 replicate plots
  - Drainage water (seepage), irrigation water, plant, potato, soil
  - Growing season 2025. New applications for 2026-27
  - Funded by Swedish Board of Agriculture (Jordbruksverket)
  - "Side project" on TFA in groundwater at farms +/- potato-growing

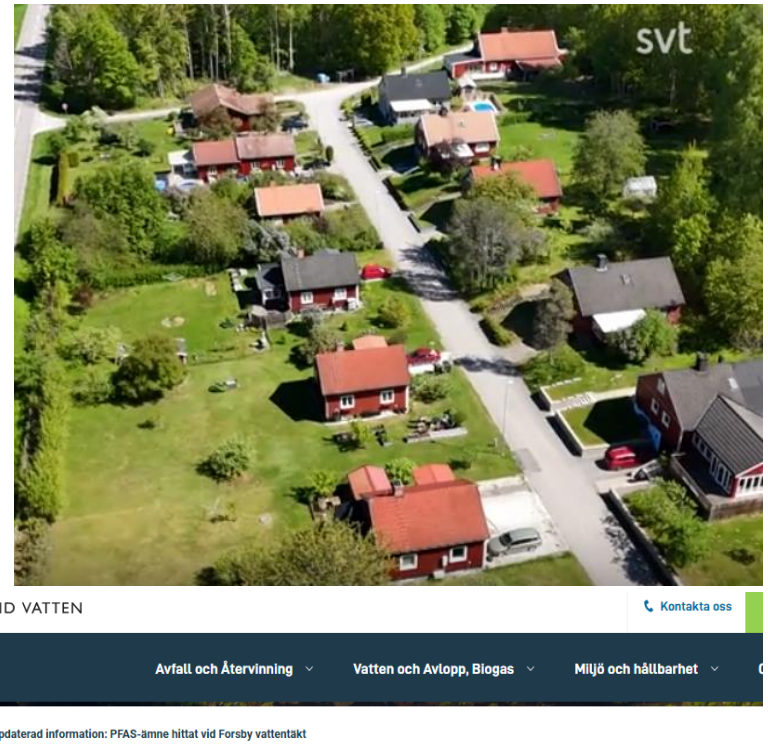


Fluazinam, wikipedia

Lilla Böslid, Hushållningssällskapet Halland, SW Sweden

PFPrA Drinking Water Case

- Small village – 29 households (Forsby, Vingåker – S Sweden)
- Small waterworks and wastewater treatment plant in area
- 30 000 ng/l PFPrA in wastewater (“leaky pipes” – water intrusion)
- PFPrA discovered as part of initial UWWTD investigation (April 25)
- 7-8000 ng/l PFPrA in drinking water
- Two water wells – one contaminated, one not
- “Normal” levels of TFA
- Source unknown – tracking will start
- Water tanks provided
- Inhabitants offered blood and urine sampling



Danish ban of ”PFAS pesticides”

No Alternatives

Produktnavn	Reg-nr.	Aktivstofnavn(e)	Frist for salg	Frist for anvendelse/ besiddelse
Propulse SE 250	18-597	prothioconazol; fluopyram	31.12.2025	30.9.2026
Vendetta	11-58	fluazinam; azoxystrobin	31.12.2025	30.9.2026
Kunshi	352-9	fluazinam; cymoxanil	31.12.2025	30.9.2026
Zignal 500 SC (tidl. Zignal)	11-35	fluazinam	31.12.2025	30.9.2026
Banjo 500 SC	396-34	fluazinam	31.12.2025	30.9.2026
Vamos	396-95	fluazinam	31.12.2025	30.9.2026
Shirlan Ultra	352-13	fluazinam	31.12.2025	30.9.2026
PRO-Tector	623-7	prothioconazol; fluopyram	31.12.2025	30.9.2026
Balaya	19-240	mefentrifluconazole	31.12.2025	16.7.2026
Himalaya Pro	623-8	mefentrifluconazole	31.12.2025	16.7.2026
Teppeki	352-5	flonicamid	28.2.2026	31.8.2026
Afinto	352-19	flonicamid	28.2.2026	31.8.2026
DFF	18-416	diflufenican	28.2.2026	30.11.2026
Legacy 500 SC	396-26	diflufenican	28.2.2026	30.11.2026
Mateno Duo SC 600	18-631	diflufenican, aclonifen	28.2.2026	30.11.2026
Sempra SC	1046-5	diflufenican	28.2.2026	30.11.2026

Alternatives available

Produktnavn	Reg-nr.	Aktivstofnavn(e)	Frist for salg i detailled	Frist for anvendelse/ besiddelse
Revyona	19-248	mefentrifluconazol	30.8.2025	31.12.2025
Othello OD	18-520	diflufenican; mesosulfuron-methyl; iodosulfuron-methyl-natrium	30.8.2025	31.12.2025
Evure Neo	396-73	tau-fluvalinat	31.10.2025	31.12.2025
Mavrik	396-82	tau-fluvalinat	31.10.2025	31.12.2025

- DK-EPA (Miljøstyrelsen) bans 33 pesticide products, incl 16 products with no alternatives
  - Decisions taken July and Sep 2025
  - Deadlines for sale and use (during 2025-26)
- 6 active substances (“PFAS pesticides”) that can form TFA
  - Fluazinam, Fluopyram, Diflufenican, Mefentrifluconazole, Tau-fluvalinate and Flonicamid
- Substances selected on basis of “TriFluPest” project
  - Report from GEUS (National Geological Surveys for Denmark & Greenland), Dec 2024
  - Batch experiments with soil demonstrating decomposition to TFA (up to 11% of theoretical content over 1 year)
- The main reason for the ban is protection of groundwater which is the major drinking water source in DK
- DK-EPA mentions that the restriction will be a big challenge for potato production, especially starch potatoes

Thanks!

Thanks for listening!

Welcome to contact me!

Questions?

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