Ultrashort PFAS – the long and the short of it!

Vision, Initiatives and Paradigm Shift

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Overview

'Forever pollution': Explore the map of Europe's PFAS contamination

- Characteristics and Invention of PFAS
- Focus on ultrashort PFAS C1-C3
- Fate & Transport of ultrashort PFAS and their precursors
- **Chemical Analysis**
- Anthropogenic Background
- Refrigerant use leading to ultrashort **PFAS** in rain
- Safer Alternatives
- **Exposure to Ultrashorts**
- **Ultrashort PFAS Toxicology**
- Summary





Projected fluorotelomer production in 2019 of 42,500 tonnes.

After Global Market Insights, 2016. Projected compound annual growth rate of 12.5% from 26,500 tonnes in 2015.

https://ipen.org/sites/default/files/documents/the global pfa s problem-v1 5 final 18 april.pdf



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PFAS Invention

- Moissan reported on perfluorocarbon synthesis in 1890
- The first perfluoroalkyl acid, trifluoracetic acid (TFA) first synthesized in 1922 by Belgian chemist Frederic Swarts at the University of Ghent (chromic acid oxidation of n-trifluoromethyl aniline)
- Trifluoroacetic acid was the strongest organic acid known at that time and described as being resistant to chemical attack
- Industrial scale synthesis of PFAS >100 tonnes p.a. during 1930's as azo dyes used in military applications.
- >250,000 synthetic organofluorine compounds reported in 1983
- Evidence for PFAS biological recalcitrance since before 1950
- Multihalogenated carbons analogous structurally to persistent component of DDT, which caused formation of EPA in 1970 after Rachel Carson & Silent Spring in 1962







Frederic Swarts (1866-1940) First PFAA synthesized 1920



Roy J. Plunkett (1910-1994) Discovery of PTFE 1938



TFA precursors - azo dyes

DDT

Per- & Polyfluoroalkyl Substances Poly-Per-Perfluoroalkyl Polyfluoroalkyl Long Chain - precursors **PFOS PFDA** Short Chain Sulphonamides **Transformation PFOA PFNA PFBS PFPeA PFHxS PFTDA** PBA PFPeS PFHxA PFHpA Polyfluoroalkyl ethers **Ethers** GenX **Cyclics** Fluorotelomers F53B **PFECHS** EE-NH₄ **Ultra Short** Side Chain Chains Biological treatment or Fluoropolymers **TFA PFPrA** chemical oxidants promote transformation



Per- & Polyfluoroalkyl Substances





Broad Spectrum PFAS

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Ultrashort Chain PFAS

- Ultrashort Chain PFAS: C1-C3 perfluoroalkyl chain length
- Over 1 million precursors to TFA
- Fluorinated refrigerants (TFA precursors) estimated to contribute a global deposition rate of 155,000 tons of TFA in rain /year, with 25-100 ng/L in rain (Boutonnet et al., 1999)
- In Norway TFA found in 219 of 247 groundwater wells up to 2.4 ppb (µg/L)
- In German tap water up to 20 ppb (μg/L), river water up to 120 ppb (μg/L)
- Chinese blood 97% detection median 8.5 μg/L
- Will not be retained by GAC and IX resins not designed to remove

Compound	Acronym	Chemical Formula	Molecular
			Weight (g/mol)
Trifluoroacetic acid	TFA	CF_3CO_2H (C2)	114.023
Perfluoropropanoic acid	PFPrA	C ₂ F ₅ CO ₂ H (C3)	164.031
Trifluoromethane sulfonic acid	TFMS	CF_3SO_3H (C1)	150.077
Perfluoroethane sulfonic acid	PFEtS	$C_2F_5SO_3H(C2)$	200.085
Perfluoropropane sulfonic acid	PFPrS	C ₃ F ₇ SO ₃ H (C3)	250.092



Refrigerant HFO R-1234yf





Ultra-Short Chains

Ultra-Short-Chain PFASs in the Sources of German Drinking Water: Prevalent, Overlooked, Difficult to Remove, and Unregulated

Isabelle J. Neuwald, Daniel Hübner, Hanna L. Wiegand, Vassil Valkov, Ulrich Borchers, Karsten Nödler, Marco Scheurer, Sarah E. Hale, Hans Peter H. Arp, and Daniel Zahn*



German drinking water health guidance value for TFA - 60 ppb target value of 10 ppb 3 out of 43 samples exceeded 10 ppb Danish drinking water standard 9 ppb

https://www.umweltbundesamt.de/sites/default/files/medien/362/d okumente/2020_10_20_uba_einordnung_tfa_leitwert.pdf



- Trifluoroacetate (TFA)
- Perfluoropropanoate
- Trifluoromethanesulfonate

ubiquitous and present at:

98% of sum target PFAS concentrations

Elevated Levels of Ultrashort- and Short-Chain Perfluoroalkyl Acids in US Homes and People

Guomao Zheng*, Stephanie M. Eick, and Amina Salamova*

15785

		dust			drinking water			serum			urine	13	
	DF	Med (Min-Max)	Contr.	DF	Med (Min-Max)	Contr.	DF	Med (Min-Max)	Contr.	DF	Med (Min-Max)	Contr.	
					Ultrasho	ort-Chain						Sci	
FA (C2)	84	220 (ND, ^b 1400)	75	95	79 (ND, 210)	84	74	6.0 (ND, 77)	57	31	ND (ND, 290)	en	
PrA (C3)	99	26 (ND, 200)	9.1	95	6.9 (ND, 19)	7.4	99	1.0 (0.14, 2.9)	9.5	56	0.051 (ND, 6.8)	1.4	
PrS (C3)	3.7	ND (ND, 53)		64	0.10 (ND, 0.40)	0.11	4.9	ND (ND, 0.013)		1.2	ND (ND, 0.85)	80	
ultrashort-chain	100	290 (37, 1400)	85	100	86 (9.3, 220)	92	100	6.9 (2.3, 78)	66	100	0.13 (0.02, 290)	2.0	
					Short	-Chain						1 2	the early ari
BA (C4)	94	14 (ND, 410)	5.0	98	2.4 (ND, 7.8)	2.6	84	0.19 (ND, 2.5)	1.8	60	0.33 (ND, 26)	9.2 B P	umospheri
BS (C4)	54	0.40 (ND, 210)	0.14	86	1.3 (ND, 0.16)	1.4	85	0.05 (ND, 0.38)	0.47	3.7	ND (ND, 0.028)		vidation
PeA (C5)	10	ND (ND, 120)		70	2.5 (ND, 7.7)	2.6	25	ND (ND, 2.2)		88	3.2 (ND, 34)	89 👻 🛡	xiuation
PeS (C5)	22	ND (ND, 15)		59	0.035 (ND, 22)	0.038	69	0.0076 (ND, 0.034)	0.071	23	ND (ND, 0.022)		
HxA (C6)	89	4.3 (ND, 290)	1.5	85	0.42 (ND, 6.1)	0.45	83	0.034 (ND, 0.10)	0.32	2.5	ND (ND, 0.09)		
HpA (C7)	81	1.7 (ND, 460)	0.60	83	0.15 (ND, 1.2)	0.10	79	0.016 (ND, 0.10)	0.10	23	ND (ND, 0.0093)		
short-chain	100	27 (1.4, 1100)	7.3	100	8.5 (0.12, 38)	7.2	100	0.41 (0.058, 3.6)	3.0	100	4.6 (0.021, 41)	98	
					Long	Chan							
HxS (C6)	73	2.7 (ND, 2200)	0.93	88	0.17 (ND, 1.1)	0.18	99	0.78 (ND, 5.4)	7.3	0			
HpS (C7)	23	ND (ND, 12)		15	ND (ND, 0.071)		96	0.099 (ND, 0.73)	0.93	0			
FOA (C8)	98	5.9 (ND, 1900)	2.1	93	0.46 (ND, 3.6)	0.49	99	0.63 (ND, 4.9)	5.9	14	ND (ND, 0.051)		
OS (C8)	95	10 (ND, 1100)	3.5	84	0.22 (ND, 1.6)	0.23	99	1.5 (ND, 33)	14	7.4	ND (ND, 0.019)		
ECHS (C8)	2.5	ND (ND, 7.5)		44	ND (ND, 0.67)		85	0.011 (ND, 0.079)	0.11	0			ΤΕΛ
FNA (C9)	64	0.65 (ND, 27)	0.23	65	0.11 (ND, 0.47)	0.11	98	0.21 (ND, 1.2)	2.0	30	ND (ND, 8.9)		IIA
FNS (C9)	7.4	ND (ND, 1.4)		2.5	ND (ND, 0.015)		1.2	ND (ND, 0.0031)		0		bub	
DA (C10)	70	1.8 (ND, 39)	0.62	49	ND (ND, 0.28)		93	0.051 (ND, 0.21)	0.48	0		s.a	
FDS (C10)	36	ND (ND, 100)		0			7.4	ND (ND, 0.019)		0		S.	
UdA (C11)	58	0.30 (ND, 15)	0.11	15	ND (ND, 0.093)		79	0.037 (ND, 0.16)	0.35	0		org	
DoA (C12)	70	1.1 (ND, 22)	0.38	25	ND (ND, 0.14)		42	ND (ND, 0.034)		0		lest	
TrDA (C13)	57	0.25 (ND, 16)	0.089	14	ND (ND, 0.13)		37	ND (ND, 0.079)		0			
TeDA (C14)	58	0.52 (ND, 13)	0.18	26	ND (ND, 0.21)		36	ND (ND, 0.043)		0			
HxDA (C16)	42	ND (ND, 8.6)		44	ND (ND, 1.0)	\frown	70	0.023 (ND, 0.13)	0.21	0			
long-chain	100	33 (0.45, 3300)	8.1	98	1.4 (ND, 5.8)	1.0	99	3.8 (ND, 35)	31	49	ND (ND, 8.9)		











Discovery and Implications of C₂ and C₃ Perfluoroalkyl Sulfonates in **Aqueous Film-Forming Foams and Groundwater**

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Supporting Information

ABSTRACT: Historically, 3M aqueous film-forming foams (AFFFs) were released at U.S. military and civilian sites to extinguish hydrocarbon-based fuel fires. To date, only C4-C10 homologues of the perfluoroalkyl sulfonic acids (PFSAs) are documented in 3M AFFFs. Perfluoroethanesulfonate (PFEtS) and perfluoropropanesulfonate (PFPrS), two ultra-shortchain PFSAs, were discovered by liquid chromatography (LC) quadrupole time-of-flight mass spectrometry. Once they were identified, PFEtS and PFPrS were then quantified in five 3M AFFFs and in one groundwater sample from each of 11 U.S. military bases by LC tandem mass spectrometry. Concentrations of PFEtS and PFPrS in the five AFFFs ranged from 7 to 13 mg/L and from 120 to 270 mg/L, respectively. For the groundwater, PFEtS was quantified in 8 of the 11 samples (11-7500 ng/L) and PFPrS in all samples (19-63000 ng/L). The high water solubility, mobility, and detection frequency of these ultra-short-chain PFSAs



indicate that groundwater contaminant plumes may be larger than previously believed, and their removal by conventional activated carbon will be challenging.



Scheurer, 2017

Hendricks, 1953

>100 ton quantities in 1930's

Refrigerants as TFA Sources in Rain



Figure 4

Estimated maximum TFA emissions in t/a for the relevant groups of chemicals*

2500 Estimates for 141 Germany 2000 emission [t/a] 1170 1500 Maximum TFA 1000 98 500 1050 84 22 -7 197 0 TFA as a basic Biocides Plant protection Refrigerants and Fluorochemicals Vet. Human chemical products pharma. pharma. blowing agents in products

Adlunger et al. UBA Background 11/2021: Reducing the input of chemicals into waters: trifluoroacetate (TFA) as a persistent and mobile substance with many sources

> Press + Press releases + Trifluoroacetic acid from fluorinated refrigerants contaminates rainwater

Trifluoroacetic acid from fluorinated refrigerants contaminates rainwater Urgent need for switch to natural refrigerants



Room air conditioners contain environmentally harmful HFCs and use a lot of electricity. Source: kanvag / Fotolia.com

As stipulated in the F-Gas Regulation, the use of climate-damaging fluorinated refrigerants and blowing agents must be significantly reduced in the European Union by 2030. Fluorinated gases are often replaced by short-lived fluorinated substances with lower Global Warming Potentials. However, these substances form trifluoroacetic acid (TFA) as a degradation product. Current rainwater measurements commissioned by the German Environment Agency (UBA) show that TFA concentrations have risen sharply since the 1990s. TFA is highly mobile, classified as hazardous to water and penetrates into groundwater and drinking water. There is currently no known method by which TFA could be removed from the water cycle by reasonable means - not even in drinking water treatment. UBA therefore recommends using natural refrigerants such as carbon dioxide or hydrocarbons.

<u>https://www.umweltbundesamt.de/en/press/pressinformation/trifluoroacet</u> <u>ic-acid-from-fluorinated-refrigerants</u>



Figure 6. TFA concentration in rainwater (at the surface). The color scale extends to the maximum value.

Select PFAS in US Rainfall



Follow up study (Kim et. al., 2022) found estimated Σ PFAS16,400 ppt in rain at Wooster, Ohio, as maximum detected

TFA PFBA PFPeA PFHxA PFHpA PFOA PFNA PFDA PFOS HFPO-DA

Ambient Anthropogenic Background

- PFAS are subject to
 - Long range transport grasshopper effect
 - Short range transport wet/dry deposition
- PFAS background is found in:
 - Surface Waters /Groundwater
 - Soils / Sediments
 - Sea Foams
 - Rain
 - Mineral waters, Beers, Ciders
- The are volatile PFAS that come back to earth in rain
- Landfills and WWTPs emit volatile PFAS – can be sources to surrounding area

In US rain:

- 16.4 ppb PFAS
- 30 ppt PFOA
- 50 ppt PFOS
- 1200 ppt TFA





Chemical Analysis





- Chemical analysis commercially available with major laboratories
- Separate chemical analytical method required
- Methods include:
 - Hydrophilic interaction liquid chromatography (HILIC)
 - Ion Chromatography with Mass Spectrometry (IC-MS)

Method Description	Analyte Description	CAS Number	MDL	Units
		750.00.0	0.404	
Short-chain analyes by PFAS-SC	2,2,3,3-TEPA	756-09-2	0.121	ug/L
	2,3,3,3-TFPA	359-49-9	0.0983	ug/L
	PFES	354-88-1	0.0926	ug/L
	PFPrA	422-64-0	0.141	ug/L
	PFPrS	423-41-6	0.134	ug/L
	Trifluoroacetic acid	76-05-1	0.416	ug/L
	TFMS	1493-13-6	0.277	ug/L





LC-MS/MS Analysis of Trifluoroacetate in Groundwater and Drinking Water using a Biozen Glycan 2.6 μm 150 x 2.1 mm column

ne presented HILI ater samples unde e LOQ is 0.0495 µ	C me r isc Iq/L.	sthod allows a fast and reliable quantification of TFA in groundwater and drinking occuratic conditions. The LOD according to DIN 32645:2008-11 is 0.0187 μ g/L and	APPLICATIONS	0	hengenen
ocument Type rget Industries chniques ands pparation Modes nases	:	Technical Notes Biophamacoulical Analysis, Pharmacoulical HPLC, HILIC Chromatography Biozan LC HILIC Biozan-Glycan		Sandara and Date	ula dan



HAZARDOUS MAATERDALS

Quantification of long-chain, short-chain, and ultrashort-chain liquid chromatography-amenable PFASs in water: Evaluation of approaches and tradeoffs for AFFF-impacted water

Journal of Hazardous Materials

Volume 466, 15 March 2024, 133591

Chuhui Zhang ^a, Shilai Hao ^a 옷 펌, Nicholas Gonda ^a, Yue Zhi ^b, Timothy J. Strathmann ^a, <u>Charles E. Schaefer ^c, Christopher P. Higgins ^a 옷 펌</u>

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Highlights

- The C18 column failed to retain ultrashort-chain PFAAs and the JJ and Acclaim columns were unsuitable for hydrophobic PFASs.
- Ultrashort-chain PFAAs comprised 1.6-18% of total measured PFCAs and PFSAs at three sites.
- Semi-quantified concentrations of suspect PFASs comprised 0.70-13% of the total PFASs.
- The C18 column captured the broadest suite of suspect PFASs in AFFFimpacted water.
- The JJ column quantified the most total PFAS mass in AFFF-impacted water.

Environmental Science Processes & Impacts



CRITICAL REVIEW

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

Insufficient evidence for the existence of natural trifluoroacetic acid

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



Refrigerants: TFA Precursors

- Hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), hydrofluoroolefins (HFOs), and hydrochlorofluoroolefins (HCFOs)
- Common refrigerants, fire extinguishing agents, and physical blowing agents
- Substitutes for ozone depleting chlorofluorocarbons (CFCs) and can transform to TFA via oxidation in the atmosphere
- Emissions of HFOs and HCFOs being substituted for HFCs and HCFCs that have a high global warming potential and HFO-1234yf is expected to be the primary compound used for refrigeration and air conditioning in the coming decades



Transformation pathway of HFC-134a and u-HFC-1234yf to TFA

Behringer et al., 2021







Ozone, Climate and environmental impact of the refrigerants

Туре	Substance	Туре	ODP ¹	GWP 20yrs ²	GWP 100yrs ²	Contain PFAS ³	TFA ⁴
Synthetic	R-12	CFC	0,82	12700	12500	No	No
Synthetic	R-22	HCFC	0,04	5690	1960	No	No
Synthetic	R-141b	HCFC	0,11	2710	860	No	No
Synthetic	R-32	HFC	0	2690	771	No	No
Synthetic	R-134a	HFC	0	4140	1530	Yes	Up to 20%
Synthetic	R-404A	HFC	0	7208	4728	Yes	Up to 20%
Synthetic	R-407A	HFC	0	4890	2262	Yes	Up to 20%
Synthetic	R-410A	HFC	0	4714	2256	Yes	No
Synthetic	R-507A	HFC	0	7290	4775		Up to 10%
Synthetic	R-245fa	HFC	0	3170	962	Yes	Up to 10%
Synthetic	R-365mfc	HFC	0	2920	914	Yes	Up to 10%
Synthetic	R-1234yf	HFO	0	1.81	0.501	Yes	100%
Synthetic	R-1234ze(E)	HFO	0	4.94	1.37	Yes	Up to 10%
Synthetic	R-1233zd(E)	HFO	0	14	3.88	Yes	2%
Synthetic	R-513A	HFO-HFC	0	1822	673	Yes	Up to 60%
Natural	R-290	HC (propane)	0	0.072	0.02	No	No
Natural	R-744	CO ₂	0	1	1	No	No
Natural	R-600a	HC (isobutane)	0	<1	<1 ⁵	No	No
Natural	R-717	HN ₃ (ammonia)	0	0	0	No	No
Natural	C ₅ H ₁₀	HC (cyclopentane)	0	0	11	No	No
Natural	R-601	HC (pentane)	0	<15	<15	No	No
Natural	R-601a	HC (isopentane)	0	<1 ⁵	<1 ⁵	No	No

¹ WMO's Scientific Assessment of Ozone Depletion, 2010.

² IPCC 6th Assessment Report, 2021.

³ ECHA, Annex XV Restriction Report

⁴ Behringer, D. et al. Persistent degradation products of halogenated refrigerants and blowing agents in the environment, Final Report, 2021.

⁵ UNEP, Refrigeration, Air Conditioning and Heat Pumps Technical Options Committee, 2022 Assessment Report.

https://ozone.unep.org/meetings/thirty-fifth-meeting-parties/side-events?arg_1=2023-10-25







Evolution of refrigerants



- Natural refrigerants were the first refrigerants to be used in cooling and heating systems.
- CFCs, HCFCs, HFCs, and HFOs have shown to have ozone, climate, multiple environmental and health effects (ODP, GWP, PFAS and TFA).
- Natural refrigerants do not have harmful impact to ozone layer, climate, environment, health and are very efficient.

https://ozone.unep.org/meetings/thirty-fifth-meeting-parties/side-events?arg_1=2023-10-25

Plant Uptake

- Plant uptake in wheat and sunflowers identified (Boutonnet at at., 1999)
- Recent publications show accumulation in roots and shoots of wheat

channe

C2:TFA C3:PFPrA Uptake mechanisms of perfluoroalkyl acids with different carbon chain lengths (C2-C8) by wheat (*Triticum acstivnm L*.)

Lu Zhang, Hongwen Sun *, Qi Wang, Hao Chen, Yiming Yao, Zhen Zhao, Alfredo C. Alder

Science of the Total Environment 654 (2019) 19-27



Fig. 3. Shoot concentration factors (SCFs) calculated from concentrations of PFAAs in shoots divided by their concentrations in the spiked nutrient solution. Mean and standard error (n = 4) are shown.

Fig. 2. Root concentration factors (RCFs) calculated from concentrations of PFAAs in roots divided by their concentrations in the spiked nutrient solution. Mean and standard error (n = 4) are shown.

HIGHLIGHTS

- Uptake and translocation of PFAAs in wheat depended on their carbon chain length.
- Higher uptake of C2, C3, and C8 PFAAs by wheat roots was observed compared to C4 and C6.
- Accumulation of PFCAs in wheat shoots decreased with their carbon chain length.
- The energy-dependent active process was the main mechanism for the uptake of PFAAs.
- Aquaporins and anion channels also contributed to the uptake of C2 and C3 PFCAs.



(Cross section of root

Carrier

Plasma

membran

Shoot concentration factors (SCFs)

GRAPHICAL ABSTRACT

channel

C2-C8:TFA/PFPrA/PFBA/PFHxA/PFOA/PFOS

Exposure / Toxicology

- Food and drinking water contribution to exposure
- European Food Standards Agency (EFSA) concerned that 'trifluoroalkyl plant protection products' expose humans to more TFA than drinking water
- Rat and Guinea Pig studies show liver effects (600-16,0000 ppm) (Felter 2018)
- No-Observed-Adverse-Effect-Level (NOAEL) of sodium trifluoroacetate for maternal toxicity in rabbits 180 mg/kg/day
 - Current margins of exposure (MoE) reported for humans are 100 (Dekanat)
 - TFA concentrations (0.1% to 0.3%) linked to reproductive toxicity with potentially harmful human health effects (German Federal Office for Chemicals (BfC))
 - Human toxicology very little known



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Plant Protection Products and their Residues

The Panel on Plant Protection Products and their Residues (PPR) provides scientific advice on the risk assessment of pesticides for operators, workers, consumers and the environment. The Panel develops and reviews guidance documents on the risk assessment of pesticides. This work supports the evaluation of active substances used in pesticides, which is carried out Rapporteur Member States and peer reviewed by EFSA staff.

PPR Panel Members are scientists from across Europe with expertise in:

- Active substances chemical and microbiological (viruses, bacteria, fungi, etc)
- Physical-chemical properties (of plant protection products and their active substances)
- Methods of analysis (of plant protection products and of their residues)
- Toxicology and regulatory toxicology
- Non dietary exposure and risk assessment (of plant protection products)
- Dietary exposure and risk assessment (of residues of plant protection products in food and feed commodities)
- Environmental fate and behaviour (of plant protection products)
- Ecotoxicology
- Ecology and population dynamics
- Ecological/Environmental exposure and risk assessment.

Archives of Toxicology (2023) 97:1069–1077 https://doi.org/10.1007/s00204-023-03454-y

MOLECULAR TOXICOLOGY



Mammalian toxicity of trifluoroacetate and assessment of human health risks due to environmental exposures

Wolfgang Dekant¹ · Raphael Dekant¹

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Abstract

While trifluoroacetic acid has limited technical uses, the highly water-soluble trifluoroacetate (TFA) is reported to be present in water bodies at low concentrations. Most of the TFA in the environment is discussed to arise from natural processes, but also with the contribution from decomposition of environmental chemicals. The presence of TFA may result in human exposures. For hazard and risk assessment, the mammalian toxicity of TFA and human exposures are reviewed to assess the margin of exposures (MoE). The potential of TFA to induce acute toxicity is very low and oral repeated dose studies in rats have identified the liver as the target organ with mild liver hypertrophy as the lead effect. Biomarker analyses indicate that TFA is a weak peroxisome proliferator in rats. TFA administered to rats did not induce adverse effects in an extended one-generation study and in a developmental toxicity study or induce genotoxic responses. Based on recent levels of TFA in water and diet, MoEs for human exposures to TFA are well above 100 and do not indicate health risks.

Sum of 'all PFAS' <500 ppt (EU) 10000 Trifluoroacetic acid (TFA) <10 ppb / 60 ppb (Germany) & Concentration (ppt) <9ppb (Denmark) / NL (RIVM) 2.2 ppb 1000

Based on

treatment system

performance, not

toxicology

Sum of PFOS, PFHxS, PFNA, PFOA <2 ppt (Denmark)

UK

.

-47 PFAS <100 ppt individually

- Sum of 20 PFAAs <100 ppt (EU)

Canada

ppt = ng/L

Europe

- Sum of 29 PFAS <30ppt (proposed)
- California
 - Broad spectrum approach for PFAS with treatment based goals
- **US** proposed MCLs
 - PFOS / PFOA 4 ppt
 - Hazard Index GenX (10) + PFBS (2000) + PFNA (10) + PFHxS (9)

International PFAS Regulations (Drinking water) Generalized Individual PFAA Drinking Water Standards



PFAS chain length / potential for bioaccumlation

2000





2200





Temporal trends of suspect- and target-per/ polyfluoroalkyl substances (PFAS), extractable organic fluorine (EOF) and total fluorine (TF) in pooled serum from first-time mothers in Uppsala, Sweden, 1996–2017[†]

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> Regulatory concerns with increasing use of alternative PFAS

> > Miaz et al., 2020

California Waterboards Non-Target Analysis of PFAS



Note: Ultrashorts PFAAs such as TFA not detected using AOF using USEPA 1621

PFAS Whole Class Restrictions

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SEC. 124. Item 3940-106-0001 of Section 2.00 of the Budget Act of 2022 is amended to read:		ead: ECHA > Nows > Archive > All news	ECHA > News > Archive > All news						
3940-106-0001—For local assistance, State Wa	News	All news							
Resources Control Board	150,000,000	Image gallery	<						
	Video library	ECHA receives PFASs restriction proposal from five national authorities							
Schedule:								Safer chemicals podcast	
(1) 3560-Water Quality		Hot topics	ECHA/NR/23/01						
(1) 5500 Water Quality	50,000,000	Corporate and visual Identity	The national authorities of Denmark,	The national authorities of Denmark, Germany, the Netherlands, Norway and Sweden have submitted a proposal					
150,000,000		CHA Articles	ECHA to restrict per- and polyfluoroal regulation. ECHA will publish the deta	ECHA to restrict per- and polyfluoroalkyl substances (PEASs) under REACH, the European Union's (EU) chemicals regulation. ECHA will publish the detailed proposal one of the broadest in the EU's history, on 7 Echruary 2023					

Of the amount appropriated in this item, \$50,000,000 shall be available for technical and financial assistance to drinking water systems to address Per- and Polyfluoroalkyl Substances (PFAS). Of this amount, up to \$15,000,000 may be used for grants, contracts, and direct expenditures to: (1) monitor all community public water systems in the state at least once, with state funding directed to accomplish testing of community public water systems serving disadvantaged and severely disadvantaged communities; (2) develop standard operating procedures for and validate a broad spectrum test for the class of PFAS; and (3) develop a treatment-based regulation for the entire class of PFAS.

he national authorities of Denmark, Germany, the Netherlands, Norway and weden have submitted a proposal to ECHA to restrict per- and polyfluoroalkyl ubstances (PFASs) under REACH, the European Union's (EU) chemicals egulation. ECHA will publish the detailed proposal, one of the broadest in the U's history, on 7 February 2023.

on the market and use of PFASs that are not adequately controlled and need to be addressed through

lelsinki, 13 January 2023 – The restriction proposal comes after the five authorities found risks in the manufacture, placement on the market and use of PFASs that are not adequately controlled and need to be addressed throughout the EU and the European Economic Area.

https://leginfo.legislature.ca.gov/faces/billNavClient.xhtml?bill_id=202120220AB178

https://echa.europa.eu/-/echa-receives-pfass-restriction-proposal-from-five-national-authorities



Poll Question

- What chain length are ultrashorts?
 - A C1-C3
 - B C3-C6
 - C C5-C9
 - D C9-C11

- Greatest exposure to PFAS from ultra-shorts
- Toxicological understanding developing
- Are ultrashort precursors in essential uses
- Ultrashorts not retained by GAC, very poorly retained by IX resins
- Regulations evolving quickly in Europe



Rapidly rising levels of TFA 'forever chemical' alarm experts

Trifluoroacetic acid found in drinking water and rain is thought to damage fertility and child development



🗅 'If you're drinking water, you're drinking a lot of TFA, wherever you are in the world,' one expert said. Photograph: Alet Pretorius/Reuters

Rapidly rising levels of TFA, a class of "forever chemical" thought to damage fertility and child development, are being found in drinking water, blood and rain, causing alarm among experts.

TFA, or trifluoroacetic acid, is a type of per- and polyfluoroalkyl substance (PFAS), a group of human-made chemicals used widely in consumer products that do not break down for thousands of years. Many of the substances have been linked to negative effects on human health.

Studies from across the world are reporting sharp rises in TFA. A major source is F-gases, which were brought in to replace ozone-depleting CFCs in refrigeration, air conditioning, aerosol sprays and heat pumps. Pesticides, dyes and pharmaceuticals can also be sources.

"Everywhere you look it's increasing. There's no study where the concentration of TFA hasn't increased," said David Behringer, an environmental consultant who has studied TFA in rain for the German government.

https://www.theguardian.com/environment/2024/may/ 01/rapidly-rising-levels-of-tfa-forever-chemical-alarmexperts



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TB 22 R (March 2023) CLA technical bulletin

CL:AIRE technical bulletins describe specific techniques, practices and methodologies relevant to sites in the UK. This bulletin describes per- and polyfluoroalkyl substances (PFAS) uses and identifies industries and activities which could potentially cause environmental impacts.

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An overview of the uses of PFAS to assist with identification of sites of concern

INTRODUCTION 1.

Per- and polyfluoroalkyl substances (PFAS) are a broad group of over 12,000 synthetic chemicals [1, 2], widely applied for bulk industrial uses and in consumer applications since the 1930s [3, 4]. As a result of their detection in drinking water supplies, PFAS are the subject of accelerating environmental regulatory concern globally.

The initial regulatory focus was on two perfluoroalkyl acids (PFAAs) perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), but attention has now widened to an array of additional PEAS, including short chain PEAS, polyfluorinated PEAS (PEAA precursors) and perfluoroalkyl ethers.

CL:AIRE Technical Bulletin TB19 Managing Risks and Liabilitie associated with Per- and Polyfluoroalkyl Substances (PFAS) should be This bulletin aims to identify industries and activities which could of PFAS-contaminated soil and groundwater.

pose a risk to environmental or human health receptors.

High concentrations of PEAS can remain at locations where PEAS 2. have been lost to ground, acting as ongoing sources to groundwater or surface waters [5-15]. PEAS may remain in soils and be associated with low permeability deposits [6] or concrete surfaces [8, 9].

Activities where the ongoing and legacy releases of liquid forms of PFAS (in solution) have likely occurred, have been prioritised, as The types of firefighting foams that contain PFAS include: these uses could result in a significant mass of PFAS release to the environment over time. Although many PFAS can be highly mobile in the environment, when released, a significant mass of amphiphilic or cationic/zwitterionic PFAS can remain at release sites and continue to represent a source of PFAS [10, 11, 16].

Some PFAS may be regarded as being ubiquitous at very low concentrations. The presence of PFAS in rain and the spreading of Class B firefighting foams continue to be stored and used for fire soils [17-21].



used as a reference document to this bulletin. It provides summary cause significant losses of PFAS to the environment, which may information on PFAS chemistry: their origin: their properties, fate and continue to act as a source of PFAS to potentially impact receptors. A behaviour; their regulation; risk assessment of PFAS; and remediation brief description of the types of PFAS that are associated with differing activities is then provided.

This technical bulletin, describing PFAS uses and potential sites of As a result of the widespread use of PFAS in multiple applications, a concern, aims to provide an overview of some of the bulk, legacy comprehensive guide to all potential source areas is not possible. A and/or dispersive uses of PEAS, to act as a guide to site review, cataloguing which PEAS may be used in multiple applications investigations of land by assisting with identification of activities and by differing industries has recently been published [22, 23]. The which may lead to PFAS being present at concentrations which could multitude of PFAS uses has been described in various publications [23-31], which provide a detailed overview.

FIREFIGHTING FOAMS

Firefighting foams containing PEAS termed fluorosurfactants have been used for extinguishment of flammable liquid (Class B) fires since 1962 [32], and continue to be widely used.

- Aqueous Film Forming Foams (AFFF) (Figure 1) and alcohol resistant derivatives (AR-AFFF)
- Film Forming Fluoroprotein Foams (FFFP) and alcohol resistant derivatives (AR-FFFP); and .
- Fluoroprotein Foams (FP) and alcohol resistant derivatives

biosolids wastes from wastewater treatment plants to land as a suppression, fire training, equipment testing and flammable vapour fertiliser, can result in widespread (low level) detections of PFAS in suppression at multiple sites where there is a fire risk from holding flammable liquids such as hydrocarbons (e.g. gasoline, kerosene, diesel, greases, tars, oils), alcohols, solvents and speciality chemicals. If a flammable liquid was or is handled or stored at any location, the

https://www.claire.co.uk/home/news/1782-pfas-bulletin

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