University of Amsterdam

PERFORCE3

Occurrence. fate. and related health risks of PFAS in raw and produced drinking water

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PFAS Production

- Synthetic chemical. manufactured since 1950.

Telomerization

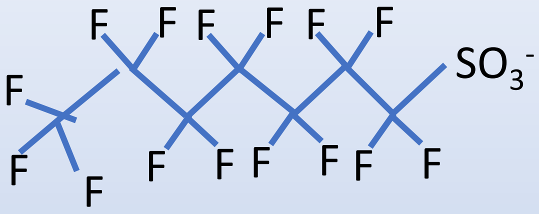
$C_2F_5I + nCF_2CF_2 \longrightarrow C_2F_5(CF_2CF_2)_n$

Electrochemical fluorination (ECF)

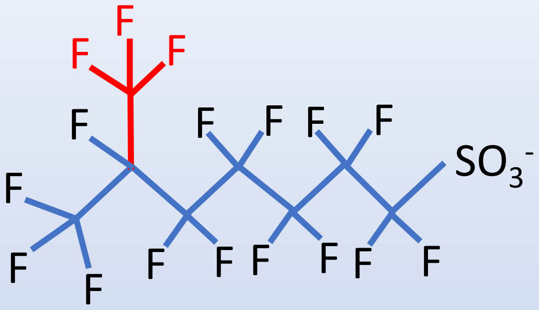
$C_nH_{2n+1}COOH + (2n+2)HF \longrightarrow C_nF_{2n+1}COF \longrightarrow$

very aggressive process with many by-products (including branched isomers and cyclic analogues)

PFOS



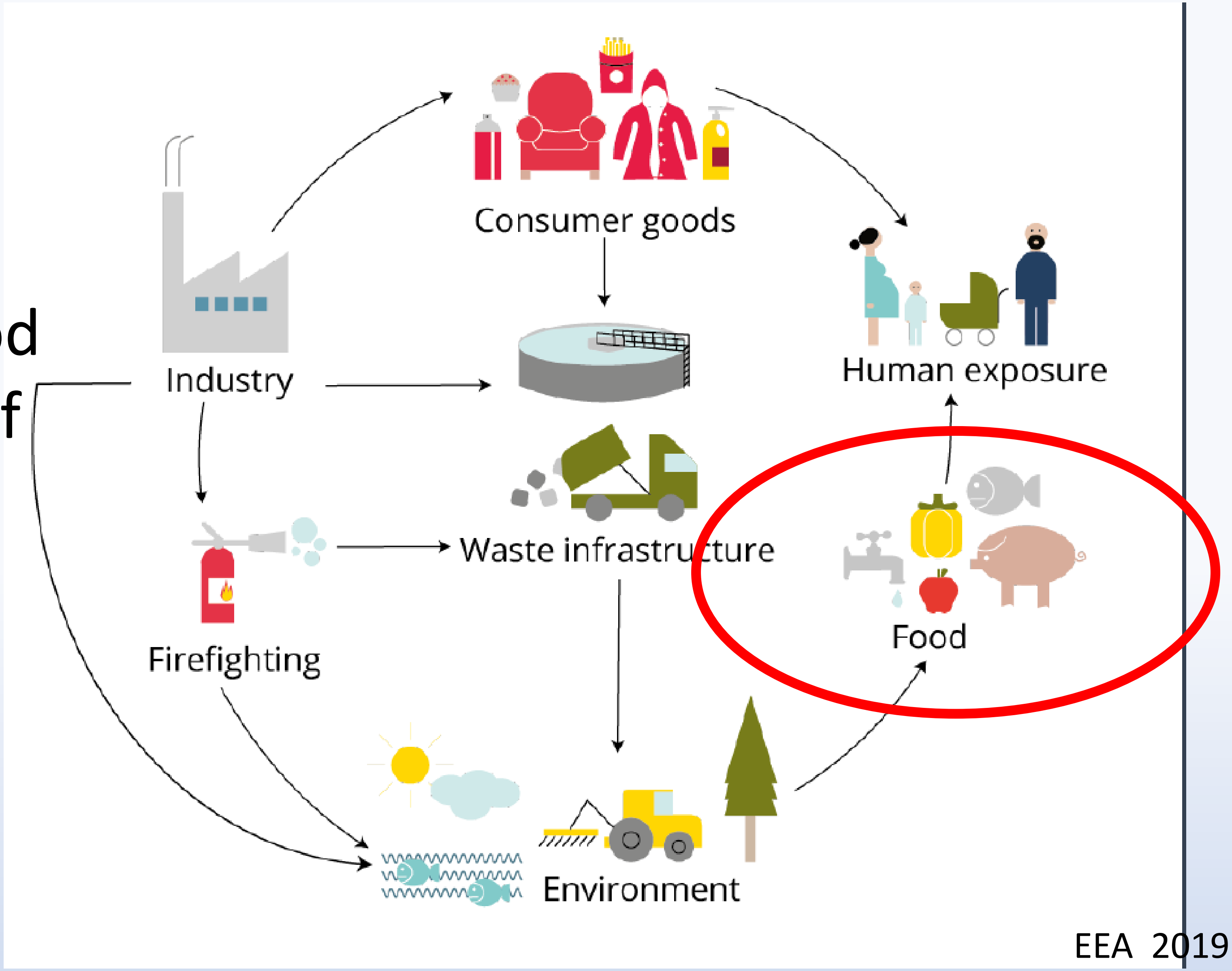
70%



30%

Human Exposure

Drinking water and food are the main sources of human exposure to PFAS (EFSA 2020)



EEA 2019

PFAS Regulation/ risk assessment

- EFSA Tolerable Weekly Intake (TWI) ng/kg bw wk

	PFOS	PFOA
2008	1050	10 500
2018	13	6
2020	4.4 For sum of (PFOS. PFHxS. PFOA. PFNA)	

- Drinking water directive (DWD) 2021
  Sum of 20 PFAS -------- 100 ng/L
  Or Total PFAS -------------- 500 ng/L

- Internationally UN : Stockholm Convention
  PFOS (Annex B 2009). PFOA (Annex A 2019).
  PFHxS as candidate to be listed in either Annex A. B. C

- Mixture assessment using **Relative Potency Factors (RPF)**

Work objective

- Developed analytical method for trace level of PFAS in drinking water (ultrashort PFAS (C1-C3) and branched isomers)

- Subject samples of Dutch drinking water to 'fluoronomic' characterization

    - With respect of:
        - Raw water sources
        - Treatment processes
        - Contamination sources; Fluorochemical plant "Dordrecht"

Work objective

Risk Assessment of Per- and Polyfluoroalkyl Substance Mixtures: A Relative Potency Factor Approach

Wieneke Bil,* Marco Zeilmaker, Styliani Fragki, Johannes Lijzen, Eric Verbruggen, and Bas Bokkers

National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands

rfluoroalkyl

hrenk, Margherita

Letter to the Editor on Bil et al. 2021 "Risk Assessment of Per- and Polyfluoroalkyl Substance Mixtures: A Relative Potency Factor Approach"

Ivonne M. C. M. Rietjens,[a] Merijn Schriks,[b,*] Corine J. Houtman,[c] Milou M. L. Dingemans,[d,e] and Annemarie P. van Wezel[f]

Response to Letter to the Editor on Bil et al. 2021 "Risk Assessment of Per- and Polyfluoroalkyl Substance Mixtures: A Relative Potency Factor Approach"

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National Institute for Public Health and the Environment, Bilthoven, The Netherlands

Chromatographic separation.

Good results

- mixed-mode WAX-1 column.
- CSH C18 column

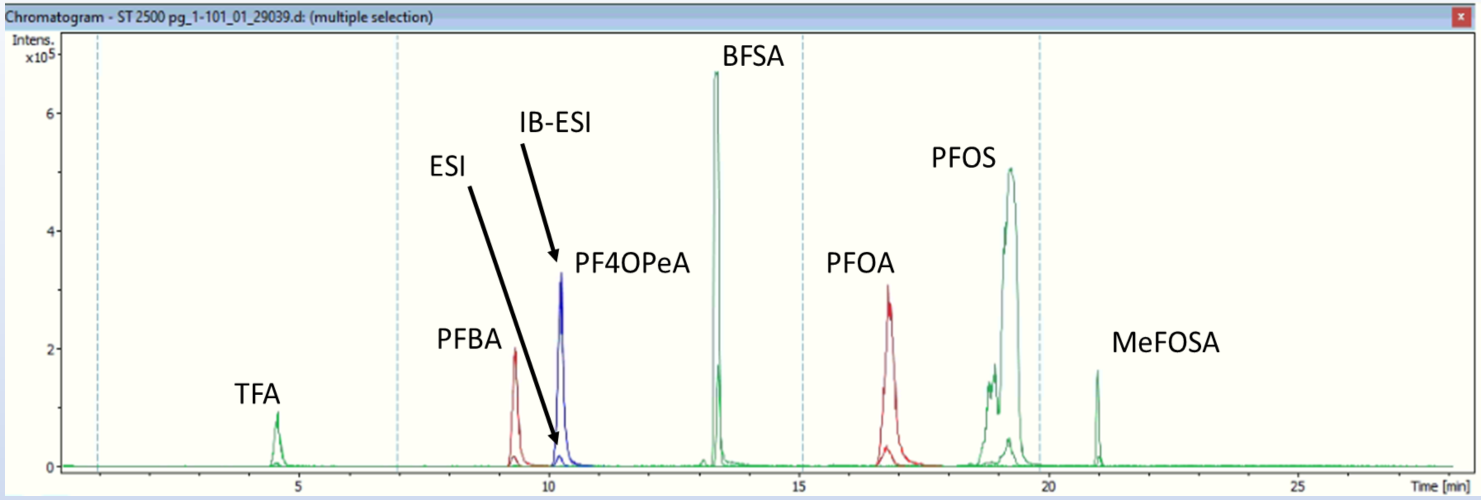
Chromatographic column	Mobile phase	Additives	Ion source
• Kinetex F5	• Methanol (MeOH)	• Ammonium acetate	• Electro Spray Ionization (ESI)
• Biphenyl	• Acetonitrile (ACN)	• Acetic acid	• Ion Booster Electro Spray Ionization (IB-ESI)
• Mixed-mode WAX	• Mixture MeOH + ACN	• Ammonia solution	
• CSH C18 column		• 1-methylpiperidine	

Instrumental optimization and matrix effect

ESI and IB

Reduce ME by adjust

the sample size and the sorbent size



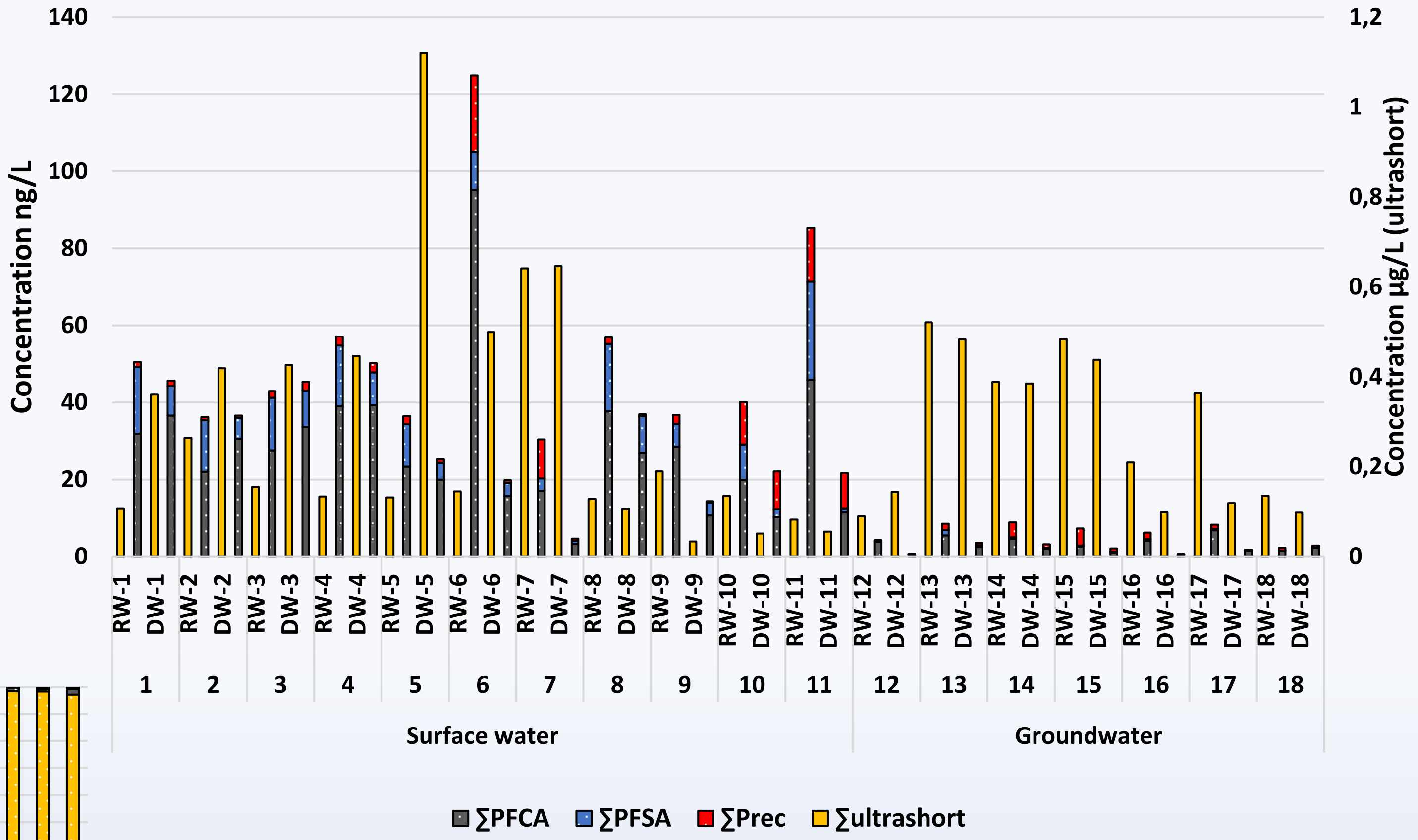
LC-HRMS chromatogram showing the different PFAS by injecting 4 ng/mL PFAS mixture into the CSH C18 column

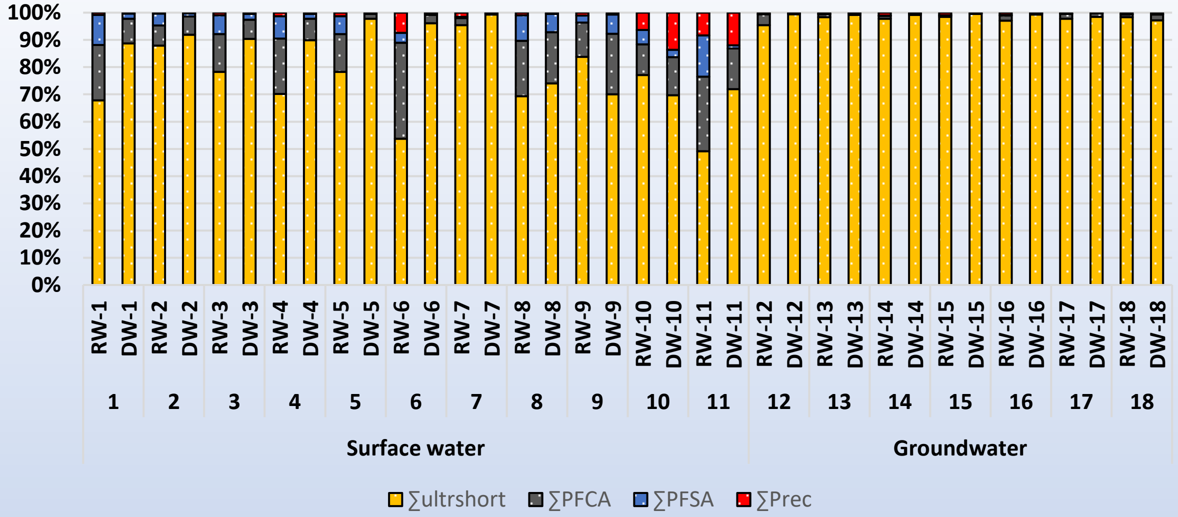
Results

56 different PFAS. including ultrashort (C2-C3). PFCA(C4-C14) PFSA(C4-C10) and a wide variety of precursors (C4-C24).

Mann-Whitney test for DGW. DSW

- Significant differences for **PFCA. PFSA. and precursors**
- No significant difference for the **ultrashort chain**



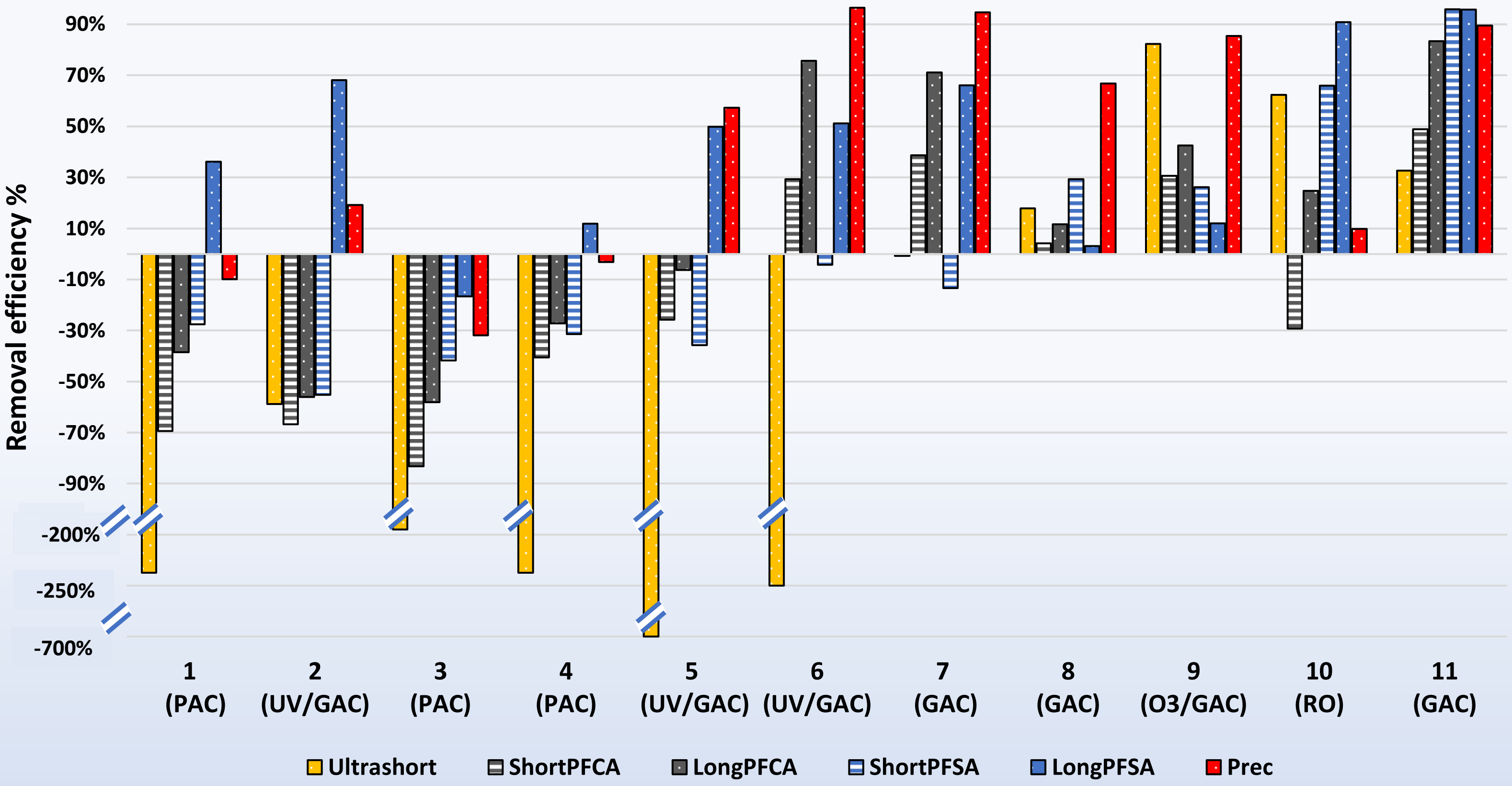


The ultrashort chain (ranged between 0.09 µg/L to 1.1 µg/L

Removal efficiency

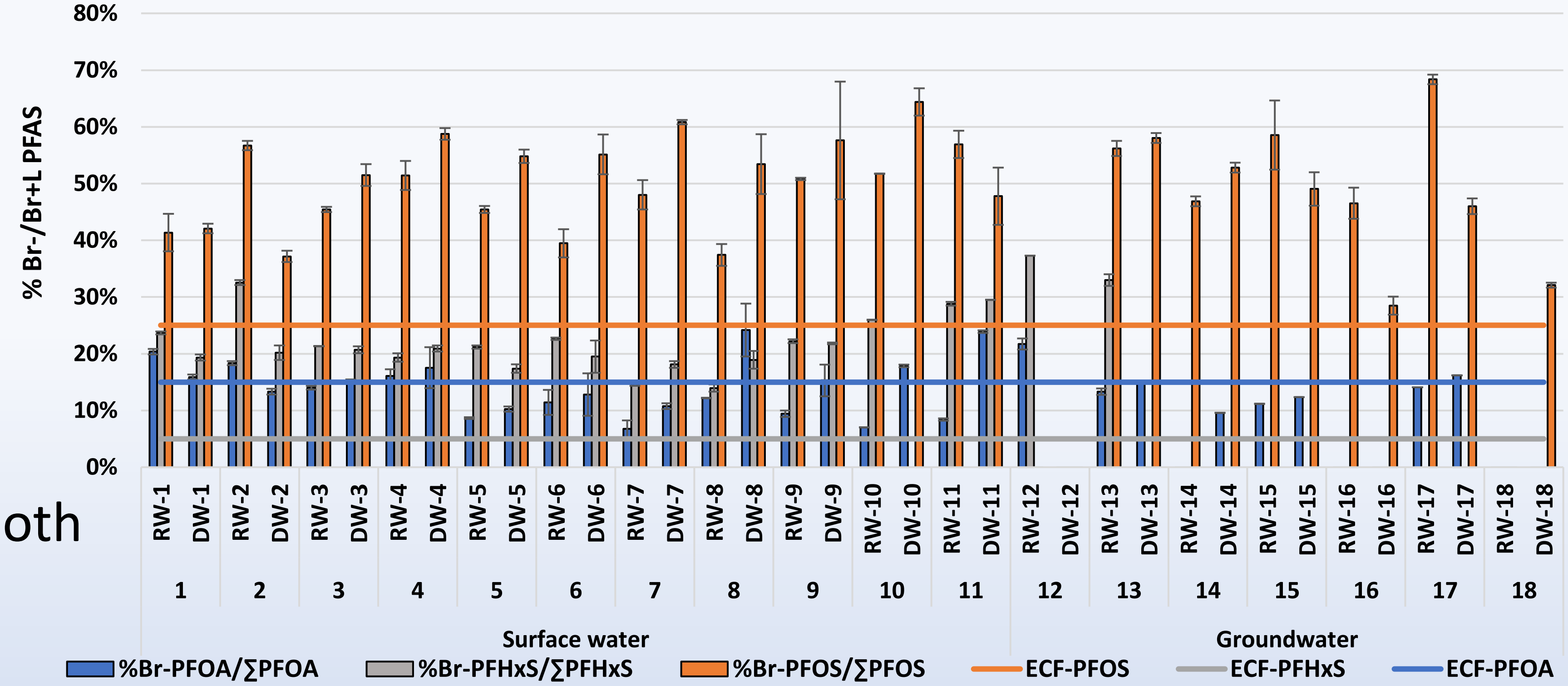
- Variety in removal even with same treatment

- Negative removal explained:
  - Different treatment setup
  - Different sorbent ages



Linear and Branched Isomers composition

<u>PFOA. PFHpS. PFHxS. PFOS. MeFOSAA. and EtFOSAA</u> were investigated separately as ∑branched (Br-) or linear (L-) isomers



No significant different for both PFOS and PFOA between different source

Risk to human health

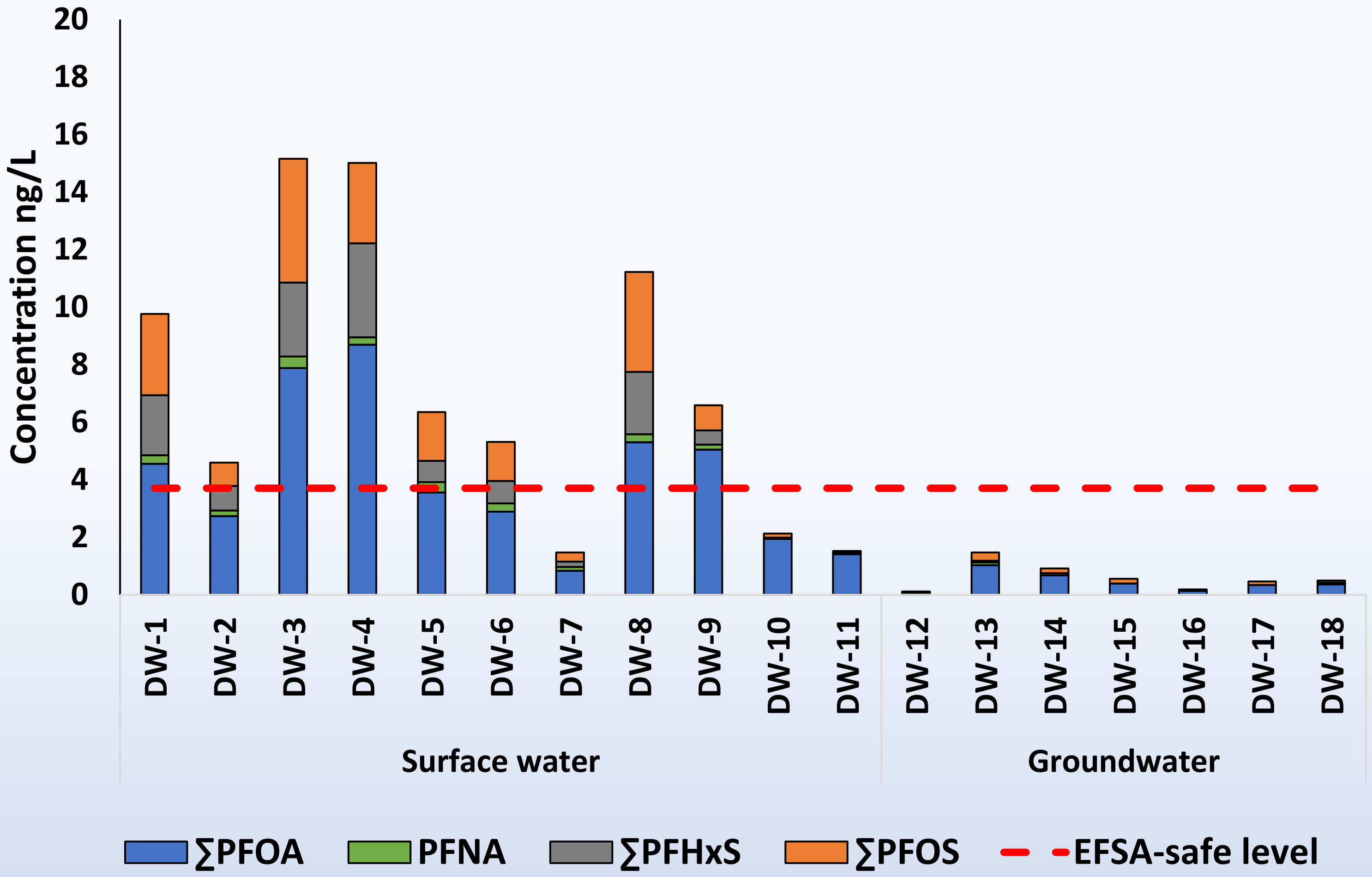
- EFAS Scientific opinion

Sum of 4-PFAS

TWI 4.4 ng/kg bw

(20% contribution form watre and 60kg bodyweight)

Safe level 3.7 ng/L



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Sum of 4-PFAS

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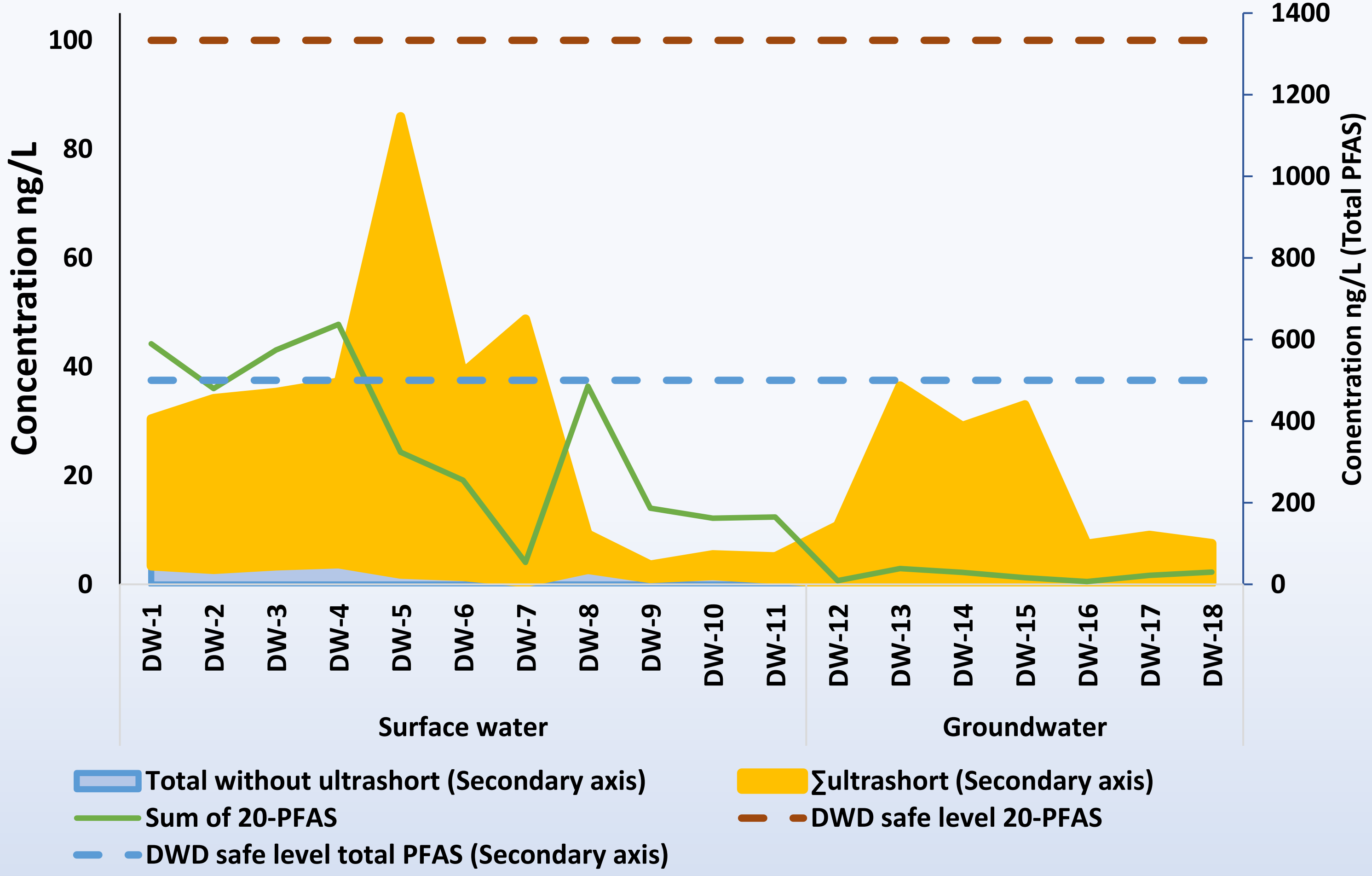
(20% contribution form watre and 60kg bodyweight)

Safe level 3.7 ng/L

- Drinking water directive 2021

value (100 ng/L) for sum of 20 PFAS

OR 500 ng/L for total PFAS



Risk to human health

Risk Assessment of Per- and Polyfluoroalkyl Substance Mixtures: A Relative Potency Factor Approach

Wieneke Bil,* Marco Zeilmaker, Styliani Fragki, Johannes Lijzen, Eric Verbruggen, and Bas Bokkers

National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands

Mixture risk assessment based on different

relative potency factor (RPFs)

proposed by

(Bil et al.. 2021. 2022. Rietjens et al.. 2022)

Source type	Sample code	Sum 21-PFAS-PEQ (ng/L) (Bil et al.. 2021)	Sum 7-PFAS-PEQ (ng/L) (Bil et al.. 2022)	Sum 7-PFAS-PEQ (ng/L) (Rietjens et al.. 2022)
Surface water	DW-1	15.9 ≤ PEQ ≤ 23	17.1	10.3
	DW-2	7.9 ≤ PEQ ≤ 11.2	7.5	4.6
	DW-3	23.9 ≤ PEQ ≤ 31.1	26.2	16.5
	DW-4	20.3 ≤ PEQ ≤ 26.8	21.8	14.5
	DW-5	12.1 ≤ PEQ ≤ 16.1	12.4	7.4
	DW-6	10.1 ≤ PEQ ≤ 13.1	10.1	6.0
	DW-7	3.7 ≤ PEQ ≤ 5.1	3.9	2.1
	DW-8	17.7 ≤ PEQ ≤ 21	19.2	11.9
	DW-9	9.1 ≤ PEQ ≤ 9.9	9.1	6.8
	DW-10	3.1 ≤ PEQ ≤ 3.6	2.4	2.2
	DW-11	2 ≤ PEQ ≤ 2.4	1.6	1.5
Groundwater	DW-12	0.1 ≤ PEQ ≤ 0.2	0.1	0.1
	DW-13	2.9 ≤ PEQ ≤ 3.7	3	1.8
	DW-14	2.9 ≤ PEQ ≤ 4.8	3.3	1.8
	DW-15	1.4 ≤ PEQ ≤ 2.4	1.7	1.1
	DW-16	0.3 ≤ PEQ ≤ 0.3	0.3	0.2
	DW-17	0.7 ≤ PEQ ≤ 0.7	0.7	0.5
	DW-18	1.6 ≤ PEQ ≤ 2.5	1.7	0.9

PEQ: perfluorooctanoic acid equivalents

Risk to human health

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	DW-18	1.6 ≤ PEQ ≤ 2.5	1.7	0.9

PEQ: perfluorooctanoic acid equivalents

Conclusion

- **Ultrashort chain** (mainly TFA) were detected in all samples and **NO** significant difference between sources.
- High **removal variability** or even **negative removal** of PFAS using the same treatment (powder/granular activated carbon).
- Higher branched isomers contribution in drinking water as compared to the originally used mixtures.
- Following **EFSA** opinion. and mixture exposure (**RPF**) assessment. additional measures will be needed to ensure safety for multiple drinking waters produced from surface water

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This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 860665.