# PFAS removal & destruction technologies

**Sanne Smith**

TU Delft

# My PhD project


SLU PERFORCE3

**Per**- and polyfluorinated substances: towards the **F**uture **O**f **R**esearch and **C**ommunication in **E**urope

Horizon 2020 International Training Network: 15 PhD students, 13 Universities, 11 partner organizations

# Content

1. Introduction
2. Removal Technologies
3. Degradation Technologies
4. PFAS research at TU Delft

# 1. Introduction

# PFAS

## According to the OECD:

Any substance that contains a **$CF_3$~** or a **~$CF_2$~** group, without any H/Cl/Br/I directly attached to it

***The PFAS we worry about in water:***

***PFAA & their precursors***
***Only ~5 % of total PFAS production!***

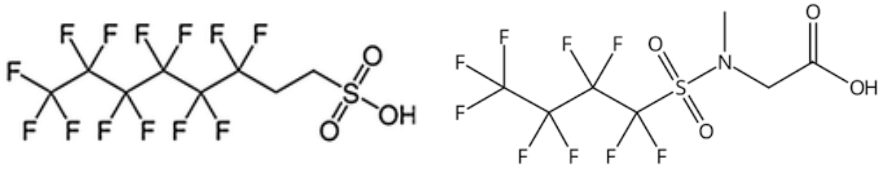
***F-gases largest group, followed by fluoropolymers***

TU Delft

OECD, 2021;
Evich et al., Science, 2022

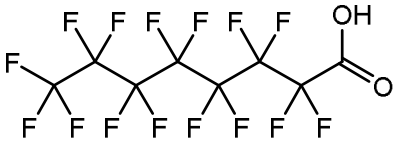
# PFAA & precursors

Precursors: can degrade to form PFAA

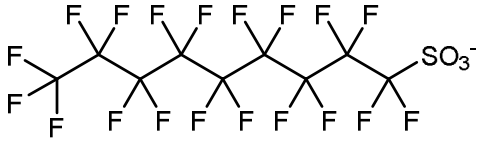


Perfluoroalkyl acid (PFAA)

Perfluorocarboxylic acids (PFCA)



Perfluorosulfonic acids (PFSA)



Long vs. short-chain: nr. of $CF_2$ moieties >~6 = long-chain (exact definition differs per group)

TU Delft

# PFAS in industrial water

## Primary manufacturing

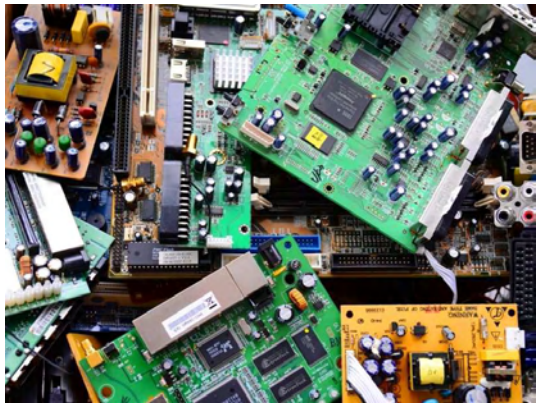
- Fluoropolymer plants
- AFFF production

## Secondary manufacturing

- Water-repellent textiles
- Paper industry
- Semiconductor industry

## Involuntary emissions

- Waste management industry, e.g. landfills
- AFFF users, e.g. biochemical industry



# Technology Readiness Levels

# 2. Removal Technologies

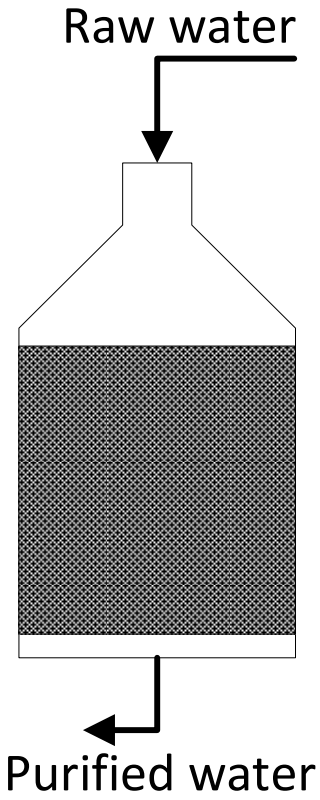
# Granular activated carbon (TRL 9)

Adsorption onto porous carbon material

Breakthrough after certain nr. of bed volumes (BV) treated

- Short-chain PFAS break through first

Competition with organic matter → earlier breakthrough



# Granular activated carbon – after breakthrough

**Regeneration** (most common)

- **Thermal** – most common
  - Off-site
  - ~10-20 % fresh GAC supplemented
- Chemical
  - In-situ
  - With HCl, NaOH, organic solvents, or mixtures

Disposal

- Incineration (mixed waste)
- Landfilling

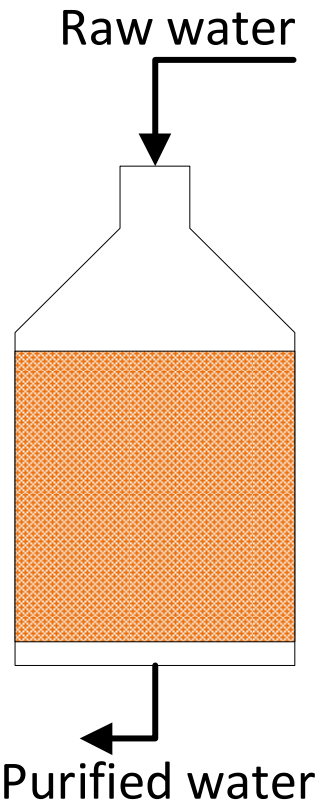
# Anion exchange (TRL 9)

Binding to synthetic resin based on electrostatic interaction

Breakthrough after certain nr. of bed volumes (BV) treated

- Binding strength can be engineered into material properties

**Shorter contact time** and **higher removal** than GAC → smaller vessels, but higher cost of sorbent



# Anion exchange – after breakthrough

Regeneration

- Thermal
- **Chemical** – most common
  - With HCl, NaOH, organic solvents, or mixtures
  - Organic solvent can be distilled off and reused
  - Remaining still-bottom requires further treatment – but is highly concentrated

**Disposal** (most common)

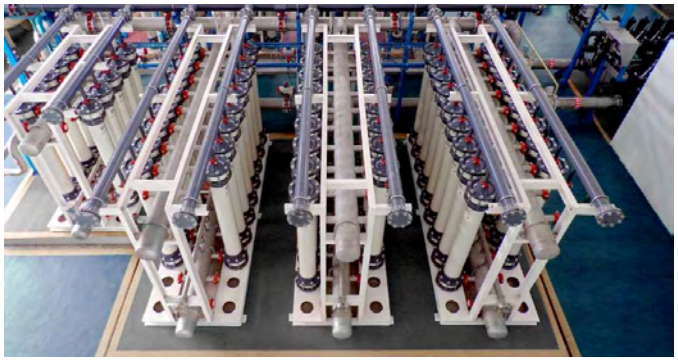
- **Incineration** – most common
- Landfilling

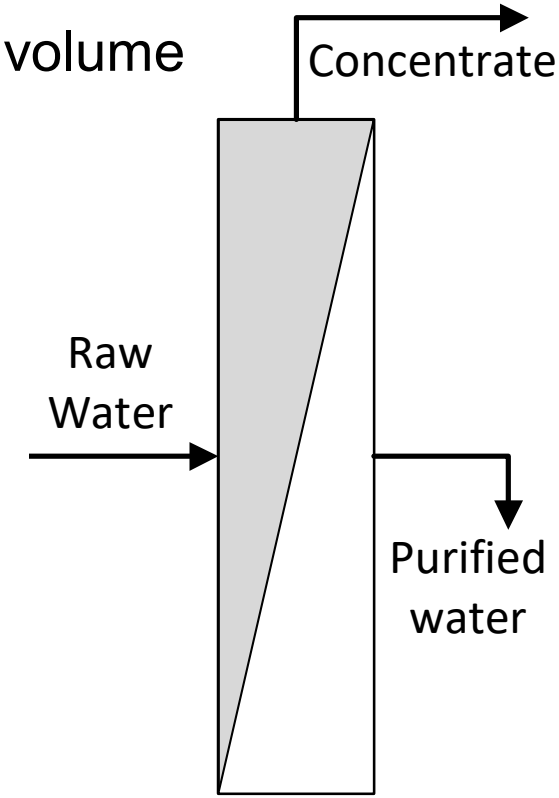
# Nanofiltration or Reverse Osmosis (TRL 9)

Membrane processes with pore size <0.1–10 nm: rejection of small molecules

Results in concentrate stream of ~10–20 % of influent volume

Higher removal than GAC/AIX, but higher OPEX





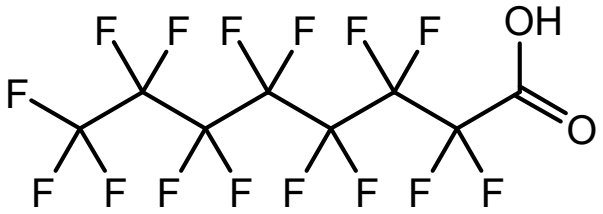
# Foam fractionation (TRL 9)

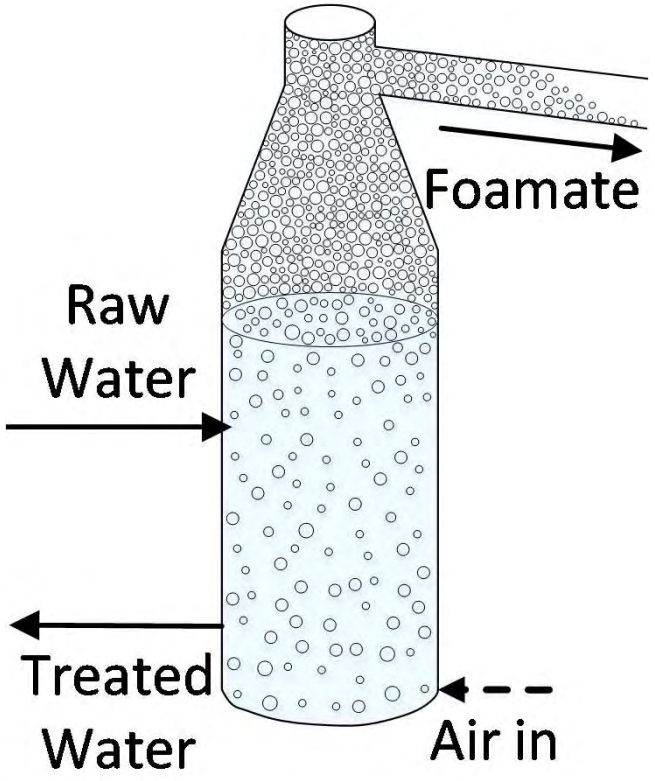
Adsorption to rising air bubbles of amphiphilic contaminants

Results in concentrated foamate stream

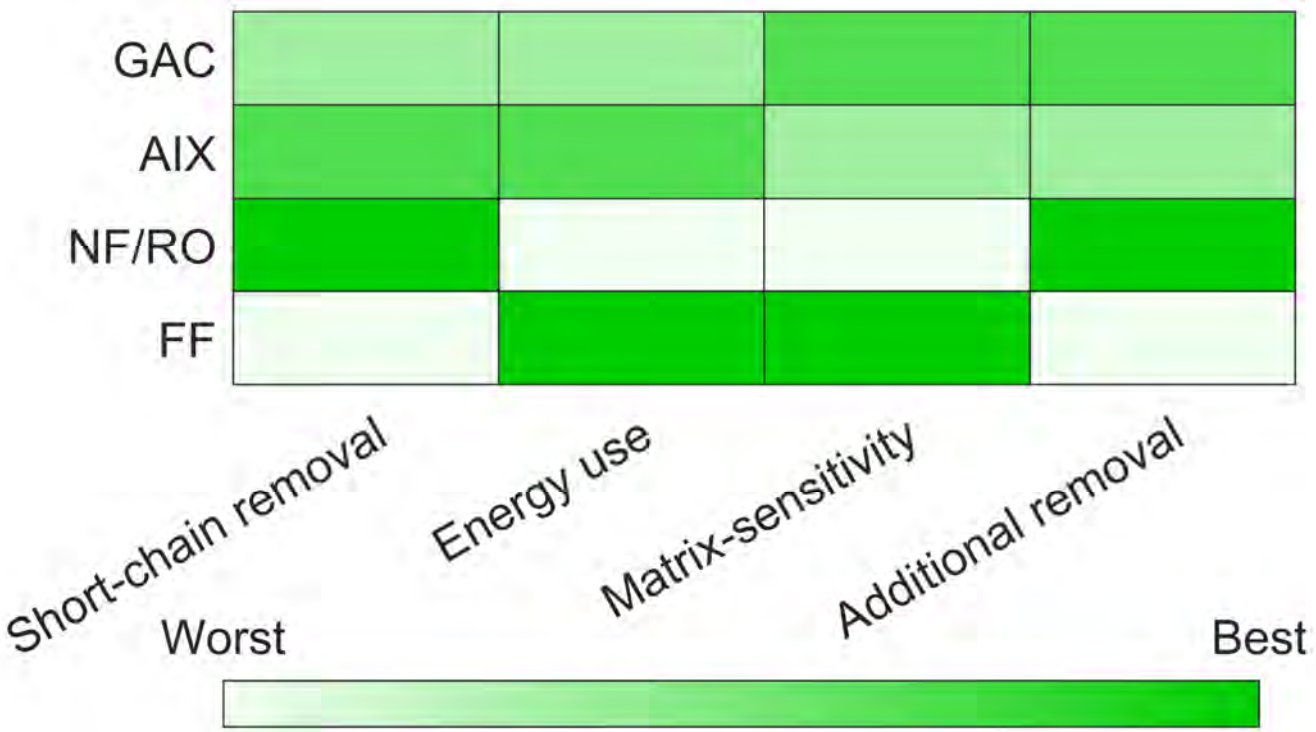
Low short-chain PFAS removal

Cheap, low matrix sensitivity, high water recovery



# Summary



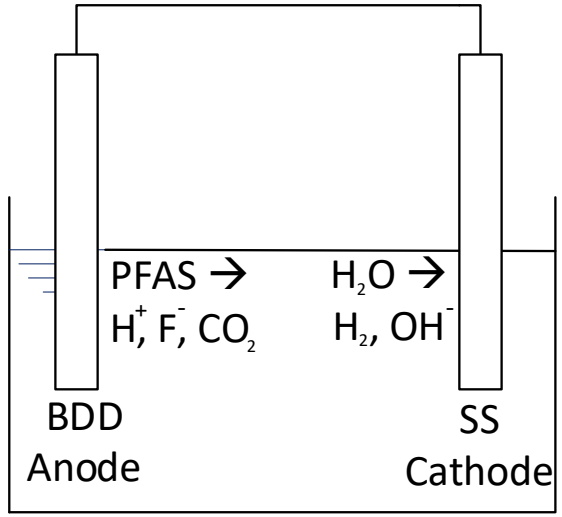

**No one-size-fits-all treatment solution!**

# 3. Degradation Technologies

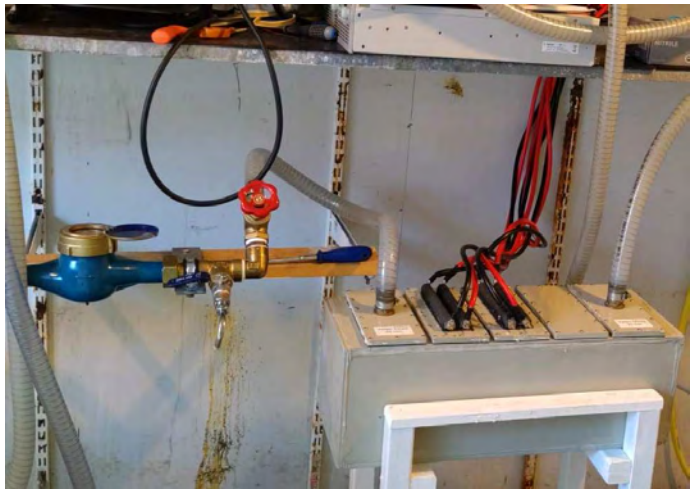
# Degradation technologies

**Electrochemical oxidation (TRL 8)**

- Degradation of contaminants on/near anode surface
- Non-active anodes: direct electron transfer to anode
- + No chemicals, small footprint, scalable
- - Low degradation of short-chains, long residence times, formation of perchlorate




Electrochemical cell



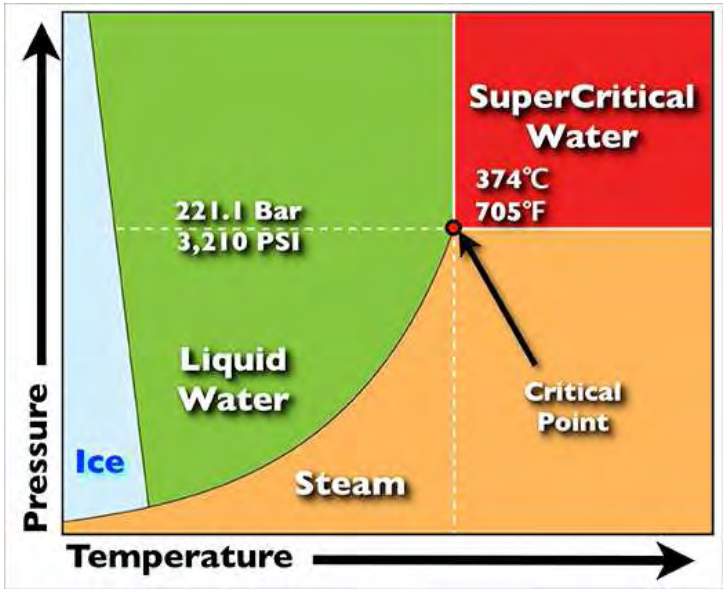
Smith et al. 2023
Radjenovic et al. 2020

# Degradation technologies

Electrochemical oxidation (TRL 8)

**Supercritical water oxidation (SCWO, TRL 9)**

- Water above critical pressure and temperature
- High solubility of organic compounds, high nr. free radicals
- +Fast (seconds), complete PFAS mineralization
- -Sensitive to corrosion, scaling, and byproduct formation, energy intensive




Krause et al. 2023

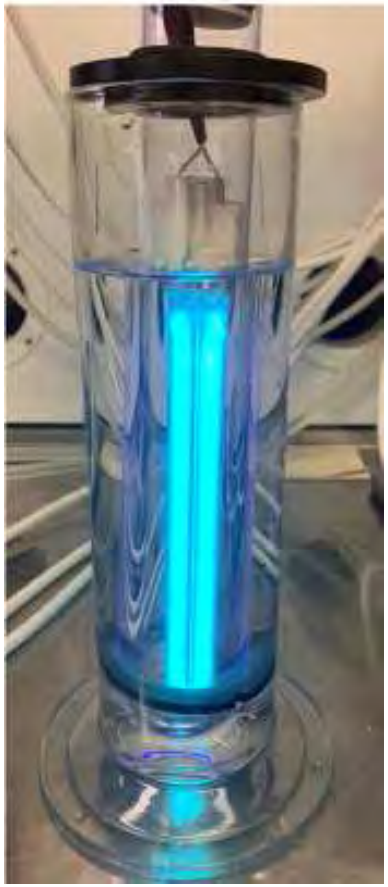
# Degradation technologies

Electrochemical oxidation (TRL 8)

Supercritical water oxidation (SCWO, TRL 9)

**Photodegradation (TRL 4)**

- Use of UV light and chemical activators/catalysts
- Photo-oxidation: persulfate, ferric iron, carbonate, …
- Photoreduction: heterogeneous catalysts, sulfite
- + UV/Sulfite photoreduction → effective for both short and long-chain PFAS
- - Forms byproducts, very matrix-sensitive



Liu et al. 2021

# Degradation technologies

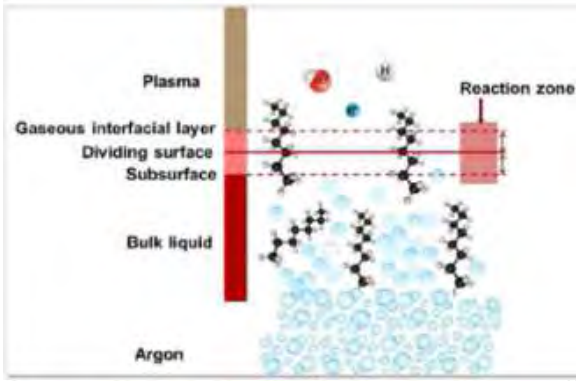
Electrochemical oxidation (TRL 8)

Supercritical water oxidation (SCWO, TRL 9)

Photodegradation (TRL 4)

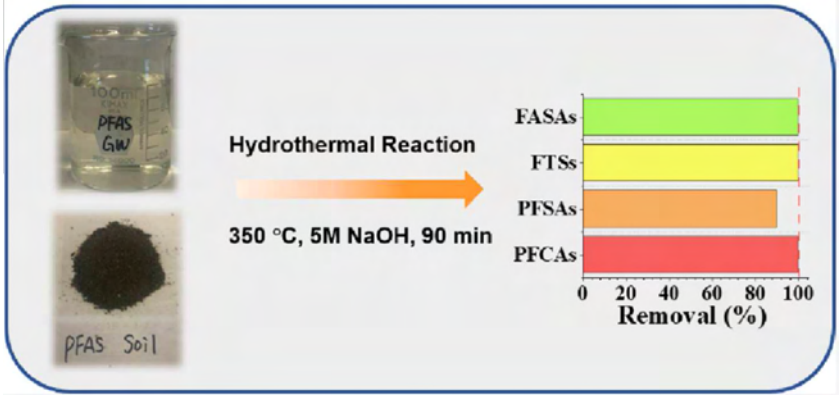
**Plasma degradation (TRL 6-9)**

- Ionized gas: generation of free electrons, free radicals, ions, photons
- Most often non-thermal plasma (higher TRL), thermal plasma also used (lower TRL)
- + Low energy use, thermal plasma is very fast
- - Matrix-sensitive, problematic scale-up




DiGuiseppi et al. 2024

# Degradation technologies




Electrochemical oxidation (TRL 8)

Supercritical water oxidation (SCWO, TRL 9)

Photodegradation (TRL 4)

Plasma degradation (TRL 6-9)

**Hydrothermal Alkaline Treatment (HALT, TRL 6-7)**

- Similar to SCWO, but subcritical conditions (170-350ºC, 2-22 MPa)
- $OH^-$ catalyzes reaction mechanism → high conc. NaOH added
- + relatively fast, full mineralization, very low matrix sensitivity
- - effluent is very alkaline, relatively energy intensive

DiGuiseppi et al. 2024 https://doi.org/10.1002/rem.21782

Hao et al. 2022

# Summary - Degradation technologies

**TABLE 1** Summary of commercially available PFAS destruction technologies.

| | Electrochemical Oxidation | Non-Thermal Plasma | UV-Activated Photoreduction | Supercritical Water Oxidation | Hydrothermal Alkaline Treatment | Thermal Arc Plasma |
|---|---|---|---|---|---|---|
| Reaction Mechanism | Oxidation | Oxidation & Reduction | Reduction | Oxidation | Nucleophilic Substitution | Oxidation |
| Reaction Time | Hours | Hours | Hours | Seconds | Minutes | Milliseconds |
| Ability to Achieve Complete Mineralization | Moderate | Moderate | Moderate | High | High | High |
| Operating Conditions | Ambient | Ambient | Ambient | High Pressure, High Temp. | High Pressure, High Temp., High pH | High Temp. |
| Treats Other Organics | Yes | Yes | Partially | Yes | Partially | Yes |
| Reagents Required | None-minimal | None-minimal | Yes | No | Yes | No |
| Representative North America-Based Technology Vendors | Axine, Aclarity, AECOM, E2Metrix, OxbyEl | DMAX Plasma | Haley & Aldrich, Enspire Solutions, Claros | 374Water, General Atomics, Revive | Aquagga | Pyrogenesis, Onvector |
| TRL Level (early 2024) | 8 | 7-9 | 6-7 | 9 | 6-7 | 6-7 |

Note – energy requirement is missing!

Depends on water matrix, but non-thermal plasma and EO typically have lowest energy demands

DiGuiseppi et al. 2024 https://doi.org/10.1002/rem.21782

# Summary - Degradation technologies

All much more energy intensive than removal technologies

Generally: less mature → scale up might be an issue

**Generate byproducts!**

- Oxyhalide anions (chlorate, perchlorate, bromate, etc.)
- Halogenated organics

**The Need to Include a Fluorine Mass Balance in the Development of Effective Technologies for PFAS Destruction**

Sanne J. Smith*, Mélanie Lauria, Christopher P. Higgins, Kurt D. Pennell, Jens Blotevogel, and Hans Peter H. Arp

Cite this: *Environ. Sci. Technol.* 2024, 58, 6, 2587−2590

Publication Date: February 5, 2024

https://doi.org/10.1021/acs.est.3c10617

Copyright © 2024 The Authors. Published by American Chemical Society. This publication is licensed under CC-BY 4.0.

Open Access

Article Views 5626 | Altmetric 13 | Citations -

LEARN ABOUT THESE METRICS

Share Add to Export RIS

PDF (3 MB) TU Delft full text

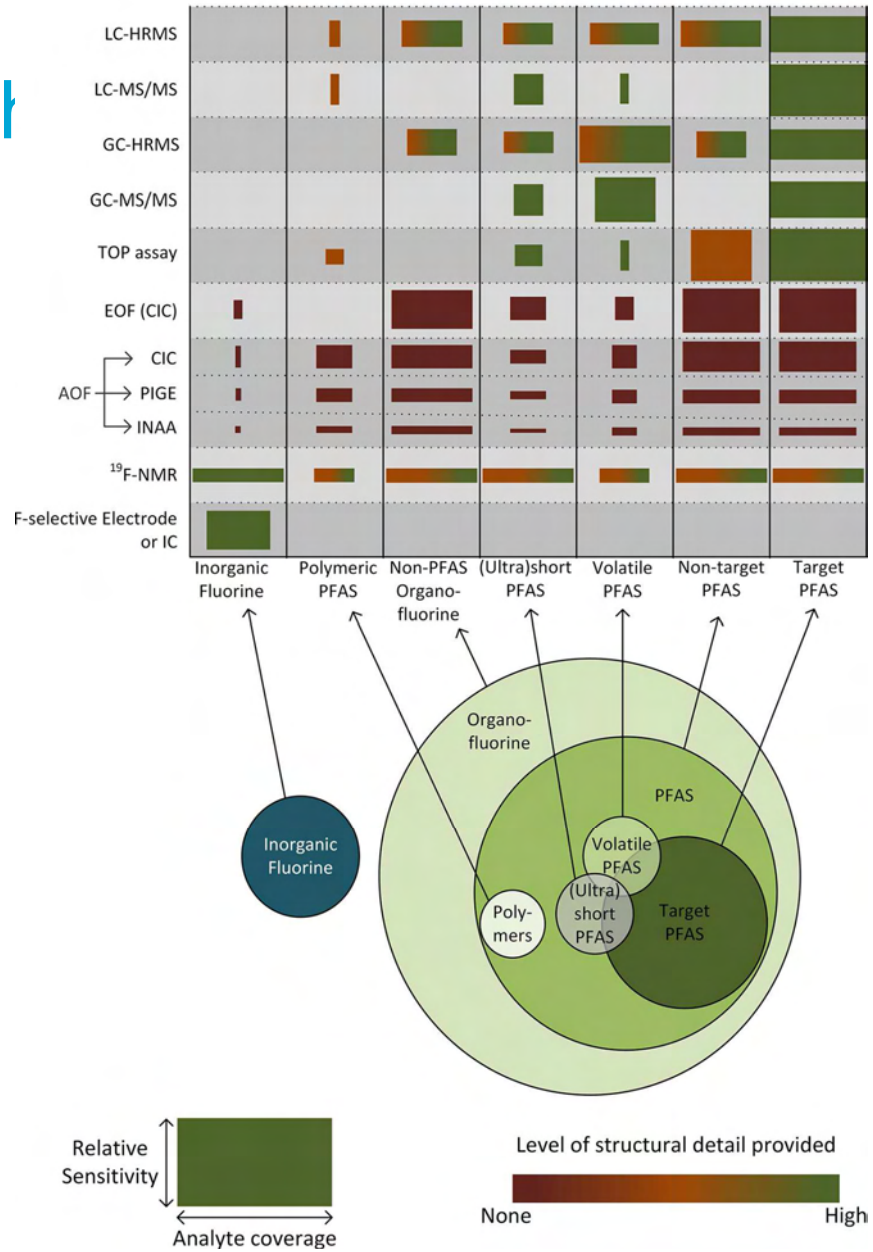
SUBJECTS: Anions, Byproducts, Degradation, Extraction, Fluorine

# How to verify destructive tecl

Simply measuring 20-40 target PFAS is **not enough**

*"Remediation can convert one problem into another, and only through efforts to complete the mass balance and understand the degradation mechanisms can we ensure that destructive technologies are benign instead of regrettable."*

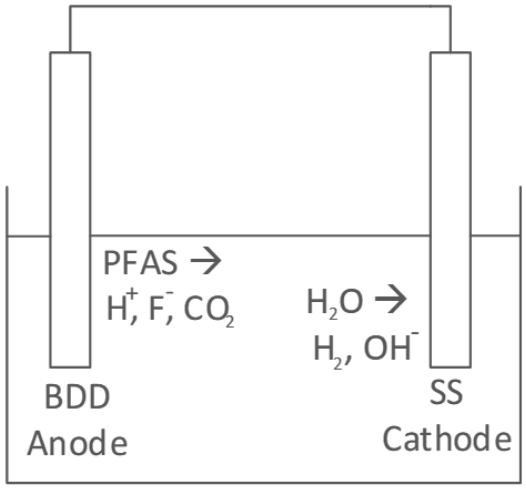
Smith et al. 2024



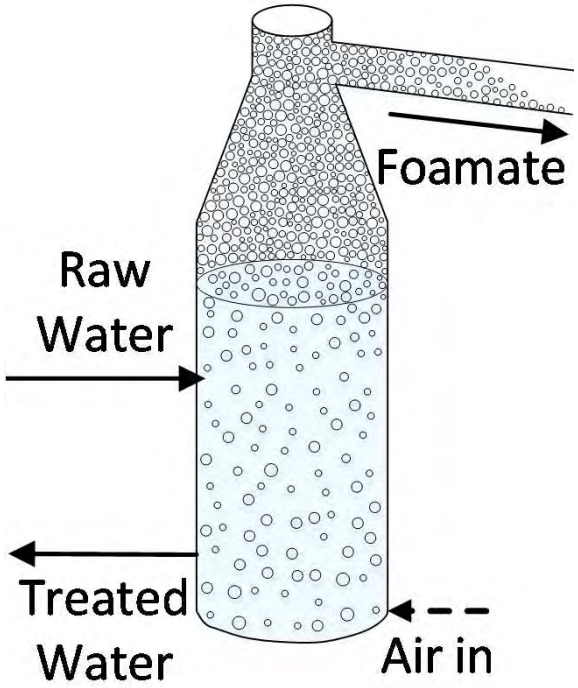
# 4. PFAS research at TU Delft

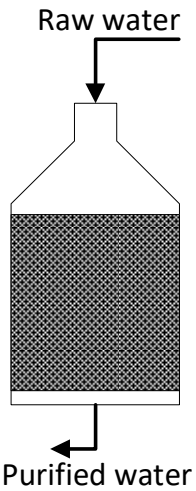
# PFAS projects at TU Delft - treatment

- Electrochemical oxidation
- Adsorption + regeneration of sorbents
- Foam fractionation




Electrochemical cell




TU Delft

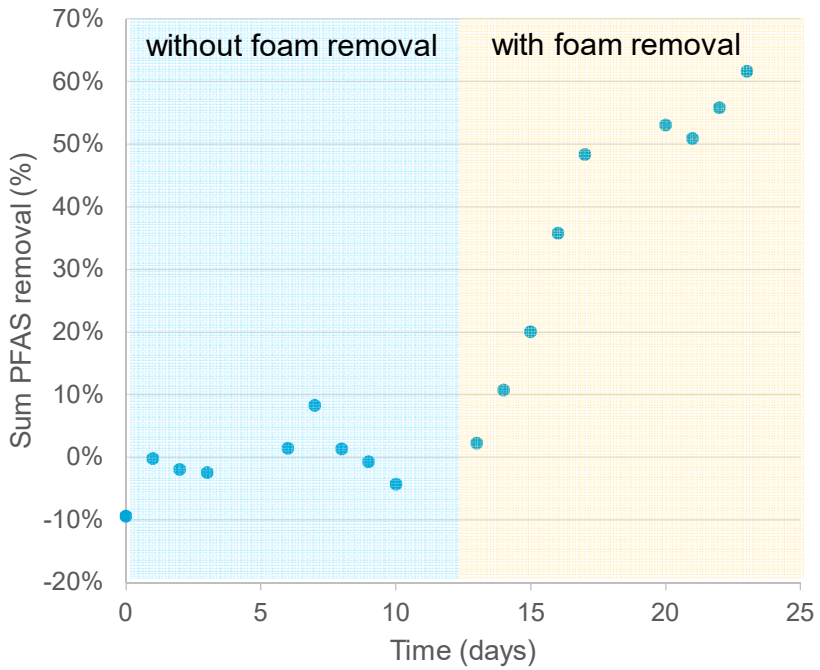
# Foam fractionation integrated in existing biological plants

Foaming occurs in many existing biological treatment processes

Removal of this foam = removal of PFAS

No additional aeration energy required

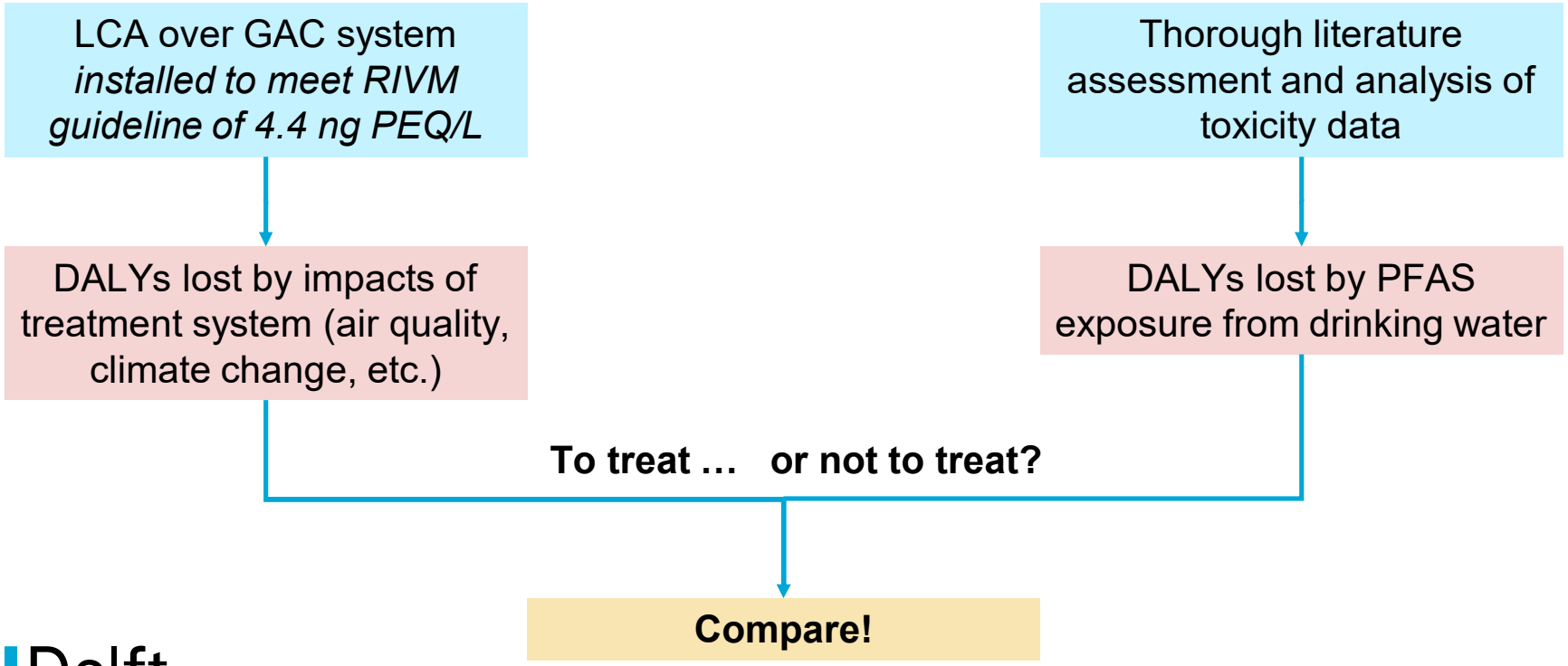
**See poster by Kay Schmidt**




# The sense of PFAS treatment…

Case: waternet drinking water production

*DALYs = disability adjusted life years*



Questions?

s.j.smith@tudelft.nl

TU Delft