

# ZeroPM approaches for water treatment: advanced adsorption and electrochemical degradation

*Marcel Riegel and Heico Schell*

*German Water Centre (DVGW-TZW)*



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101036756.

# Treatment Options for Water

Process engineering grouping:

1. Adsorption

2. Flocculation

3. Liquid-liquid separation /  
pre-concentration

4. Destruction

E  
x  
a  
m  
p  
l  
e  
s

- ①
  - Activated Carbon (AC)
  - Ion Exchange (IEX) (single use)
- ②
  - PFAS specific flocculants
  - Reverse Osmosis / Nanofiltration
- ③
  - Foam Fractionation
  - IEX (including regeneration)
  - AC (including controlled desorption)
- ④
  - Electrochemical degradation
  - Plasma destruction

# Treatment Options for Water

Process engineering grouping:

1. Adsorption
2. Flocculation
3. Liquid-liquid separation / pre-concentration
4. Destruction

E x a m p l e s

- ①
  - Activated Carbon (AC)
  - Ion Exchange (IEX) (single use)
- ②
  - PFAS specific flocculants
  - Reverse Osmosis / Nanofiltration
  - Foam Fractionation
- ③
  - IEX (including regeneration)
  - AC (including controlled desorption)
- ④
  - Electrochemical degradation
  - Plasma destruction

# Introduction: Activated Carbon (AC)

- State of the art for (drinking) water treatment
- Limitations:
  - Short chain carboxylic acids (PFBA & PFPeA) are poorly adsorbable
  - High DOC (dissolved organic carbon) competes for adsorption sites
    - ⇒ Short operating times
    - ⇒ frequent material changes
    - ⇒ high treatment costs

# Introduction: Ion Exchange (IEX)

- Higher product price (5 to 10 times higher than AC)
  - Faster adsorption kinetics  $\Rightarrow$  smaller filter columns  
 $\Rightarrow$  lower investment cost
  - Higher capacity for PFAS  $\Rightarrow$  **longer operation times** than AC
    - PFOS: 10 x longer than AC
    - PFOA: 5 x longer than AC
    - PFHxA: 4 x longer than AC
    - PFPeA: 2 x longer than AC
    - PFBA: 1.5 x longer than AC
- $\Rightarrow$  Less advantages for removing short chain PFAS

# Introduction: Ion Exchange (IEX) / 2

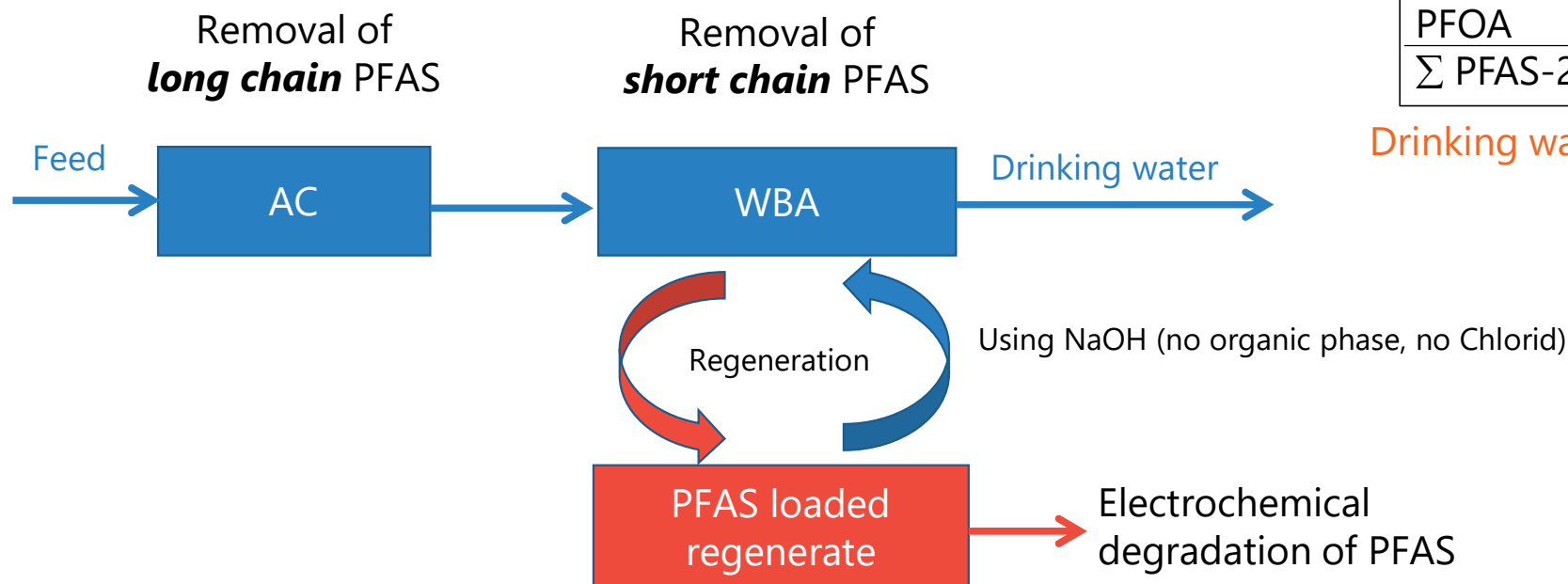
- IEX can be regenerated and used multiple times (dishwasher)
- Strongly basic anion exchangers (SBA):  
higher affinity to PFAS  
⇒ regeneration only possible using an organic phase (EtOH)
- Weakly basic anion exchangers (WBA):  
lower affinity to PFAS  
⇒ regeneration possible with NaOH
- Short chain PFAS are easier to eluate from IEX than long chain PFAS

# Technical Approach in ZeroPM

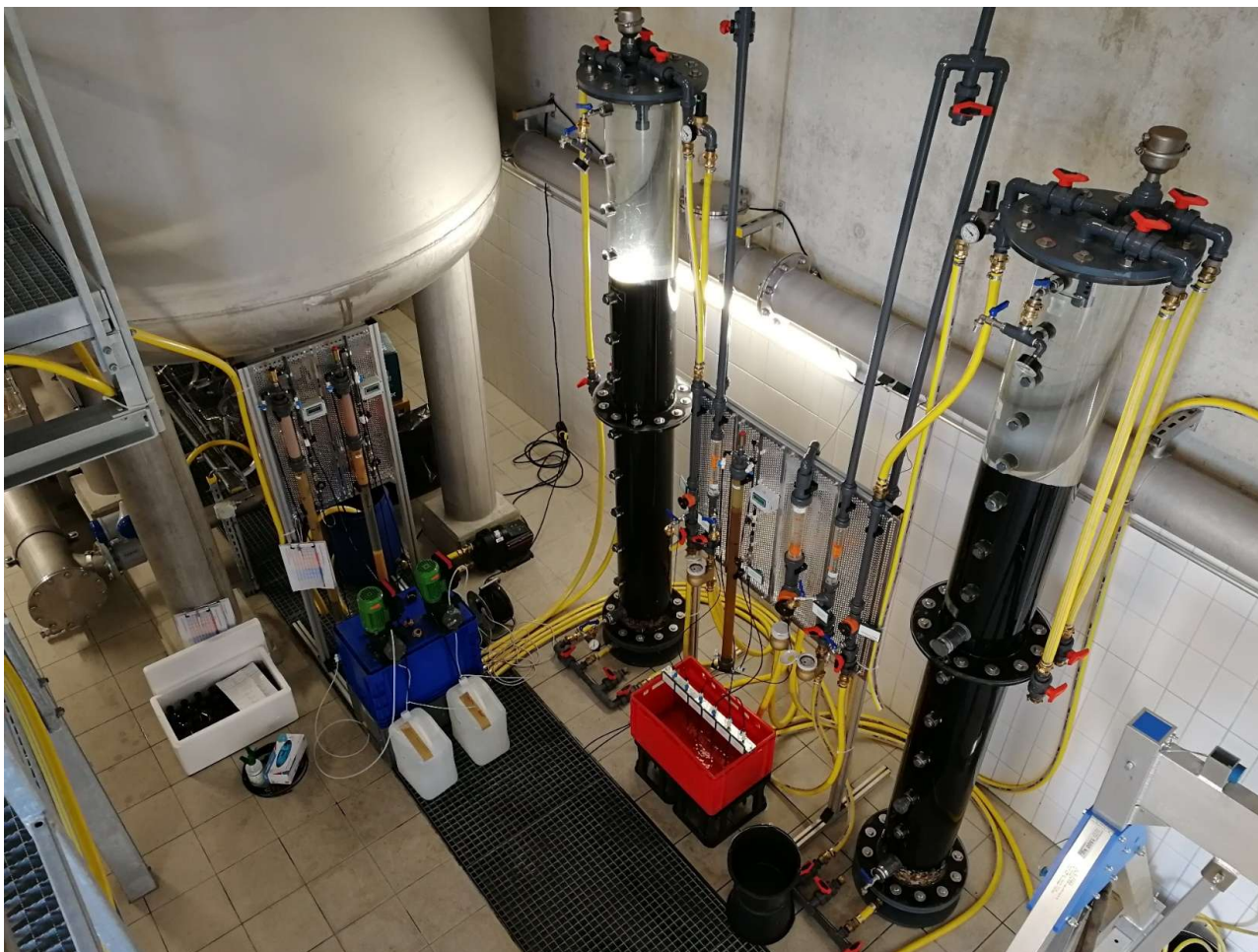
Ground water PFAS contamination:

PFBA	30 ng/L
PFPeA	100 ng/L
PFHxA	100 ng/L
PFHpA	40 ng/L
PFOA	200 ng/L
Σ PFAS-20	450 ng/L

Drinking water limit: 100 ng/L



# Pilot plant



## AC

$$V = 130 \text{ L}$$

$$Q = 660 \text{ L/h}$$

$$= 5 \text{ BV/h}$$

$$\text{EBCT} = 12 \text{ min}$$

$$v_F = 10 \text{ m/h}$$

## IEX

$$V = 2 \text{ L}$$

$$Q = 20 \text{ L/h}$$

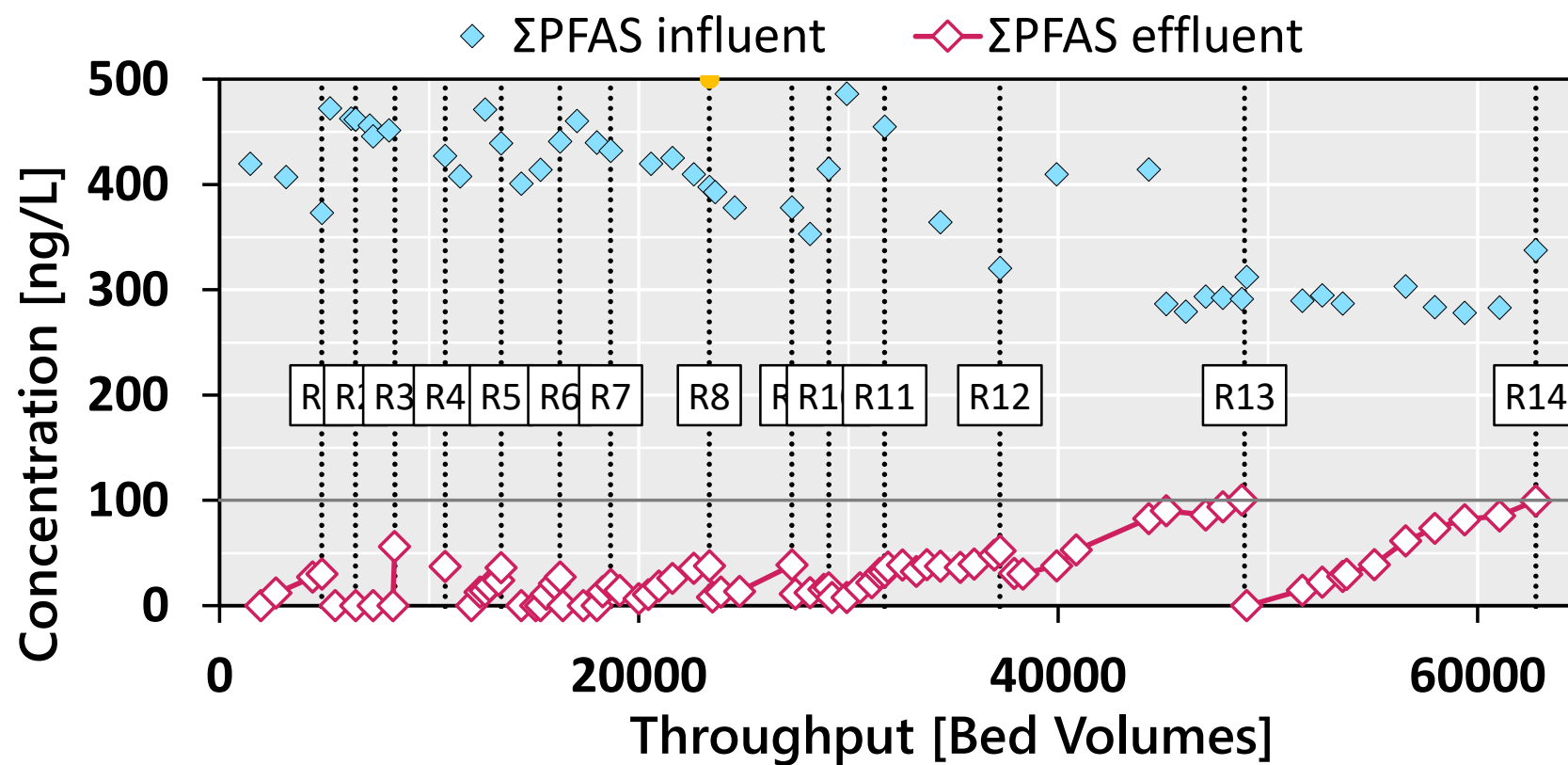
$$= 10 \text{ BV/h}$$

$$\text{EBCT} = 6 \text{ min}$$

$$v_F = 10 \text{ m/h}$$

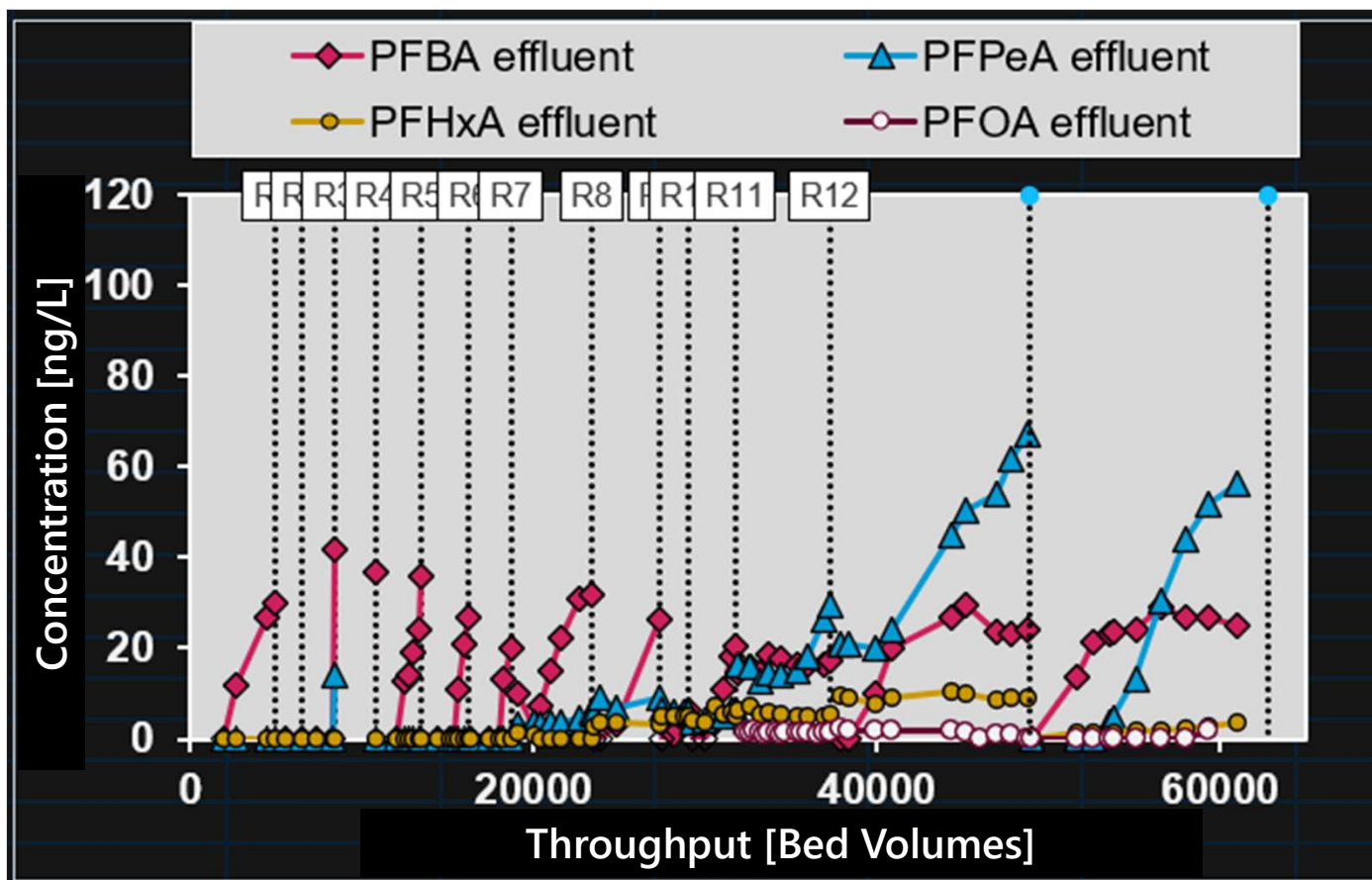


# Performance AC + IEX

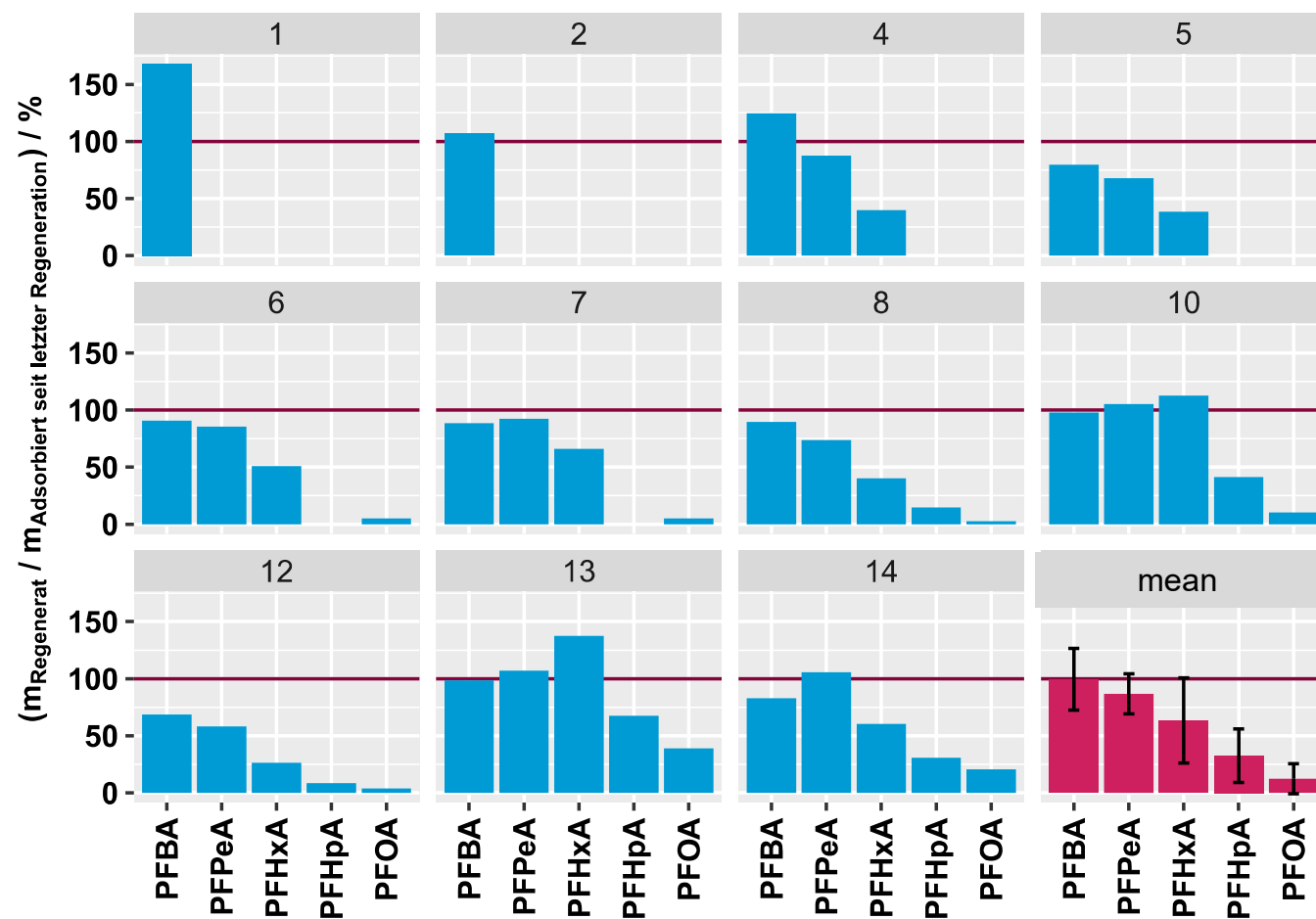


Regeneration period:  
1 week to  
2.5 month

# Performance IEX



# IEX Regeneration mass balance



Variation of regeneration procedure:

- NaOH 0.01 – 1 mol/L
- V: 10 – 30 BV

# Technology evaluation

- Long chain and short chain PFAS can effectively removed  
Limits ( $\Sigma$  PFAS-20 and  $\Sigma$  PFAS-4) can be reached
- 14 Regenerations without noticing losses in capacity  
(although PFOA and PFHxA are not completely eluted)
- Operating time of IEX until material replacement is at least 70,000 BV

IEX with regeneration

• VRF: 100 – 750

Reverse Osmosis

5

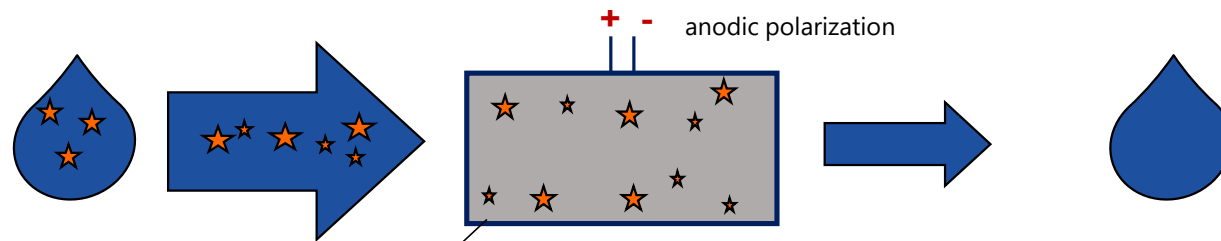
VRF... Volume Reduction Factor  
=  $V(\text{feed}) / V(\text{concentrate})$

# Evaluation of costs

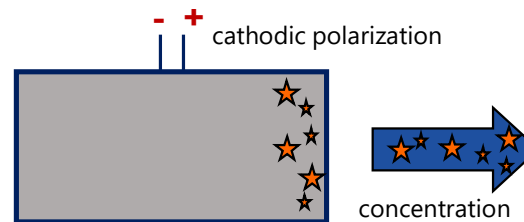
- Benchmark: Activated Carbon
- Advantage of AC + IEX:  
AC operation time can be prolonged (factor 3)
- To be cost neutral:  
500,000 BV have to be treated with IEX (including regeneration)  
until IEX replacement (70,000 BV have been demonstrated)
- Additional costs for treatment of regenerate  
⇒ Process more expansive than AC

# Objective

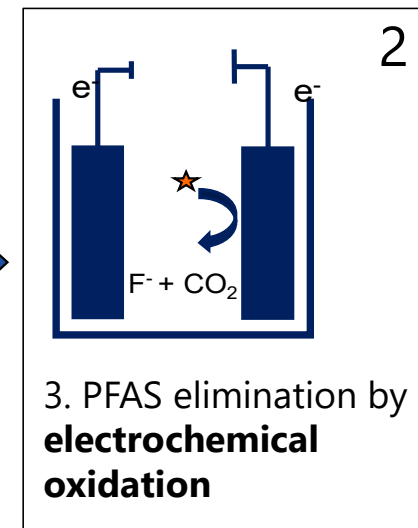
- Development, optimization and **combination of techniques** for the removal of PFAS from groundwater and drinking water
- Combination of two processes:



1. Removal from water by **electrosorption**



2. Regeneration of filter by **electrodesorption**



★ = PFAS

Ad- and desorption tests with **granulated activated carbon (GAC)** in a **flow-through cell**

Enhancement of adsorption/desorption by **polarization** of the GAC



# Electrosorption/-desorption

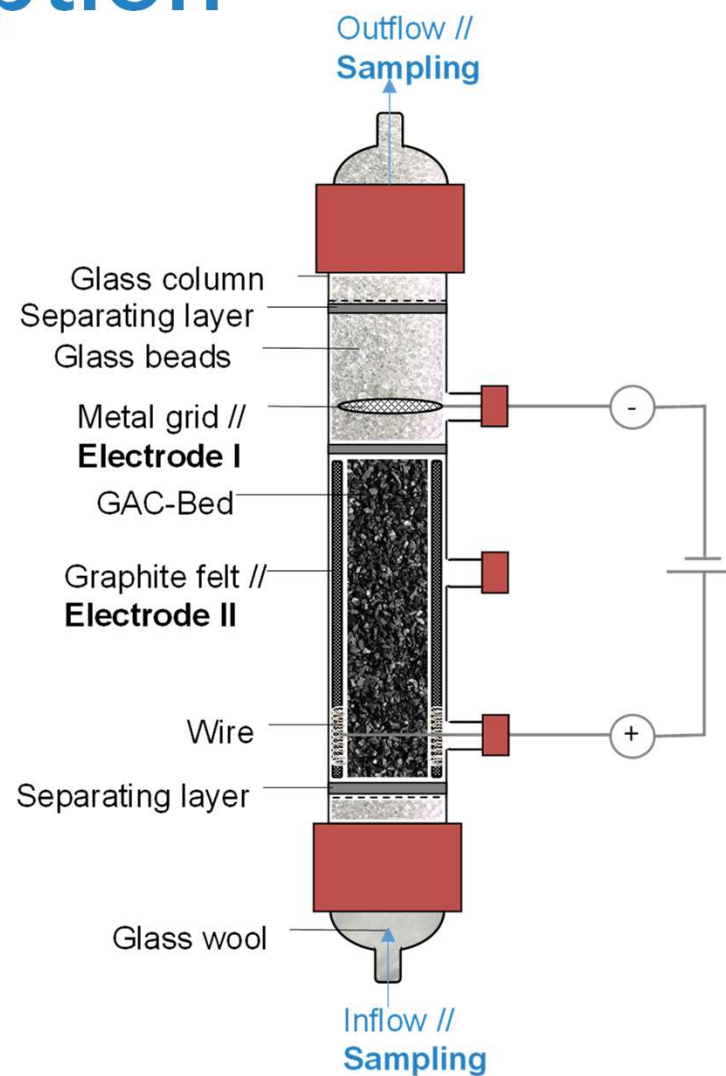
Analyte: **PFAS-mixture each 100 µg/L**

Matrix: **Na<sub>2</sub>SO<sub>4</sub>-solution**

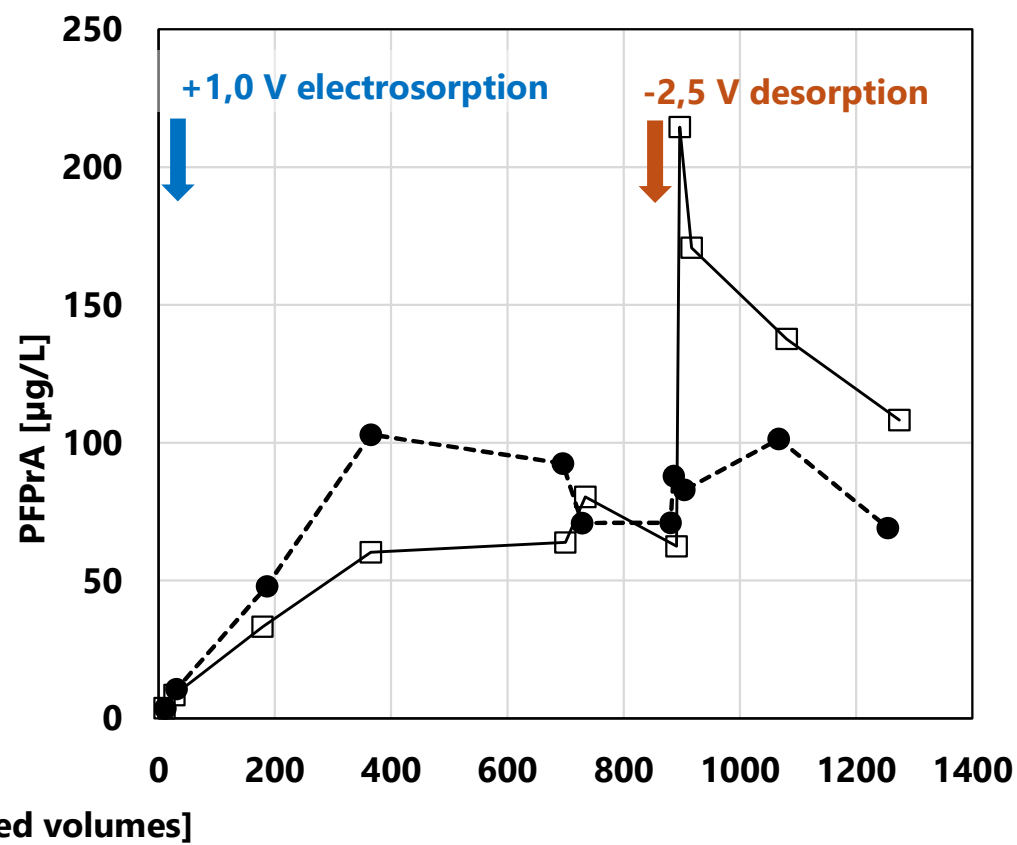
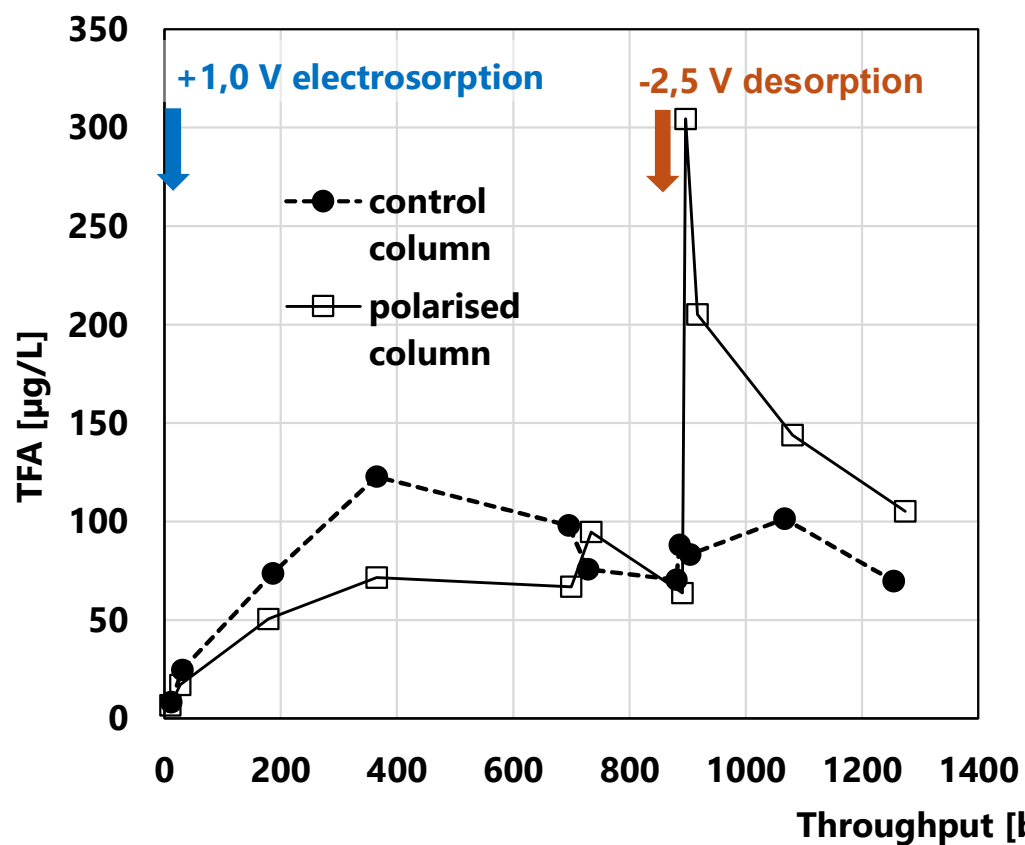
Filter material: **granulated activated carbon**

Polarization adsorption: **+1,0 V**

Polarization desorption: **- 2.5 V**



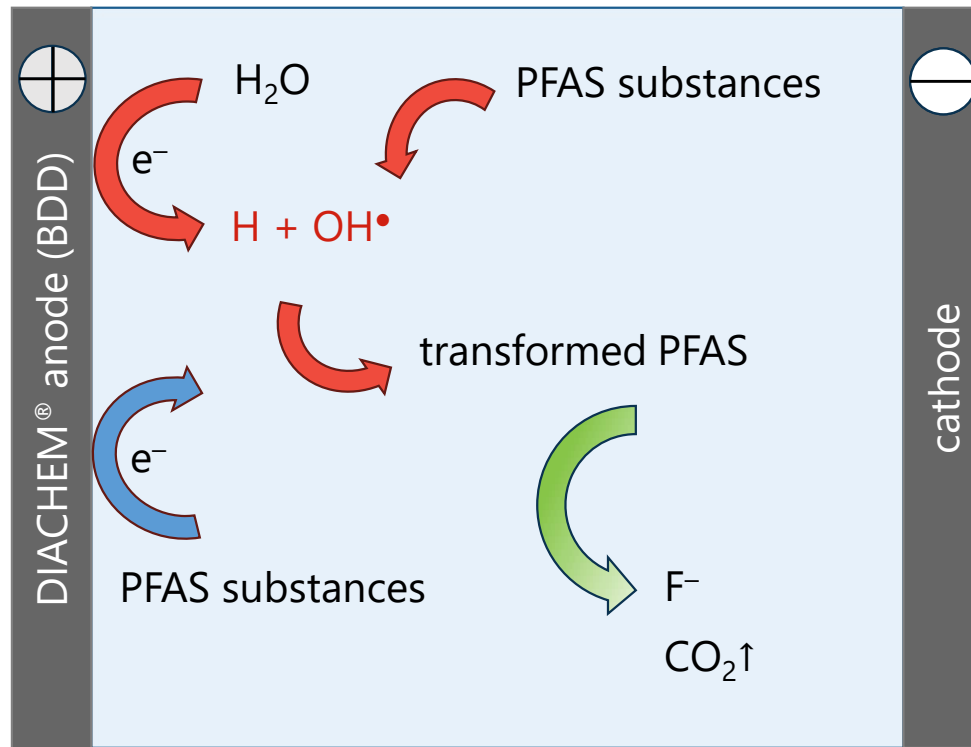
# Electrosorption/-desorption



Effluent concentrations



# Electrochemical PFAS destruction



## Pathway 1:

## Oxidation by hydroxyl radical

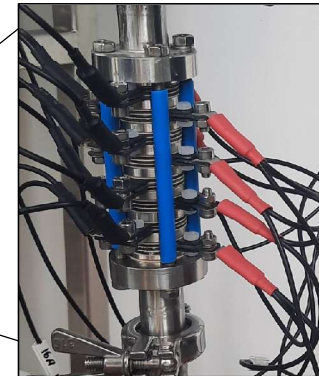
## Pathway 2:

## Direct destruction at BDD anode

*Literature:* Oxidative Destruction of Perfluorooctane Sulfonate Using Boron-Doped Diamond Film Electrodes von K. E. Carter, J. Farrel in Environmental Science and Technology 42(16):6111-5 · 2008 <https://doi.org/10.1021/es703273s>

Electrochemical degradation of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in groundwater. Trautmann, A. M.; Schell, H.; Schmidt, K. R.; Mangold, K-M; Tiehm, A. in Water science and technology 71 (10), S. 1569–1575. 2015 <https://doi.org/10.2166/wst.2015.143>.

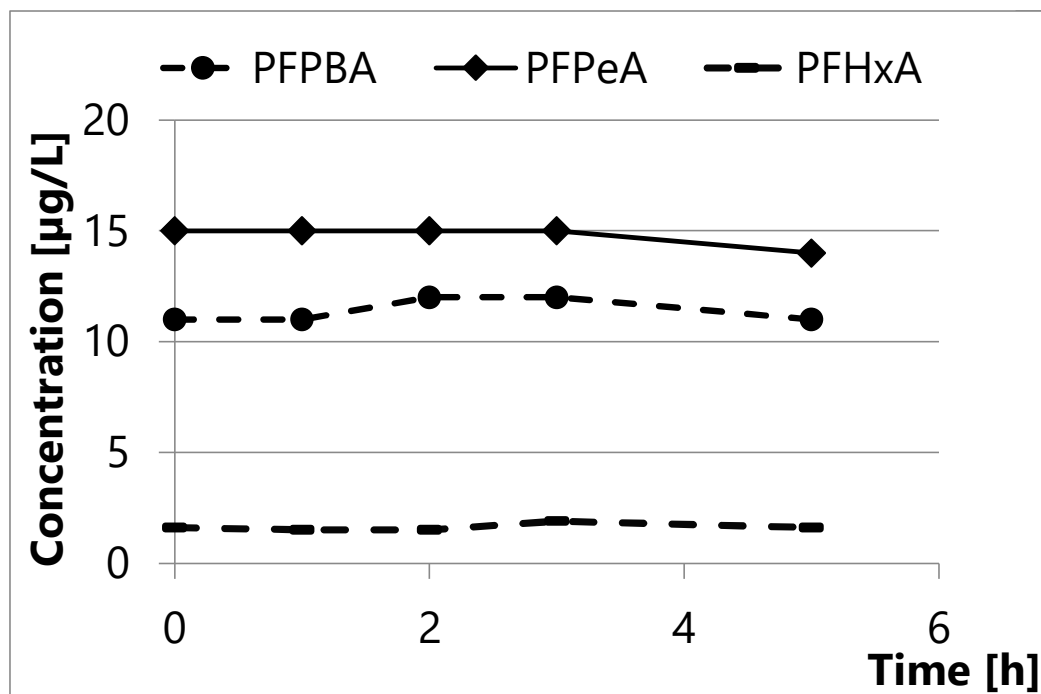
# PFAS destruction – Equipment – System



electrolysis plant: 20 L scale

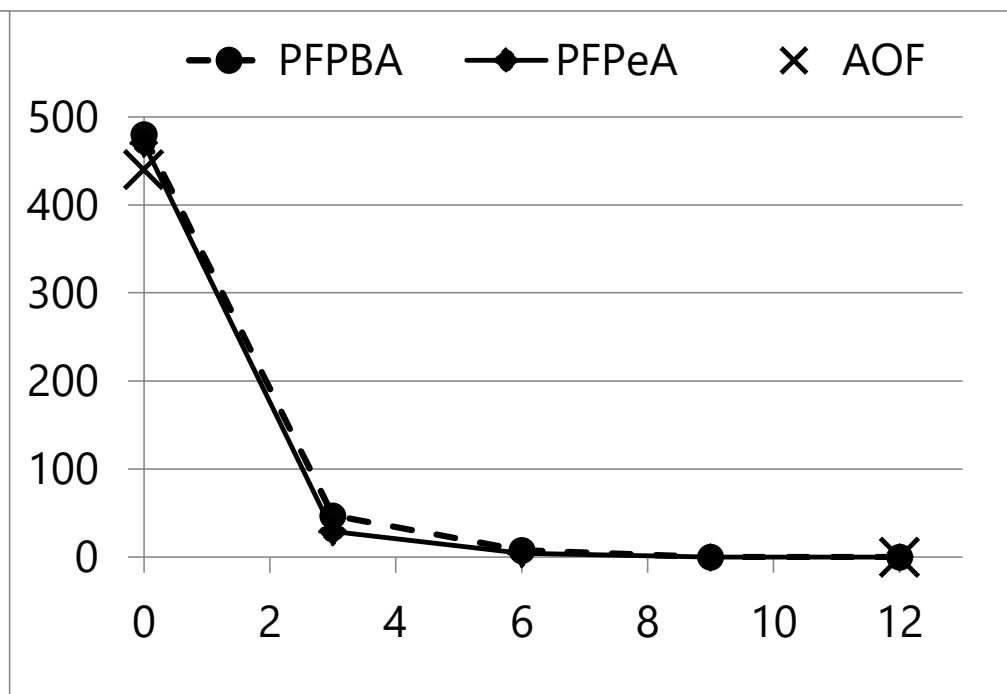
- ECWP with 8 electrode packages

# Electrochemical elimination of short-chain PFAS in IEX regenerates



**Regenerate IEX 0,8 - 1 M NaOH**

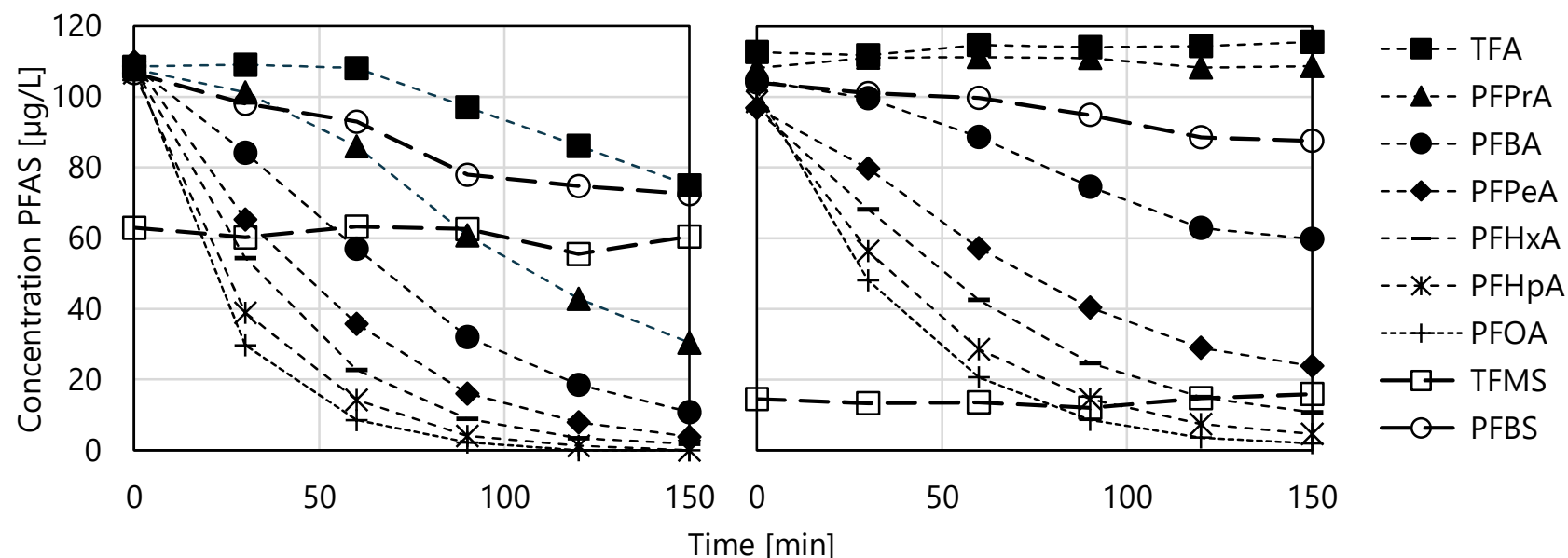
cond.  $\kappa \approx 150$  S/cm  
Scale: 10 L  
 $I = 2$  A



**Synthetic regenerate 2 mM NaOH**

cond.  $\kappa \approx 470$   $\mu$ S/cm  
Scale: 10 L  
 $I = 1.5$  A

# Electrochemical elimination of short-chain PFAS in drinking water



Scale: 10 L

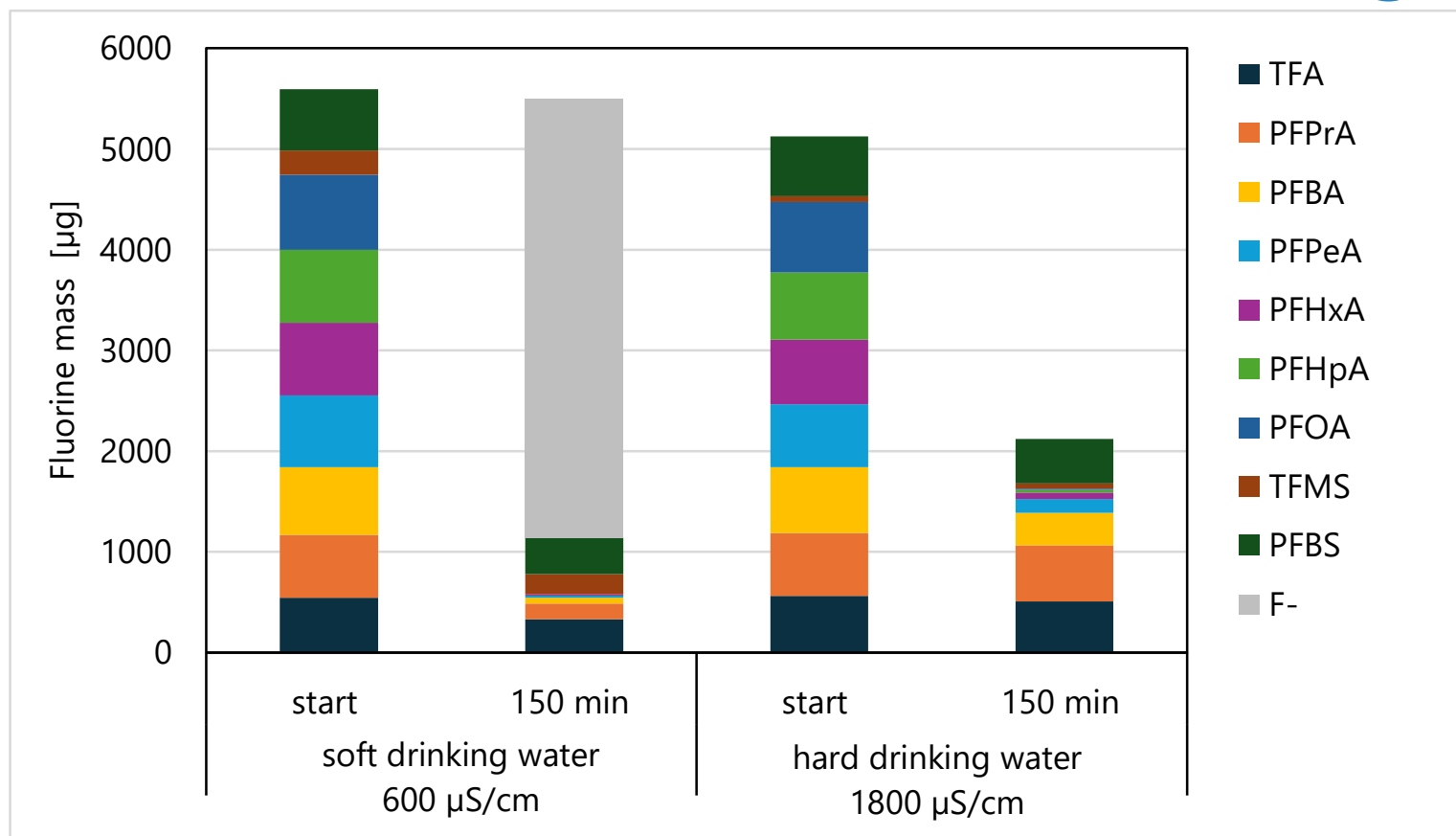
Soft drinking water  $\kappa \approx 600 \mu\text{S/cm}$

$I = 1.5 \text{ A}$

Initial PFAS conc.:  $100 \mu\text{g/L}$  each

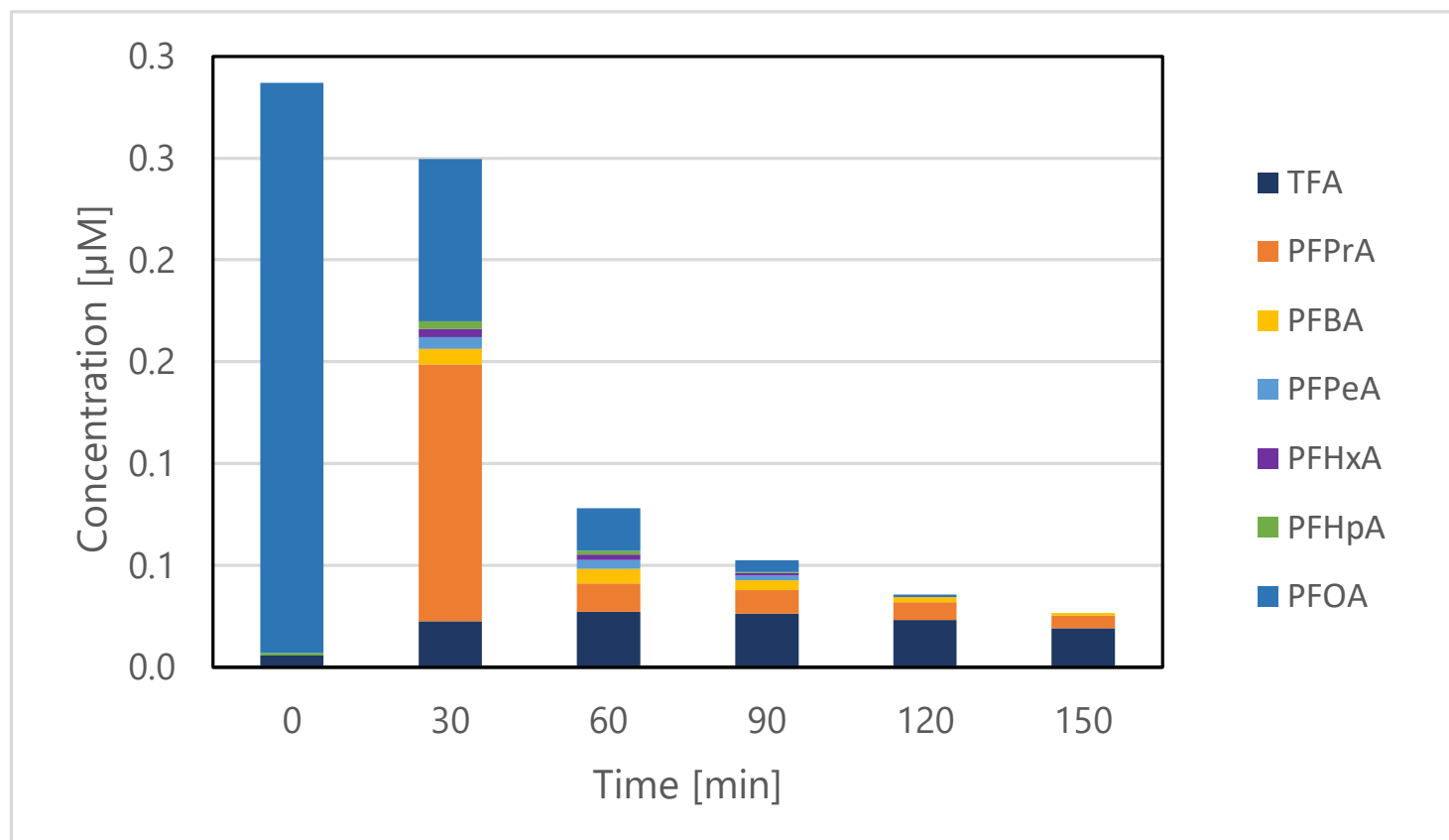
Hard drinking water  $\kappa \approx 1800 \mu\text{S/cm}$

# Elimination of short-chain PFAS in drinking water



**Stoichiometric fluorine (from PFAS) and measured fluoride (free ions) relative to the total volume**

# Formation of transformation products



**PFOA as single substance**

Scale: 10 L

Soft drinking water  $\kappa \approx 600 \mu\text{S}/\text{cm}$

$I = 1,5 \text{ A}$

Initial PFAS conc.:  $100 \mu\text{g}/\text{L}$  PFOA

# Summary electrochemical polarisation and oxidation

- Better electrosorption is shown mainly with the ultra-short PFAS
- As the ultra-short PFAS can only be insufficiently retained with GAC, electrosorption offers a possibility to achieve better sorption capacities
- PFAS are electrochemically oxidised and mineralized
- Long PFCA molecules are transformed into shorter ones
- The shorter the molecule, the more energy is required
- The higher the conductivity of the matrix, the more energy is required
- National project started to modify GAC for better electrosorption properties and the biological degradation of harmful by-products from electrolysis will be investigated.

# Zer◻PM



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101036756.