EU Green Week
PARTNER EVENT

Special Symposium on PFAS elimination from Drinking Water

Rastatt / Karlsruhe
12.-13. June 2024

#WaterWiseEU






ZeroPM

STADTWERKE RASTATT

DVGW | TZW Technologiezentrum Wasser

THE TREATMENT OF PFAS CONTAMINATED WATER

ZeroPM PFAS Symposium, 12.-13.06.2024

Marcel Riegel

DVGW | TZW Technologiezentrum Wasser

PFAS-ELIMINATION DURING DRINKING WATER TREATMENT

Effective processes:

- Adsorption
  - Activated carbon
- Dense membrane filtration
  - Nanofiltration (NF)
  - Reverse Osmosis (RO)

Ineffective processes:

- Bank Filtration
- Air Stripping
- Flocculation
- Iron Removal
- Ultrafiltration (UF)
- Oxidation (O_3, $KMnO_4$)
- Disinfection (Cl_2, UV)

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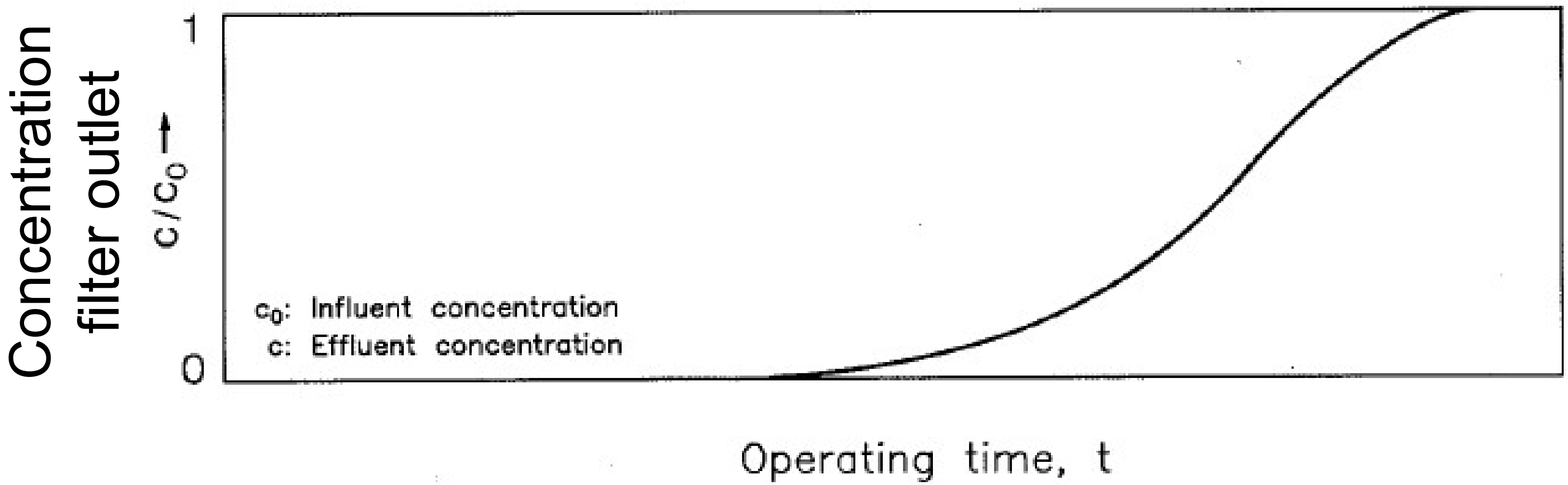
AKTIVATED CARBON FILTRATION

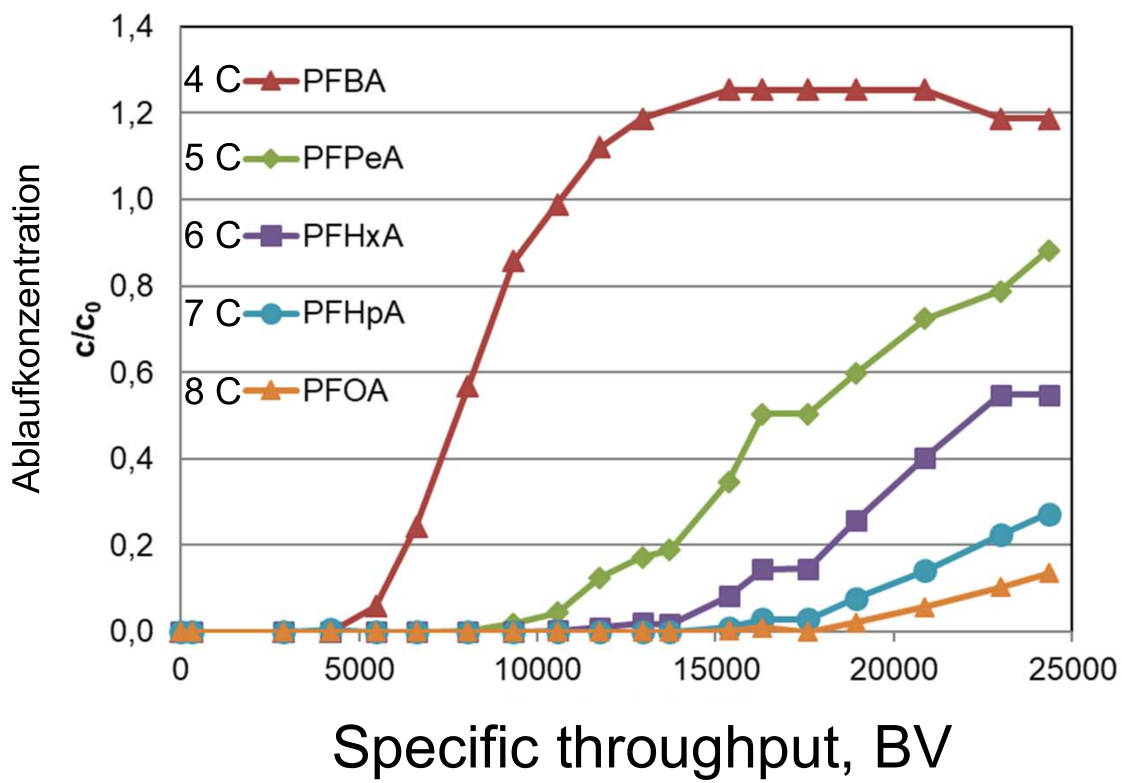
- Removal of every substance = Breakthrough curve



- Start of breakthrough depends on various factors,
  ⇨ mainly on **adsorption behaviour of the selected substance**

HS0

PFAS: DIFFERENT LEVELS OF ADSORBABILITY



- Short chain carboxylic PFAS are much more difficult to remove

⇨ If short chain PFAS have to be removed, frequent AC changes are necessary

⇨ Type of PFAS contamination is important

TZW

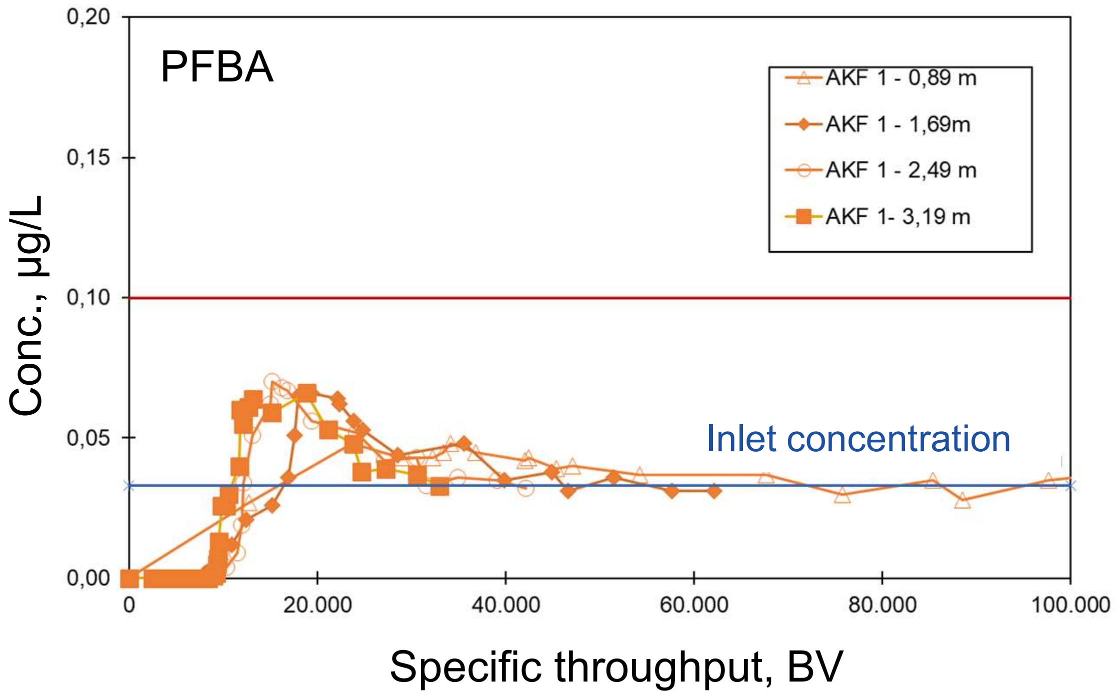
Slide 5

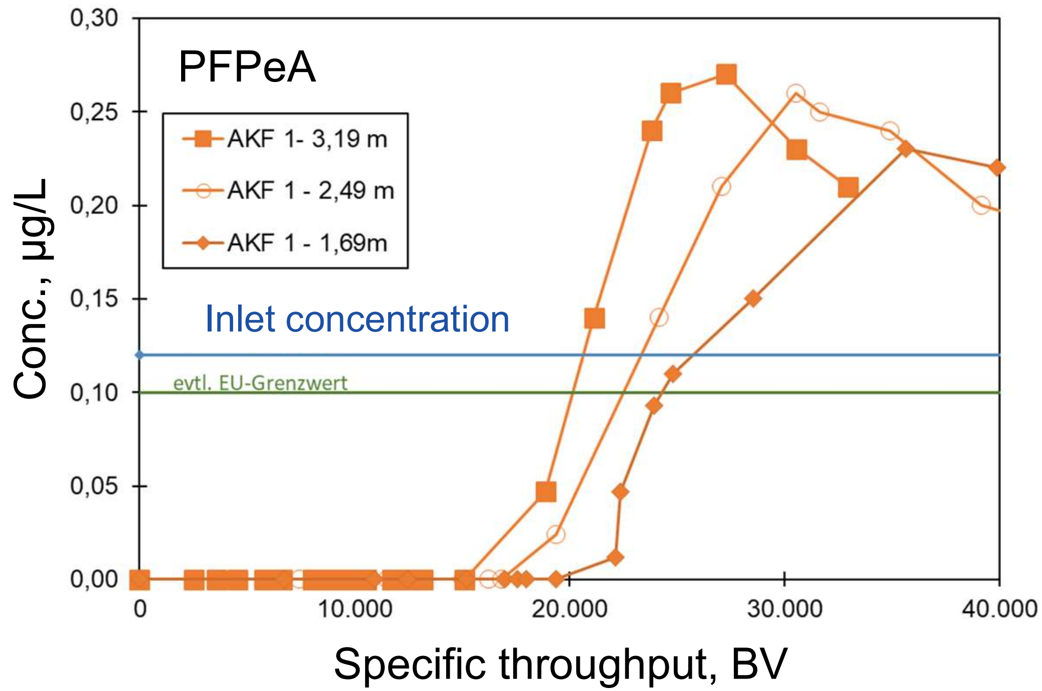
HS0 Should it be short chain carboxylic acids? Rather than PFAS

"If short chain PFAS need to be removed, the AC filter needs to be changed frequently"
Hale, Sarah, 2024-06-11T10:43:10.936

PROBLEM WITH SHORT CHAIN PFCA

Chromatography effect due to substance **replacement**





PFCA…perfluorated carboxylic acids HS0

TZW

Slide 6

HS0 Perfluoroalkyl carboxylic acids

Not perfluorated ......
Hale, Sarah, 2024-06-11T10:43:59.782

PFAS FATE AFTER ADSORPTION

- After AC replacement ⇨ thermal treatment
  - Combustion
  - Reactivation and Reuse
- Total destruction of PFAS ⇨ sufficient temperature and time
- Transformation into fluoride (F^-)

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HS0

GENERAL TREATMENT OPTIONS (GROUNDWATER, WASTEWATER, …)

Process engineering grouping:

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

Riegel, M., Egner, S., Sacher, S.: Review of water treatment systems for PFAS removal. Concawe Report no. 14/20 (2020)

Slide 8

HS0 https://www.concawe.eu/wp-content/uploads/Rpt_24-8.pdf

This is a nice report too! See who wrote it 😆

Hale, Sarah, 2024-06-11T10:45:22.038

HS0

1. ADSORPTION

- Activated carbon
- Ion exchange (single use)
- Other materials (modified organo-clay „FluoroSorb“)
- Material mixtures

Marco Müller

Björn Dinges

Fiona Rückbeil

Ronit Erlitzki

Challenges:

- High selectivity and capacity for PFAS
- Short-chain PFAS are difficult to adsorb
- Competition with other water constituents (DOC or sulphate)

Symposium Presentations

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Slide 9

HS0

I would change Ronits to "Full scale results"
Not sure I get what mixtures are
Hale, Sarah, 2024-06-11T10:47:44.502

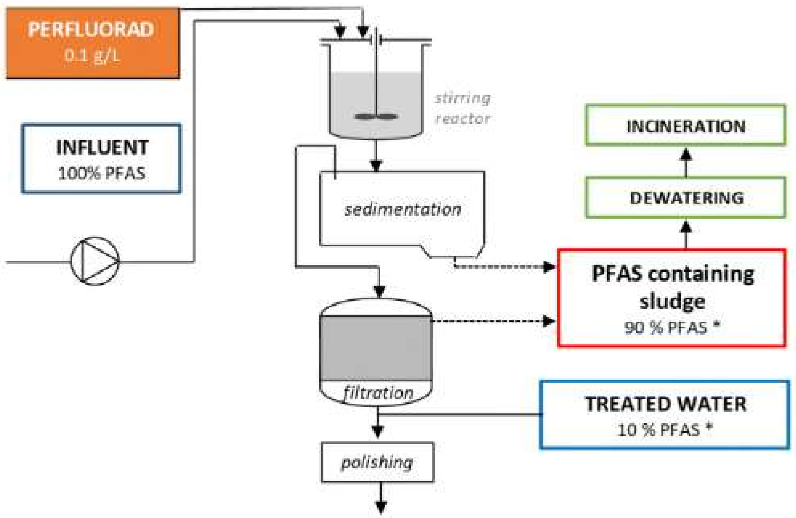
HS0

2. FLOCCULATION

Providers are (for example):

- PerfluorAd
- InSite

- Pre-Treatment
- Longer operation times for downstream AC filters



- Only for use in Groundwater remediation
- Flocculation chemicals not suitable for use in drinking water
- PFAS-containing flocculation sludge
  - Landfilling
  - Incineration

TZW

Slide 10

HS0 "Flocculants are not suitable for use....."

Also what is flocculation sludge? Is it PFAS contaminated sludge where a flocculant has been added?
Hale, Sarah, 2024-06-11T10:49:29.648

3. LIQUID-LIQUID SEPARATION

- Reverse Osmosis / Nanofiltration
- Ion exchange (including regeneration) — Lukas Lesmeister
- Activated carbon (including controlled desorption) — Anett Georgi
- Foam fractionation — Helena Hinrichsen
- Distillation

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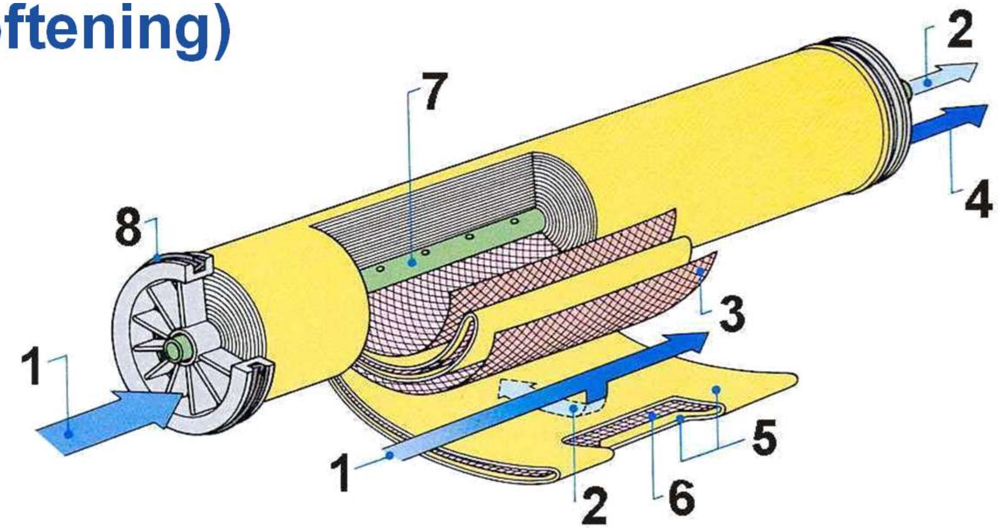
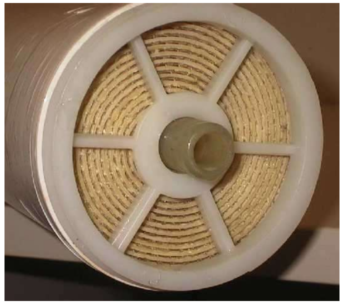
TREATMENT WITH REVERSE OSMOSIS (RO)

Primary purpose: Desalination (softening)

- ‘Pore diameter’ approx. 0.1 nm
- Pressure difference: approx. 8 bar
- Retention of
  - dissolved salts
  - almost all water constituents
- Permeate = ‘distilled’ water
- = Separation process
  - Permeate: free of ‘all’ ingredients
  - Concentrate: contains all ingredients



Quelle: Toray



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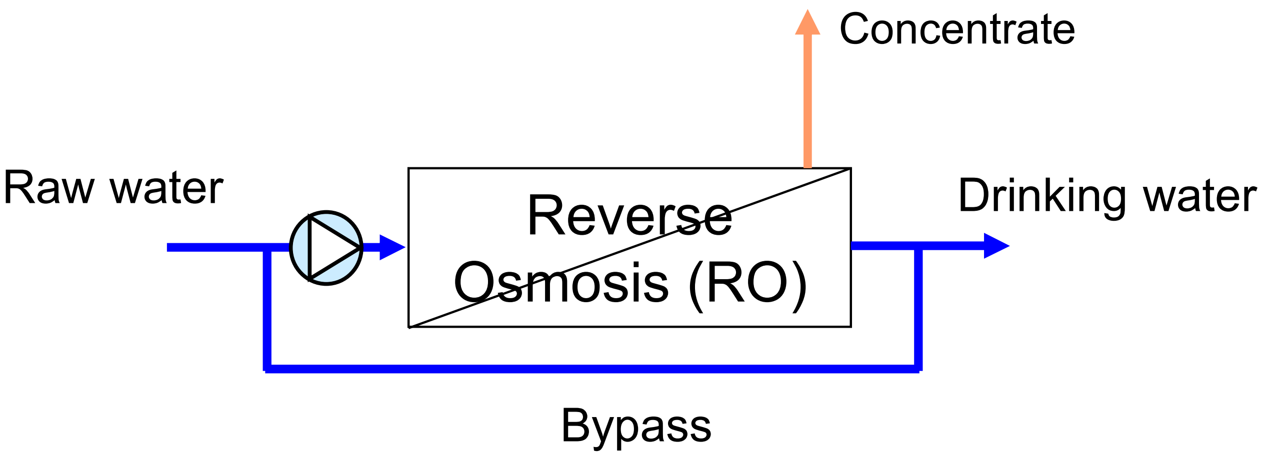
HS0

PFAS-ELIMINATION WITH RO

- Reverse osmosis removes 100 % of PFAS
- Use of RO for softening: only in bypass mode
- Removal in bypass: 0 %
- Bypass share: approx. 50 %
- **Total PFAS removal: 50 %**



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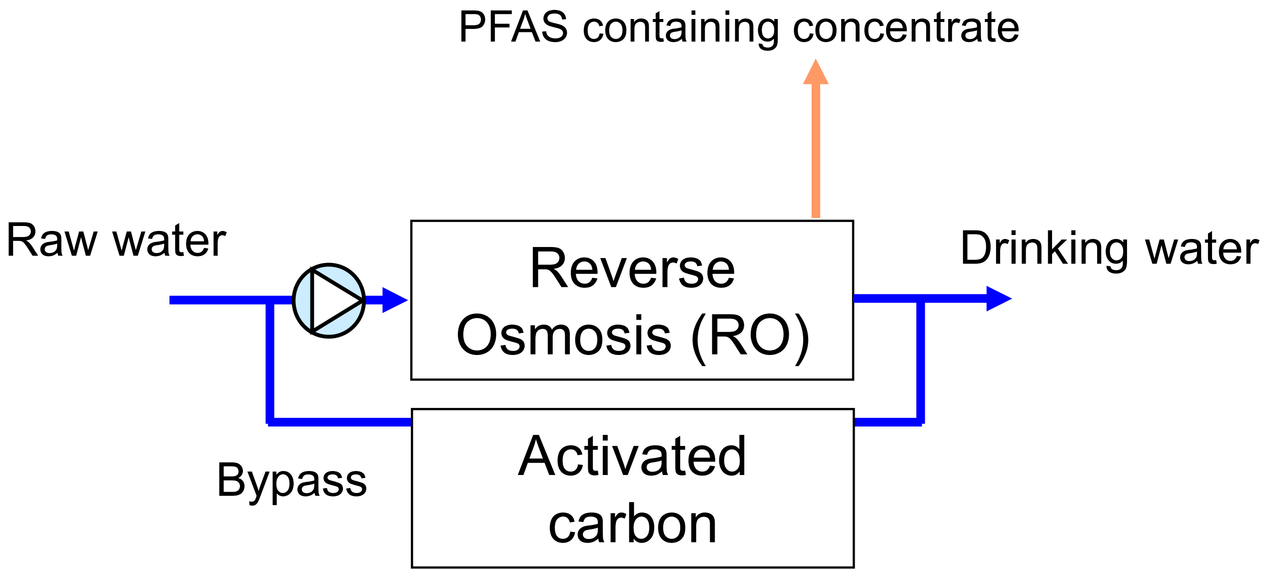
Slide 13

HS0 You can remove the - between PFAS and elimination
Hale, Sarah, 2024-06-11T10:50:23.999

INCREASING THE REMOVAL RATE



- Bypass treatment using activated carbon
- Full stream treatment with RO

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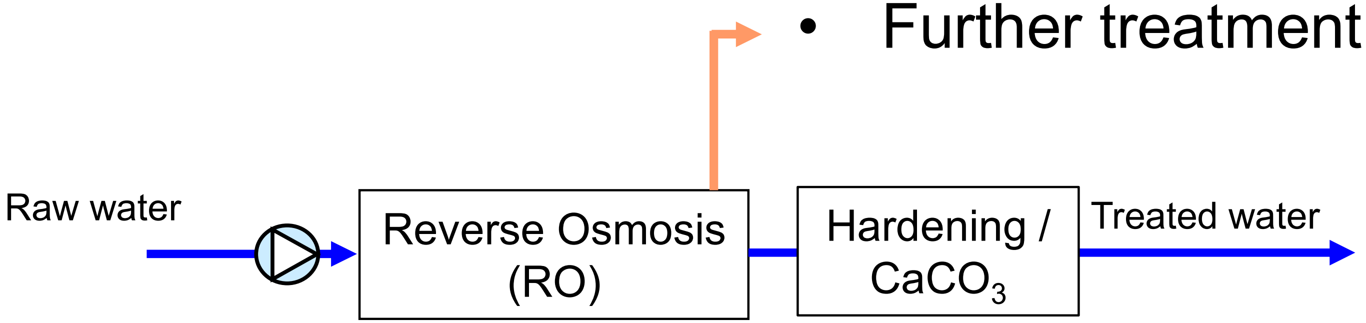
FULL STREAM TREATMENT

PFAS containing concentrate

- 20 % of the raw water volume
- Further treatment

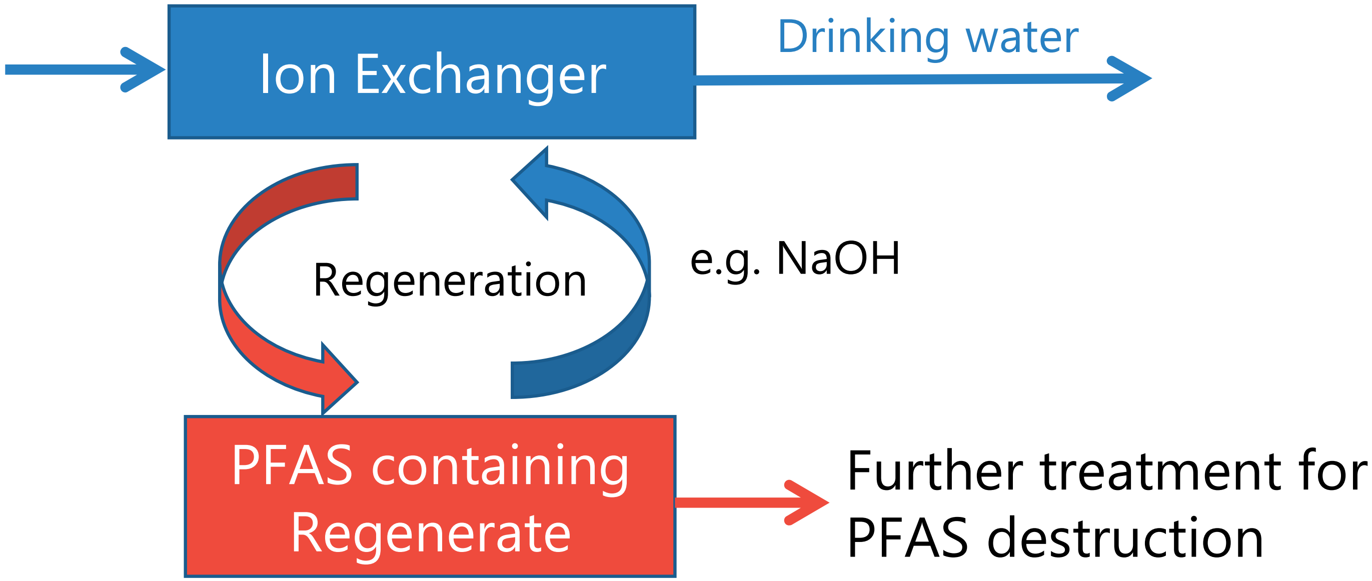


Additional water treatment for hardening

Higher water demand (20 %)

HS0

ION EXCHANGER INCLUDING REGENERATION



Problem: Regeneration of well absorbable long chain PFAS only possible using organic solvents

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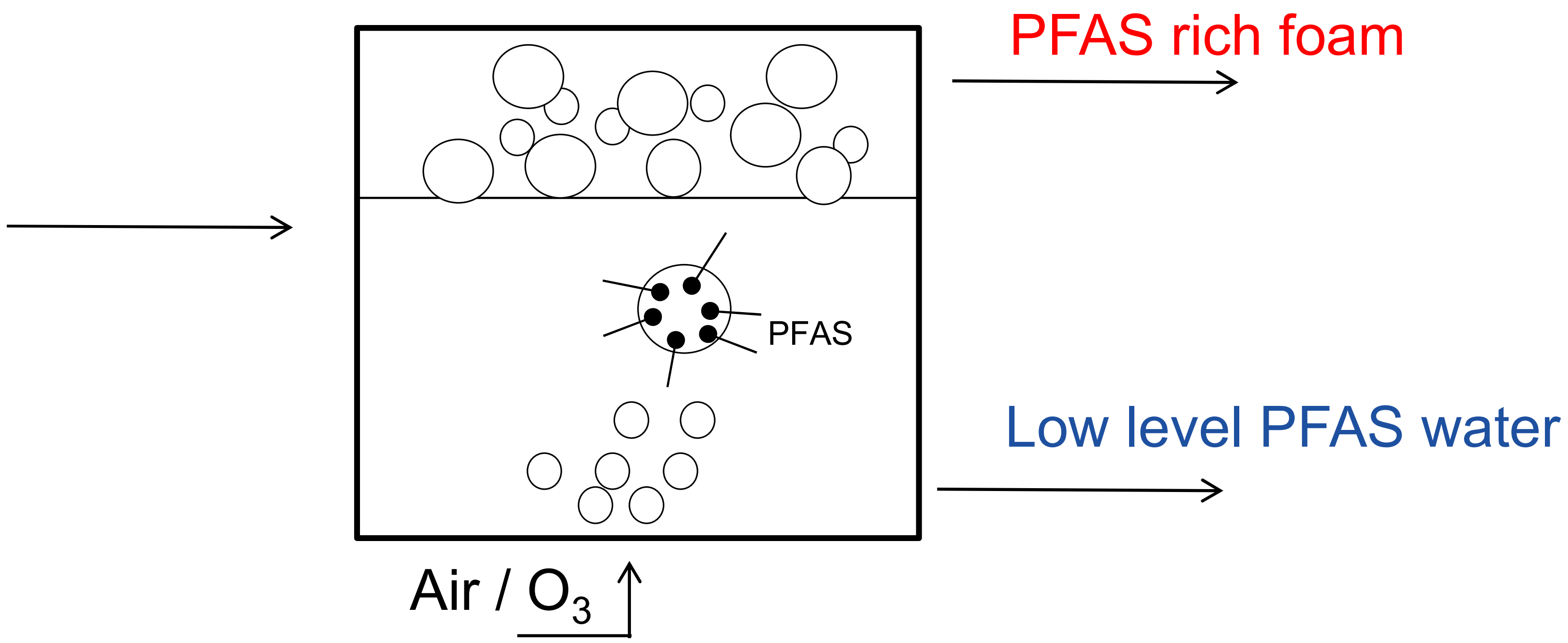
Slide 16

HS0 Problem: Regeneration of highly adsorbable....
Hale, Sarah, 2024-06-11T10:51:09.309

FOAM FRACTIONATION



- separation mechanism due to surfactant properties of PFAS
- *ex-situ* (reactor) and *in-situ* (well, only with air)
- O_3: Oxidation of precursors to PFAS

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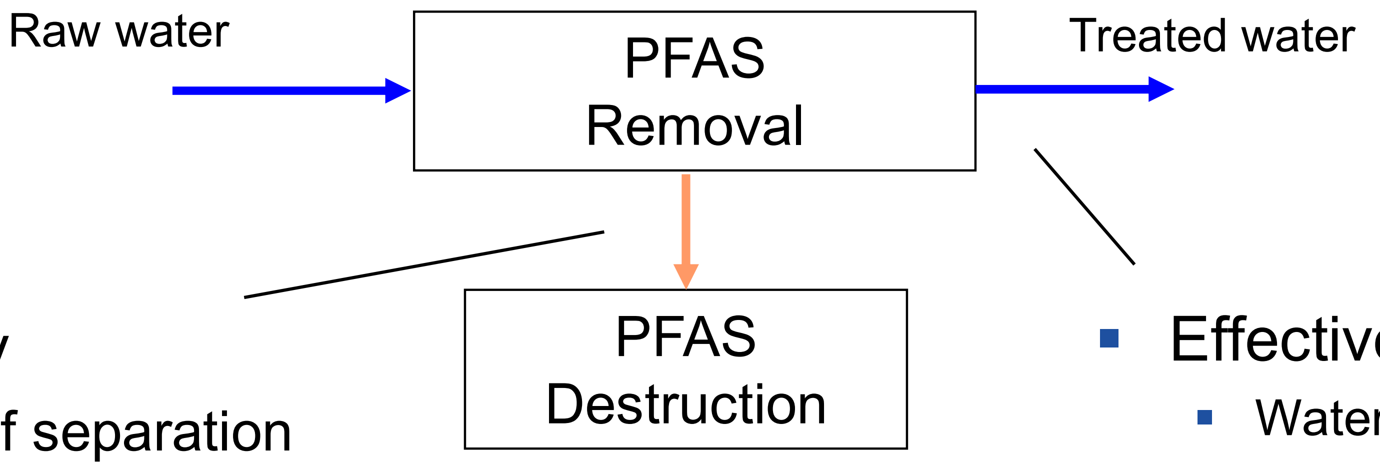
GENERAL EVALATION OF LIQUID-LIQUID SEPARATION



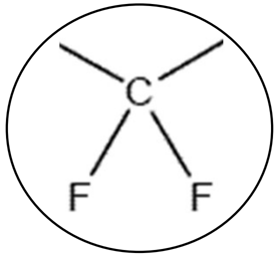
- Efficiency
  - Yield of separation processes
  - Energy required for destruction

- Effectiveness
  - Water quality, PFAS concentration in treated water

4. DESTRUCTION

Barbara Behrendt-Fryda
& Lara Stelmaszyk

- Electrochemical Oxidation / Degradation
- Sono-chemistry
- Oxidation processes (AOP using sulphate radicals)
- Plasma destruction
- Incineration



- C-F-bond: very stable

- High energy costs
- Pre-concentration necessary (liquid-liquid separation)
- By-products

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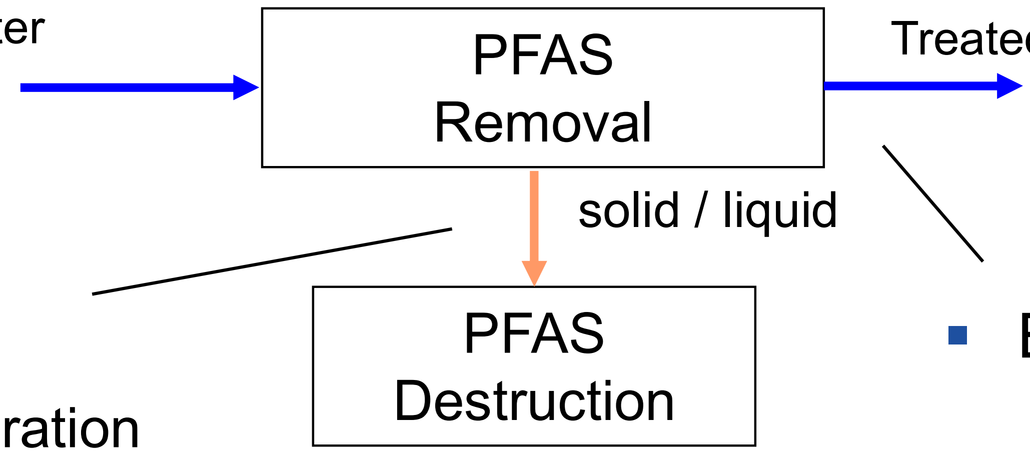
CONCLUSTIONS OF PFAS ELIMINATION OUT OF WATER



- Efficiency
  - Yield of separation processes or operation time and costs by adsorption
  - Energy required for destruction

- Effectiveness
  - Water quality, PFAS concentration in treated water

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Using GAC for PFAS & Reactivation

Product Development for best results and Mineralization of PFAS

Marco Müller – Head of Activated Carbon Application & Quality Assurance

Agenda

- Short introduction into activated carbon
- Product Development for best results against PFAS
- Results on the most important, short chain length substances
- Reactivation of spend carbon
- Mineralize PFAS during the reactivation

HYDRAFFIN®

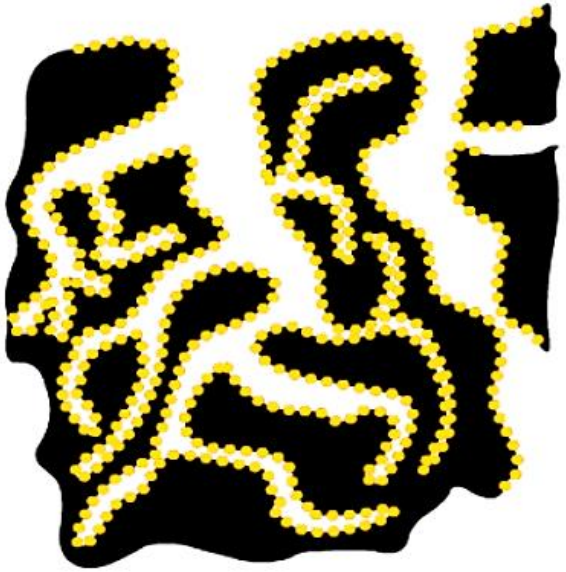
granular & powdered types for efficient treatment of all types of water

Characteristics of Activated Carbon

Main characteristics in water applications

- Iodine number (mg/g)
- Apparent density after backwash and drainage (kg/m^3)
- Pore size distribution (proportion of micro-, meso- and macropores)
- Granulation (mm) or (mesh)
- Chlorine half value length (cm)
- Hardness (wt.%)
- .....

Iodine number



Pore radius
0,25 nm

Product Portfolio at a glance

The main granulated **Hydraffin**® products for water treatment according customer requirements

Hydraffin®	CC 8x30	CC 8x30 plus	XC 30	A 8x30	30 N
Application	Drinking water			Waste water	
COD	●	●	●●●	●●●	●●
BTX / PAH	●●●	●●●	●●●	●●	●●
Halogenated HC	●●●	●●	●●	●	●●
Chlorine & Ozone	●●●	●●	●●	●	●●
Micro pollutants	●	●●	●●	●●●	●
Odour & taste	●●●	●●●	●●●	●	●●
PFAS	●	●●●●*	●●	●●●●*	●●

* Specially developed for the adsorption of PFAS

DONAU CARBON

PFAS - new development Hydraffin CC 8x30 plus

PFAS at a glance

- The danger of this group of substances with its over **10,000** different individual substances is becoming more and more an issue. Per- and polyfluorinated alkyl compounds (PFAS) are suspected of harming people and the environment. PFAS are manufactured industrially and can be found in many everyday items such as textiles, carpets, cosmetics and firefighting foams. They enter the environment during production, further processing, use and disposal. Due to the knowledge of their **influence on people's health**, the demand for high-quality activated carbons remains high.

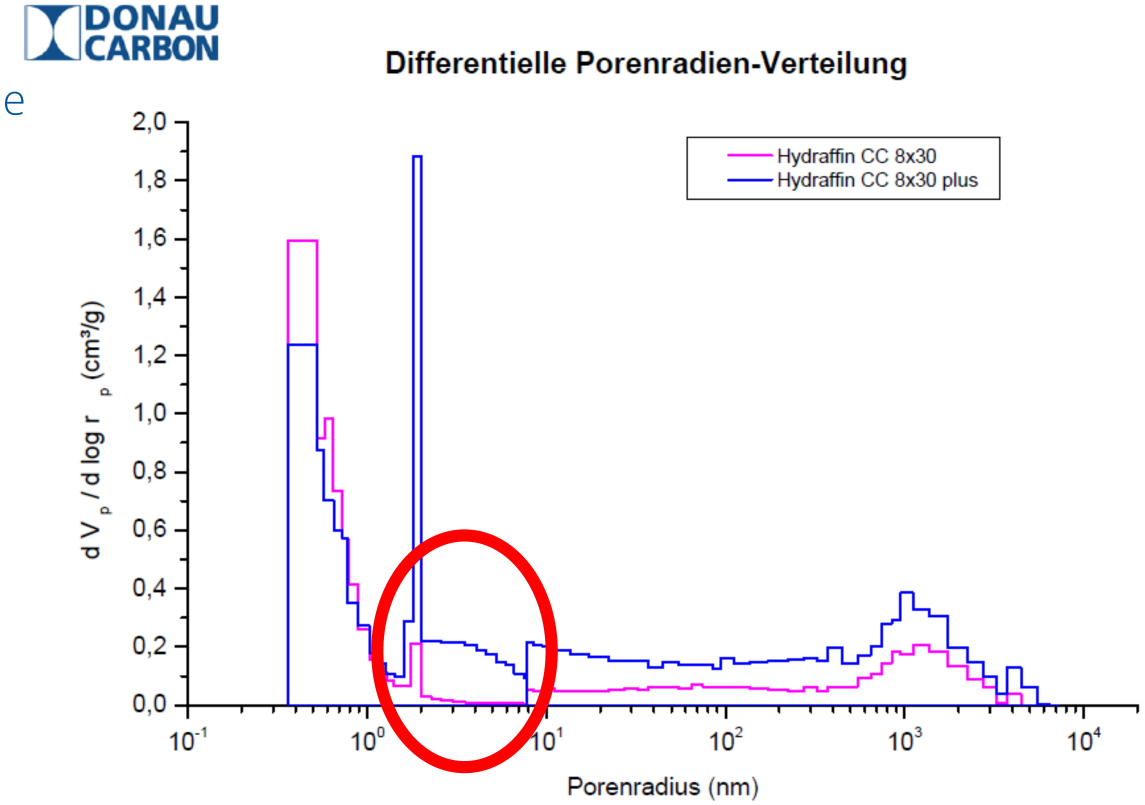
Substance Shortname	Molecular formula	perfluorinated chain length
PFBA	C4HO2F7	short
PFPeA	C5HO2F9	short
PFHxA	C6HO2F11	short
PFHpA	C7HO2F13	short
PFOA	C8HO2F15	long
PFNA	C9HO2F17	long
PFDA	C10HO2F19	long
PFBS	C4HO3F9S	short
PFHxS	C6HO3F13S	long
PFHpS	C7HO3F15S	long
PFOS	C8HO3F17S	long

PFAS - new development Hydraffin CC 8x30 plus

Comparison of the pore size distribution of the new development

Hydraffin CC 8x30 plus vs. Hydraffin CC 8x30

→ Conclusion: Pore size matters!



Aktivkohle	Rohstoff	BET	Porenvolumen	Mikroporen	Mesoporen	Makroporen
Hydraffin CC 8x30	Kokosnussschalen	1126	0,699	0,441	0,073	0,185
Hydraffin CC 8x30 plus	Kokosnussschalen	1158	0,824	0,446	0,153	0,225

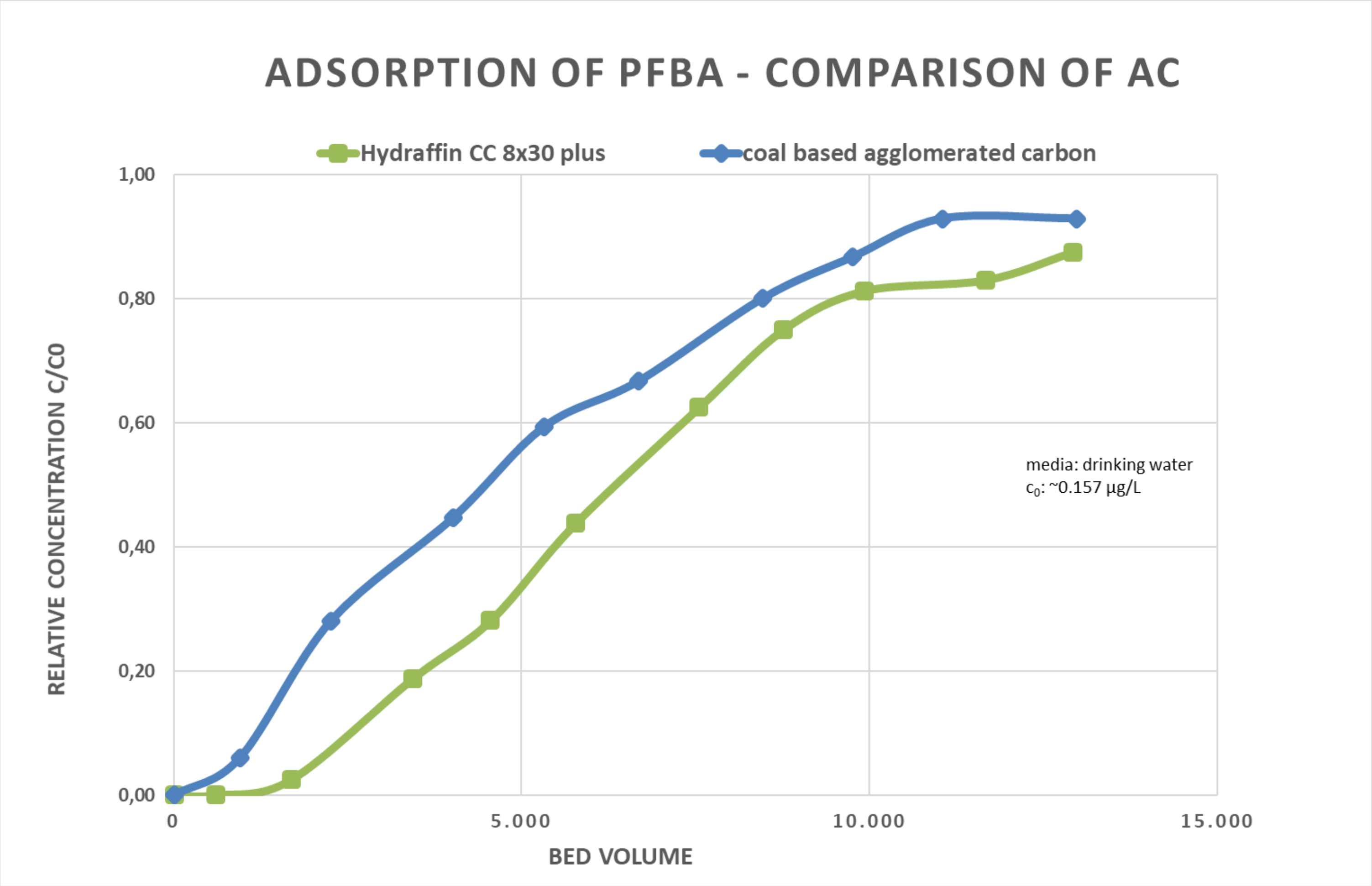
PFAS - new development Hydraffin CC 8x30 plus

- Drinking water

Sum PFAS-20:

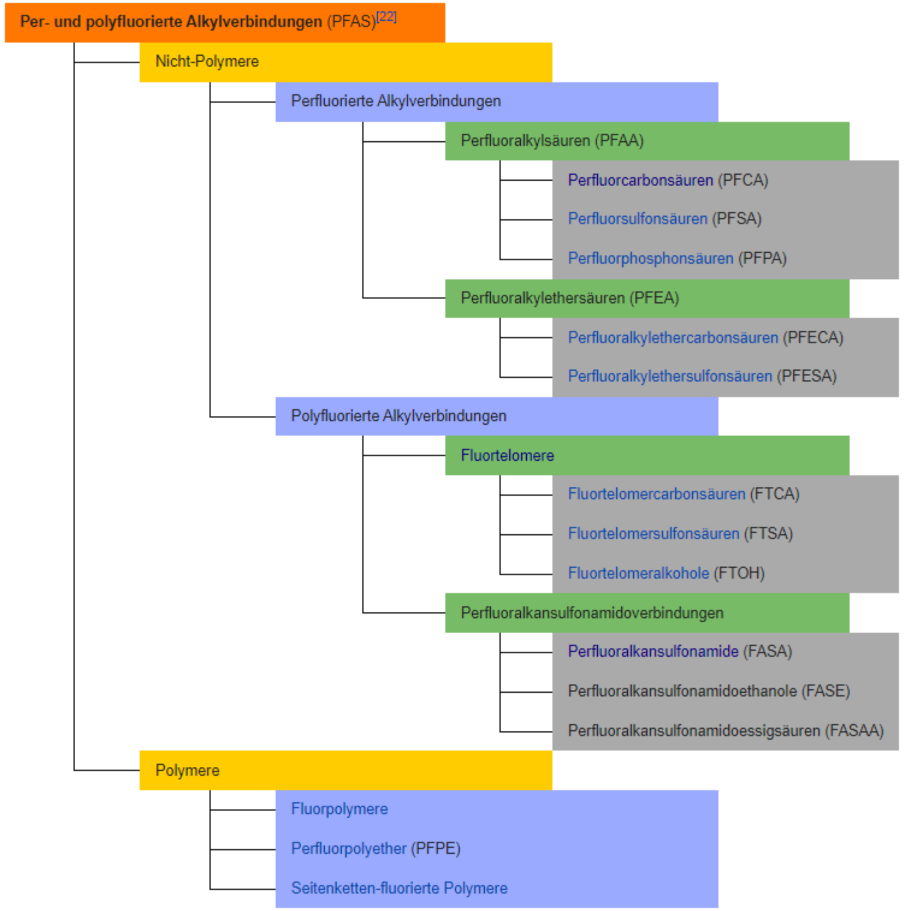
Limit: 100 ng/L

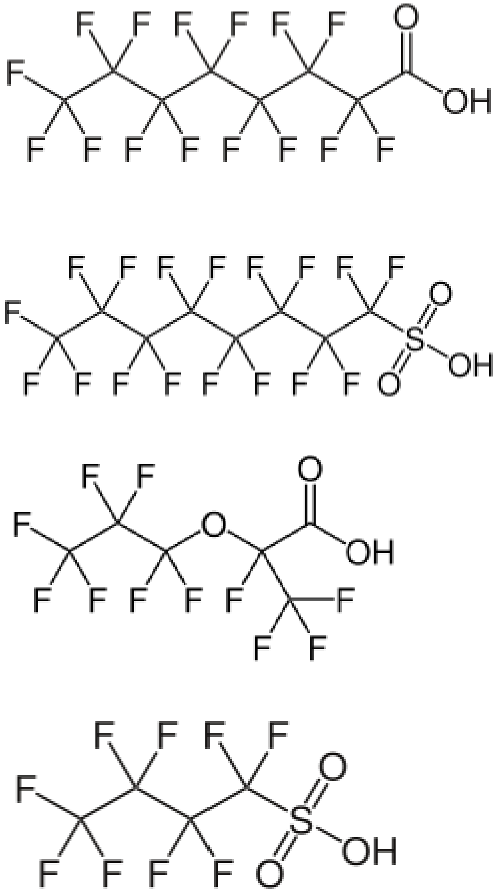
Start: 01/26



DONAU CARBON

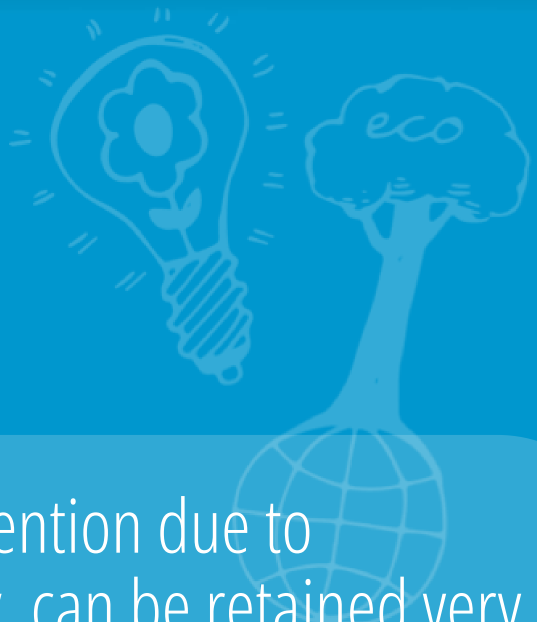
PFAS – reactivation of Hydraffin





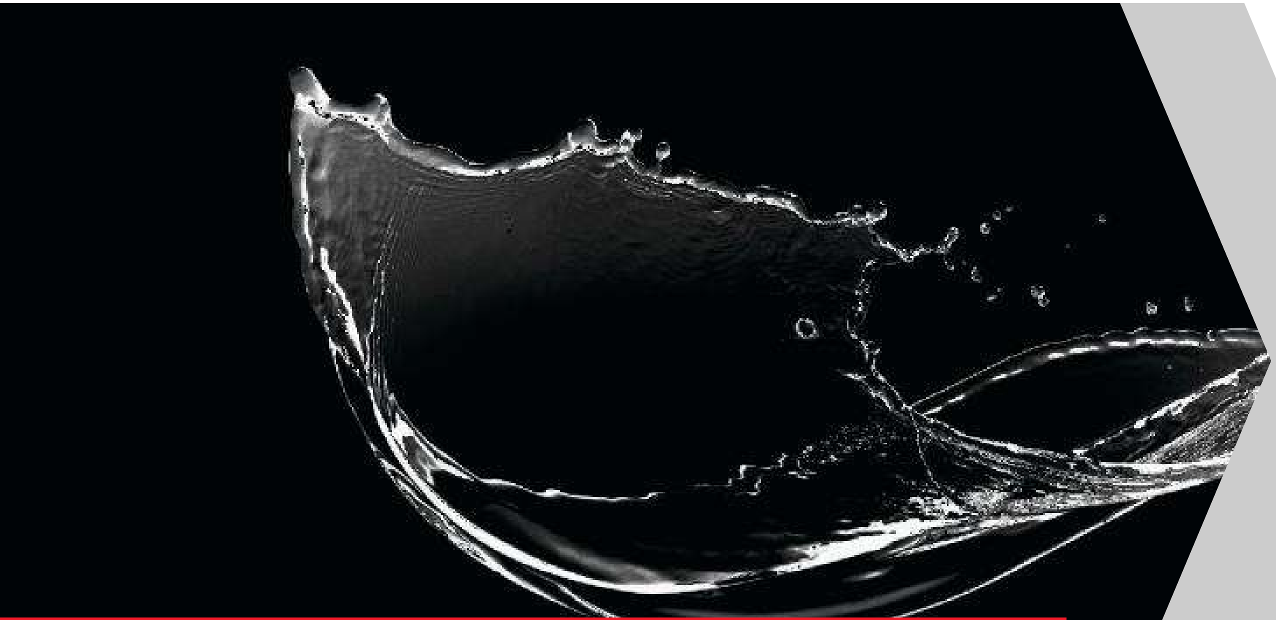
Shortname	PoP-Regulation (EU) 2019/1021
PFOA	1 mg/kg
PFOS	50 mg/kg
HFPO-DA (GenX)	k. A.
PFHxS	1 mg/kg

Conclusion



- Short-chain PFAS, which are the focus of attention due to coadsorption and lower adsorption capacity, can be retained very well using **Hydraffin CC 8x30 plus**.
- **Reactivation** frees the **Hydraffin** activated carbon from PFAS and demineralises it so that the "chemical of the century" is removed from the environment

DONAU CARBON



Lewatit® ion exchange resins for PFAS remediation: Challenges & Removal

Dipl.-Ing. Björn Dinges, Technical Marketing Manager, LANXESS Deutschland GmbH

ZerOPM Rastatt, June 12, 2024

Versatile specialists – comprehensive product portfolio provides advanced solutions

LANXESS
Energizing Chemistry

Products and brands

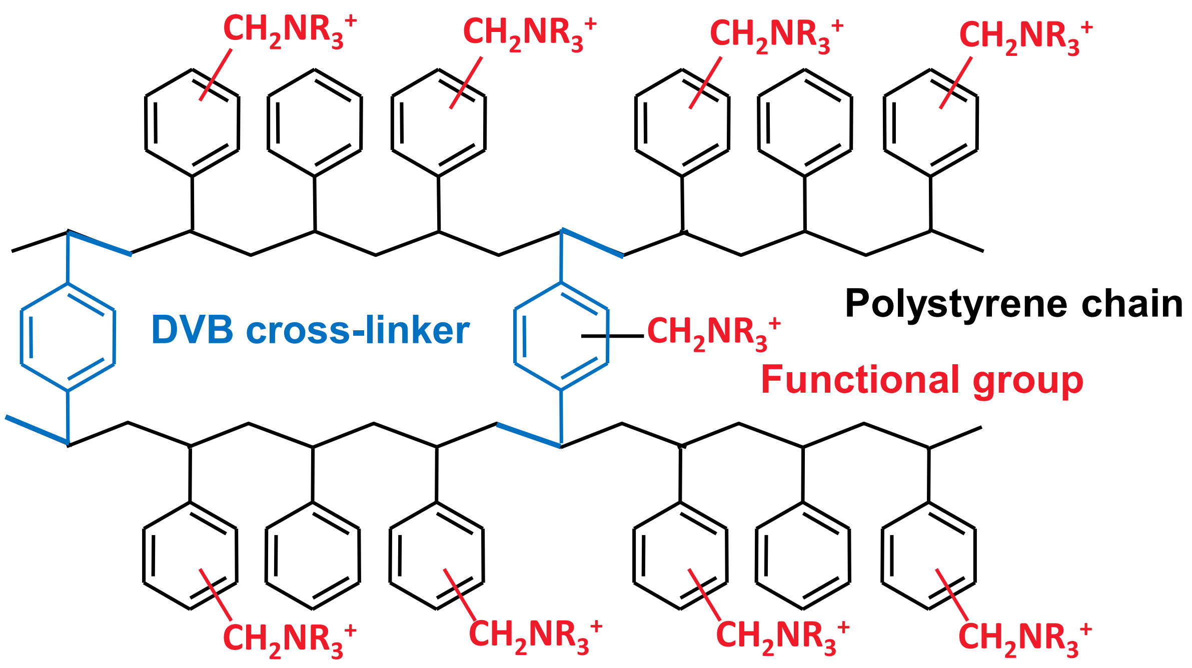
Lewatit®; Lewatit® Scopeblue	▪ Ion exchange resins, adsorbers, and functional polymers for use in many industries and applications
Bayoxide®	▪ Granular iron oxide adsorbers for water treatment
LewaPlus®	▪ Software for designing and optimizing ion exchange resin plants

Customer industries

The general structure of ion exchange resins

LANXESS
Energizing Chemistry

Structure of IX resins made from a styrene-DVB copolymer

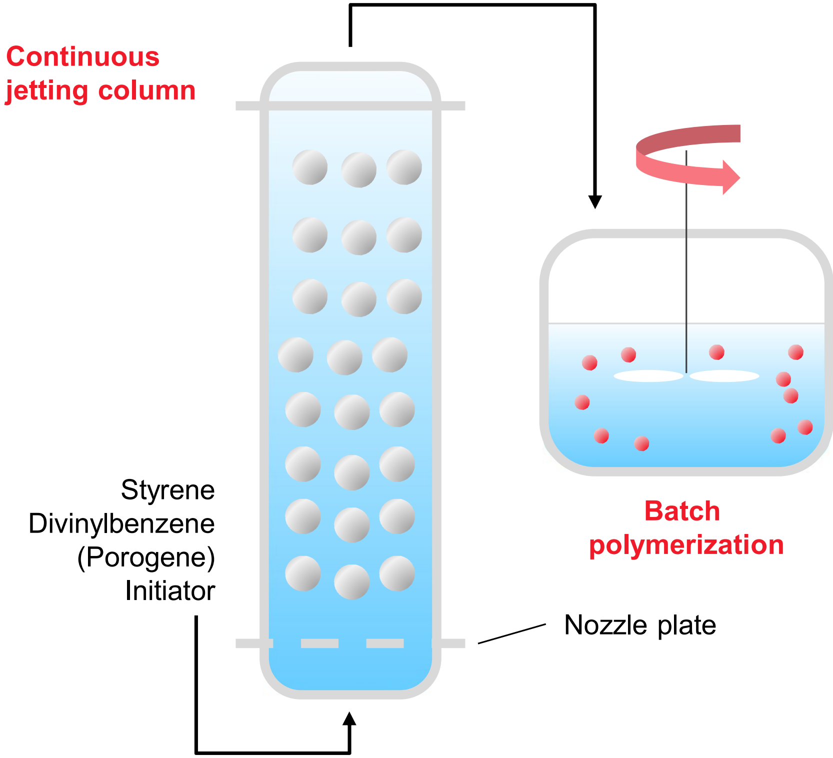


- Synthetic ion exchange beads consist of an organic copolymer material
- Polymer chains are linked to form a three-dimensional network
- Cross-linker connects different polymer chains to enhance physical strength
- Each monomer unit carries a functional group

Monodisperse droplet generation by jetting process

Stable scaffolds for demanding metals processing applications!

Formation of monodisperse droplets



Description

- Continuous process
- Raw materials are fed through a nozzle plate at the bottom of the column
- The resulting monomer jet is chopped into droplets of the same size
- Particle size can be controlled by adjustment of the whole width of the nozzle plate
- The droplets formed at the bottom start to encapsulate as they proceed to the column head
- Polymerization of the monodisperse encapsulated droplets is completed afterwards

Bead size distribution: HD vs. MD

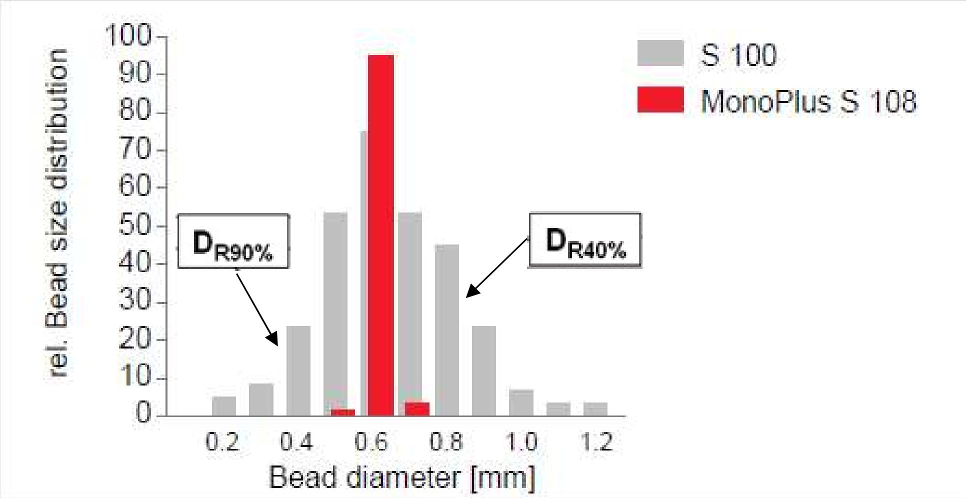
A flexible portfolio of solutions for critical separation challenges

Physical Properties

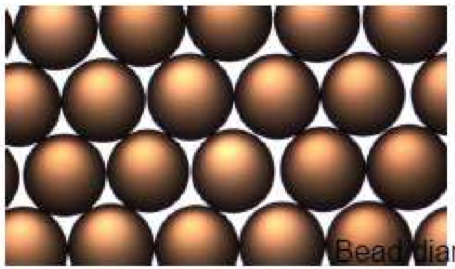
- **Critical parameters are:**
  - **Diameter d [mm]**
  - **Fines d < 0.315 [mm]**
  - **Uniformity coefficient UC**

effective bead size = $D_{R90\%}$	= 0,52 mm	= 0,58 mm
Uniformity coefficient = $D_{R40\%}/D_{R90\%}$	= 0,72mm / 0,52 mm 1,38 (HD)	= 0,62 mm / 0,58 mm 1,07 < 1,1 (MD)

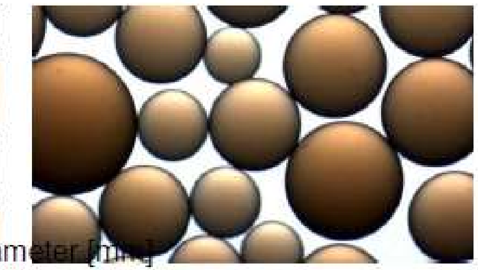
The UC is an indicator how homogenious the beads are. UC<1.1 means very low content of fines that would block the colomn nozzles and low content of bigger beads that are less stabile and that cause uneven loading profile.



Lewatit® MonoPlus S 108



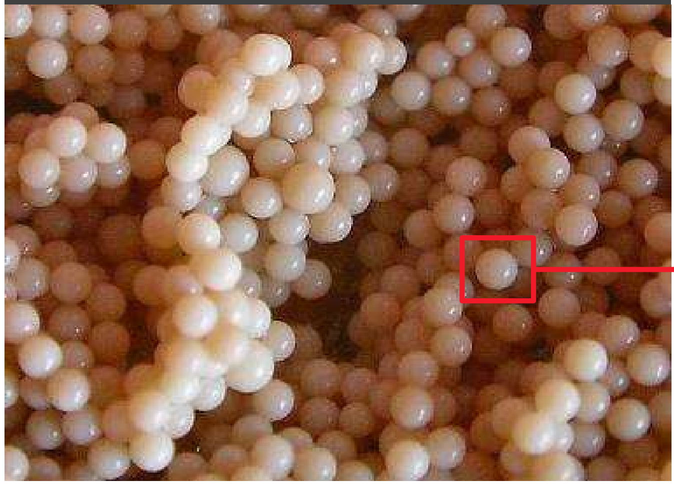
Lewatit® S 100



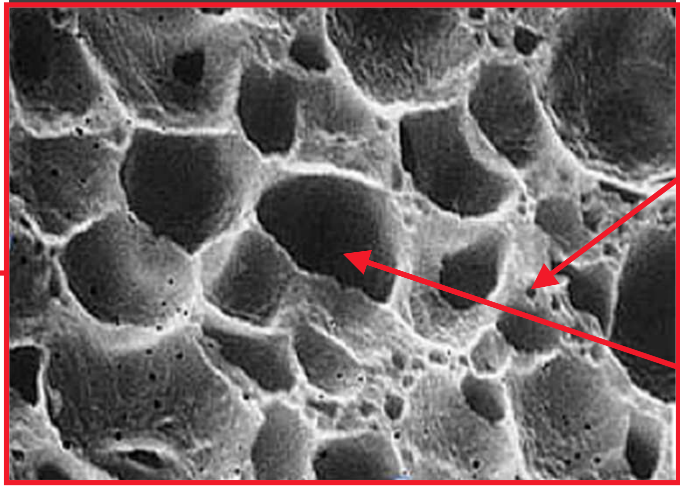
The structure of macroporous resins

Small opaque beads are actually of a highly permeable sponge-like structure

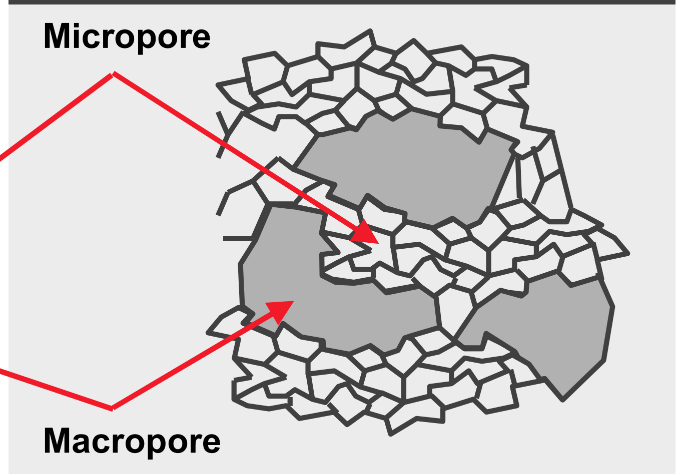
Microscopic image



SEM

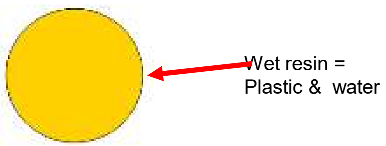


Schematic structure

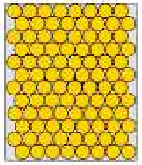


Ion Exchange resin terminology

Physical Properties

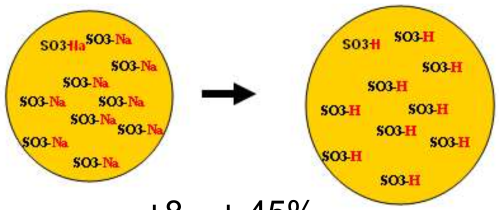


Density = $\frac{\text{mass of a bead [g]}}{\text{Bead volume [ml]}}$



Bulk Density = $\frac{\text{mass of one liter of beads}}{\text{one liter}}$

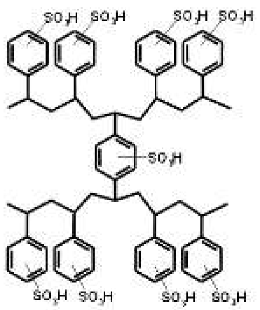
Volume change



+8…+ 45%

- **The higher the resin density the more polymer is sold. With this high crosslinkage (low water retention) the resins swell less during operation and regeneration.**
- **Especially customers who order material in the swollen form have to take care when they compare total capacities of products.**

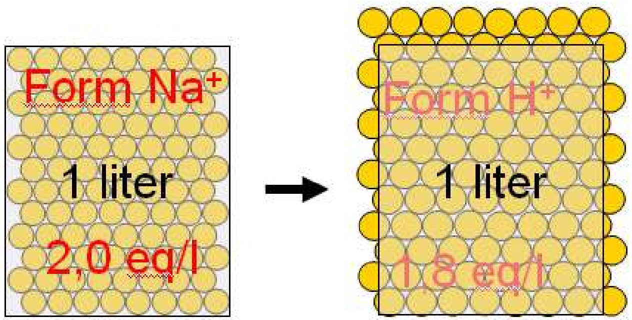
Crosslinkage

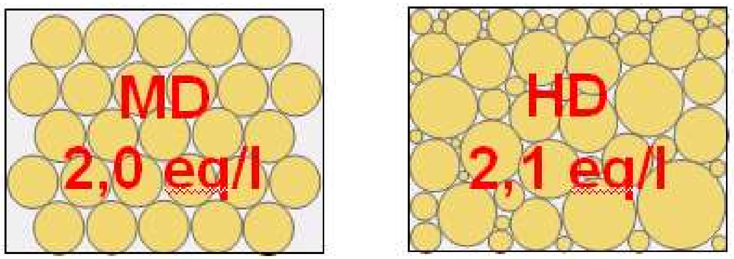


- **Crosslinkage range typical 4-20%**
- **Crosslinkers maintain the resin shape**
- **In non-oxidative media, resins cannot dissolve**
- **Dependant on solvant polarity, they either swell or shrink**

Ion Exchange Resin Terminology

Chemical Properties - Total Resin Capacity





- **Customers have to understand the relationship between the total amount of functional groups in the volumetric measured resin matrix (eq/ liter resin) and the delivered ionic form. In this example the strong acidic cation resin swells after acid regeneration by +8%, so the total capacity of the resin is reduced by -8%.**

- **Also important is the amount of fines, to avoid a blocking of the nozzles customer who order heterodisperse resin have to backwash the material more intensive. The small beads that affect the total resin capacity result have to be washed out and the real capacity of the material is lower.**

- **F.e. is the theoretical cupper capacity of Lewatit TP207:**

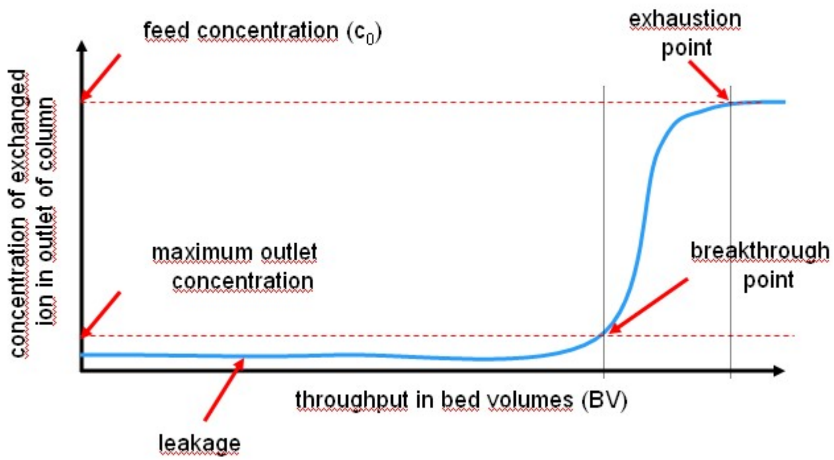
$$TC'(g/L) = \frac{TC\,(eq/L) * MG\,(g/mol)}{charge\,(eq/mol)} = \frac{2.2 * 65}{2} = 71.5\ g_{Cu}/l_{resin}$$

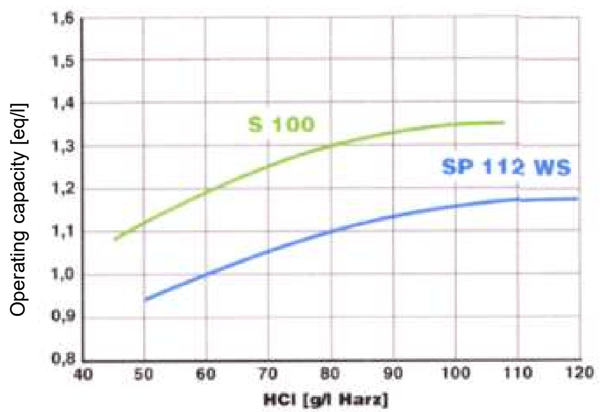
Basic Design Parameters

Chemical Properties - Operating Capacity

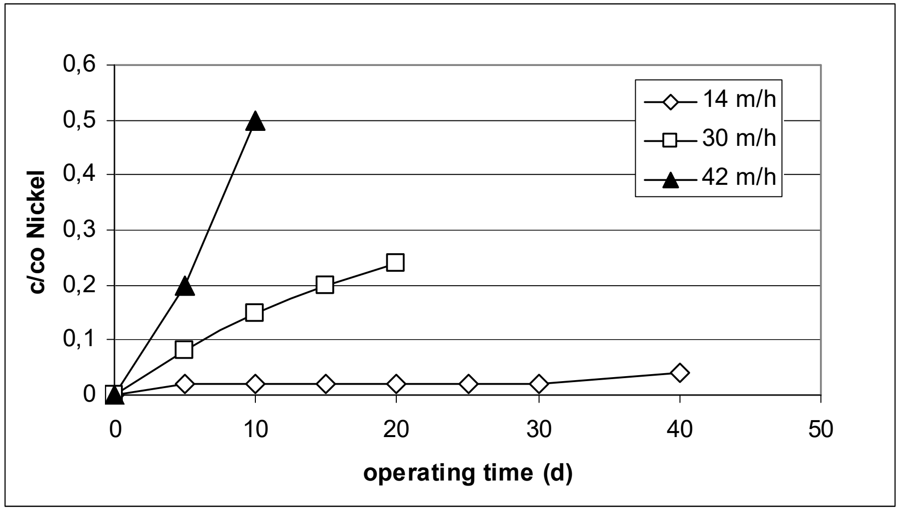
Parameters with influence on OC:

- **Total capacity of resin & resin age**
- **Feed concentration of removed species**
- **Competing ions**
- **Feed velocity**
- **pH**
- **Setting of break through point**
- **Hydrodynamics in filter**
- **Depth of regeneration**
- **Temperature**
- **Oxidative state of ion (Fe(II), Fe(III))**
- **Complexing agents in solution…**



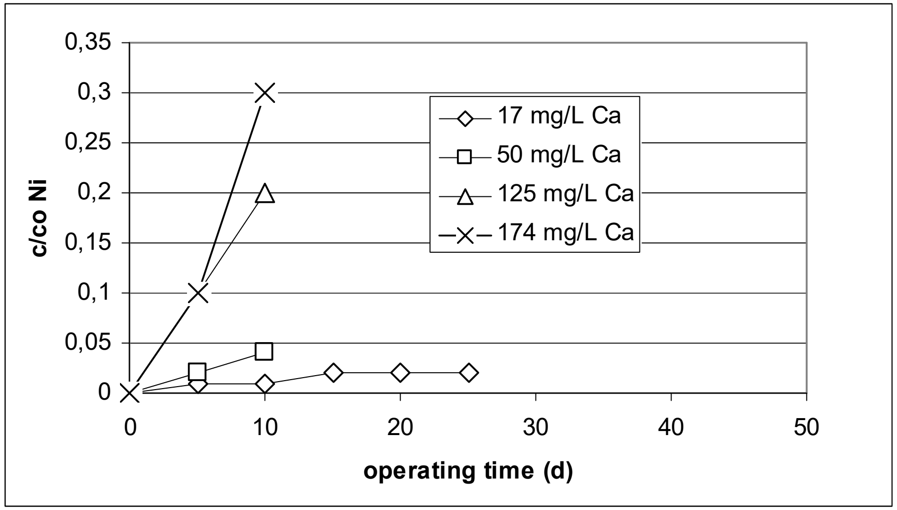


Influence of Velocity on breakthrough



IX= Lewatit TP 207; Co(Ni) = 120 - 153 µg/l, c(Ca) = 45 - 51 mg/L, pH = 7.5 - 7.9

Influence of Competing Ions on breakthrough



IX= Lewatit TP 207; Co(Ni) = 81 - 140 µg/l, c(Ca) = 45 - 51 mg/L, vF = 29 - 30 m/h, pH = 5.3 - 7.4

Basic Design Parameters

des Vorlagentextes zu bearbeiten

Pressure Loss

Specific pressure loss	(15 °C) approx. kPa*h/m²	1.0
Pressure loss	max. kPa	200

$$\Delta p\ [kPa] = h\ [m] \times v\ [m/h] \times F_V \times F_T \times F_R$$

- h = Resin bed depth [m]
- v = Linear velocity [m/h]
- F_V = Velocity factor [from diagram 1]
- F_T = Temperature factor [from diagram 2]
- F_R = Resin factor (specific pressure drop) from table 1 [kPa x m^{-2} x h]

Diagram 1 Velocity Factor

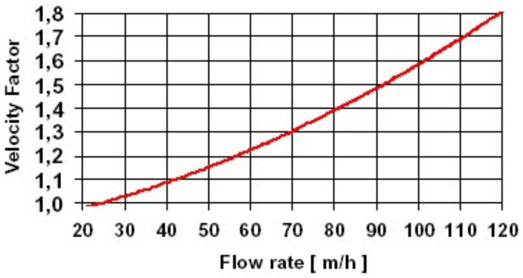
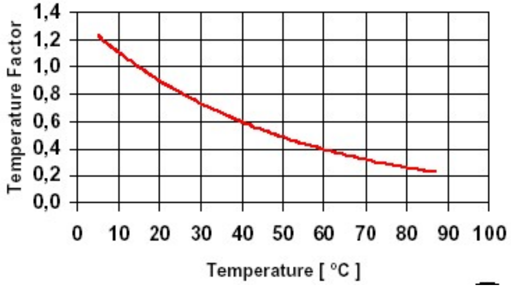
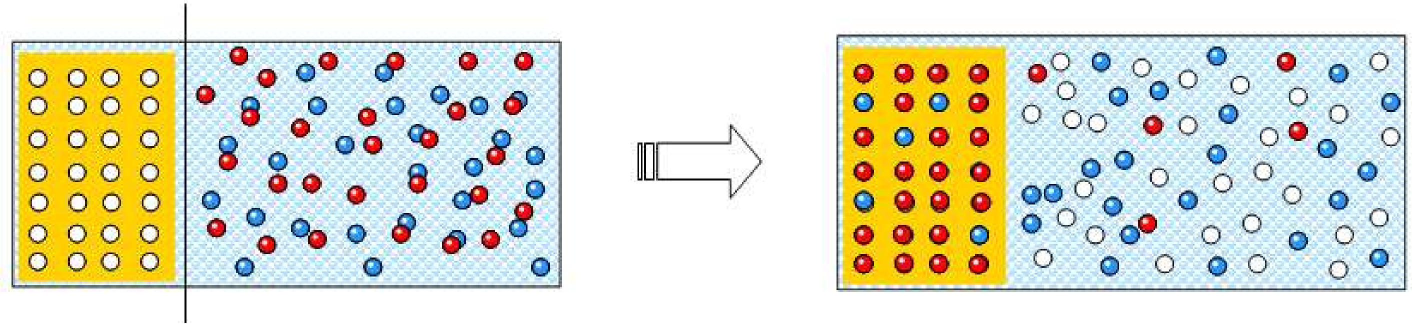


Diagram 2 Temperature Factor



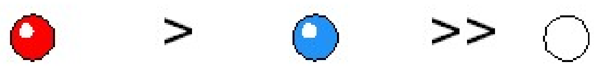
Ion Exchange Resin Terminology

Definition of Selectivity



- **Selectivity describes the tendency of certain ion species (e.g.) of being adsobed on an ion exchange material ( ) in comparison to other ionic species (e.g. ,)**

Selectivity Series:



Ion exchange resin terminology :Selectivity as…

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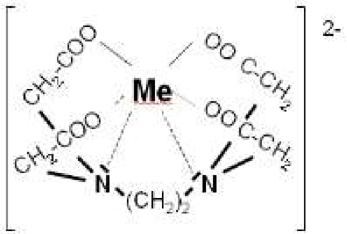
Energizing Chemistry

Complexation reaction (IDA resin)

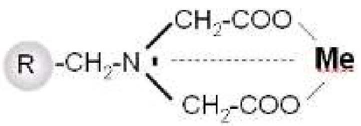
Homogenic reaction

Me^{2+} + $EDTA^{4-}$ ⇌



Heterogenic reaction

Me^{2+} + (R) -IDA^{2-} ⇌



Lewatit M+TP 207

Heavy metals, alkali earth metals

Fe^{3+}>Cu^{2+}> H^+> Hg^{2+} >Pb^{2+}>Ni^{2+}>Zn^{2+}>Cd^{2+}>Co^{2+}>Fe^{2+}>Mn^{2+}>>Ca^{2+}>Mg^{2+}>Sr^{2+}>Ba^{2+}>>> Alkalis

heavy metals > earth-alkali metals >>> alkali metals

For comparison the **SAC selectivity:**

● - SO_3Na

Ba^{2+}> Pb^{2+}> Sr^{2+}> Ca^{2+} >Ni^{2+}>Cd^{2+}> Cu^{2+} > Co^{2+}> Zn^{2+} >Fe^{2+}>Mg^{2+}>Mn^{2+}> Alkalis > H^+

earth-alkali metals > heavy metals > alkali metals > H^+

Precipitation reaction

Homogenic reaction

Me^{2+} + S^{2-} ⇌ MeS↓

Me^{2+} + 2 (R) -CH_2-S^- ⇌ ((R) -CH_2-$S)_2$ -Me

selectivity: heavy metals, noble metals

Heterogenic reaction

Me^{2+} + SO_4^{2-} ⇌ $MeSO_4$ ↓

Me^{2+} + (R) -SO_3^{2-} ⇌ (R) -SO_3 Me

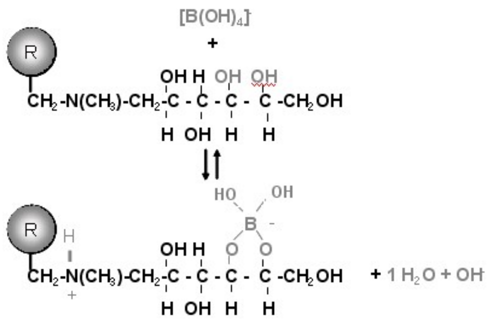
selectivity: earth alkali metals, lead, ….

condensation reaction

Homogenic reaction

$B(OH)_3$ + 3 EtOH ⇌ $B(OEt)_3$ + 3 H_2O

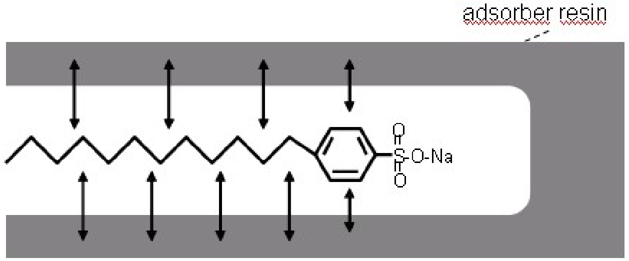
Heterogenic reaction



selectivity: boron, oxyanions, ….

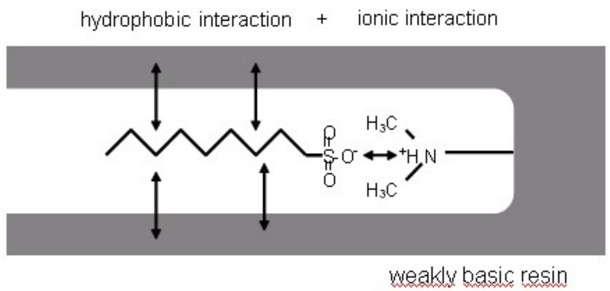
Ion exchange resin terminology : Selectivity as…

Hydrophilic interaction



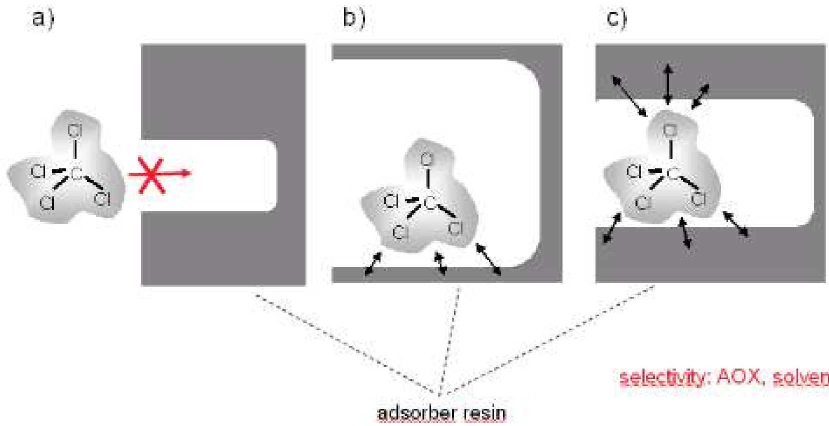
selectivity: surfactants, BTEX, …

Hydrophilic interaction



selectivity: surfactants, tannins, lignins …

Size exclusion



selectivity: AOX, solvents

Acid / Base reaction

Soft base likes to react with soft acid not with hard acids

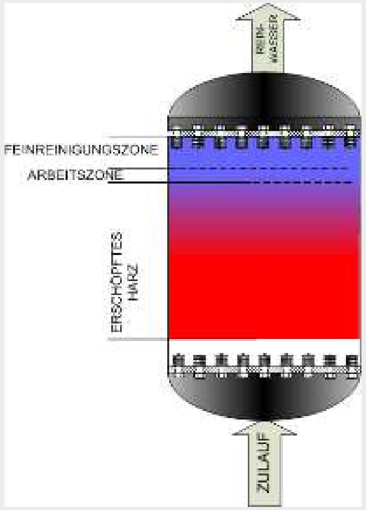
$$R\text{-}N(CH_3)_3Cl + NO_3^- \rightleftarrows R\text{-}N(CH_3)_3NO_3 + Cl^-$$

$$R\text{-}N(CH_2\text{-}CH_2\text{-}CH_3)_3Cl + NO_3^- \rightleftarrows R\text{-}N(CH_2\text{-}CH_2\text{-}CH_3)_3NO_3 + Cl^-$$

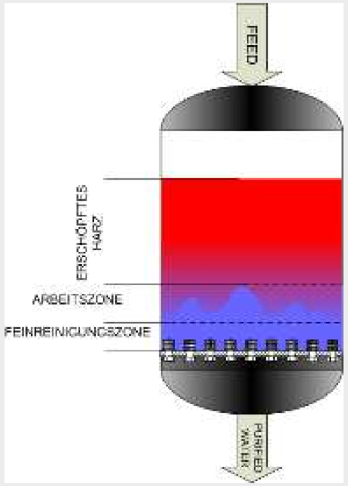
selectivity: perchlorate, nitrate, borate, iodide ….

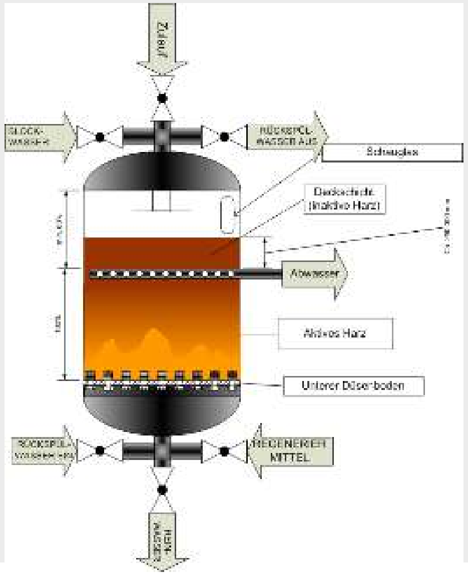
Vessel Technologies

Countercurrent



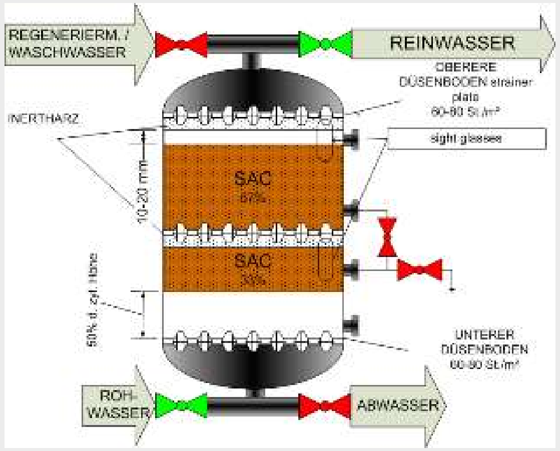
Cocurrent



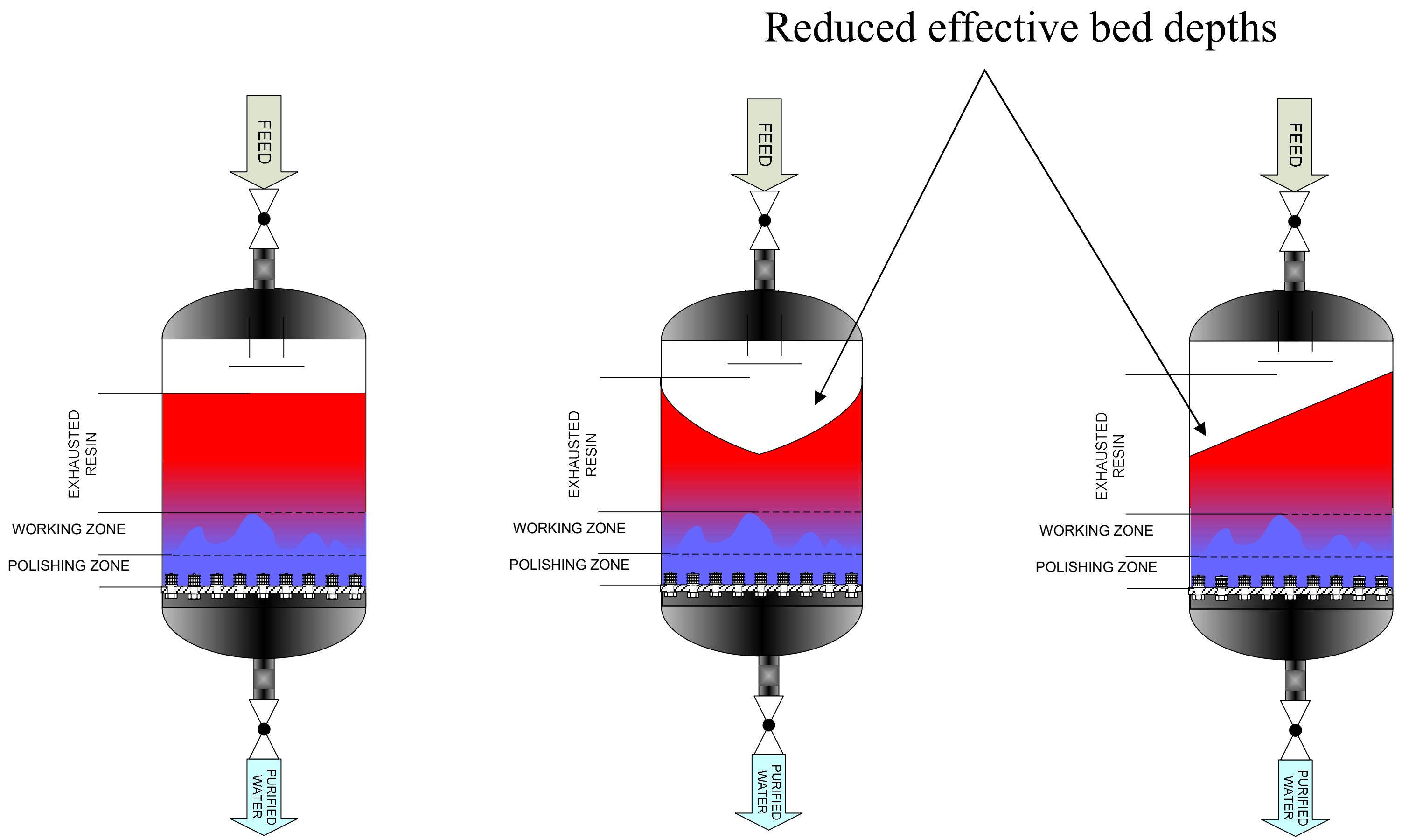


Countercurrent-counter pressure

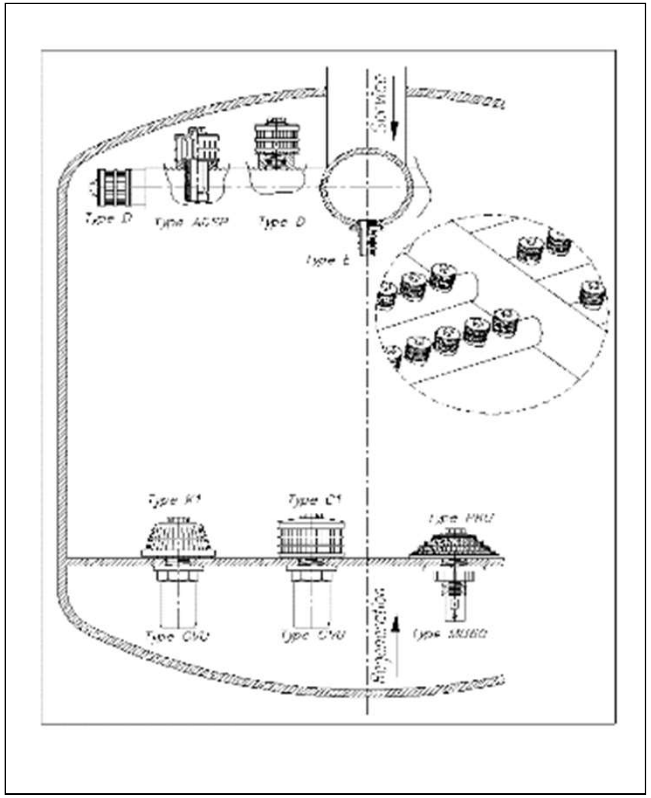
Liftbed

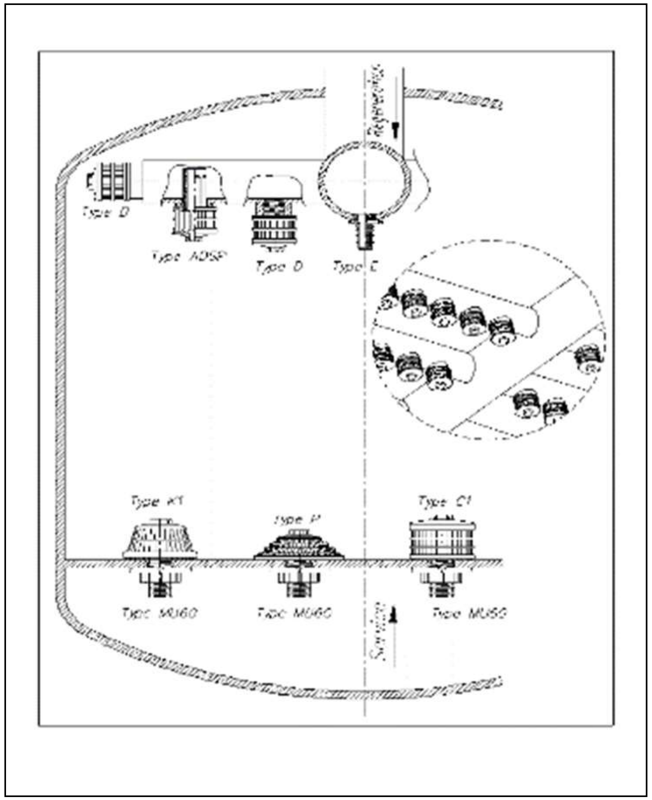


Flow Patterns



Filter Nozzles





Key properties of ion exchange resins

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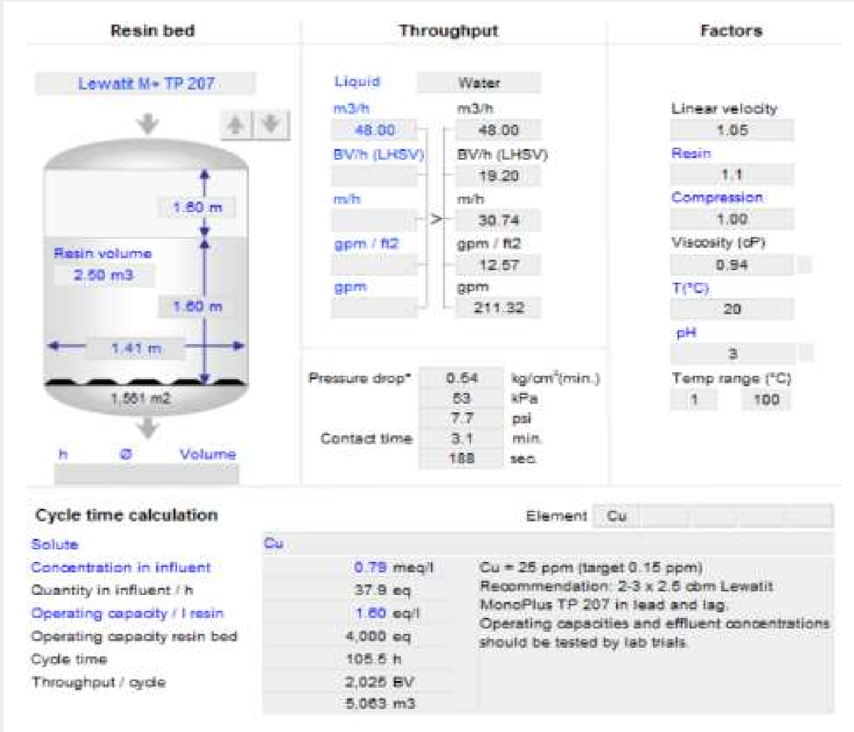
Energizing Chemistry

Precise control of resin parameters for critical separation challenges

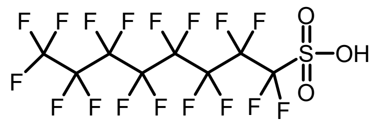
- Functional group (type of chelating)
- Polymer Matrix (styrenic or acrylic)
- Morphology (gel or macroporous)
- Crosslinking
- Bead size (mono- vs. heterodisperse)
- Kinetics
- Resin swelling



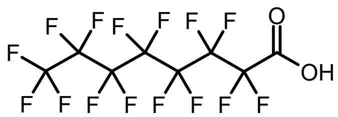
Chemical structures of most critical Per- and Polyfluorinated Alkyl (PFAS) substances

Highly efficient resin for the removal of toxic anions such as perchlorate, chlorate, and bromate

Long chain

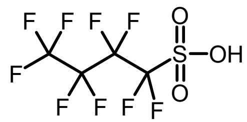


Perfluorooctanesulfonic acid (PFOS)
MW = 500 g/mol

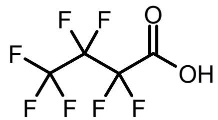


Perfluorooctanoic acid (PFOA)
MW = 414 g/mol

Short chain



Perfluorobutanesulfonic acid (PFBS)
MW = 300 g/mol



Perfluorobutanoic acid (PFBA)
MW = 214 g/mol

A high-performance ion exchange resin required in order to remove mixture PFAS

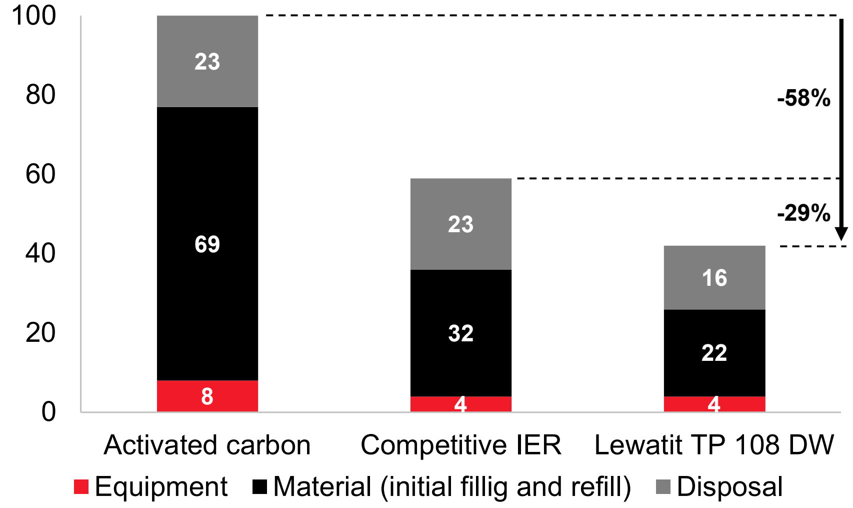
Options for treatment of PFAS

Ion exchange is most efficient technology especially for short chain PFAS!

Reverse osmosis/ nanofiltration	▪ Effectively removes even smaller chain PFAs ▪ Capex cost is high ▪ Operating cost and energy consumption is high ▪ Results in a relatively large waste stream
Granulated activated carbon	▪ Low-cost media difficult to change and expensive to reactivate ▪ Large footprint ▪ Low selectivity short chain PFAS results short cycles frequent exchanges
Ion exchange	▪ Fast kinetics, small vessels, ▪ Spent material is easy to be exchanged ▪ Very high selectivity, long cycles, low exchange rate

Cost Calculation using Lewatit® TP 108 DW, a competitor ion exchange resin (IER), and activated carbon

Costs in %
Normalized to AC costs



Lewatit® PFAS resins

LANXESS Energizing Chemistry

Lewatit® TP 108 DW NSF 61	▪ **Very high selectivity to PFAS** ▪ Especially effective against short-chains, e.g., PFBA types ▪ Not recommended for regeneration ▪ NSF 61 Certified for drinking water application
Lewatit® MonoPlus TP 109 New	▪ **High selectivity to PFAS species** ▪ Macroporous structure for improved kinetics, **fouling resistance and easier regeneration** ▪ **Monodisperse resin bead size** for improved hydraulics ▪ Optimum functional group hydrocarbon chain length for balance PFAS removal and regeneration ▪ High regeneration efficiency 70% methanol + 1% NaCl[1]
Lewatit® MP 62 WS New **Lewatit® MP 62 WS Eco**	▪ Medium selectivity for PFAS species weak base anion exchange resin, short chains **regenerated NaOH** ▪ Suitable for highly PFAS-contaminated waters such as point sources or aquifers ▪ Macroporous structure for improved kinetics, fouling resistance and easier regeneration ▪ A high operating capacity and total capacity (≥1.7 eq/l), ideal as a pretreatment resin ▪ 24% greenhouse gas savings[2] due to usage of ISCC[2] Plus certified styrene in accordance with mass balance approach

[1] Deng et al. Water Research 2010, 44, 5188

[2] Compared to standard Lewatit® based on fossil monomer (acrylonitrile/styrene). ISCC refers to International Sustainability & Carbon Certification

Required resins and filter arrangements

LANXESS
Energizing Chemistry

Wastewater leachates from hot spots
(PFAS influent: ppm-ppb)

1

Activated carbon removal of natural organic matter

Macroporous regenerable:
Lewatit® MP 62 WS and
Lewatit® MonoPlus TP 109
Regenerable working filter

PFAS selective Lewatit® TP 108 and Lewatit® K 6362 polishing, especially short chain PFAS

Purified water

2

RO unit

Selective Lewatit® TP 108 Polishing

concentrate

Lewatit TP 108 single use or Lewatit® MonoPlus TP 109
Regenerable

Ground water
(PFAS influent: ppt)

Activated carbon removal of natural organic matter

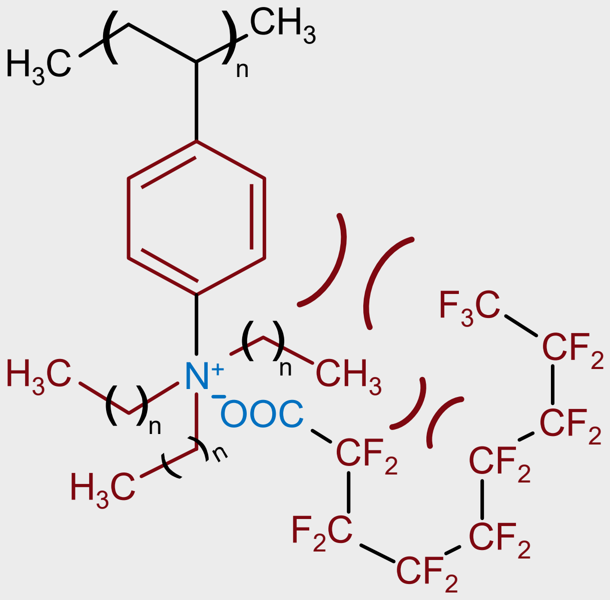
Selective Lewatit® TP 108
Polishing, longest cycle time
lowest leakage

Purified water

Interactions of PFAS with anion exchange resins

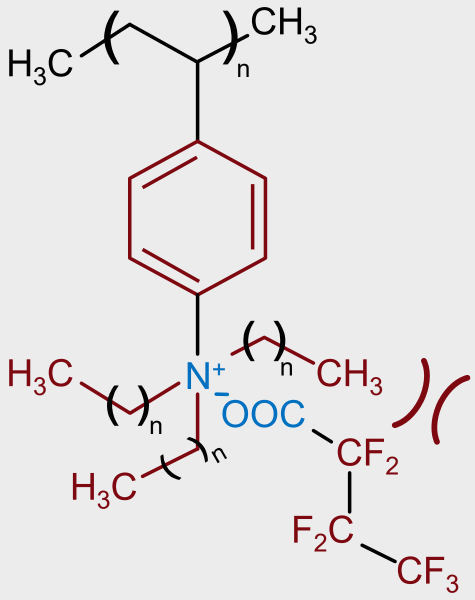
Strongest interaction between Lewatit® TP 108 DW and long chain PFAS

Strong interactions between Lewatit® TP 108 DW and PFNA



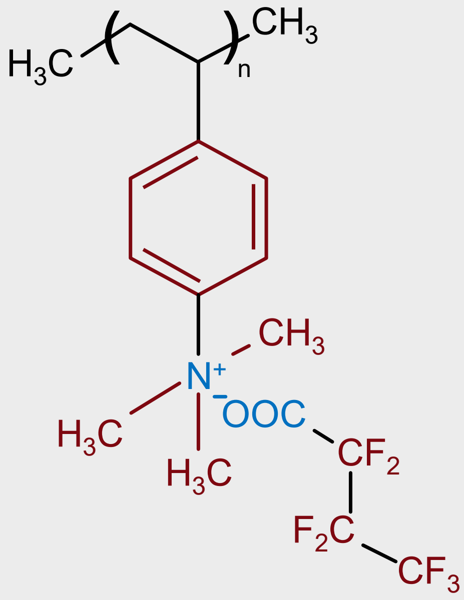
)(Hydrophobic interaction

Medium interactions between Lewatit® TP 108 DW and PFBA



n > 1

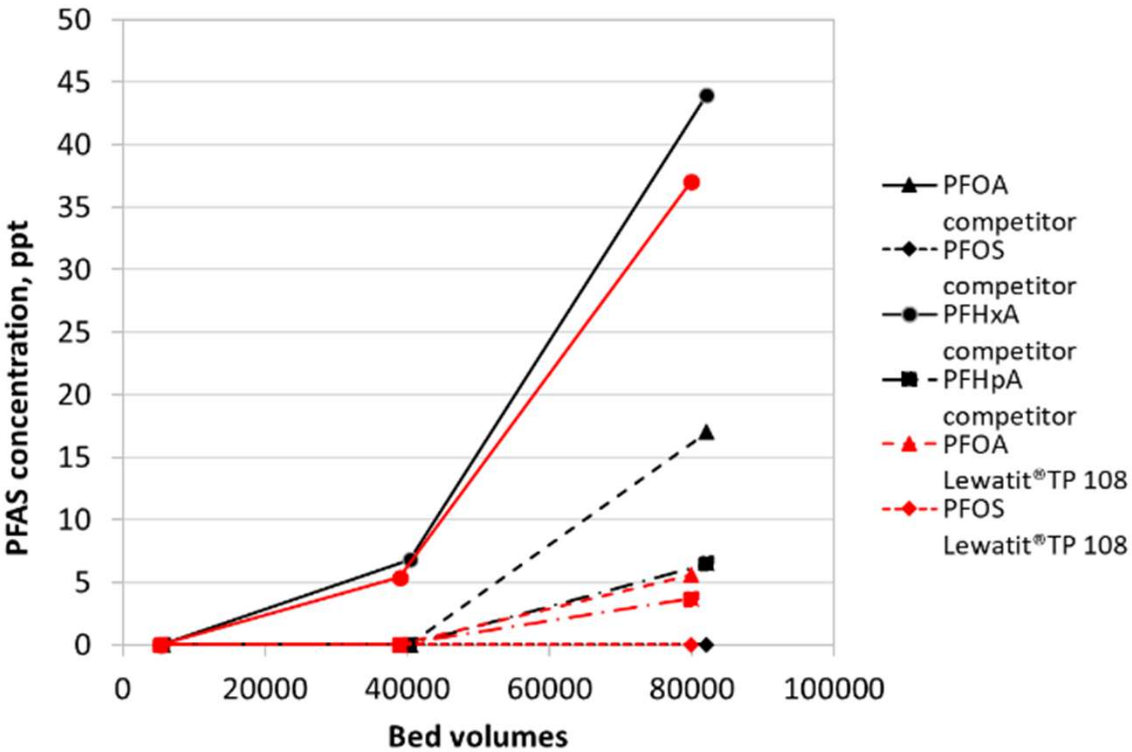
Weak interaction between Lewatit® K 6362 and PFBA



Ionic interaction

Warminster plant comparison

Lewatit® TP 108 offers longer lifetime than competitor resin



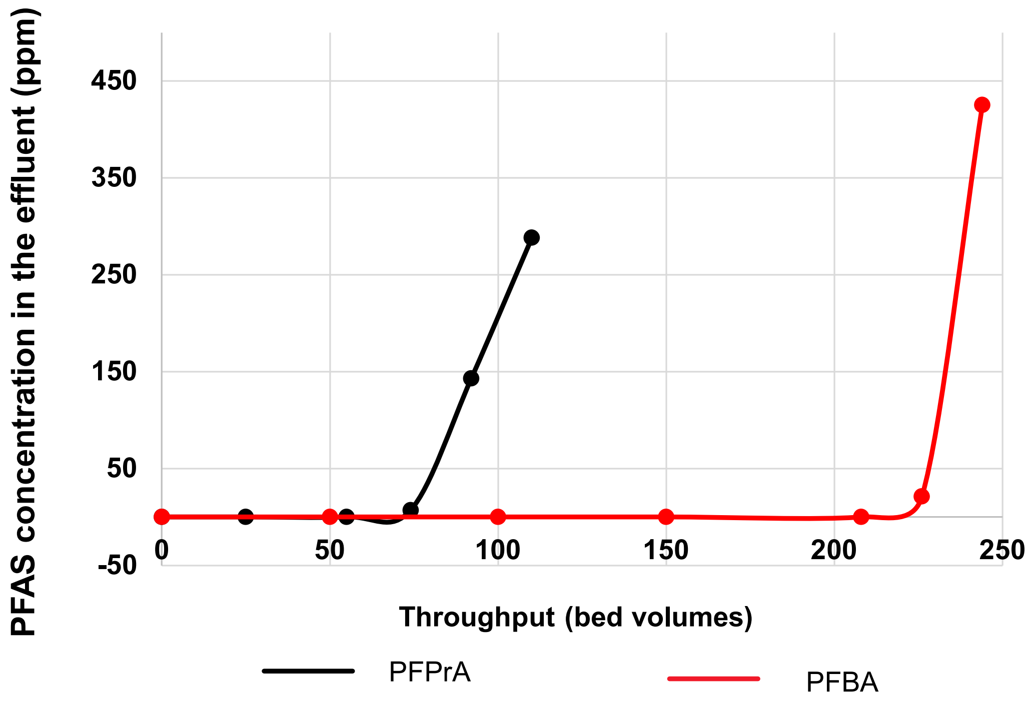
1.5 L, 30 BV/h PFOS 429 ppt, PFHxA 80 ppt, PFOA 174 ppt, PFHxS 110 ppt

PFPrA[1)] and PFBA[2)] removal from process stream

Lewatit® MP 62 WS outperforms with high loading capacity and efficient regeneration using 4% NaOH

operating conditions	
applied form	free base form
$PFPrA_{feed}$	103 ppm
$PFPrA_{loading\ capacity}$	10.3 g/L
$PFBA_{feed}$	602 ppm
$PFBA_{loading\ capacity}$	145 g/L
Volume	900 L
pH	2
SV	2 BV/h
Reg.	4% NaOH, 3-4 BV
Configuration	merry-go-round

PFPrA and PFBA removal by Lewatit® MP 62 WS



Reliable and efficient PFAS removal for several years at waste water plant in Germany

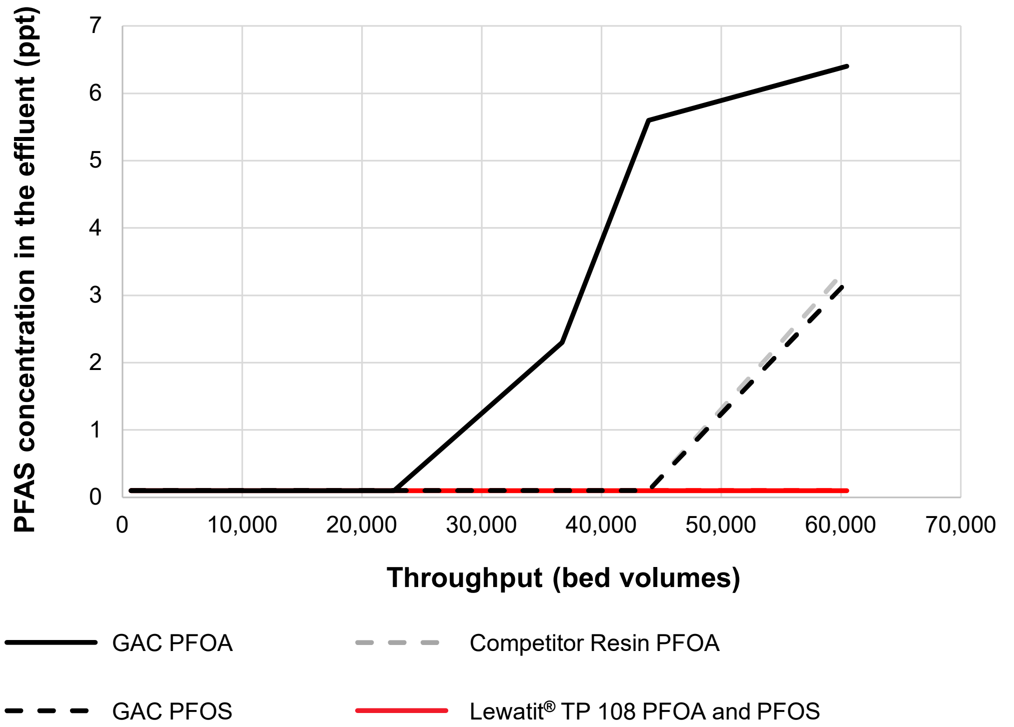
1) Perfluoropropanoic acid 2) Perfluorobutanoic acid

PFOA and PFOS removal from ground water

Lewatit® TP 108 DW offers longer lifetime than competitor resin and activated carbon

Operating Conditions	
Resin in Cl form	
PFOS	61 ppt
PFOA	44 ppt
Volume	75 L
pH	7
SV	15 BV/h
Temp	20°C
Breakthrough	> 1 ppt

PFOA and PFOS removal pilot in Italy



Lewatit® TP 108 DW offers longer lifetime than competitor resin

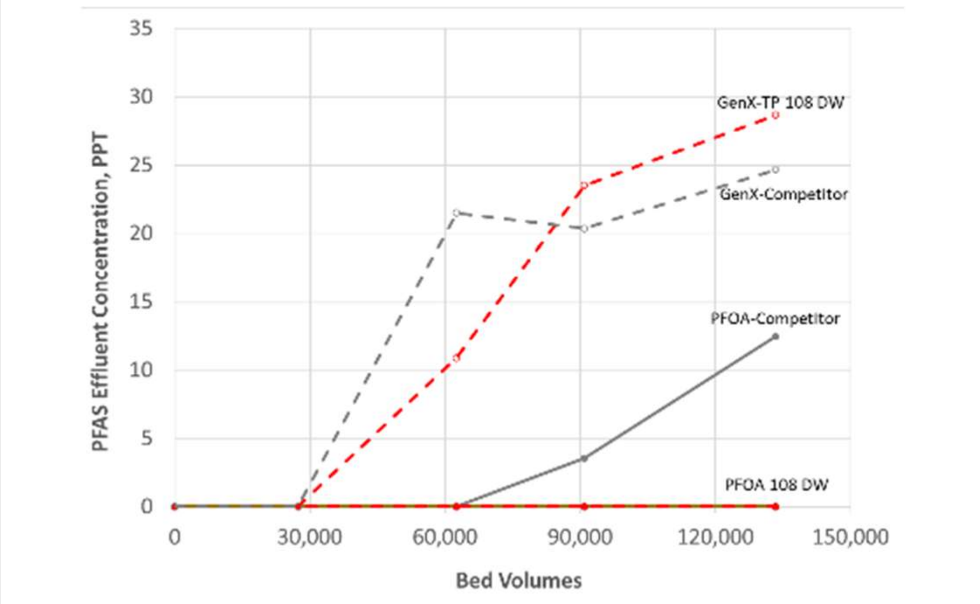
Pilot Trial in a River Water Project, USA

- 20 BV/Hour
- EBCT = 3 min
- Competitor resin is a gel type non-regenerable PFAS resin

IX Resins	Bed Volumes	PFOS, ppt	PFOA, ppt	PFBS, ppt	PFHxS, ppt	PFNA, ppt	GenX, ppt	PFHxA, ppt	PFHpA, ppt
	Raw Water	20.8	23.5	6.1	9.3	5.9	28.7	64.9	42.5
TP 108 DW	27,400	ND	ND	ND	ND	ND	ND	ND	ND
TP 108 DW	62,500	ND	ND	ND	ND	ND	10.9	7.8	ND
TP 108 DW	90,900	ND	ND	ND	ND	ND	23.5	37.0	6
TP 108 DW	133,400	ND	ND	ND	ND	ND	28.7	68.7	11.5
A Competitor Resin	27,400	ND	ND	ND	ND	ND	ND	ND	ND
A Competitor Resin	62,500	ND	ND	ND	ND	ND	21.5	16.9	2.5
A Competitor Resin	90,900	ND	3.5	ND	ND	ND	20.3	37.6	15.7
A Competitor Resin	133,400	ND	12.5	ND	ND	ND	24.6	50.6	26.3

PFOA and GenX Removal

- PFOA (feed) = 23.5 ppt; GenX (feed) = 28.7 ppt



ND: non-detect

Lewatit® TP 108 DW offers longer lifetime than competitor resin

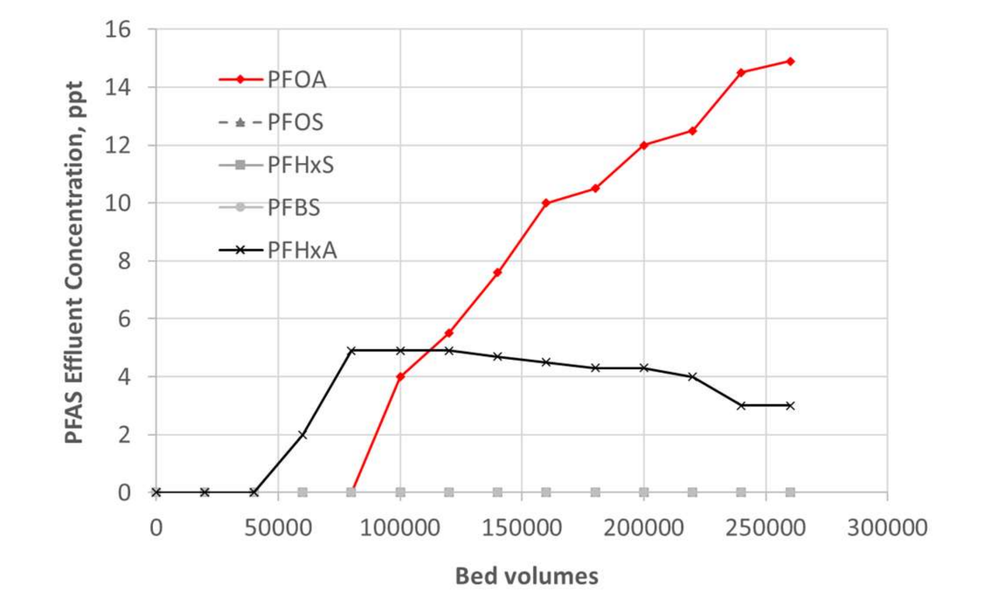
California OCWD Pilot Data (Phase 2)

- 30 BV/hour, run for about 19 months
- EBCT = 2min

Bed Volumes (BV)	PFOA	PFOS	PFHxS	PFBS	PFHxA
Avg. Influent conc., ppt	20.1	24.5	10.3	14.9	4.5
0	ND	ND	ND	ND	ND
20,000	ND	ND	ND	ND	ND
40,000	ND	ND	ND	ND	ND
60,000	ND	ND	ND	ND	2
80,000	ND	ND	ND	ND	4.9
100,000	4	ND	ND	ND	4.9
120,000	5.5	ND	ND	ND	4.9
140,000	7.6	ND	ND	ND	4.7
160,000	10	ND	ND	ND	4.5
180,000	10.5	ND	ND	ND	4.3
200,000	12	ND	ND	ND	4.3
220,000	12.5	ND	ND	ND	4
240,000	14.5	ND	ND	ND	3
260,000	14.9	ND	ND	ND	3

19 Month Trial

- PFOS, PFHxS and PFBS didn't breakthrough



ND: non-detect

Lewatit® TP 108 DW offers the highest capacity for most PFAS species found in drinking water sources

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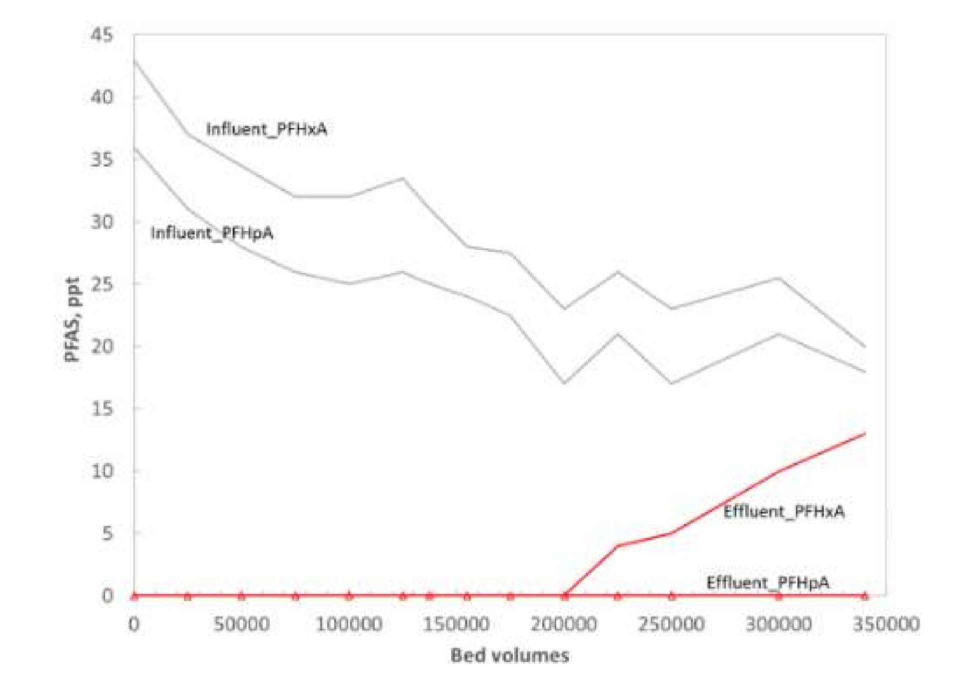
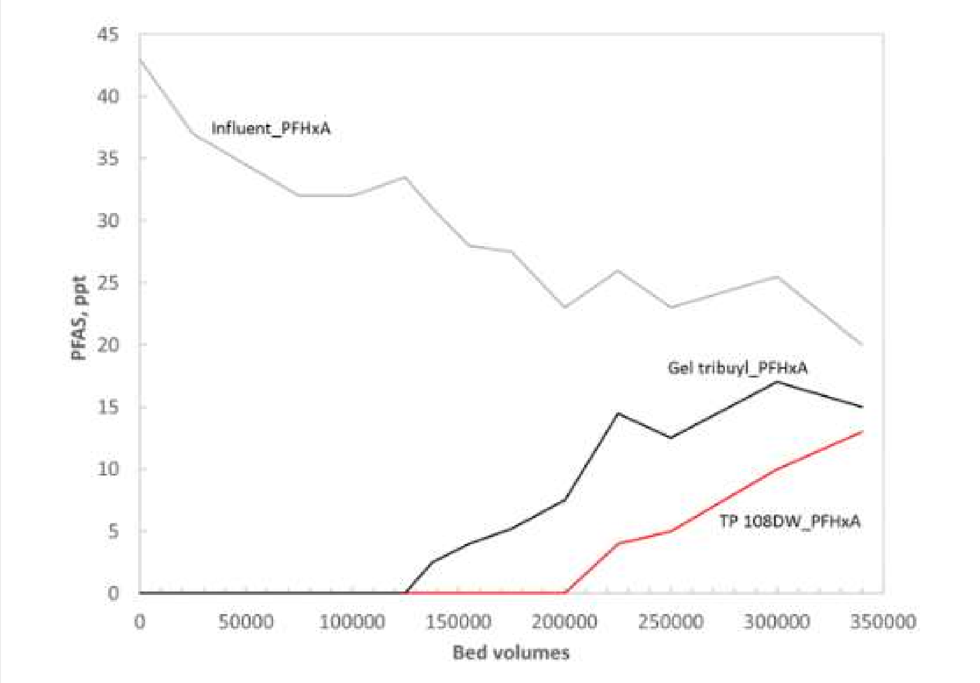
PFHxA and PFHpA breakthrough curves generated USA



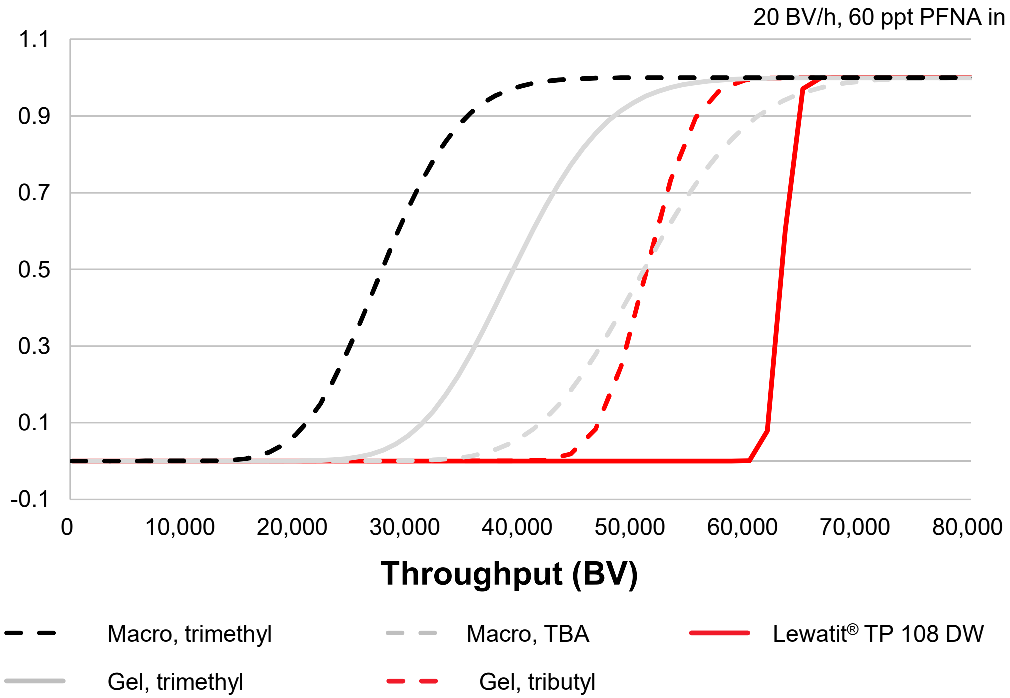
PFHxA breakthrough curves generated USA



Resin performance for PFAS application
Simulated breakthrough curves by use of Klinkenberg model

LANXESS
Energizing Chemistry

PFNA breakthrough curves



Conclusions

- Lewatit® TP 108 DW best resin to be used as single use polisher: longest cycle time and lowest leakage
- Macroporous resins, shorter cycle times and higher leakage values due to lower total capacity
- Technique established that yields fast access to breakthrough curves 2-3 weeks instead of 15 weeks for traditional method

$$\frac{C}{C_f} \approx \frac{1}{2}\left[1 + erf\left(\sqrt{\tau_1} - \sqrt{\xi} + \frac{1}{8\sqrt{\tau_1}} + \frac{1}{8\sqrt{\xi}}\right)\right]$$

$$\xi = \frac{kKu}{z}\left(\frac{1-\varepsilon_0}{\varepsilon_0}\right) \qquad \tau_1 = k\left(t - \frac{z}{u}\right)$$

Case study at fire training site Australia

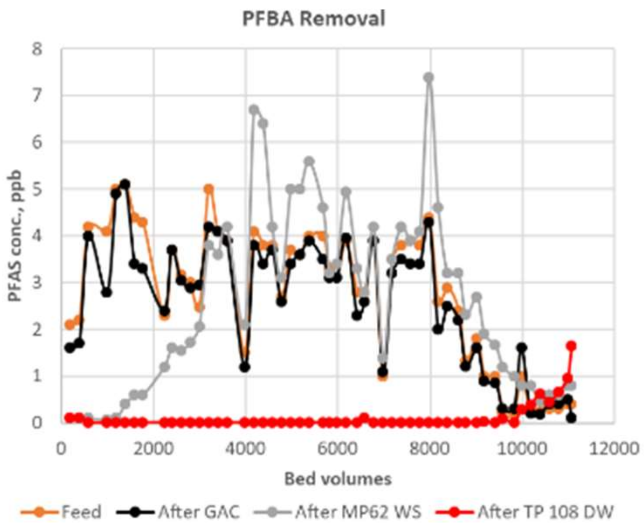
One of the most successful PFAS water treatment plants

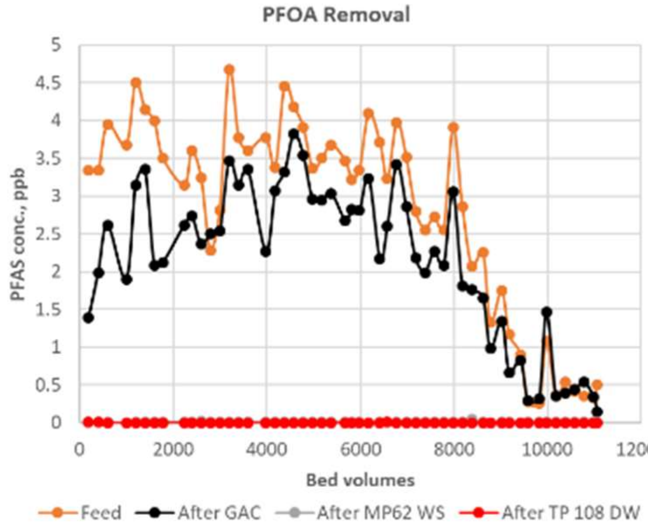
Containerized PFAS treatment plant

Characteristics

- Training using aqueous fire-fighting foam (AFFF) containing per- and poly-fluoroalkyl substances (PFAS)
- PFAS leached into groundwater
- Discharge criteria for **long and short-chain PFAS** to comply with
- Processes: oxidation, pH adjustment, flocculation, solids separation, media filtration, ion exchange and adsorption

PFAS treatment in a fire-fighting facility





Lewatit® TP 108 DW reduced most PFAS compounds to non-detect!

PFAS treatment summary

- Influent: total PFAS up to 200 ppb
- **Effluent targets**
  - PFOS and PFHxS combined total less than 0.07 ppb
  - PFOA less than 0.56 ppb
  - PFBA to non-detect level up to 10,000BVs
- 20 m^3/hour flow rate
- In operation for 12 months and treating nearly 14 million gallons of water
- Deemed one of the most successful PFAS water treatment plants in Australia

Operational Guidelines

LANXESS
Energizing Chemistry

Recommended Operational Conditions

- Total suspended solids in the feed < 0.5 ppm
- Pressure drop <150kpa to prevent mechanical stress on the resins
- Free chlorine < 0.05 ppm: effective pre-treatment is required to prevent irreversible chemical damage to the resins
- Presence of other oxidants e.g., ozone, permanganate and etc are not tolerable- same as above
- Organic as TOC < 1 ppm: effective pre-treatment is required to prevent fouling of the resins and prevent poor performance
- Oil & grease are not tolerable- same as above
- Heavy metals: <0.05 ppm

Design Considerations

- Specific flow rate: 10-20 BV/hour
- Vessels: 8 ft, 12 ft diameter vessels are typical
- Cross-sectional linear velocity: > 5 m/hour
- Bed depth: minimum 3 ft
- Backwash: not recommended except startup
- Pretreatments
  - High TOC: GAC, Acrylic resin pre-filter
  - High PFAS concentration: regenerable resins as pre-filters
- Configuration
  - Lead/lag

Overview of LANXESS resins and adsorbers for drinking water applications

LANXESS Energizing Chemistry

Strong portfolio of Lewatit® ion exchange resins for critical water purification challenges

Pollutant		Chelating resin	Strong base anion resin (SBA)					Ferric hydroxide adsorber
		Lewatit® MonoPlus TP 207	Lewatit® TP 107	Lewatit® TP 108 DW	Lewatit® TP 106	Lewatit® S 5128	Lewatit® DW 630	Bayoxide® E33 / E33 HC
Heavy metals	HM	■						
Chromium	CrO_4^{2-}		■					
Nitrate	NO_3^-				■			
Per- and polyfluoroalkyl substances	PFAS			■				
Perchlorate	ClO_4^-				■			
Natural organic matter	NOM					■		
Uranium	$UO_2(SO_4)_2^{2-}$						■	
Arsenic	AsO_4^{3-}							■

Country specific potable water approval certificates can be received as manufacture's declaration.

Please get in contact with us

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Energizing Chemistry

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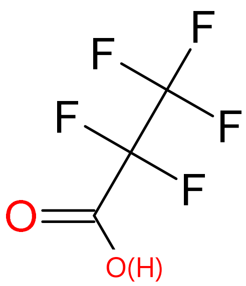
ZeroPM treatment approach: Two step treatment with activated carbon and regenerable anion exchanger

Special Symposium on PFAS elimination, 12.6.2024, Karlsruhe/Rastatt

Lukas Lesmeister, Dr.-Ing. Marcel Riegel

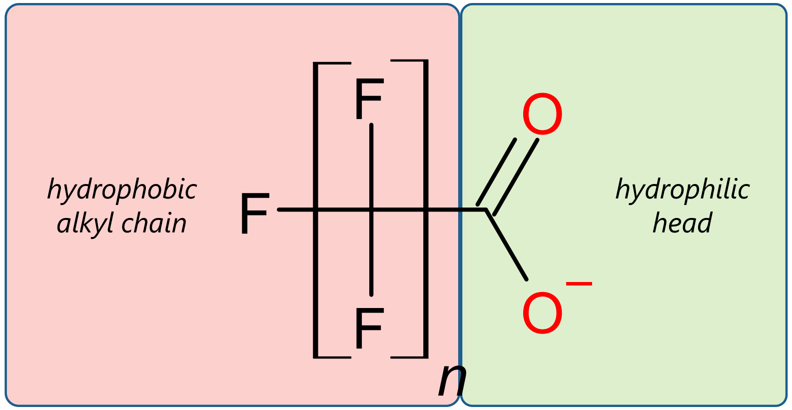
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101036756.

Perfluoroalkyl acids (PFAA)



PFBA

Terminal degradation products

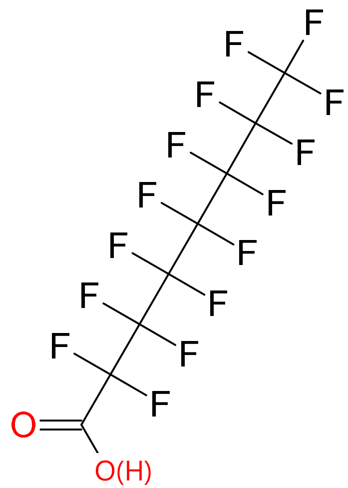


$n = C_F = 3 \rightarrow$ PFBA 4 C atoms

$n = C_F = 4 \rightarrow$ PFPeA 5 C atoms

$n = C_F = 5 \rightarrow$ PFHxA 6 C atoms

…

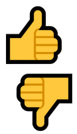


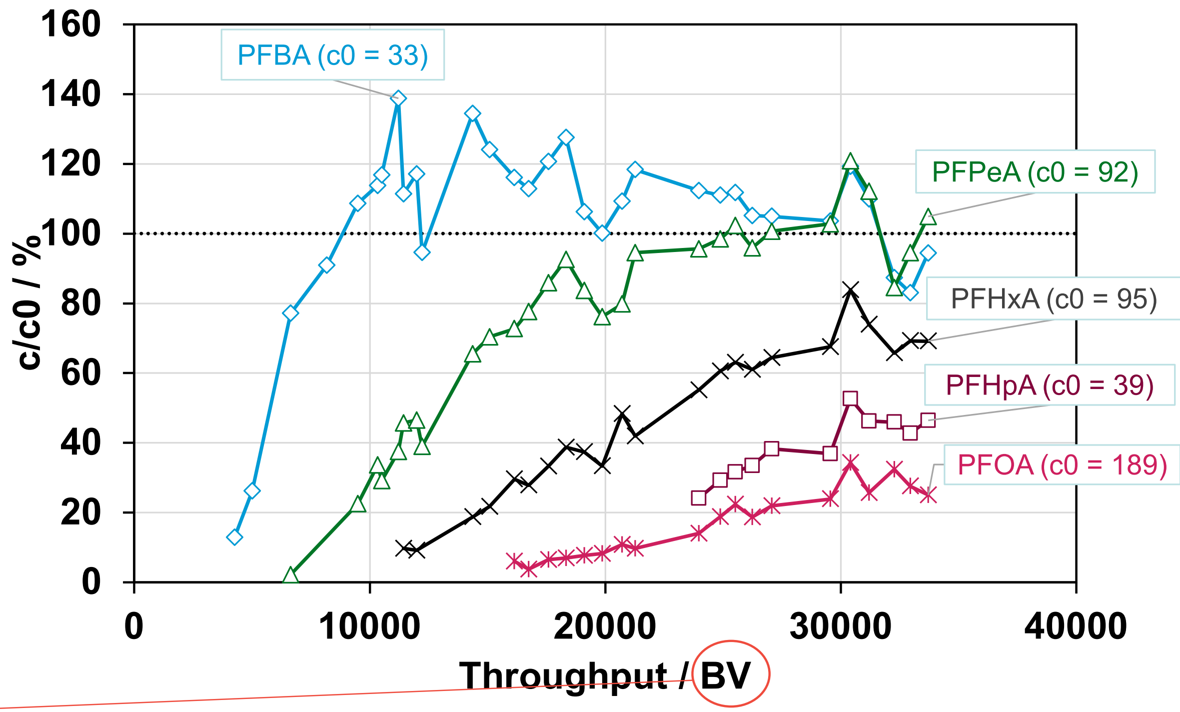
PFOA

Current Situation

Removal of
long chain PFAA

Long chain PFAA
Short chain PFAA





1 bed volume (BV) = volume of water equal to the volume of the filter bed

Abb.: Relative effluent concentrations in GAC filter in pilot plant, h = 2 m, flow = 5 BV/h, v_F = 10 m/h, c_0 in ng/L.

Impact of the new DWD

Removal of
long chain PFAA

Long chain PFAA 👍
Short chain PFAA 👎

⇨Up to 80 % reduced operating time (presence of short chain PFAA)

⇨Additional effort & costs

- Former guidance values (LW), health orientation values (GOW)

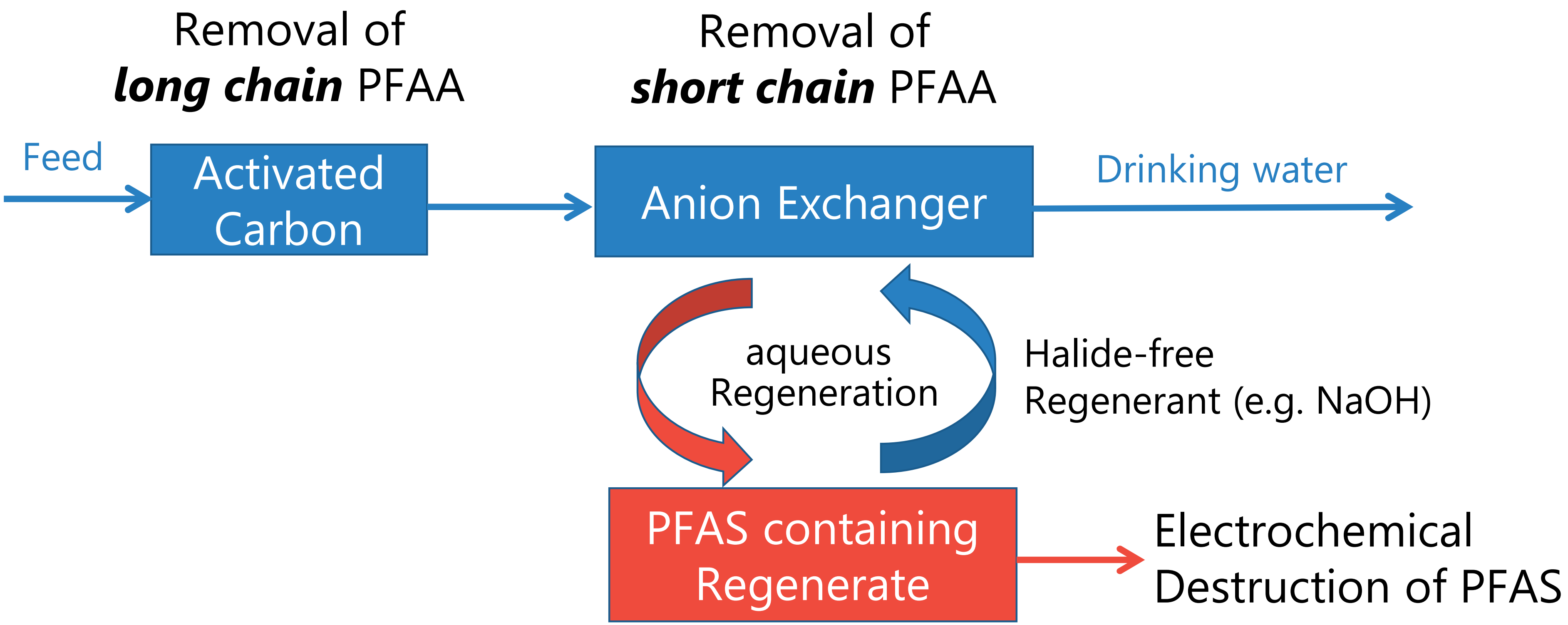
Substanz		C	perfluorinated, C_F	LW, µg/L	GOW, µg/L
PFBA	Perfluorobutanoate	4	3	10	-
PFPeA	Perfluoropentanoate	5	4	-	3.0
PFHxA	Perfluorohexanoate	6	5	6	-
PFHpA	Perfluoroheptanoate	7	6	-	0.3
PFOA	Perfluorooctanoate	8	7	0.1	-

New threshold, RL 2020/2184/EU

Σ_{20} PFAS = 0.1 µg/L

Approach in the EU ZeroPM project

Approach in the EU ZeroPM project



Selection of suitable test resins

- Comparison of adsorption and desorption on different anion exchange resins (16 resins, 5 manufacturers) in the laboratory

Test in pilot plant:

- ➢ Weakly basic resin (Purolite A111, regenerable)
- ➢ Strongly basic resin (Lewatit MonoPlus M600, regenerable)
- ➢ PFAS-specific strongly basic resin (Amberlite PSR2+, not regenerable)

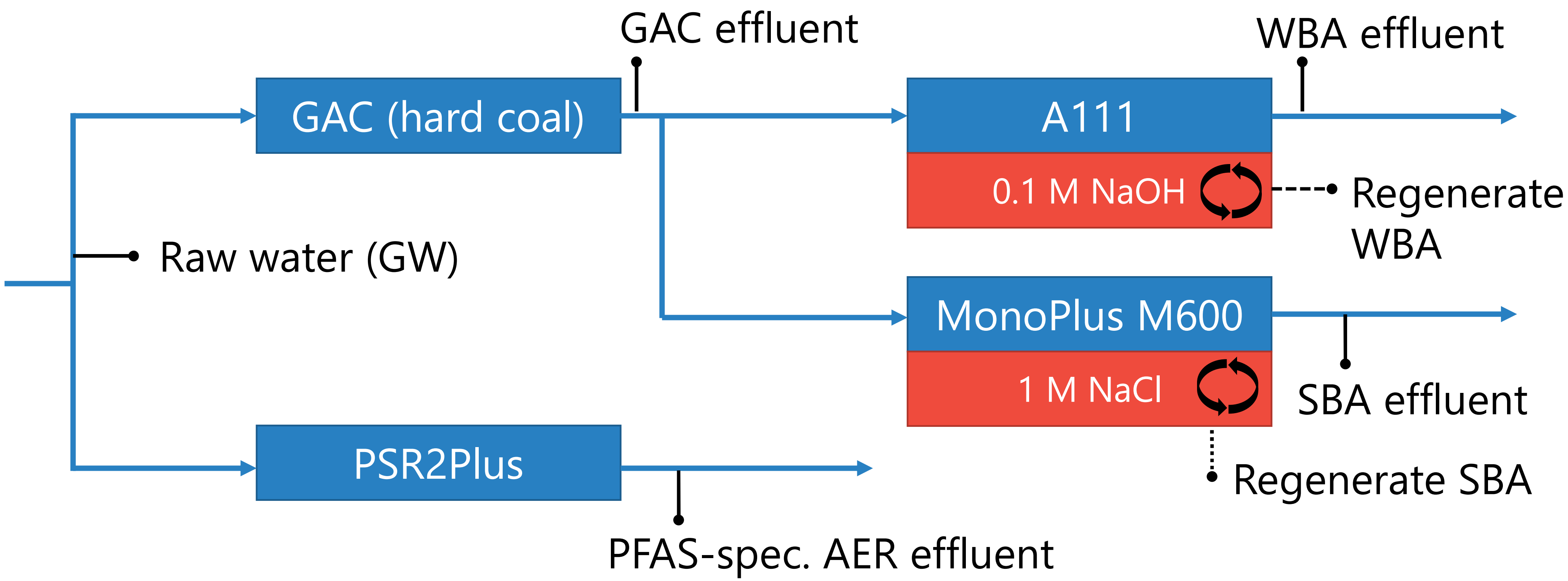
Water matrix

Threshold ΣPFAS-20 = 100 ng/L

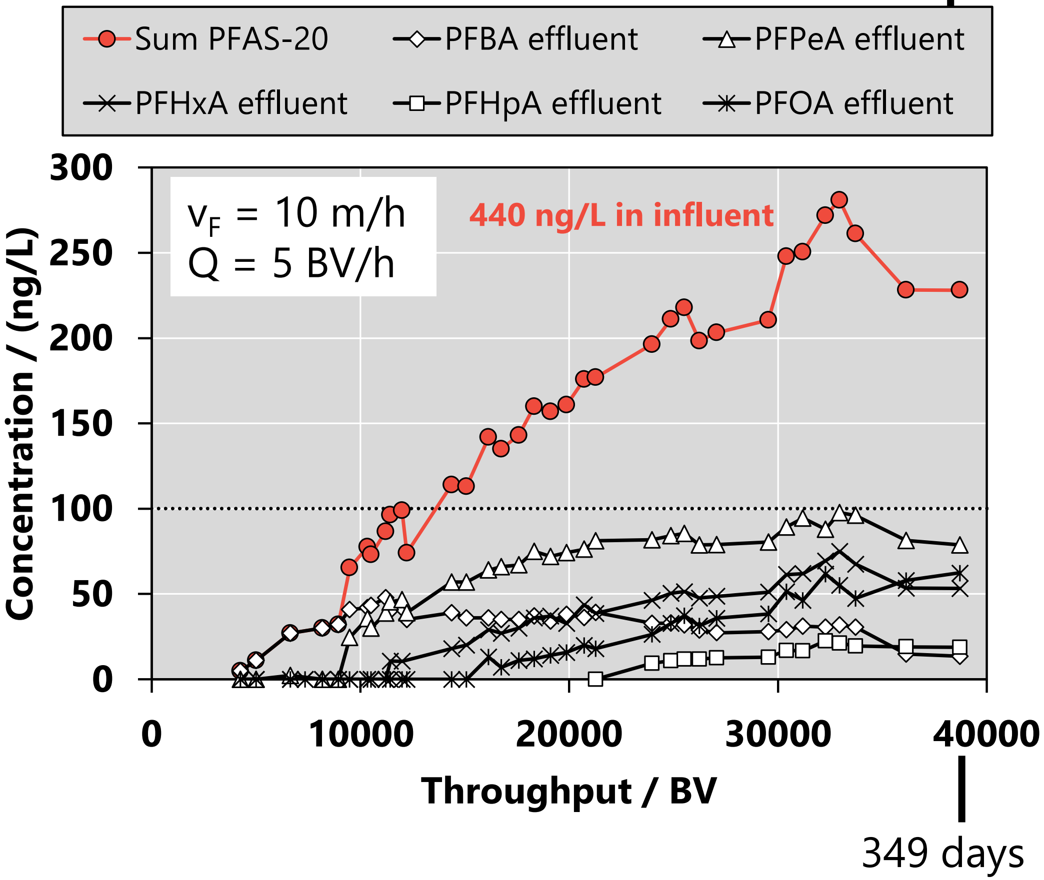
Parameter	Unit	Mean
pH	-	6.2
Temperature	°C	12
El. Conductivity	µS/cm	301
TOC	mg/L	0.58
Total hardness	°dH	6.6
Total hardness	mmol/L	1.18
Sulphate	mg/L	24.7
Chloride	mg/L	19.5
Nitrate	mg/L	27.1

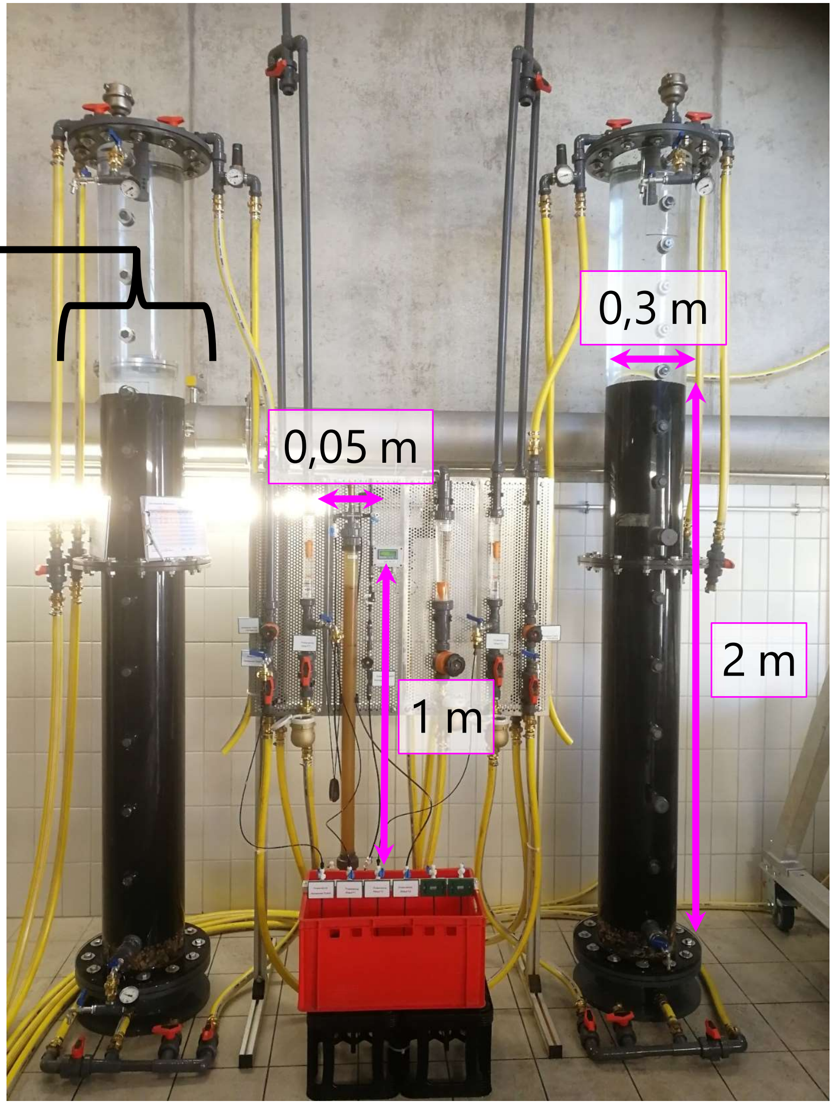
Parameter	Unit	Mean
TFAA	ng/L	907
PFPrA	ng/L	18
PFBA	ng/L	32
PFPeA	ng/L	91
PFHxA	ng/L	94
PFHpA	ng/L	39
PFOA	ng/L	187
ΣPFAS-20	**ng/L**	**442**

Scheme of the pilot plant

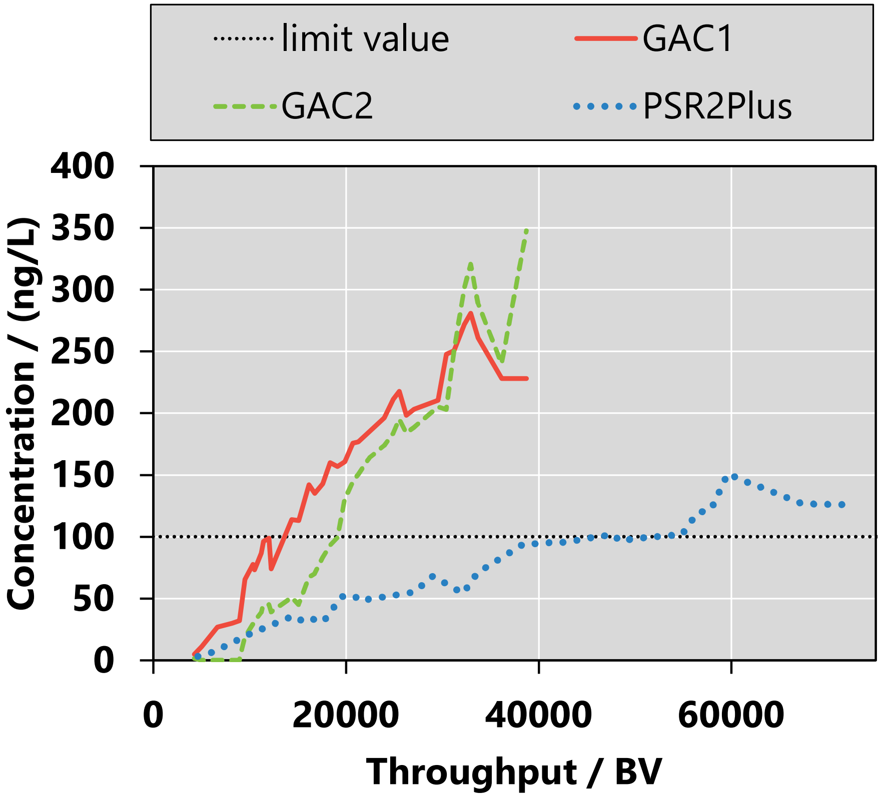


GAC-Filter (hard coal)





Effluent ΣPFAS comparison

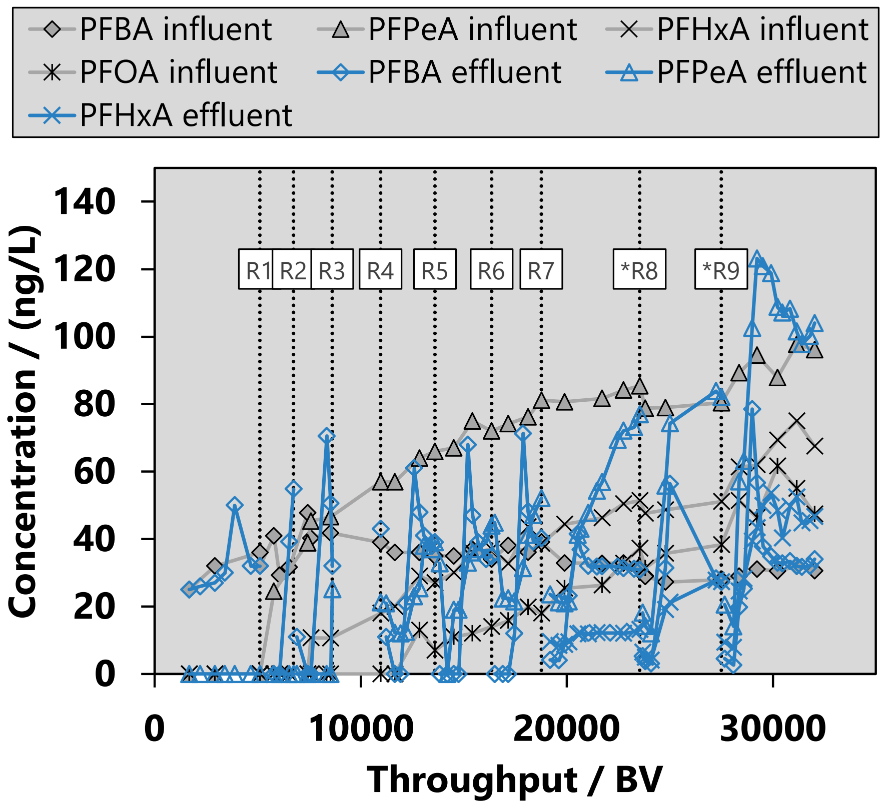


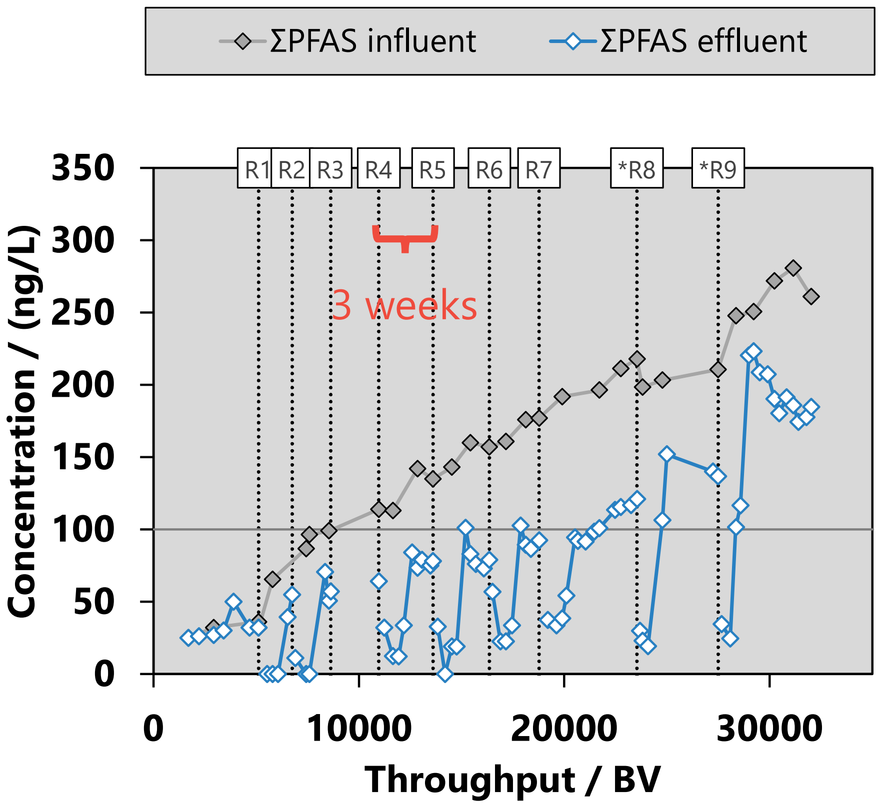
- GAC1: Hard coal
- GAC2: Coconut shell-based

Table: Comparison of flow parameters.

Parameter	GAC	PSR2Plus
v_F / (m/h)	10	10
Throughput / (BV/h)	5	10

Strongly basic anion exchanger, M600



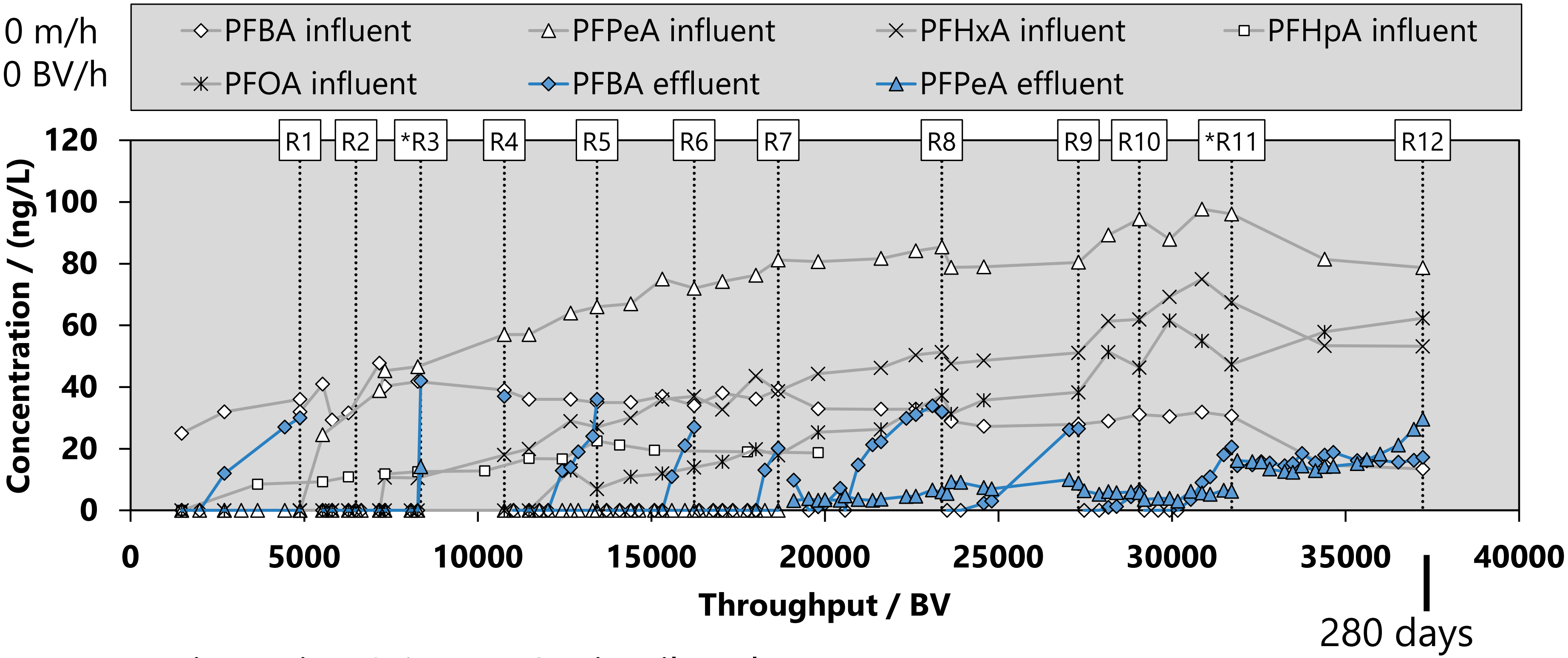


- R, regeneration using 1 M $NaNO_3$ in pilot plant
- *R8 and R9: regeneration using 1 M NaCl.

v_F = 10 m/h BV_{Reg} = 10
Q = 10 BV/h

Weakly basic anion exchanger, A111

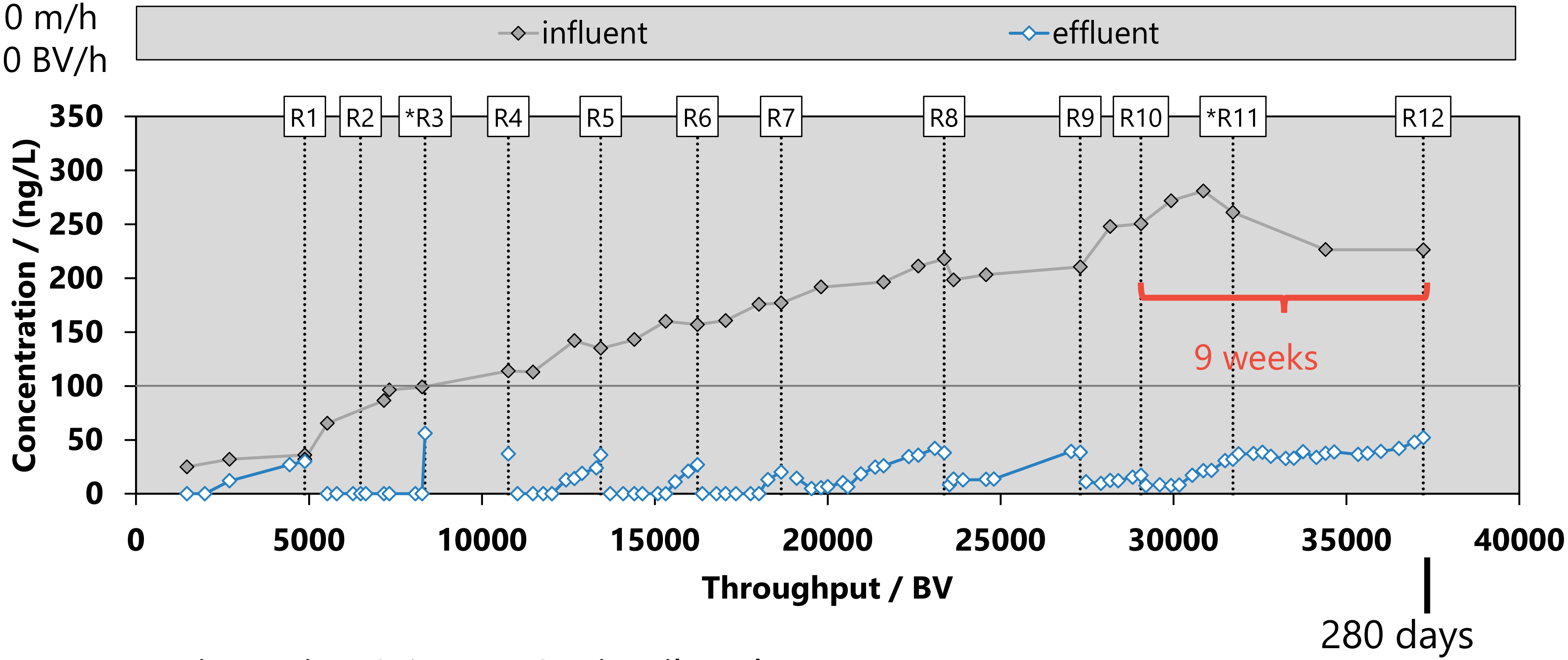
v_F = 10 m/h
Q = 10 BV/h



- R, regeneration using 0.1 M NaOH in pilot plant BV_{Reg} = 10
- *R3 and R11: regeneration using 0.01 M NaOH.

Weakly basic anion exchanger, A111

v_F = 10 m/h
Q = 10 BV/h



- R, regeneration using 0.1 M NaOH in pilot plant BV_{Reg} = 10
- *R3 and R11: regeneration using 0.01 M NaOH.

Process evaluation (example)

<u>Assuming regeneration every 3 weeks:</u>

- 10 080 L treated drinking water
- 25 L regenerate → process efficiency: 99.8%
- 60 L flush water cut-off → process efficiency: 99.1%

<u>Comparison with reverse osmosis treatment:</u> approx. 80%

Without consideration of additional treatment of regenerates or concentrates

Conclusions / outlook

- Process evaluation:
  - Effective: PFAA concentration in the effluent < 100 ng/L ✓
  - Efficient: > 99% ✓
  - Treatment costs: materials, specific costs **pending**

- Treatment of Regenerate **pending**

Team

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Coordinator

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Doctoral student

Julian Schmid
Technician

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

Thank you for your attention!

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EU Green Week

HANDLING A PFAS GROUNDWATER CONTAMINATION: EXPERIENCE OF A WATER UTILITY

Symposium on PFAS elimination from Drinking Water

12th June 2024

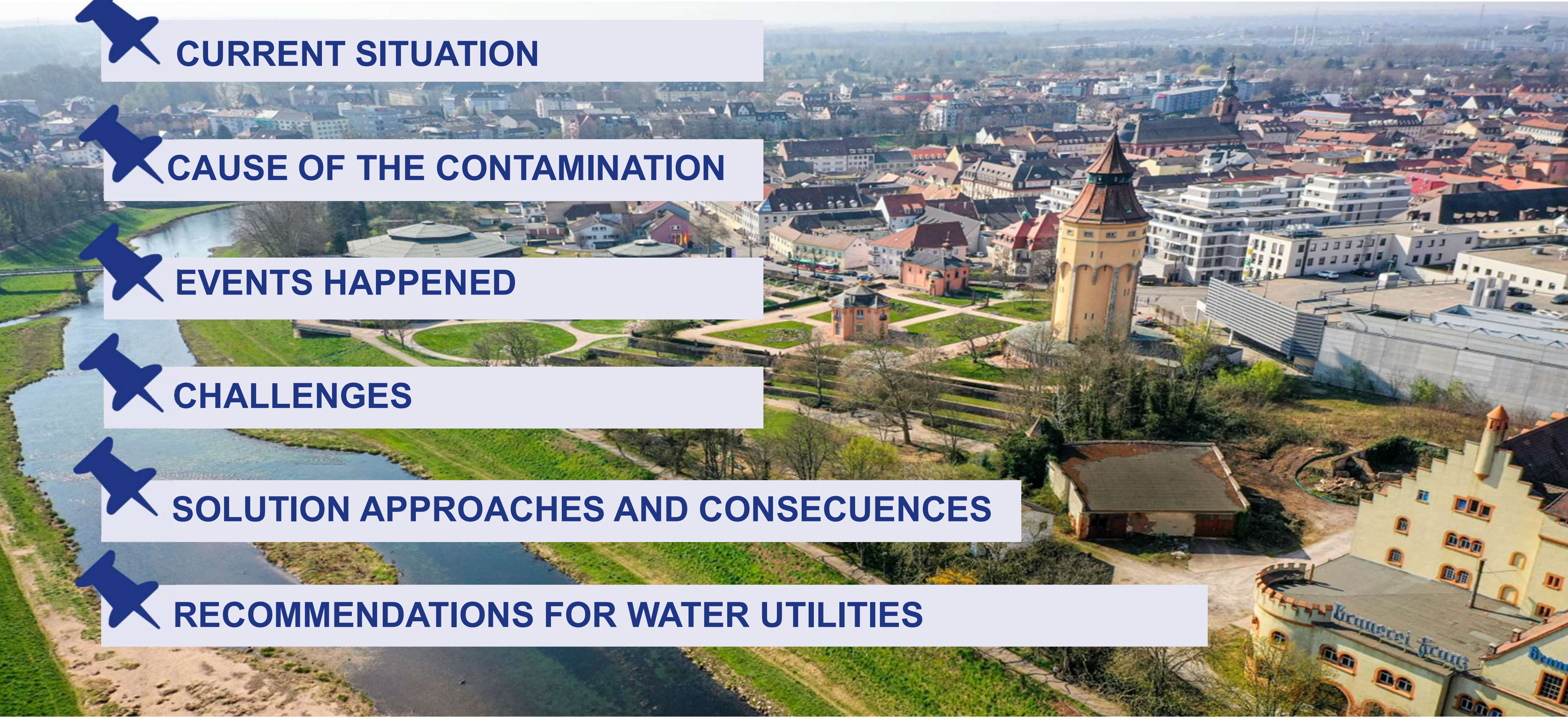
Rastatt, Germany

ZerOPM

STADTWERKE RASTATT

STADTWERKE RASTATT AS AN EXAMPLE OF ENGAGEMENT

- Highlights of a real example of a public utility that has effectively managed a PFAS contamination
- Challenges of PFAS, drinking water regulations and water supply responsibilities
- Immediate measures and actions taken: investigation, best technologies, expert involvement, investment and treatment optimization
- Crisis Management: priorities, decision making
- Ensure a reliable water supply: long term efforts and continuous engagement



- CURRENT SITUATION
- CAUSE OF THE CONTAMINATION
- EVENTS HAPPENED
- CHALLENGES
- SOLUTION APPROACHES AND CONSECUENCES
- RECOMMENDATIONS FOR WATER UTILITIES

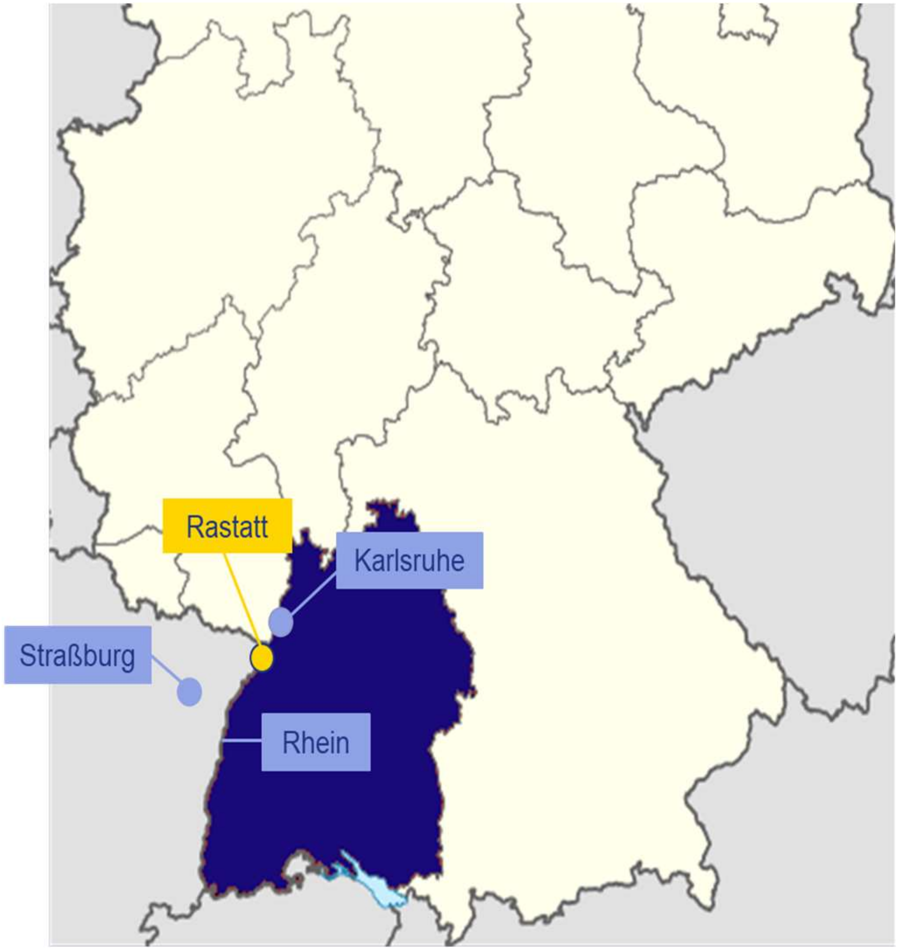
CURRENT SITUATION

► PFAS discovered in groundwater well in 2012 by chance of a full water-analysis

► PFAS contamination in the region "Mittelbaden" is one of the biggest environmental scandal in Germany

► The groundwater and soil remediation is economically impossible

► Measures taken regarding PFAS removal made it possible to ensure a safe water supply



CURRENT SITUATION

SOIL

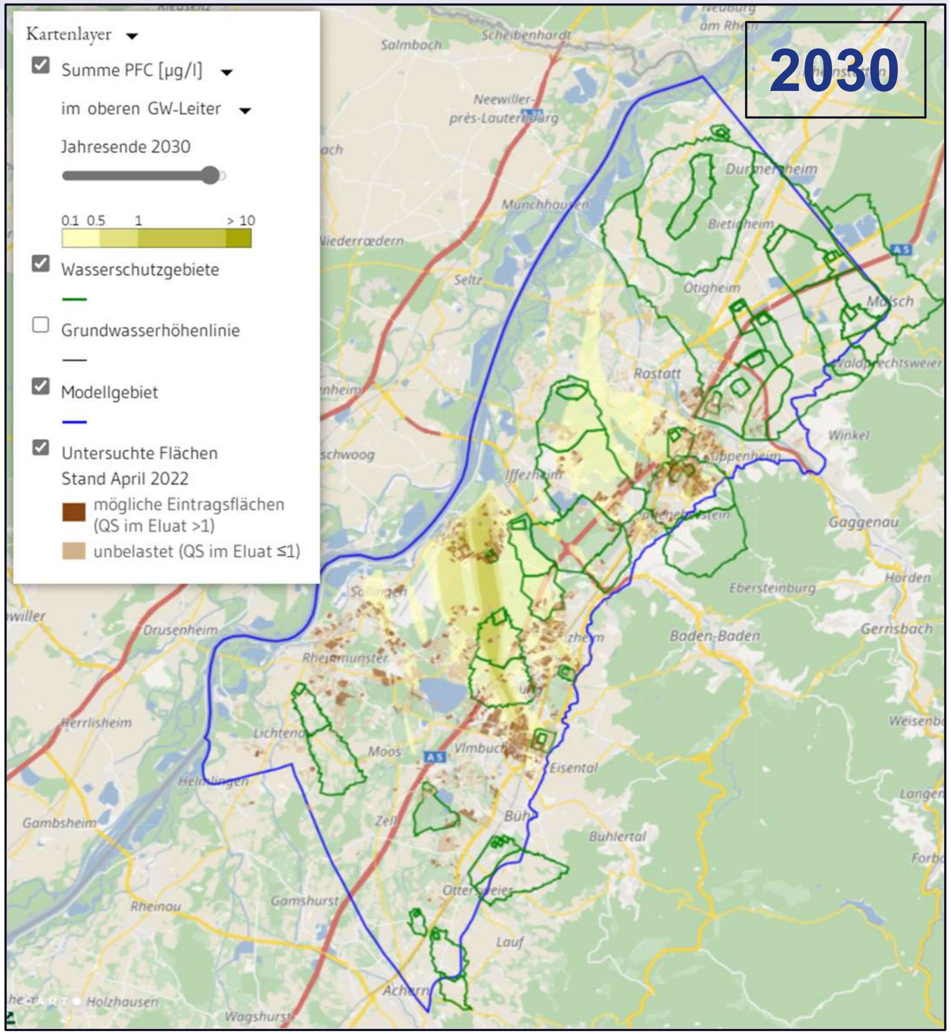
1.100 hectares contaminated with PFAS so far

11% of the total agricultural land

GROUNDWATER

170 million m^3

58 km^2 of groundwater surface (Lake Starnberg)



CURRENT SITUATION

SOIL

1.100 hectares contaminated with PFAS so far

11% of the total agricultural land

GROUNDWATER

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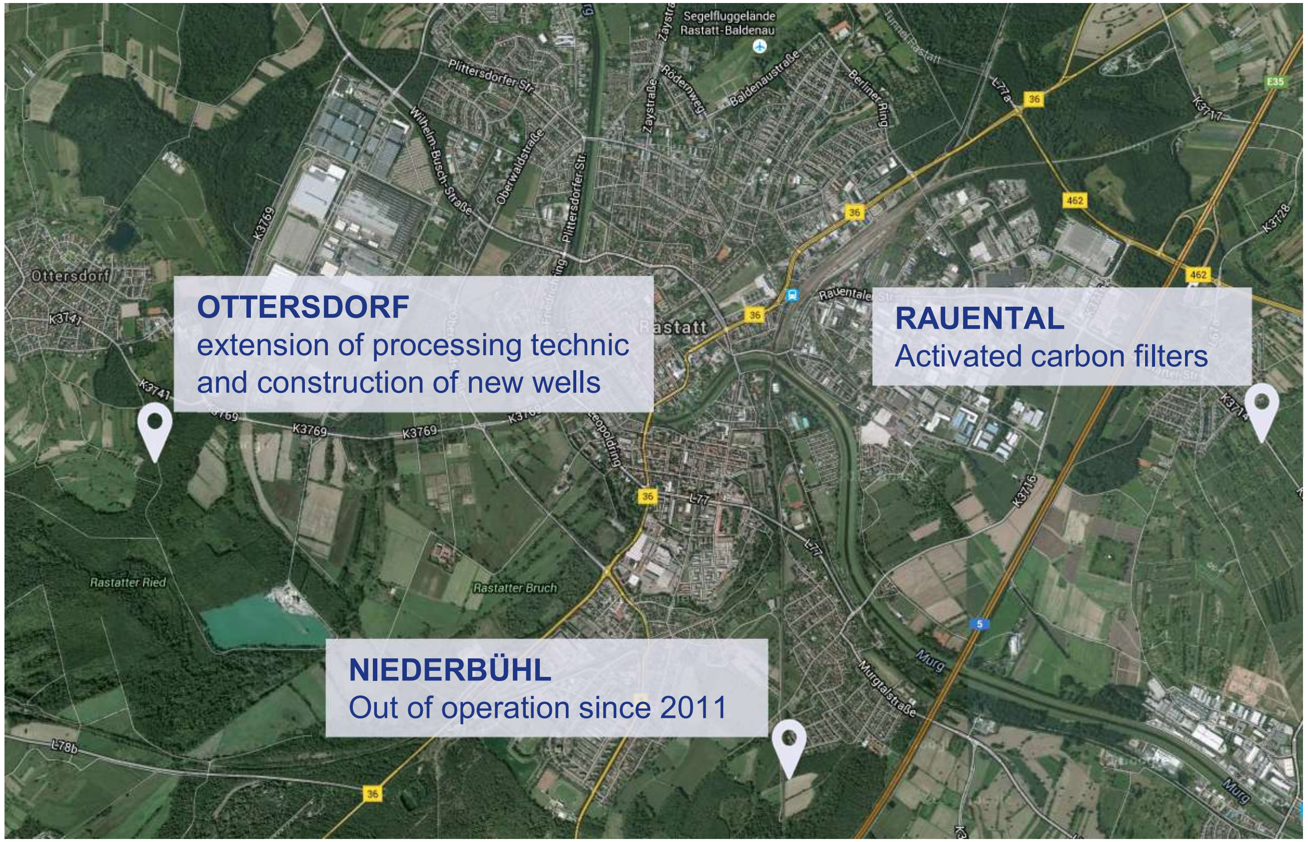
58 km^2 of groundwater surface (Lake Starnberg)

CURRENT SITUATION OF WATER TREATMENT PLANTS



Measures taken for safe water:

- ►Inter-municipal pipe connections
- ►New internal pipelines
- ►Treatment technology: activated carbon filters in treatment plants
- ►PFAS-Monitoring
- ►Construction of new wells
- ►Further research for most economical solutions

CAUSE OF THE CONTAMINATION

WHO?

► A compost company from Baden-Baden

WHAT?

► Experts conclusion: the contamination was most likely due to compost distribution on fields mixed with paper sludge

HOW?

► Spreading PFAS-containing compost over large areas of agriculture land between 2000 and 2006

EVENTS HAPPENED

2012-2013

- PFAS discovered by chance in water analysis
- Criminal complaint
- Public communication
- Information exchange with specialists and authorities

2014-2015

- Search for financing
- Research for treatment technologies
- Groundwater models
- Activated carbon in water treatment
- Inter-municipal connection pipeline

2016-2017

- Completion of redundancy
- First Symposium in Rastatt
- First juristic verdict
- Expert opinion on health

2018-2019

- Civil action against polluter
- Further PFAS Symposiums
- Appeals to state
- Request for financing
- Public communication

2020- 2021

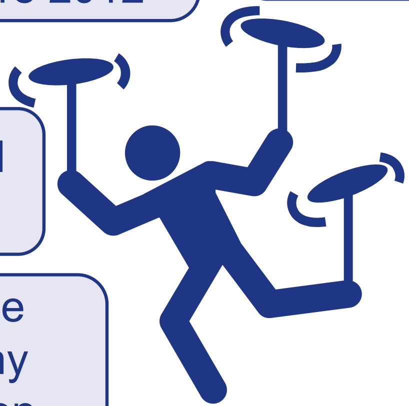
- Rejection for the sewage sludge compensation fund
- Revision of the EU Drinking Water Directive
- Participation and statement on water management planning

2022-ongoing

- Reconstruction of water treatment plant in Ottersdorf
- Legal action against Baden-Württemberg
- Oral hearing of damages claim

CHALLENGES

- Difficult removal due to the special properties of PFAS
- Ensuring drinking water supply
- Ensuring water quality
- Advancing prevention through appeals to legislation
- Find and contact experts
- Lack of practical experience with PFAS before 2012
- PFAS-Monitoring and Analysis
- Find the polluter
- Research for treatment technologies
- Develop technical solutions
- Investigation and evaluation of health effects
- 'Polluter pays' principle applicable?
- Determine the extent of damage
- Save the company reputation
- Fight for financing and funding
- Take legal actions
- Inform stakeholders
- Definition of fair water prices
- Future challenges
- Fight for clarifying the legal situation
- Giving consumers security



ZerOPM STADTWERKE RASTATT

CHALLENGES

Difficult removal due to the special properties of PFAS

Ensuring drinking water supply

Ensuring water quality

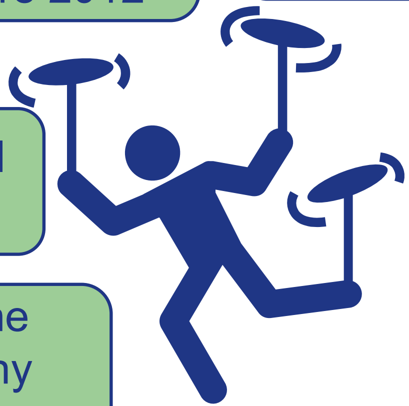
Advancing prevention through appeals to legislation

Find and contact experts

Lack of practical experience with PFAS before 2012

PFAS-Monitoring and Analysis

Find the polluter



Research for removal technologies

Develop technical solutions

Investigation and evaluation of health effects

'Polluter pays' principle applicable?

Determine the extent of damage

Save the company reputation

Fight for financing and funding

Take legal actions

Inform stakeholders

Definition of fair water prices

Future challenges

Fight for clarifying the legal situation

Giving consumers security

SOLUTION APPROACHES

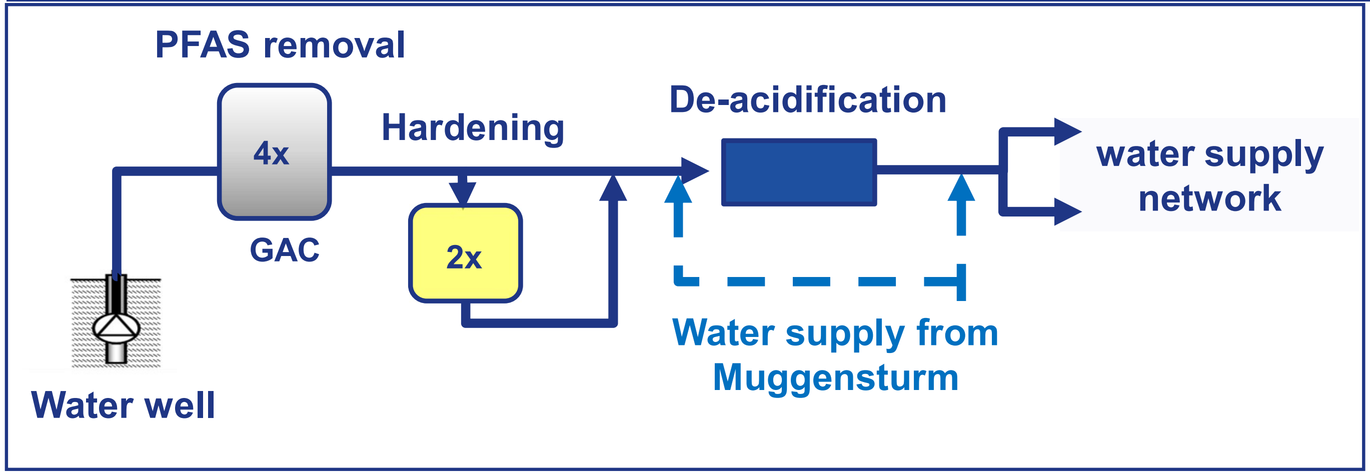
TECHNICAL SOLUTIONS

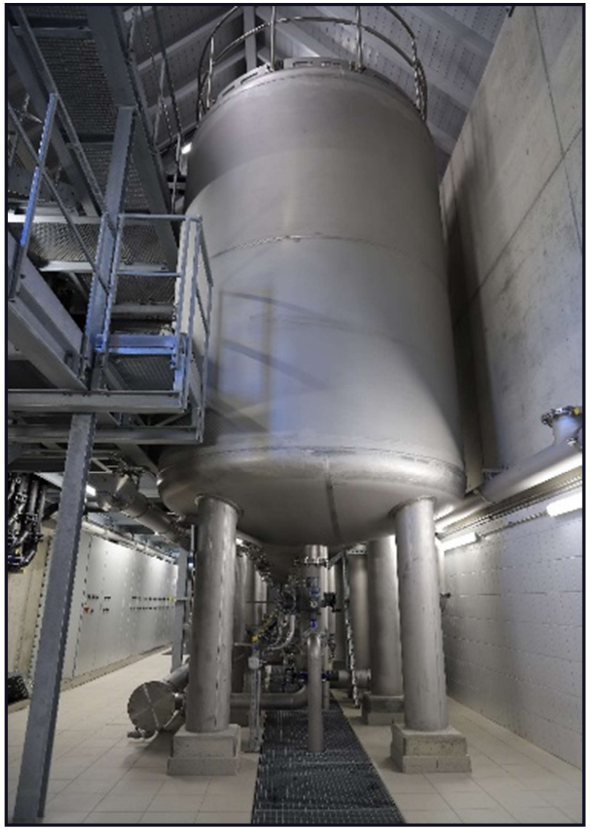
► First urgent measure	⇨ Water wells were taken out of operation
► Research	⇨ Feasibility study for best technologies ⇨ Activated carbon for PFAS removal
► Extension of damage	⇨ Groundwater models ⇨ Water, soil and groundwater analysis
► Engineering	⇨ Interconnection pipeline for redundancy ⇨ Reconstruction of water treatment plants ⇨ Construction of additional water wells
► PFAS-Monitoring	⇨ Over 35 measuring points

SOLUTION APPROACHES

SOLUTION APPROACHES

ACTIVATED CARBON TECHNOLOGY IN WATER TREATMENT PLANT IN RAUENTAL





- **4 filters** with granulated activated carbon (GAC)
- **25 tons** of activated carbon
- **250 m^3/h** treatment capacity
- **2,33 kg of PFAS** removed to date

SOLUTION APPROACHES

RESEARCH PROJECTS

- ► Research projects with activated carbon and ion exchangers
- ► Effectiveness test with ion exchangers for short-chain PFAS removal
- ► Collaboration in the EU project ZeroPM

COMMUNICATION AND NETWORKING

- ► Networking for PFAS cases
- ► Specialist reinforcement
- ► Information exchange with authorities and water utilities
- ► Transparent communication with public stakeholders
- ► Symposiums with technical and legal experts
- ► Communication with the Environment Agency and politicians

Zer◯PM STADTWERKE RASTATT

SOLUTION APPROACHES

LEGAL ACTIONS

- ► Criminal complaint against unknown person
- ► Civil action in 2019 for damages for amount of 6.5 million € against the compost manufacturer
- ► Legal action against the state of Baden-Württemberg
- ► Application for compensation from the National Sewage Sludge Compensation Fund
- ► Lawsuit against water management plan

BADISCHE NEUESTE NACHRICHTEN

Kraichgau | Pforzheim | Erleben | Nachrichten

BNN bei WhatsApp | Newsletter | Sporttabellen

Mittelbaden / Bühl

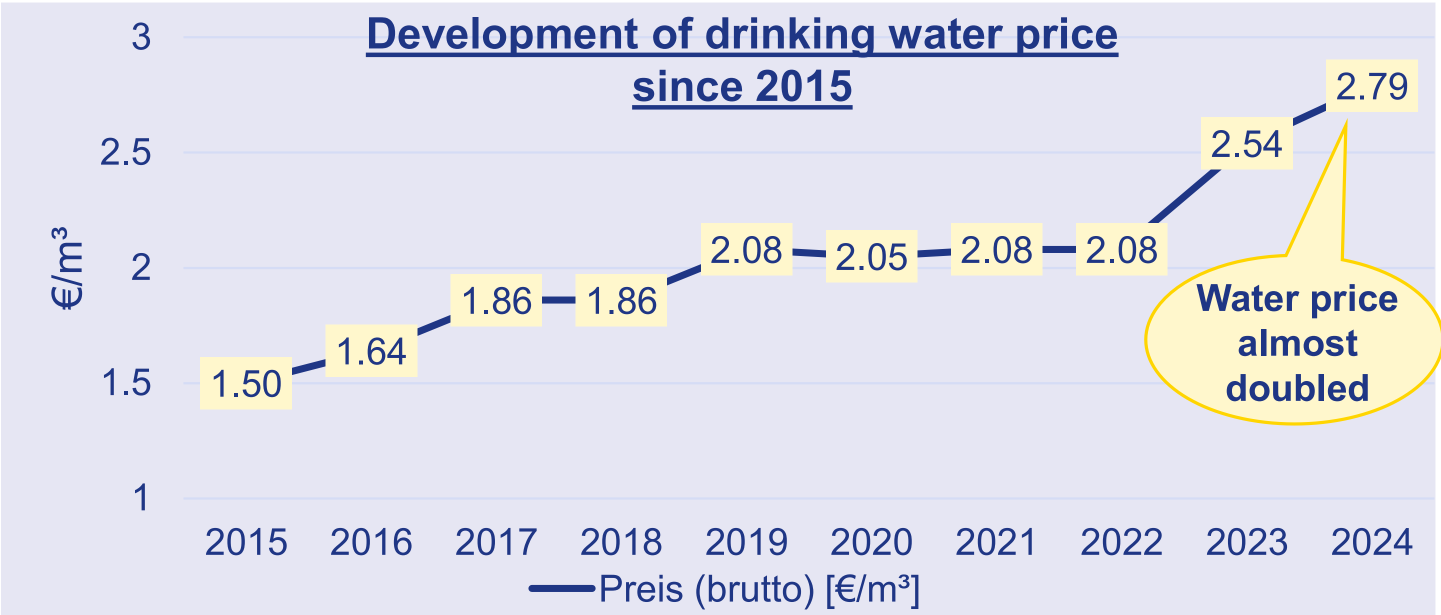
130 Hektar belastete Fläche

Kosten durch PFAS-Belastung im Grundwasser: Stadt Bühl und Stadtwerke Rastatt klagen gegen Land

Die Stadtwerke Rastatt und die Stadt Bühl klagen vor dem Verwaltungsgerichtshof Baden-Württemberg gegen das Land Baden-Württemberg wegen der Belastung des Grundwassers in Mittelbaden mit PFAS, bislang bekannt als PFC.

CONSECUENCES OF ACTIONS TAKEN FOR PFAS REMOVAL

COMPLEXER OPERATION + HIGHER COSTS = HIGHER WATER PRICES



Total net costs 2012 -2023

Investment	**11,2 M €**
Operation costs	**4,1 M €**
Total	**15,3 M €**

2024

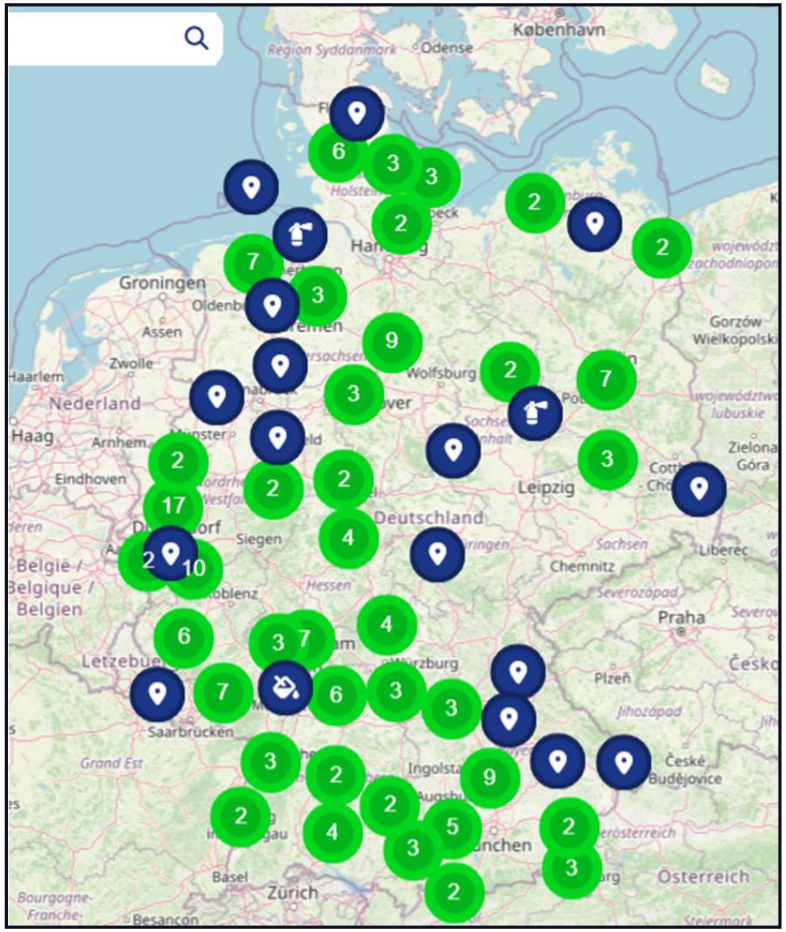
OUR SOLUTION APPROACHES

CONSECUENCES OF NEW LIMITS OF THE EU DRINKING WATER DIRECTIVE 2020/2184

EU WATER DIRECTIVE 2020/2184
PFAS Total < 0,5µg/L
Sum of PFAS-20 < 0,1µg/L
GERMAN DRINKING WATER DIRECTIVE
Sum of PFAS-20 < 0,1µg/L
Sum of PFAS-4 < 0,02µg/L

- ► Shorter service life of activated carbon: more frequent filter changes and regeneration cycles
- ► Reduction of the adsorption efficiency of activated carbon due to short-chain PFAS
- ► Research for more cost-efficient processes
- ► Higher demand for laboratory analysis
- ► Staff training

UNFORTUNATELY, WE ARE NOT THE ONLY ONE…



Research results of Stadtwerke Rastatt (2022):

- ► 187 cases of PFAS contamination in Germany
- ► 50% related to extinguishing water or foam use
- ► Greatest damage caused by soil application
- ► Groundwater is the most affected by PFAS
- ► 23 water utilities in Germany are dealing with PFAS contamination caused by extinguishing foams

RECOMMENDATIONS FOR WATER UTILITIES

► **DETERMINATION OF POLLUTION**

Analytics, groundwater models

► **ENSURING THE WATER SUPPLY**

Reconstruction of water treatment plants, investment, redundancy

► **IMPLEMENTATION OF TECHNICAL SOLUTIONS**

Testing, feasibility studies, research, experts support, training

► **PROTECTING REPUTATION**

Public relations, documentation, legal measures

► **CONVEYING SECURITY**

Consumer protection and public and transparent communication

- ► **FUNDING/ SUPPORT**
- ► **PRICE POLICY**
- ► **LEGAL PROCEDURES**
- ► **TRANSPARENT COMMUNICATION**
- ► **COOPERATION WITH AUTHORITIES**

CONCLUSIONS

- ► Public water utilities are forced to “remove” PFAS from the environment
- ► Uncertain and unknown duration of the cost increase and contamination
- ► Technical and legal processes due to PFAS contamination leads to considerable costs
- ► Citizens and municipalities assume the costs through water price increases
- ► The new limits for PFAS leads to further expenses and efforts for water utilities

UNKNOWNS

- ► How could such cases of contamination be avoided in the future?
- ► How long will the contamination last ?
- ► What responsibilities should PFAS manufacturers take ?
- ► Will PFAS be banned in future ?

THANK YOU!

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STADTWERKE
RASTATT

Agenda

Wednesday 12th June Time	Activity	Location
12.30 – 14.50	Presentations	BadnerHalle
15.00 – 16.00	Free time	
16.00 – 18.30	Buses to the Rauental water works for tours	Buses depart from BadnerHalle at 16.00. Group one will arrive back at around 17.15 and group two by 18.15
18.30 – late	Dinner	Avocado Restaurant, Karlstraße 38, 76437 Rastatt

Thursday 13th June Time	Activity	Location
8.15	Depart for TZW	Buses depart from BadnerHalle at 8.15!
9.15	Presentations	TZW, Karlsruher Str. 84, 76131 Karlsruhe
15.30	End of event	

Back up

ERFOLG: NEUE GRENZWERTE

EU-Trinkwasserrichtlinie hinsichtlich PFAS	Erfüllt von	Deadline
Umsetzung der neuen Grenzwerte für PFAS in die Deutsche Trinkwasserverordnung	Mitgliedstaaten	24. Juni 2023
Festlegung technischer Leitlinien bzgl. der Analyseverfahren zur Überwachung von „PFAS gesamt“ und „Summe PFAS“	EU-Kommission	12.Januar 2024
Klärung des Parameters „PFAS gesamt“	EU-Kommission	12. Januar 2024
Umsetzung der nötigen Maßnahmen	Mitgliedstaaten	12. Januar 2026

PFAS EU-Verbotsverfahren: Anfang 2023 veröffentlichte ECHA Vorschlag zur EU-weiten Beschränkung von PFAS, der aktuell wissenschaftlich bewertet wird. Die Beschränkungen sollen 2026/27 in Kraft treten.

Deutsche Trinkwasserverordnung hinsichtlich PFAS	Erfüllt von	Deadline
Summe PFAS-20 < 0,1µg/L	Deutsche Wasserversorger	12. Januar 2026
Summe PFAS-4 < 0,02µg/L	Deutsche Wasserversorger	12. Januar 2028

HERSTELLERVERANTWORTUNG

- Wichtige Quellen von PFAS-Emissionen sind die Hersteller von Fluorchemikalien und/ oder Fluorpolymeren sowie Karton- und Papierfabriken
- Die europäische Chemikalienagentur ECHA eröffnet Konsultation zur Beschränkung von PFAS
- **EU-Kommission verbietet alle PFAS als Gruppe** in Feuerlöschschäumen sowie in anderen Verwendungszwecken und Zulassung ihrer Verwendung, es sei denn, dass sie für die Gesellschaft unerlässlich sind
- Derzeit keine Einstufung oder Aufnahme der kurzkettigen PFAS, da bisher keine Toxizität nachgewiesen werden konnte
- **Ersatzstoffe sind kritisch:** nach dem Verbot der PFAS werden Ersatzstoffe auf dem Markt gebracht die jedoch nur unzureichend auf gesundheitliche Auswirkungen getestet wurden. Als Beispiel ist die GenX-bezogene Chemikalie
- In den USA werden PFAS-Hersteller bereits verklagt
- Deutsche Industrieverbände warnen vor einer Gefährdung der EU-Klimaziele bei einem umfassenden Verbot von sogenannten Ewigkeits-Chemikalien

WIE KANN PFAS IM TRINKWASSER ENTFERNT WERDEN?

ZeroPM STADTWERKE RASTATT

Wirksame Verfahren:

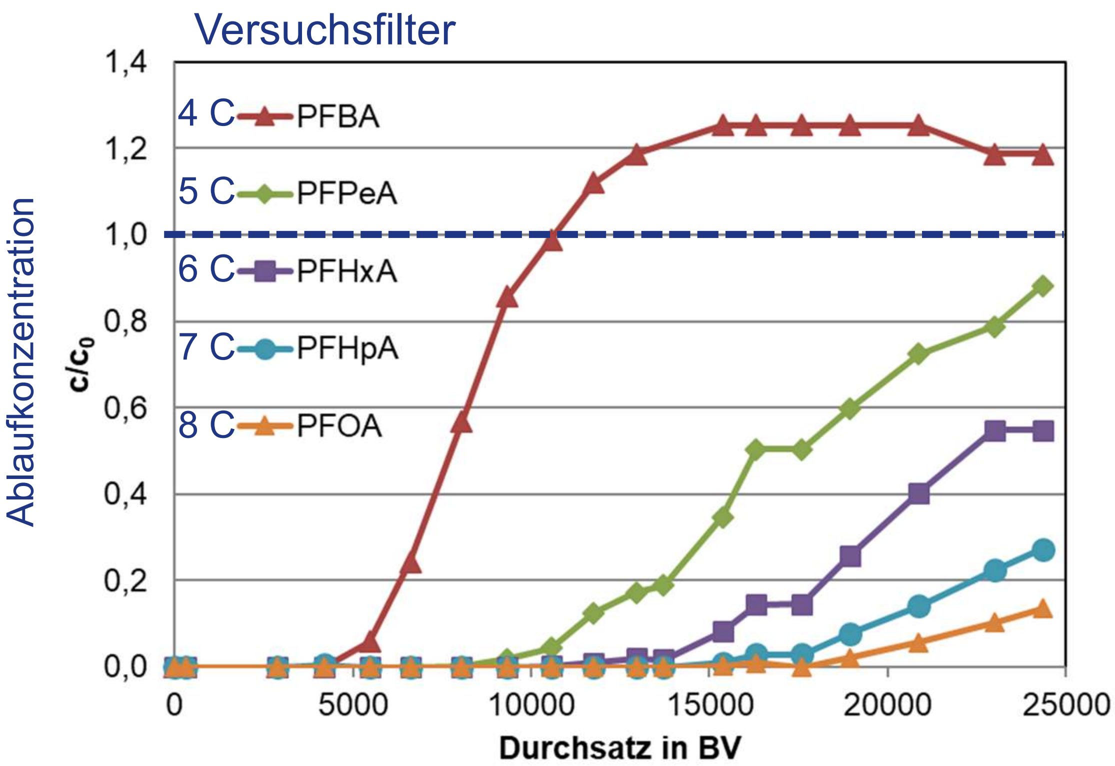
- Adsorption
  - Aktivkohle
  - (Ionenaustausch)
  - (Bentonit)
- Membranfiltration
  - Nanofiltration (NF)
  - Umkehrosmose (UO)

Unwirksame Verfahren:

- Uferpassage
- Belüftung
- Flockung
- Enteisenung
- Ultrafiltration
- Oxidation (O_3, $KMnO_4$)
- Desinfektion (Cl_2, UV)
- ….

AKTIVKOHLE: WIE KANN DAS GUT FUNKTIONIEREN?

-> **Pilotversuche** bei den SW Rastatt, um Erfahrungen zur großtechnischen Umsetzung zu bekommen.

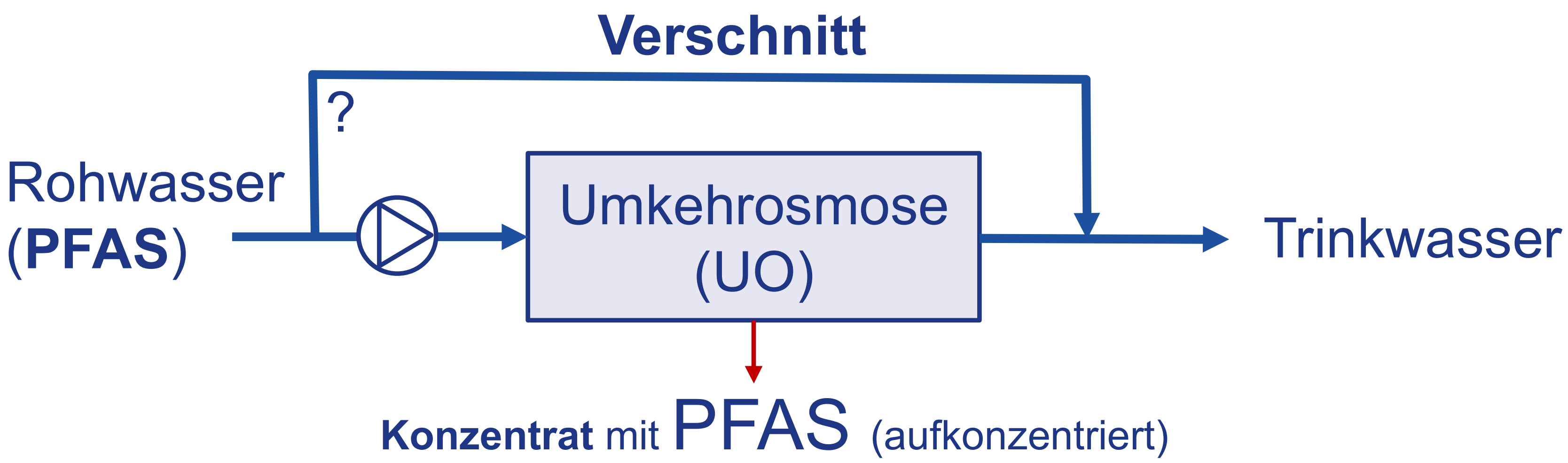


- Effizienz abhängig von der Kettenlänge
- Kurzkettige PFAS sind deutlich schlechter entfernbar
- Chromatographie-Effekt

⇨ Häufige Aktivkohlewechsel

ERFAHRUNGEN MIT DER MEMBRANTECHNIK

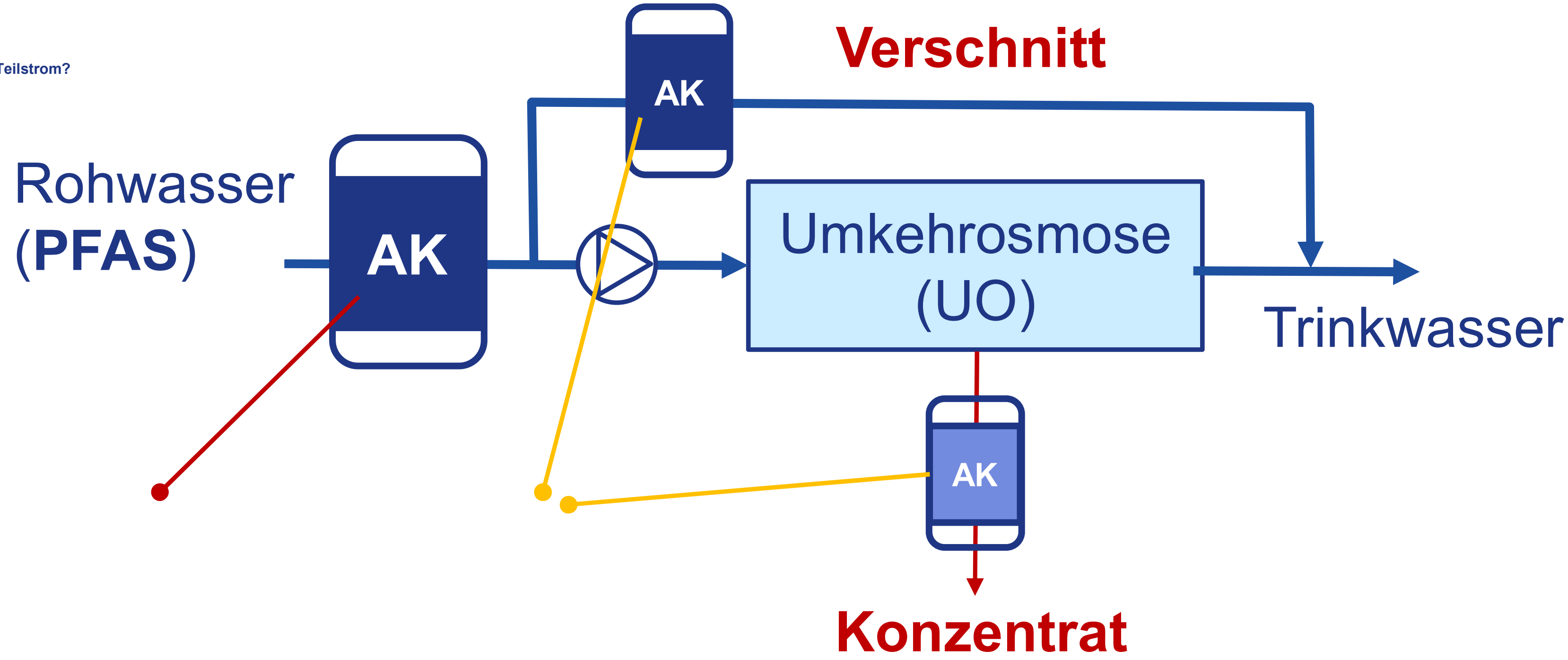
- Die Umkehrosmose entfernt **nahezu 100 %** der PFAS
- **Verschnitt** muss PFAS-frei sein



KONSEQUENZ FÜR DIE MEMBRANTECHNIK

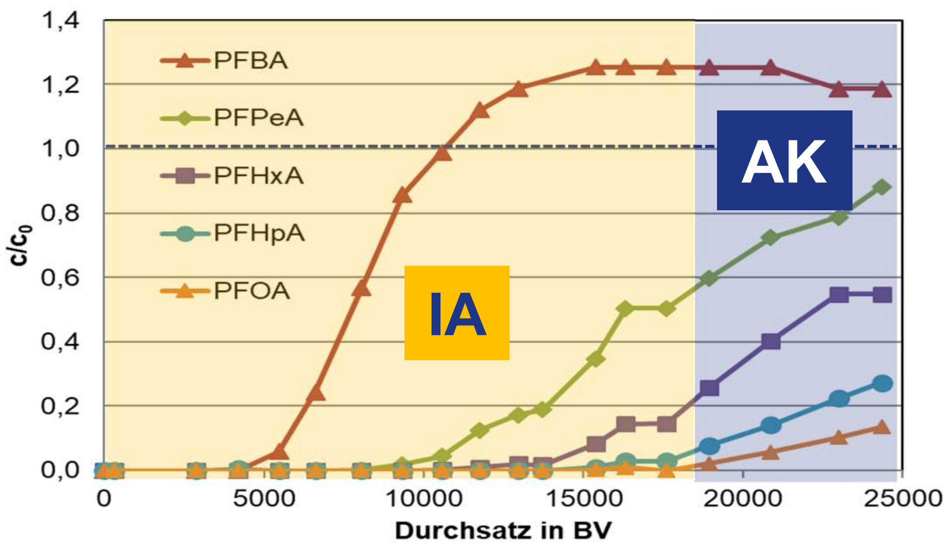
- Es muss ein Adsorptionsverfahren zur Entfernung von PFAS eingesetzt werden -> zusätzlicher Aufwand

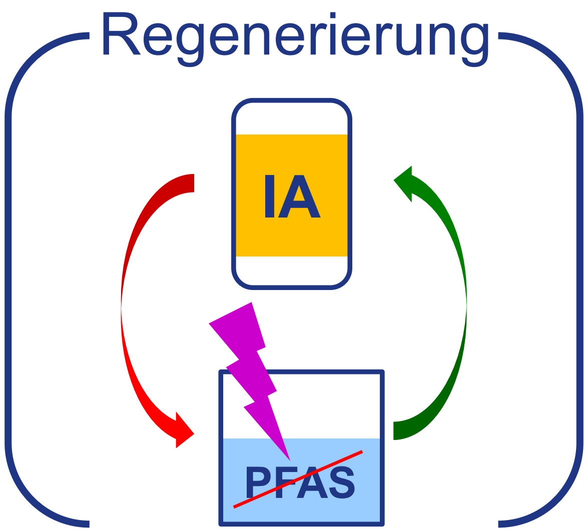
Vollstrom oder Teilstrom?



WEITERE FORSCHUNG & ENTWICKLUNGEN

– Die Hoffnung gilt dem **Ionenaustausch**:





EU Green Week

PARTNER EVENT

ZeroPM Special Symposium on PFAS elimination from drinking water

Rastatt / Karlsruhe

12th and 13th June 2024

#WaterWiseEU

DVGW | TZW Technologiezentrum Wasser | ZeroPM

An introduction to the PFAS problem and ZeroPM's approach to solve it

Sarah Hale
TZW
sarah.hale@tzw.de

DVGW | TZW Technologiezentrum Wasser

ZeroPM

The PFAS problem

North Yorkshire town has UK's highest concentration of 'forever chemicals'

PFAS contamination recorded in groundwater on Angus Fire site in Bentham, and includes chemicals with known health impacts

Bentham is home to the Angus International Safety Group – locally known as
Photograph: Rob Whitrow/Rob Whitrow/Ends Report

Jersey people with high PFAS levels could get treatment

21 October 2023

PFAS, used in firefighting foam, leaked into the area by the airport's fire training ground in the early 1990s

Experts have recommended that a blood treatment is offered to Jersey people with high levels of PFAS.

Experts call for tighter limits on 'forever chemicals' in water

18 October 2023 · Comments

;tallard
:ience reporter, BBC News

its are needed on levels of 'forever chemicals' in UK drinking
h are potentially harmful to human health, experts have warned.

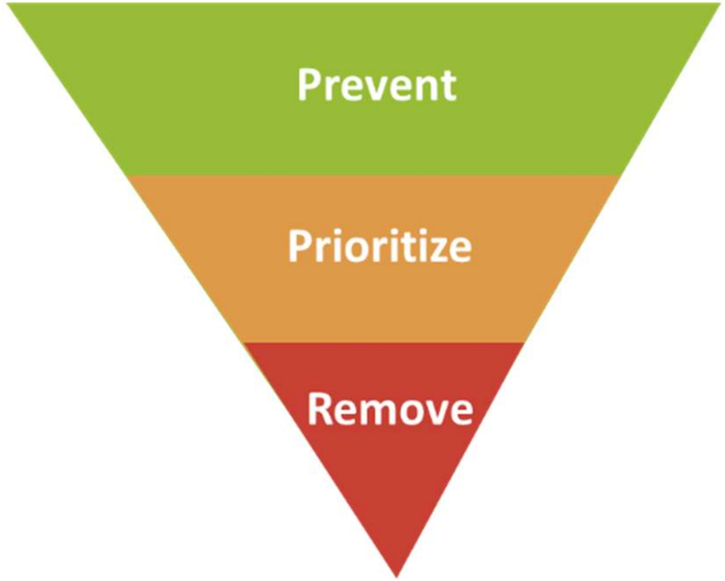
The ZeroPM approach to solve it

DVGW | TZW Technologiezentrum Wasser

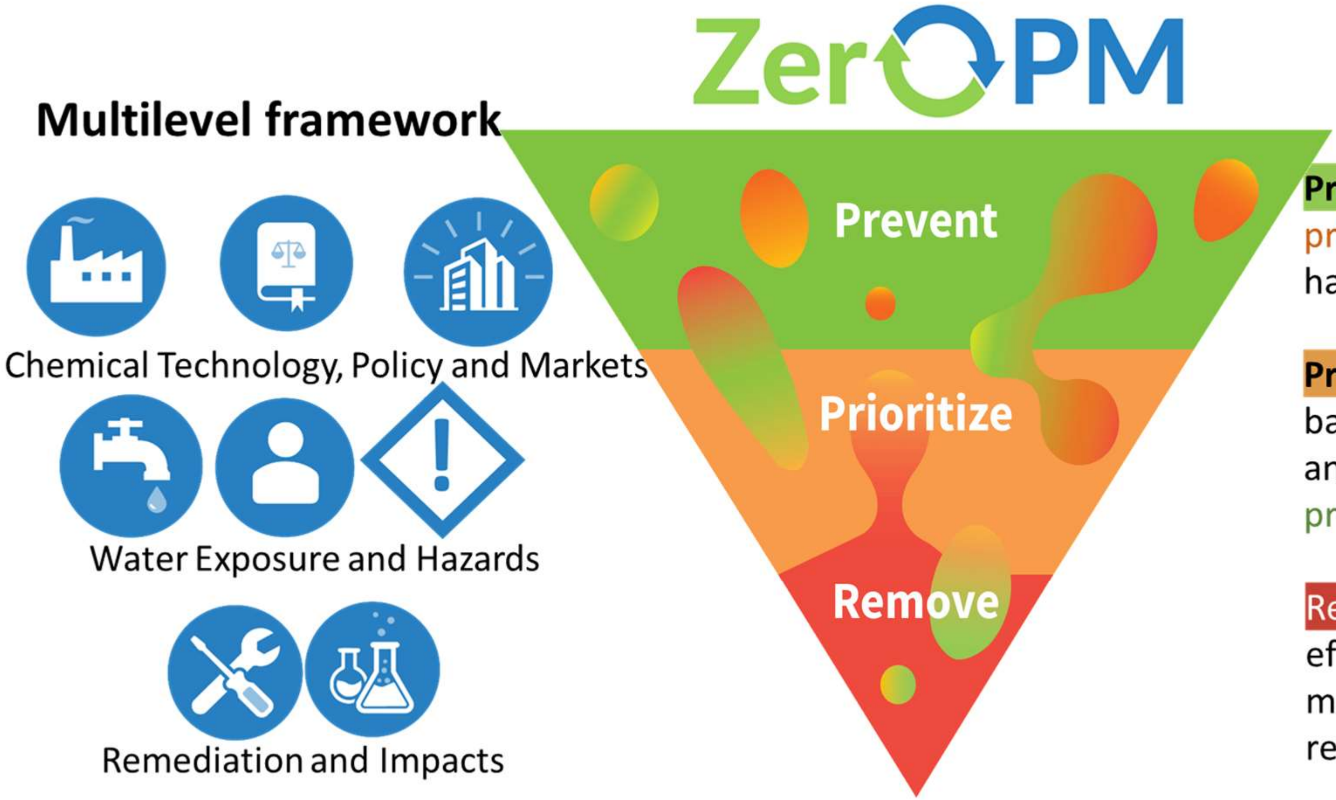
ZeroPM

Zero pollution of persistent, mobile substances

- ZeroPM will interlink and synergize three strategies to protect the environment and human health from **<u>persistent, mobile</u>** substances: **Prevent**, **Prioritize** and **Remove**.



ZeroPM's concept



Interlinked Strategy

Preventing regrettable substitution for prioritized PM substances, by assessing hazards, sustainability, exposure and removal.

Prioritizing PM substances and groups based on intrinsic properties, exposure, and hazard to select those substances to prevent and remove most urgently

Removing prioritized PM substances via effective, sustainable and safe remediation methods, that prevent unfocused remediation effort

WP2 Alternatives Assessment

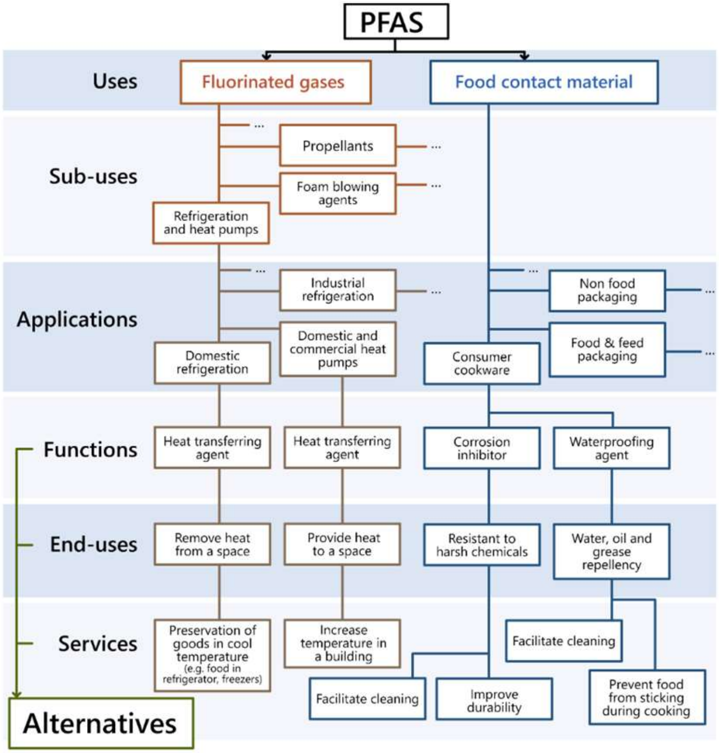
Objective: to provide **safer chemical alternatives to non-essential uses** of PM substances

- for each use of substances of concern, the database provides its chemical function, end-use function, and function as a service

Use categories
Active pharmaceutical ingredients
Biocidal product
Building and construction products
Consumer mixtures
Cosmetics
Electronics and semiconductors
Energy sector
Fluorinated gases
Food contact materials
Lubricant
Medical devices
Metal products manufacture and metal plating
Petroleum and mining
Plant protection products
Ski wax
Transport
Textile, upholstery, leather, apparel, and carpets (TULAC)

ZeroPM Alternatives Database

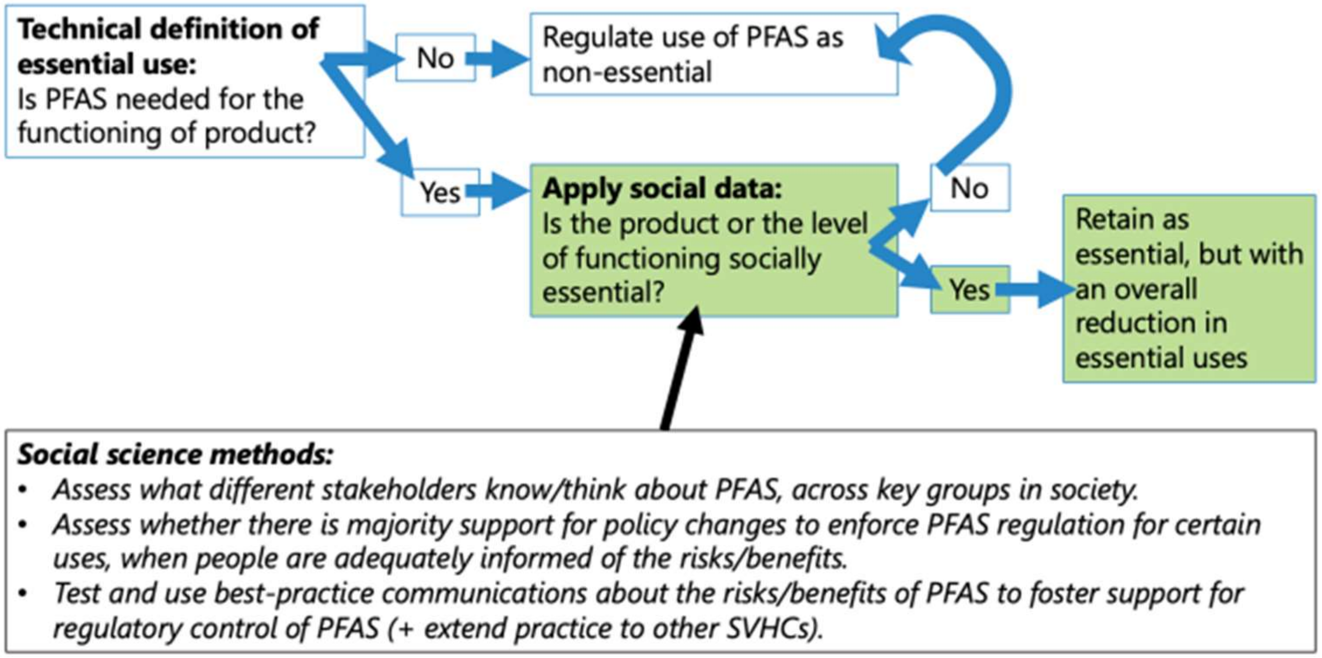
sent into the public consultation for the broad PFAS restriction



General structure of the ZeroPM alternatives database for PFAS - Examples of fluorinated gases and food contact material

WP2 Alternatives Assessment

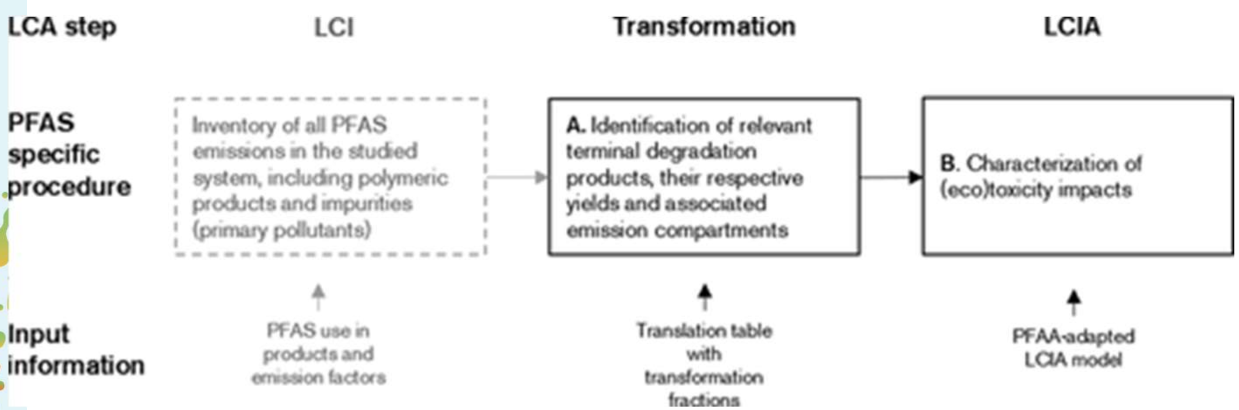
- Social perceptions
- An extra layer of essentiality beyond technical function
- Relevant for assessing diverse stakeholder perspectives (industry, general public, policy)



Suffill et al. Environ. Sci. Europe. 2024

WP2 Overall Sustainability Considerations

- Consider life cycle impact analysis with alternatives assessment
- Also consider technology and impacts of water removal technology



Holmquist et al. Environ. Sci. Technol. 2020, 54, 10, 6224-6234

Energy intensive reverse osmosis facility to eliminate PFAS at the Rastatt test site to make drinking water potable

WP3 Policy

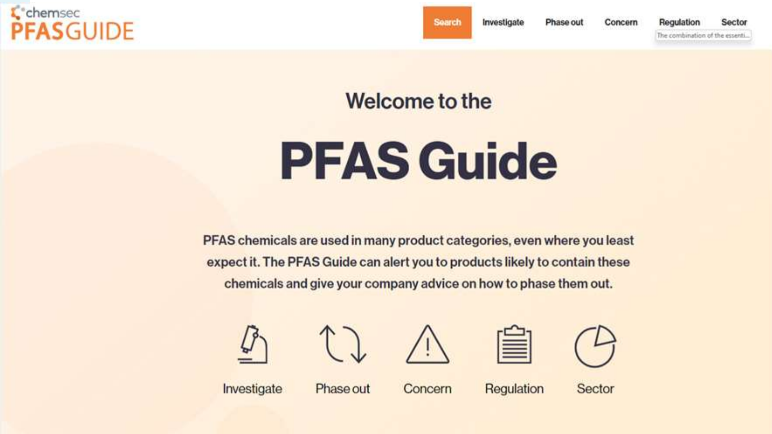
Objective: to **stimulate and support policy changes** to more effectively tackle PM substances

- ZeroPM Regulatory Watch
- Policy actions tailored to groups of PM/PFAS substances, uses or sectors facilitating a transition towards zero pollution from PM substances
- Design roadmaps for groups of PM substances, uses or sectors
- To promote implementation of PM substance assessment into EU legislation engaging all relevant stakeholders

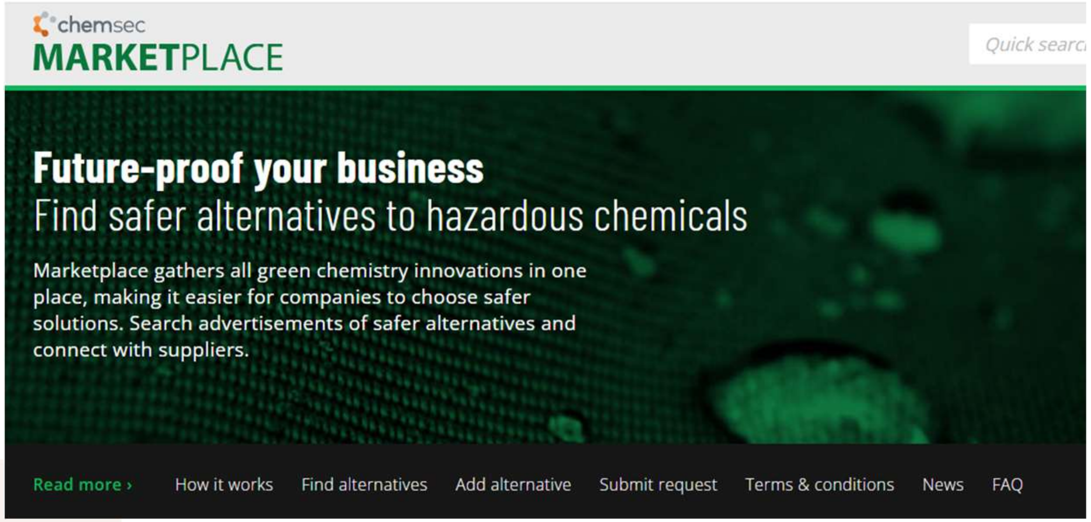
https://zeropm.eu/regulatory-watch/

WP4 Market Transition

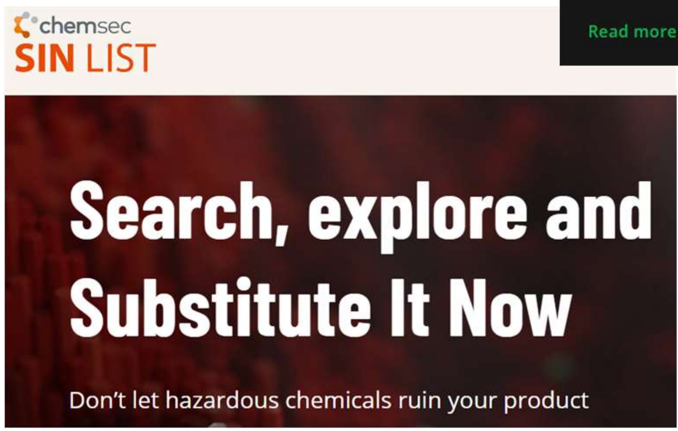
Objective: to **catalyse a market transition** away from harmful PM substances



https://pfas.chemsec.org/



https://marketplace.chemsec.org/



https://sinlist.chemsec.org/

SIN List helps you identify the most relevant PFAS and other hazardous substances to start substituting (before regulators make you)

WP4 Market Transition

- Map PFAS in products to provide information to companies
- Existing reports, databases and publications
- The investigate section lists and explains typical PFAS uses showing red flags where these uses are suspected to contain PFAS.
- There is a section on supply chain communication explaining how and what to ask suppliers about PFAS.
- There is a section with a basic introduction to different methods for chemical analysis of PFAS in different types of products.
- The phaseout section gives a short introduction to substitution and alternatives assessment and links to further resources on this.
- There is a short summary of the regulatory situation for PFAS in the EU and the US.
- There are also links to good reports by others about PFAS and how to substitute PFAS in different sectors, such as Paints, Textiles, Food Packaging, Construction and more.
- There is also a database where you can search for sectors, products, uses and functions to understand if you have "PFAS hotspots" in your business

WP5 Substance Grouping

Objective: To **prioritize PM substances and substance groups** on the global chemical market for prevention and removal

- **PFAS Tree to navigate PFAS on Pubchem** (>7 million!)
  https://pubchem.ncbi.nlm.nih.gov/classification/#hid=120

PubChem Classification Browser

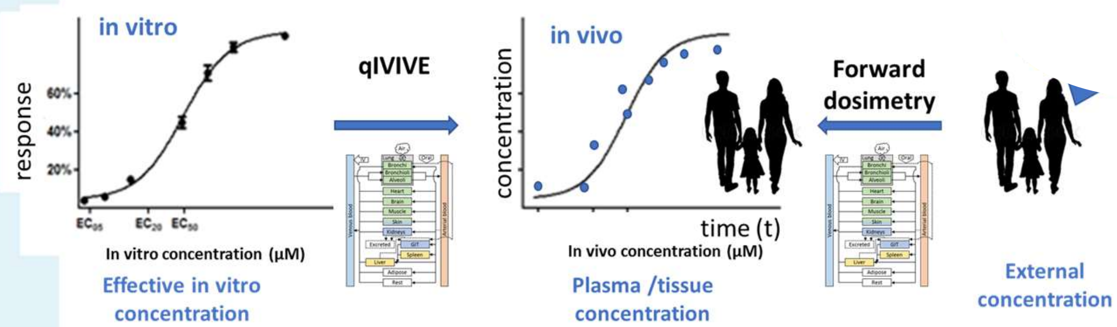
Browse PubChem: PFAS and Fluorinated Compounds in PubChem Tree

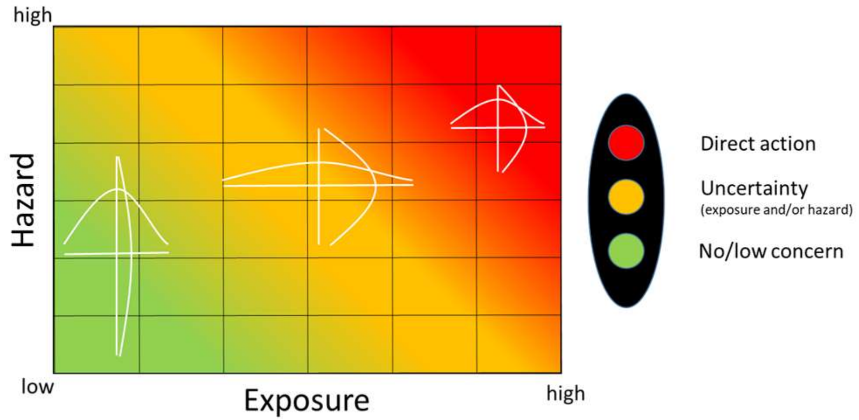
- PFAS and Fluorinated Compounds in PubChem 21,410,924
  - OECD PFAS definition 6,540,217
  - Organofluorine compounds 20,417,012
  - Other diverse fluorinated compounds 125,621
  - PFAS and fluorinated compound collections 1,789,296
  - PFAS breakdowns by chemistry 7,497,118
  - Regulatory PFAS collections 26,943

[Navigating over 6 million PFAS! A walk through the PFAS tree with Emma Schymanski - YouTube]()

WP6 Risk Assessment

Objective: To **characterise and quantify impacts** of PM substances on human health and the environment





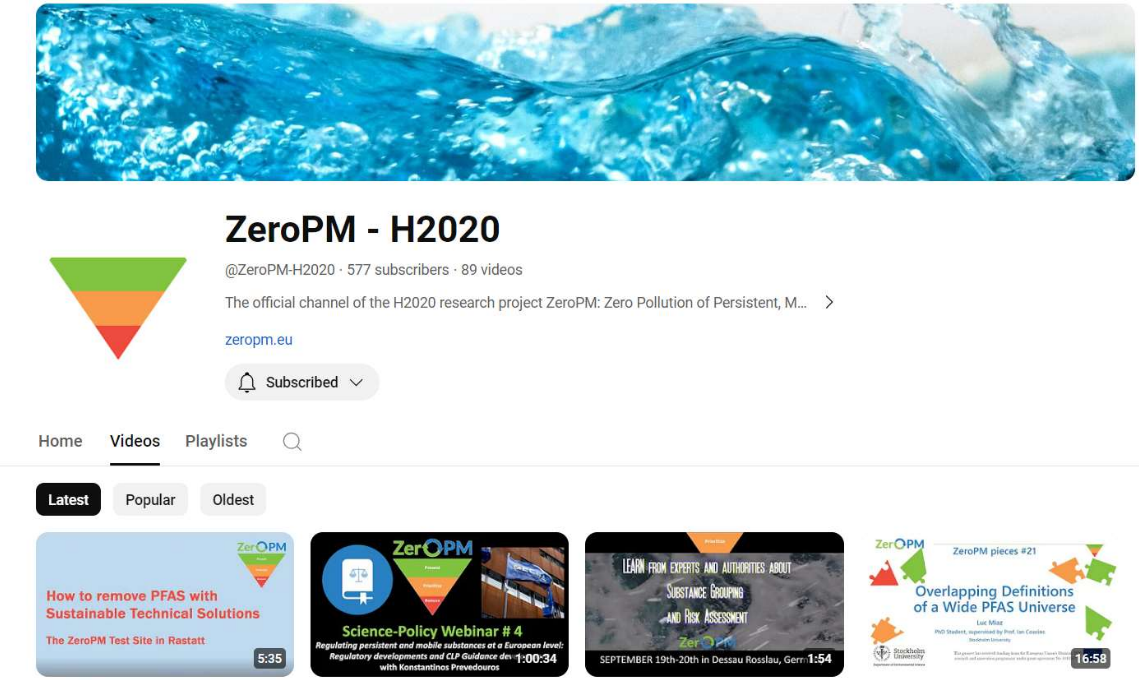
WP7 Technical Solutions

Objective: to demonstrate **how and if** legacy and prioritized PM substance pollution **can be remediated**

- Developing passive sampler for PFAS and PMT/vPvM monitoring
- Pilot scale testing of water treatment solutions to PFAS and PMT substances
  - Coupling AC with regenerative ion-exchange and electrochemical degradation
- Pilot scale testing of sludge treatment for PFAS and PMT substances
  - using hydrothermal carbonization (HTC)

WP8 Dissemination and Communication

Objective: to spread and embed ZeroPM's results with our stakeholders



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

Thank you for attending and look out for our next webinar, film, event or opportunity to participate

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ZeroPM

PFAS occurrence and monitoring – Insights from the NORMAN network

Ian J Allan
Emma R Knight
Bert van Bavel

Norwegian Institute for Water Research

This presentation

- Introduction to the NORMAN network
  - Organisation
  - Activities (JPAs)
  - Databasing
- PFAS sampling and passive sampling in water
  - Introduction to passive sampling
  - Passive samplers tested/developed in ZeroPM

NORMAN network

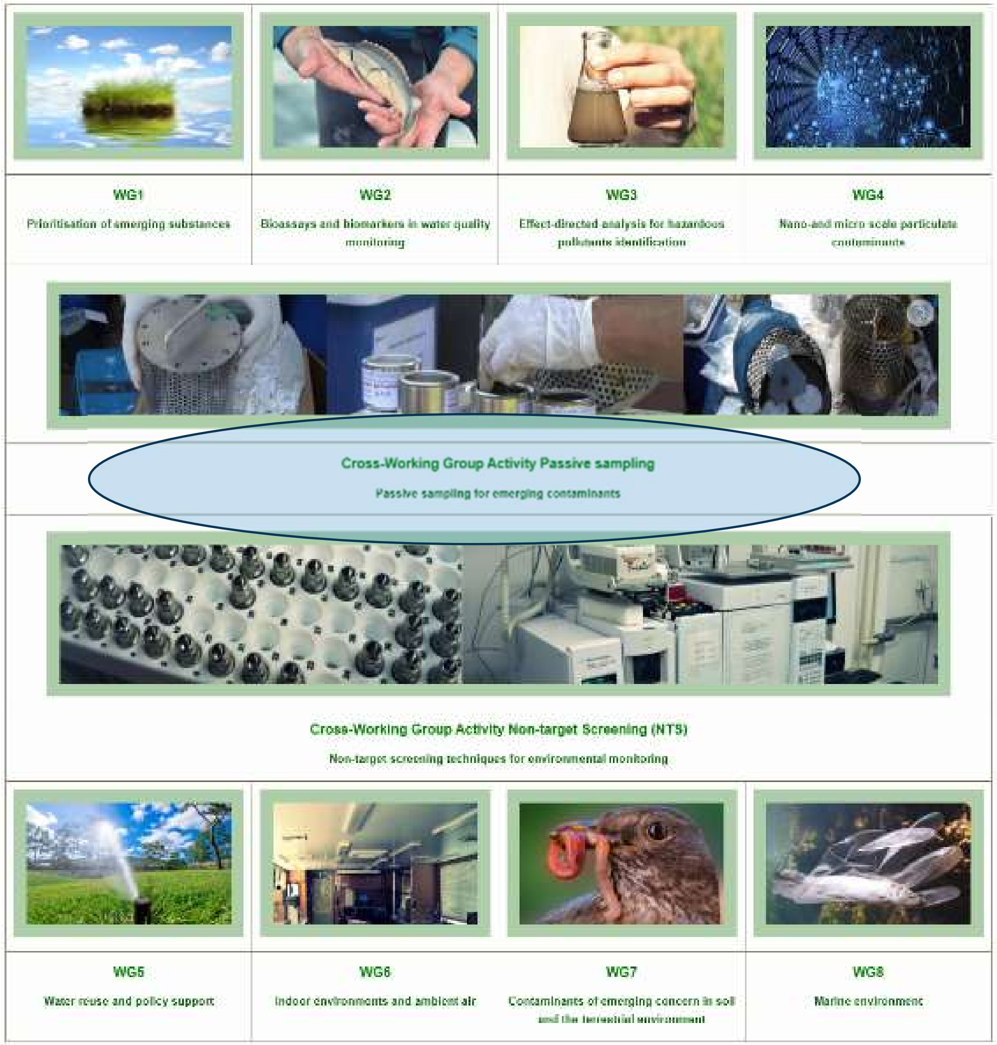
WELCOME TO THE NORMAN NETWORK | NORMAN (norman-network.net)

- Started as a EU 6th FP project and became a self-sustaining network of reference and research laboratories and related organisations involved in ermerging contaminant (bio)monitoring in 2009
- The network has grown over the years to include many stakeholders dealing with emerging substances
  - National authorities
  - Reference laboratories
  - Research centres and academia
  - Industrial stakeholders
- Objectives of NORMAN:
  - Exchange of information and data collection on emerging environmental substances;
  - Validation/harmonisation of common measurement methods and monitoring tools
  - Maintenance/development of knowledge of emerging pollutants by stimulating coordinated, interdisciplinary projects on problem-oriented research and knowledge transfer

Joint Programme of Activities

NORMAN driving force: Valeria Dulio and Jaroslav Slobodnik

NORMAN working groups



Past output of the **cross-working group activity on passive sampling**

- JPAs
- Workshop/discussions
- Position papers
- research cooperation e.g. with ILS …

Inter-laboratory mass spectrometry dataset based on passive sampling of drinking water for non-target analysis | Scientific Data (nature.com)

Position paper on passive sampling techniques for the monitoring of contaminants in the aquatic environment – Achievements to date and perspectives - ScienceDirect

Mobile dynamic passive sampling of trace organic compounds: Evaluation of sampler performance in the Danube River - ScienceDirect

Towards the review of the European Union Water Framework Directive: Recommendations for more efficient assessment and management of chemical contamination in European surface water resources - ScienceDirect

Databases in NORMAN

Chemical occurrence data

→PFOS in surface water (River water)

Over 50 000 entries for 2010-2024

SEARCH All Databases

Searching for individual substance or group(s) of substances in all databases

Note: Click on a link below to go to an individual database home page

SARS-CoV-2 in sewage

A database with the latest information on SARS-CoV-2 in sewage across Europe and internationally; including a common protocol for

Substance Database

A merged list of NORMAN substances; Central Database to access various lists of substances for suspect screening and prioritisation

Suspect List Exchange

Central Database to access various lists of substances for suspect screening and prioritisation

Digital Sample Freezing Platform

A database of mass chromatograms obtained by LC-HR-MS for retrospective screening of environmental samples

Substance Factsheets

A summary information on individual substances from all NORMAN Database System modules

Show 200 entries

ID	Substance	Concentration	Unit	Ecosystem/Matrix	Sampling Site/Station	Sampling Date	Country
3927679	Perfluorooctanesulfonic acid (PFOS)	< LoQ		Surface water - River water	Pont de la D219 au Vert	2010/08/30	France
3927710	Perfluorooctanesulfonic acid (PFOS)	< LoQ		Surface water - River water	Pont de la D219 au Vert	2010/09/20	France
3927741	Perfluorooctanesulfonic acid (PFOS)	< LoQ		Surface water - River water	Pont de la D219 au Vert	2010/10/11	France
3927772	Perfluorooctanesulfonic acid (PFOS)	< LoQ		Surface water - River water	Pont de la D219 au Vert	2010/11/02	France
3927803	Perfluorooctanesulfonic acid (PFOS)	< LoQ		Surface water - River water	Pont de la D219 au Vert	2010/11/22	France
3927834	Perfluorooctanesulfonic acid (PFOS)	< LoQ		Surface water - River water	Pont de la D219 au Vert	2010/12/13	France
3927987	Perfluorooctanesulfonic acid (PFOS)	< LoQ		Surface water - River water	Pont de St-Faziol	2010/08/30	France
3928018	Perfluorooctanesulfonic acid (PFOS)	0.5	µg/l	Surface water - River water	Pont de St-Faziol	2010/09/20	France
3928049	Perfluorooctanesulfonic acid (PFOS)	1.1	µg/l	Surface water - River water	Pont de St-Faziol	2010/10/11	France
3928080	Perfluorooctanesulfonic acid (PFOS)	0.68	µg/l	Surface water - River water	Pont de St-Faziol	2010/11/02	France
3928111	Perfluorooctanesulfonic acid (PFOS)	1.9	µg/l	Surface water - River water	Pont de St-Faziol	2010/11/22	France
3928142	Perfluorooctanesulfonic acid (PFOS)	0.52	µg/l	Surface water - River water	Pont de St-Faziol	2010/12/13	France
3929590	Perfluorooctanesulfonic acid (PFOS)	< LoQ		Surface water - River water	Pont de la D144 à Merpins	2010/08/30	France
3929621	Perfluorooctanesulfonic acid (PFOS)	< LoQ		Surface water - River water	Pont de la D144 à Merpins	2010/09/20	France

NORMAN network: PFAS work

Date	Activity	Type
2009	3rd Interlaboratory study on perfluorinated compounds in water, fish and sludge *Organised by: NORMAN and QUASIMEME (IVM-VU University, Amsterdam)*	ILS
2020	Proficiency test 5/20 - TW S3 - TW S4 – PFC in drinking water *Organised by: IWW and AQS Baden-Württemberg, Germany*	ILS
2021	PFAS Analytical Exchange *Organised by: Environment Agency (UK) in collaboration with Aarhus University (DK), Finnish Environment Institute SYKE (FI), IWW Water Centre (DE), Norwegian Environment Agency (NO), Örebro University (SE), University of the Basque Country (ES), VITO NV (BE), Wageningen Food Safety Research (NL)*	International exchange
2022	PFAS suspect HRMS lists and lists of PFAS-containing products *Organised as a part of the NORMAN JPA 2022 by QAEHS – the Queensland Alliance for Environmental Health Science, The University of Queensland, Australia; IRSA-CNR - Water Research Institute of the National Research Council of Italy and University of Amsterdam, The Netherland*	Survey/ international exchange
2022	Proficiency Test 2/22 - TW S7 – Trifluoroacetic acid in drinking water *Organised by: AQS Baden-Württemberg at Institute for Sanitary Engineering, Water Quality and Solid Waste Management, University of Stuttgart, Bandtäle 2, 70569 Stuttgart-Büsnau, Germany*	ILS
2022	PFAS analytical exchange - TOP Assay Method Comparison *Organised by: Environment Agency (UK) In collaboration with University of the Basque Country, Vito NV, Fraunhofer IME, Örebro University, Wageningen University & Research, Luleå University of Technology, German Federal Environment Agency, The French National Centre for Scientific Research*	Exchange
2022	Proficiency Test PT 7/22 TW S4 – PFAS according to EU drinking water directive *Organised by: AQS Baden-Württemberg at Institute for Sanitary Engineering, Water Quality and Solid Waste Management, University of Stuttgart, Bandtäle 2, 70569 Stuttgart-Büsnau, Germany and IWW Water Center, Moritzstr. 26, 45476 Mülheim an der Ruhr, Germany*	ILS

ILS on target and non-target PFAS analysis of passive sampling and water extracts (2023-2025)

OBJECTIVE

Better understand the performance, reproducibility, and robustness of PS and NTS methods for PFASs, for the advancement of these tools in compliance and risk assessment frameworks.

OVERVIEW

JPA 2023

Phase 1

- Deploy one type of passive samplers at one site in Australia
- QAEHS to extract and homogenise samplers.
- QAEHS to send extracts to participants
- Analysis for target and/or NTA – **Deadline 30 January 2024**

JPA 2024

Phase 2

- Deploy different samplers at a site/s in EU
- Participants to receive samplers they will extract, plus homogenised extracts
- Analysis for target and/or NTA – **to begin Early 2024**

Number of participating labs: 29 institutions, 16 different countries!

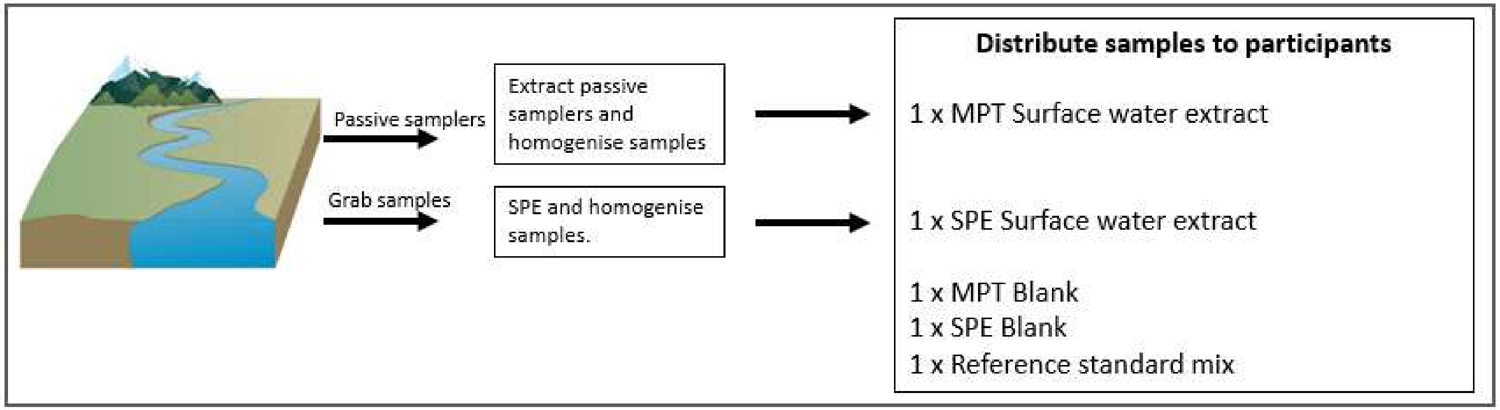
Dr Sara Gorji, QAEHS, Australia s.ghorbanigorji@uq.edu.au

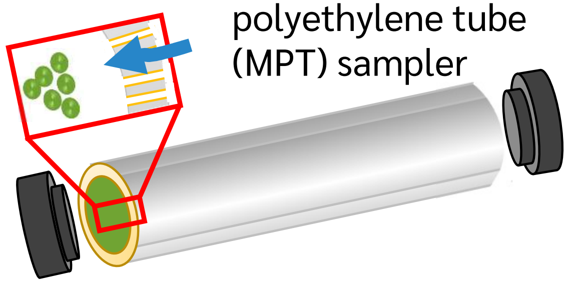
Dr Sarit Kaserzon, QAEHS, Australia k.sarit@uq.edu.au

ILS on target and non-target PFAS analysis of passive sampling and water extracts (2023-2025)

One passive sampling configuration for target and suspect/non-target screening. The aims are to examine the following:

(i) Type of PFAS that can be monitored using passive sampling devices and SPE
(ii) Comparativeness of analytical methods (i.e., chromatography-mass spectrometry methods)
(iii) Effectiveness of extended suspect screening workflows for the detection of PFAS in PS extracts and comparativeness of the processing methods using a set list of target and spiked PFAS as well as expanded NTA reporting from each participating laboratory.





Dr Sara Gorji, QAEHS, Australia s.ghorbanigorji@uq.edu.au
Dr Sarit Kaserzon, QAEHS, Australia k.sarit@uq.edu.au

Passive sampling

- Passive sampling measures a concentration of contaminant

  Dissolved or labile in water

  Based on diffusive processes
- In/ex situ measurements of trace contaminants:

  Dissolved/labile in water, in sediment/soil pore waters

  That are bioaccessible
- Integrative monitoring over periods of days to months
- Improved limits of detections and simplified matrix composition

Conceptual model

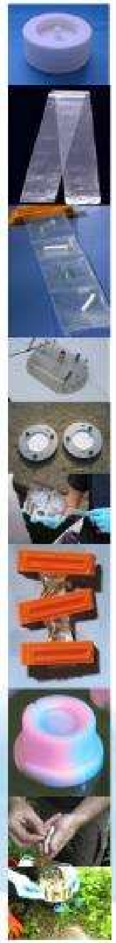
Diffusive boundary layer

Membrane

Sorbent

Water

Concentration



Passive sampling operation

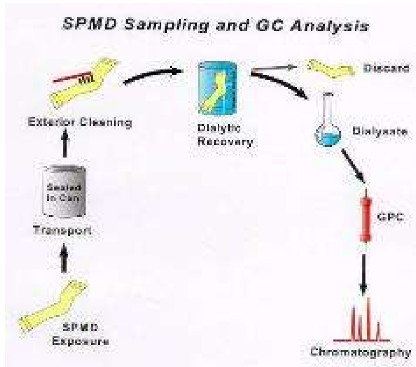
Sampler deployment

Exposure for days-months

Sampler Retrieval

Sampler selection

Sampler Extraction and analysis

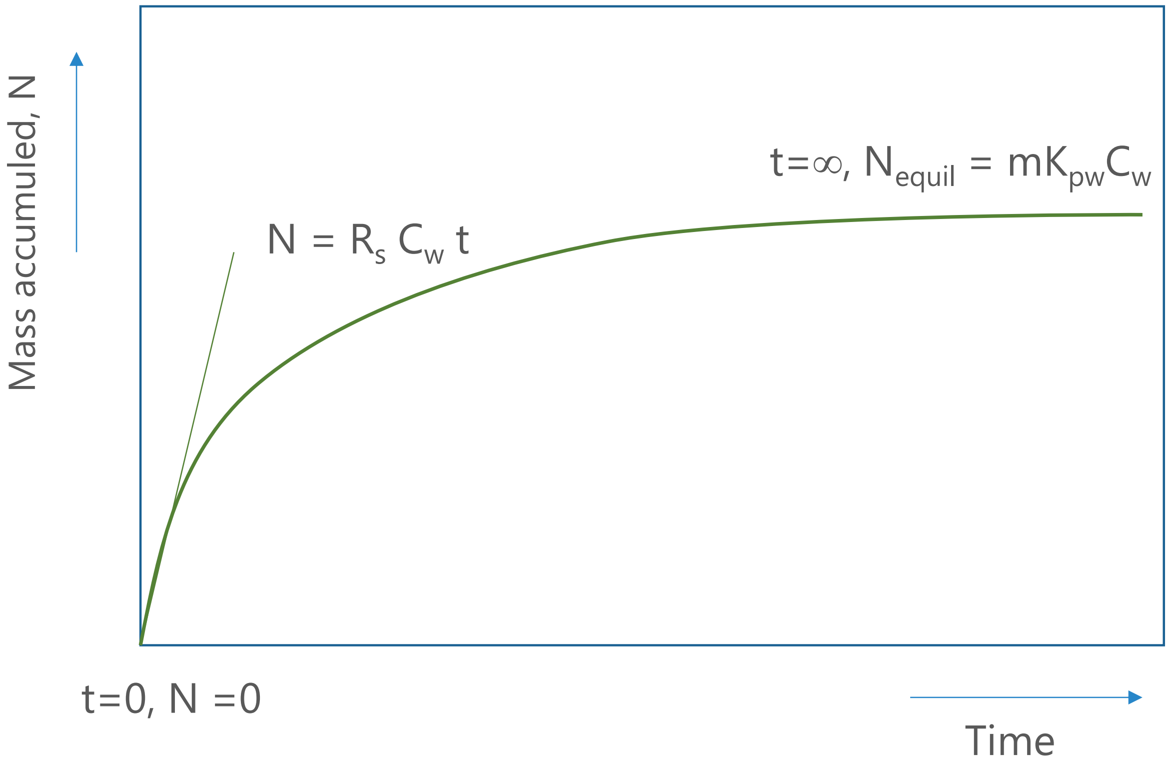


Modelling...

Calculation of concentration, C_W

Principle of accumulation into passive samplers

Contaminant accumulation in time



1st order kinetics

$$N = N_{equil}(1 - \exp(-k_e t))$$

$$R_s = \frac{m_{acc}}{C_w t}$$

Example of passive sampling for PFAS

Randselva deployments – upstream and downstream former industial site (paper producing factory)

- Papercup production
- Contaminated soil and ground water
- Contaminated sediment dowsnstream of the industrial site

POCIS exposures for 63 days, 400 mg mix of OASIS WAX & HLB :

	Exposure 2	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFHxS	PFOS	brPFOS	PFOSA	etFOSAA	8:2 FTS	10:2 FTS
	Sample	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
Site 1	Mean	0.002	0.008	0.001	0.001	0.001	0.001	0.003	0.003	0.000	0.001	0.001	0.001
	(%RPD)	*116*	*10*				*5*	*9*	*6*		*68*		
Site 2	Mean	0.001	0.010	0.002	0.002	0.002	0.002	0.006	0.005	0.001	0.001	0.001	0.001
	(%RPD)		*25*				*40*	*30*	*35*	*20*	*51*		
Site 3	Mean	0.007	0.036	0.045	0.029	0.007	0.002	0.029	0.014	0.004	0.019	0.003	0.002
	(%RPD)	*8*	*27*	*27*	*38*	*47*	*164*	*47*	*35*	*50*	*84*	*126*	*77*

DGT exposures for 21 days: **No detections**

	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFHxS	PFHpS	PFOS	brPFOS	PFOSA	FOSAA	meFOSAA	etFOSAA	6:2 FTS	8:2 FTS	10:2 FTS
	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
Site 1	4.3	2.2	2.2	2.2	2.2	2.2	1.7	0.4	0.7	0.4	0.4	0.4	1.1	1.1	1.1	1.1	1.1	1.1
Site 2	4.3	2.2	2.2	2.2	2.2	2.2	1.7	0.4	0.7	0.4	0.4	0.4	1.1	1.1	1.1	1.1	1.1	1.1
Site 3	4.3	2.2	2.2	2.2	2.2	2.2	1.7	0.4	0.7	0.4	0.4	0.4	1.1	1.1	1.1	1.1	1.1	1.1

Viul/Randselva PFAS contamination

Groundwater concentrations measured with DGT

Exposure 2	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFHxS	PFHpS	PFOS	brPFOS	PFOSA	FOSAA	meFOSAA	etFOSAA	6:2 FTS	8:2 FTS	10:2 FTS
Code	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
GWB 14	3.9	30	114	125	32	14	1.5	7.2	13	86	231	106	20	4.9	603	0.4	30	14
GWB 13	8.1	75	239	114	36	4.9	0.6	1.5	0.7	18	26	0.7	0.4	0.4	1.7	12	37	0.4
GWB 12	1.4	20	97	148	11	1.6	0.6	1.3	0.7	23	31	0.4	0.4	0.4	1.2	0.4	5.1	0.4
GWB 11	2.8	21	64	158	38	6.6	0.6	1.5	2.3	120	74	14	0.6	0.4	1.7	0.4	17	0.4
GWB 10	12	87	306	599	91	0.7	0.6	10	11	37	149	1.0	0.8	0.4	10	0.4	4.4	27
GWB 6	1.4	0.7	0.7	0.7	0.7	0.7	0.6	0.1	0.2	0.1	0.1	0.1	0.4	0.4	0.4	0.4	0.4	0.4
GWB 2	18	68	151	150	13	1.3	0.6	0.5	0.2	4.5	6.6	0.1	0.4	0.4	0.4	1.0	5.1	0.4

When data were below LOQ, LOQs are given in grey

Estimated PFAS emissions between the three sampling sites in Randselva

Table 4. Estimated PFAS emissions to the river two river stretches

	Flux/emission to the river (mg d^{-1})*		
	ΣPFAS	PFOS	PFOA
Between sites 1 and 2	39-219	13-68	
Between sites 2 and 3	1618 (700-3500)	212 (97-483)	476 (185-925)

*Based on the longest passive sampler exposure (exposure 2). The "mean" value for F between Sites 2 and 3 is given based on R_s for POCIS-Nylon of 1.5, 1.2 and 1.9 L d^{-1} for Sites 1, 2 and 3, respectively. The range in brackets is based on R_s values of 1 and 5 L d^{-1}. Detailed data are given in Appendix 9.

PS for PFAS and other PM substances

POCIS 

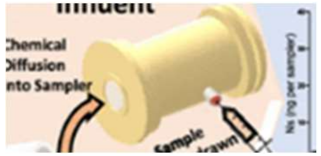
Sorbent sandwiched between two membranes (~ 40 cm^2)

MPT 

Sorbent enclosed in microporous PE tube (15 cm^2)

DGT 

Hydrogel/PES membrane & sorbent gel layer (3.14 cm^2)

G-TIP 

Sampling cell with small opening for sampling (~ 3 cm^2)

Hale et al. (2021). Using passive samplers to track per and polyfluoroalkyl substances (PFAS) emissions from the paper industry: laboratory calibration and field verification. Frontiers in Environmental Science, 621.

Verhagen et al. (2021). Multisite Calibration of a Microporous Polyethylene Tube Passive Sampler for Quantifying Drugs in Wastewater. Environmental Science & Technology, 55(19), 12922-12929.

Liu et al. (2021). In situ measurement of an emerging persistent, mobile and toxic (PMT) substance-Melamine and related triazines in waters by diffusive gradient in thin-films. Water Research, 206, 117752.

Verhagen et al. (2020). Time-integrative passive sampling of very hydrophilic chemicals in wastewater influent. Environmental Science & Technology Letters, 7(11), 848-853.

Passive sampler development in ZeroPM

Membrane transfer
- Diffusion cell
- Film stack
- Inert?

Affinity and capacity
- Batch sorption (K_d)

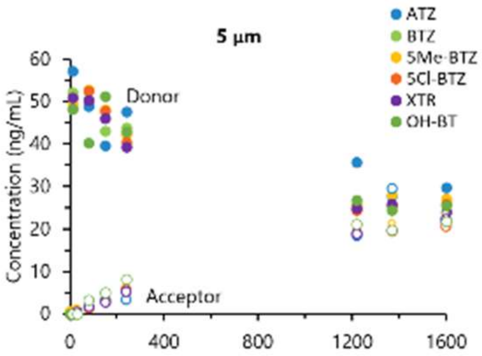
Calibration
- Lab scale
- Sampling rates (Rs)
- Linear uptake?

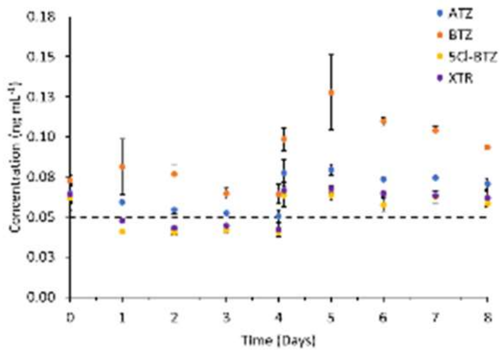
Monitoring
- One size does not fit all

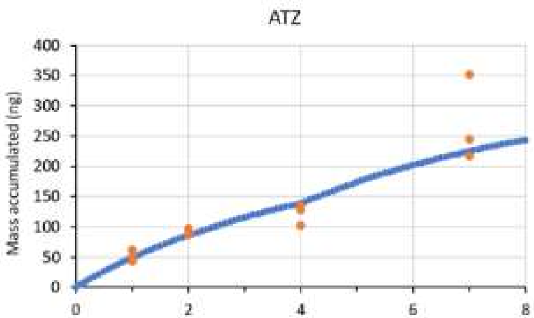
Performance criteria:

- Appropriate time window for integrative monitoring
- R_s that are insensitive to the level of water turbulences experienced during *in situ* exposures in water/ deployment
- High affinity and selectivity for analytes of interest
- Adequate sensitivity, limits of detection/quantification

PS calibrations in ZeroPM







Field deployment of PS at drinking water plants

Exposures to

- Raw water
- After ozonation
- After AC filtration
- After pilot plant treatment

Deployment of

- DGTs
- POCIS
- MPT
- Silicone to check hydrodynamics

Acknowledgements

- Chiara Scapuzzi
- Environmental Chemistry Section, NIVA
- Aud Helland (COWI)
- Tom Telefsen (COWI)
- ZeroPM project

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The University of Queensland
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ZeroPM

Prevent

Prioritize

Remove

NIVA

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

PFAS contamination in Rastatt and Baden-Baden

Joshua Walter - PFAS-Geschäftsstelle

Amt für Umwelt und Gewerbeaufsicht Landkreis Rastatt

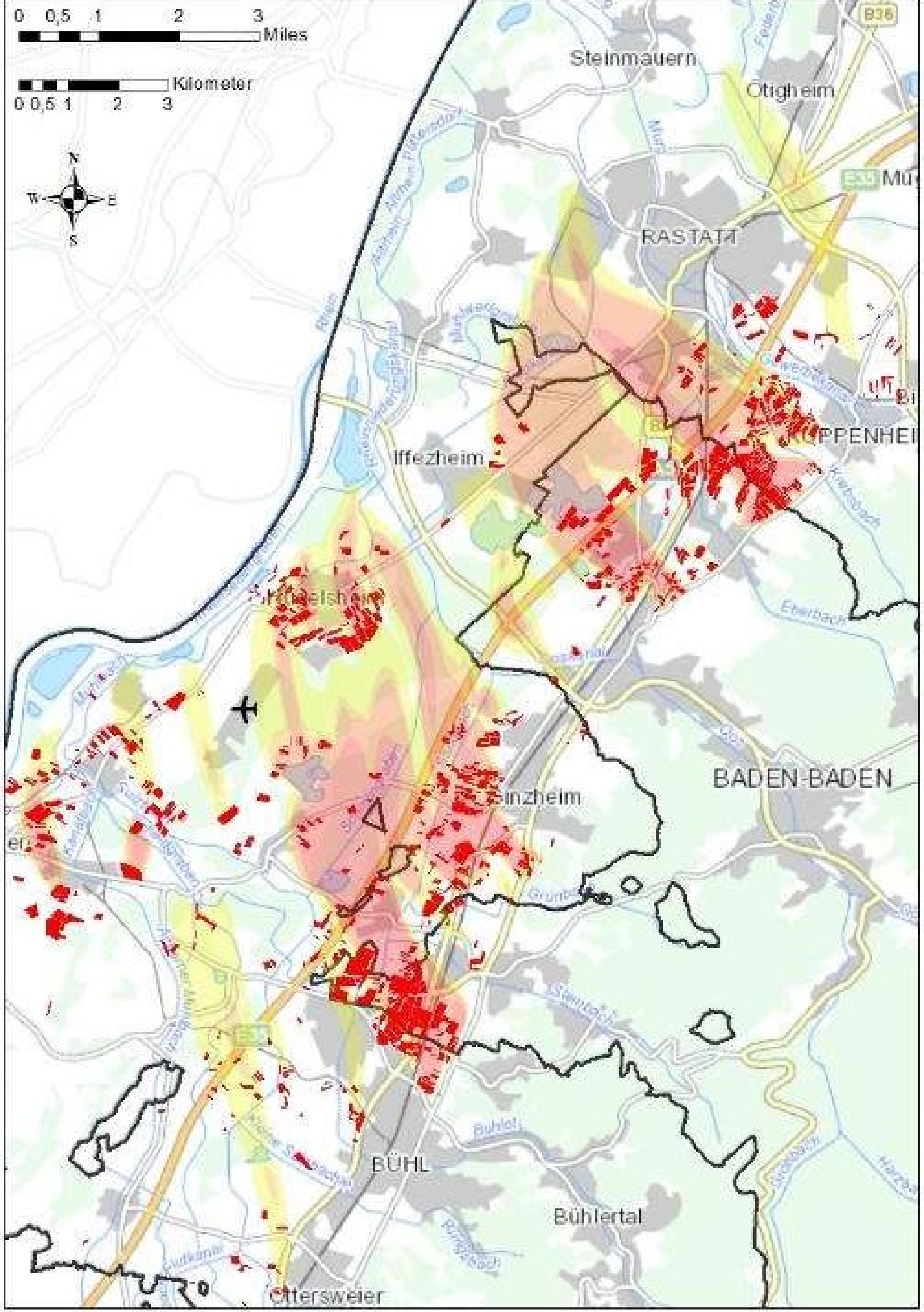
13.06.2024

Agenda

- Introduction
- Extent of the PFAS contamination
- Cause of the PFAS contamination
- Effects on soil and agriculture
- Effects on ground and surface water
- Effects on drinking water supply
- Outlook

Extent of the contamination

- 8000+ Soil analyses of 3113 ha
- 1105 ha contaminated farmland
- >10.000 groundwater analyses
- 180 mio m³ contaminated groundwater



Source: LUBW, https://www.lubw.baden-wuerttemberg.de/wasser/PFAS-karten-online, modified, 31.3.22

Cause of the contamination

- Papersludge as agricultural fertilizer
  - During 1999-2008
  - presumably: 100.000-200.000 tons
  - Waste disposal




Source B.Übelin

How could this happen?

- Win-Win-Situation?
- Excessive application
- Lack of legal limits for PFAS
- Lack of analytical tools

Effects on the district

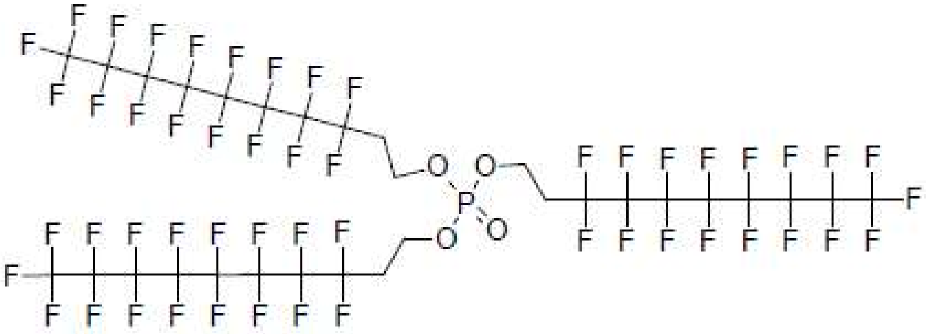
Soil

Health

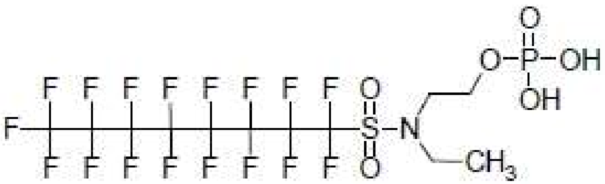
- Large scale soil sampling (2013-2023)
  - 3113 ha sampled
  - 1105 ha contaminated
  - Of which 480 ha are highly contaminated
- TOPA (300+ Samples)
- Research projects

Precursors

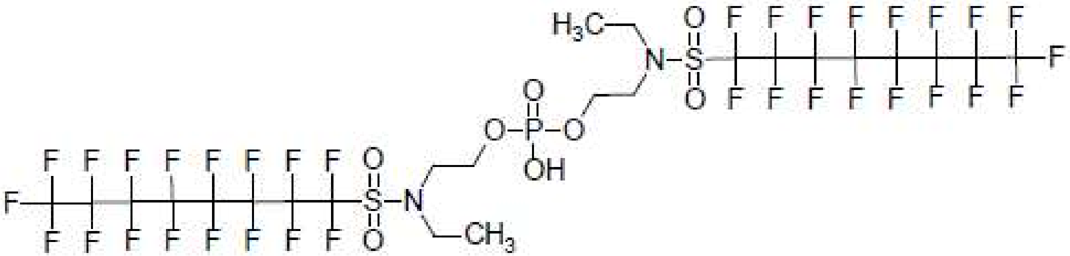
8:2 triPAP



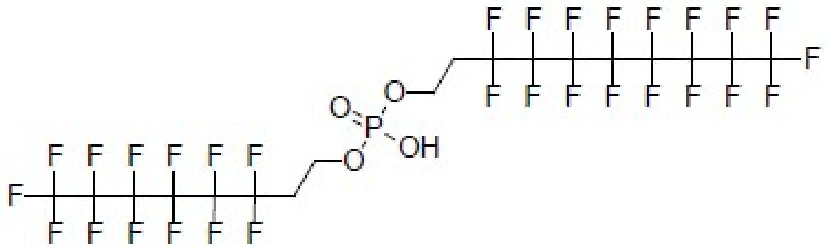
monoSAmPAP



diSAmPAP



6:2/8:2 diPAP



Quelle: Entwicklung eines fluorspezifischen Gruppenparameters „EOF“ für Boden und weitere Feststoffmatrices. DVGW-Technologiezentrum Wasser, 2017

Source: J. Walter

Soil

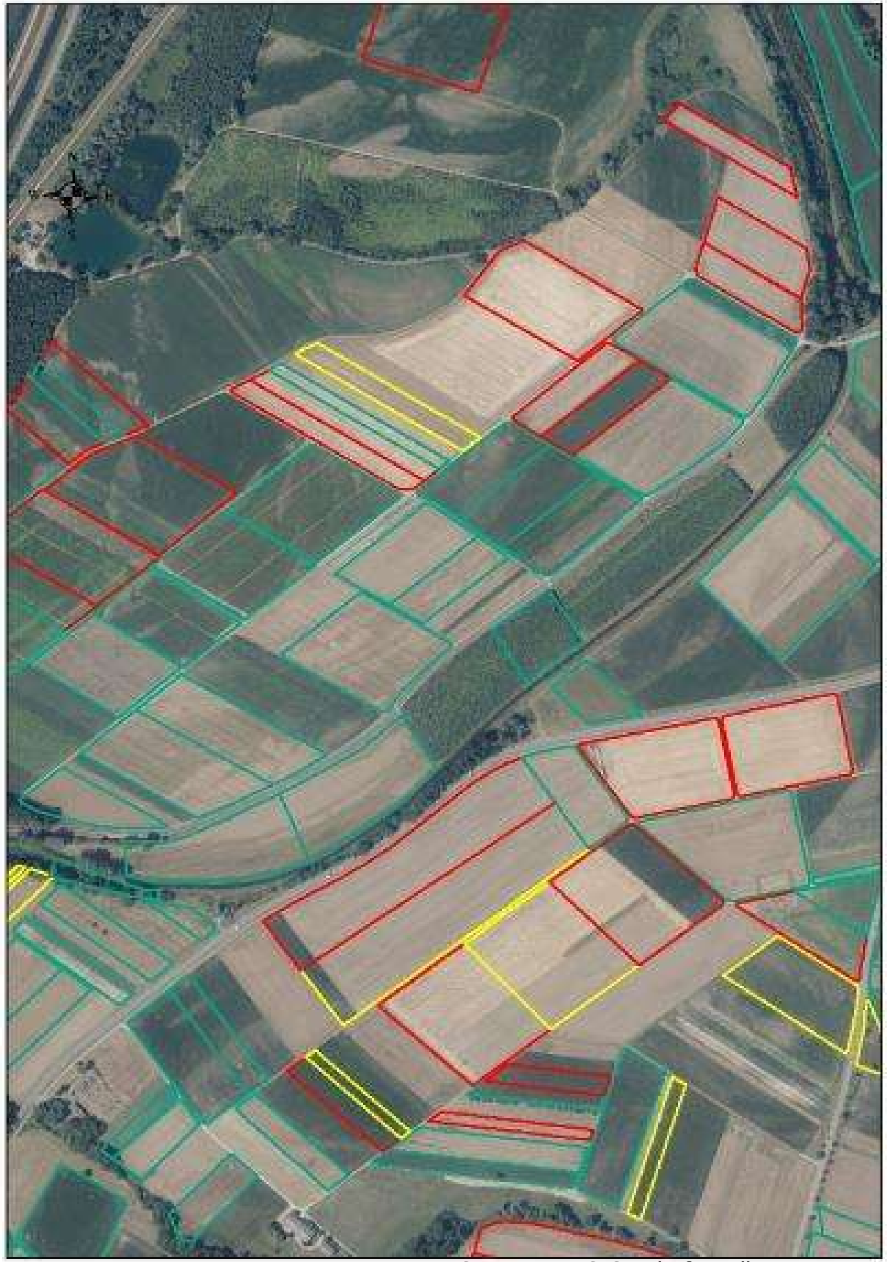
Health

- Agriculture
- Construction
- Disposal

Source: J. Walter

Soil

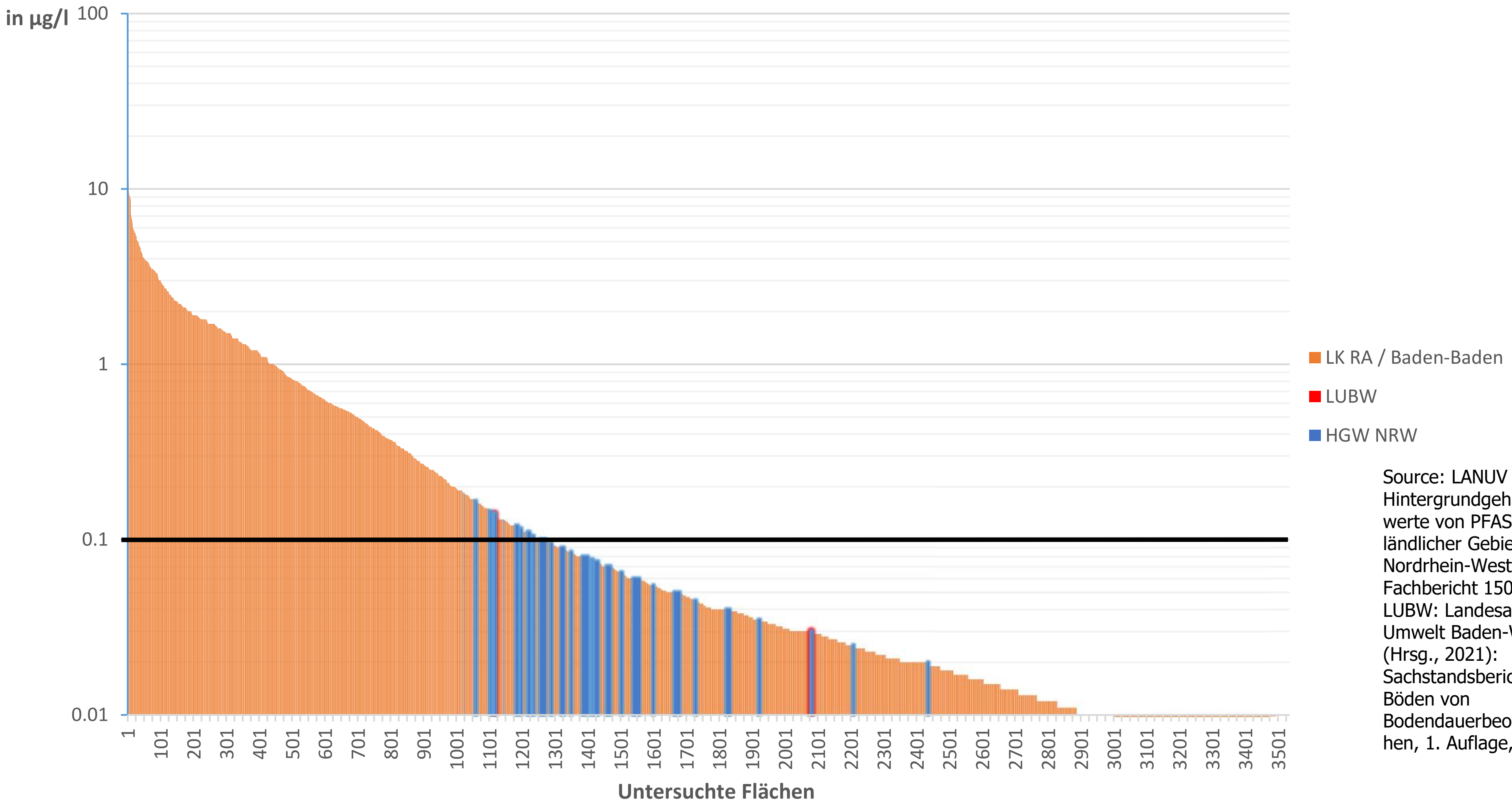
- Remediation
  - Sealing
  - Excavation
  - Research



Source: PFAS-Geschäftsstelle

Soil

- PFOA: Limit values and background contamination



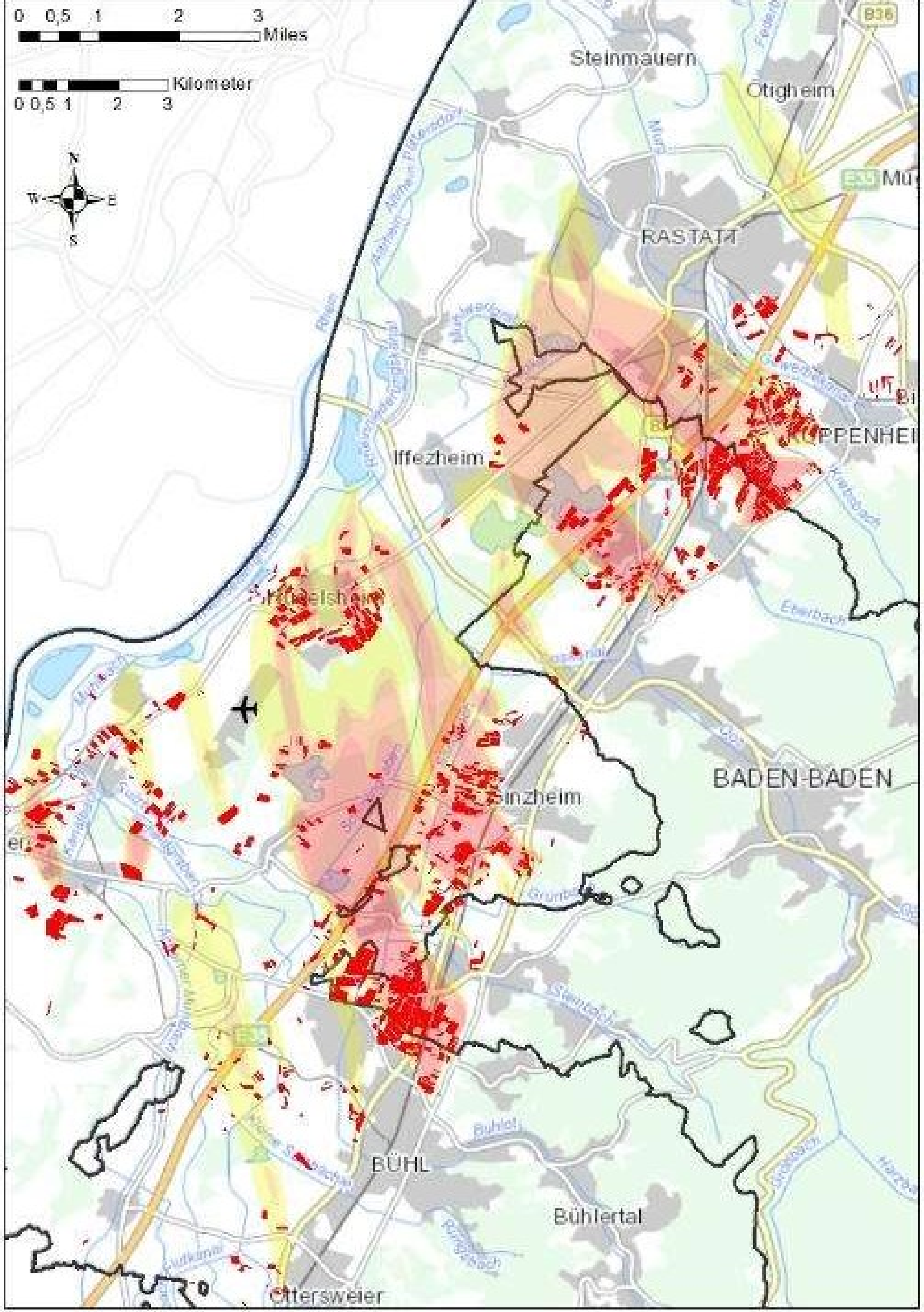
Source: LANUV NRW: Hintergrundgehalte und -werte von PFAS in Böden ländlicher Gebiete in Nordrhein-Westfalen LANUV-Fachbericht 150, 2023
LUBW: Landesanstalt für Umwelt Baden-Württemberg (Hrsg., 2021): Sachstandsbericht: PFAS – in Böden von Bodendauerbeobachtungsflächen, 1. Auflage, Karlsruhe

Groundwater

- Groundwater model
- (Agricultural) Watering
- Dewatering

Source: LUBW, https://www.lubw.baden-wuerttemberg.de/wasser/PFAS-karten-online, 31.3.22

Source: J. Walter



Source: LUBW, https://www.lubw.baden-wuerttemberg.de/wasser/PFAS-karten-online, modified, 31.3.222

Surfacewater

Ground water

- Monitoring
- Fishing
- Bathing

Source: J. Walter

Soil

Health

- Domestic water supply
- Public water supply
  - Restructuring
  - Filter
  - Monitoring

Health

- Blood testing 2018 - 2020 - (2023)
- Exposure via drinking water
- PFOA in blood plasma [µg/l]

year	min	max	median
2018 (n= 120)	2,5	71,2	15,6
2020 (n= 101)	1,1	50,6	12,7

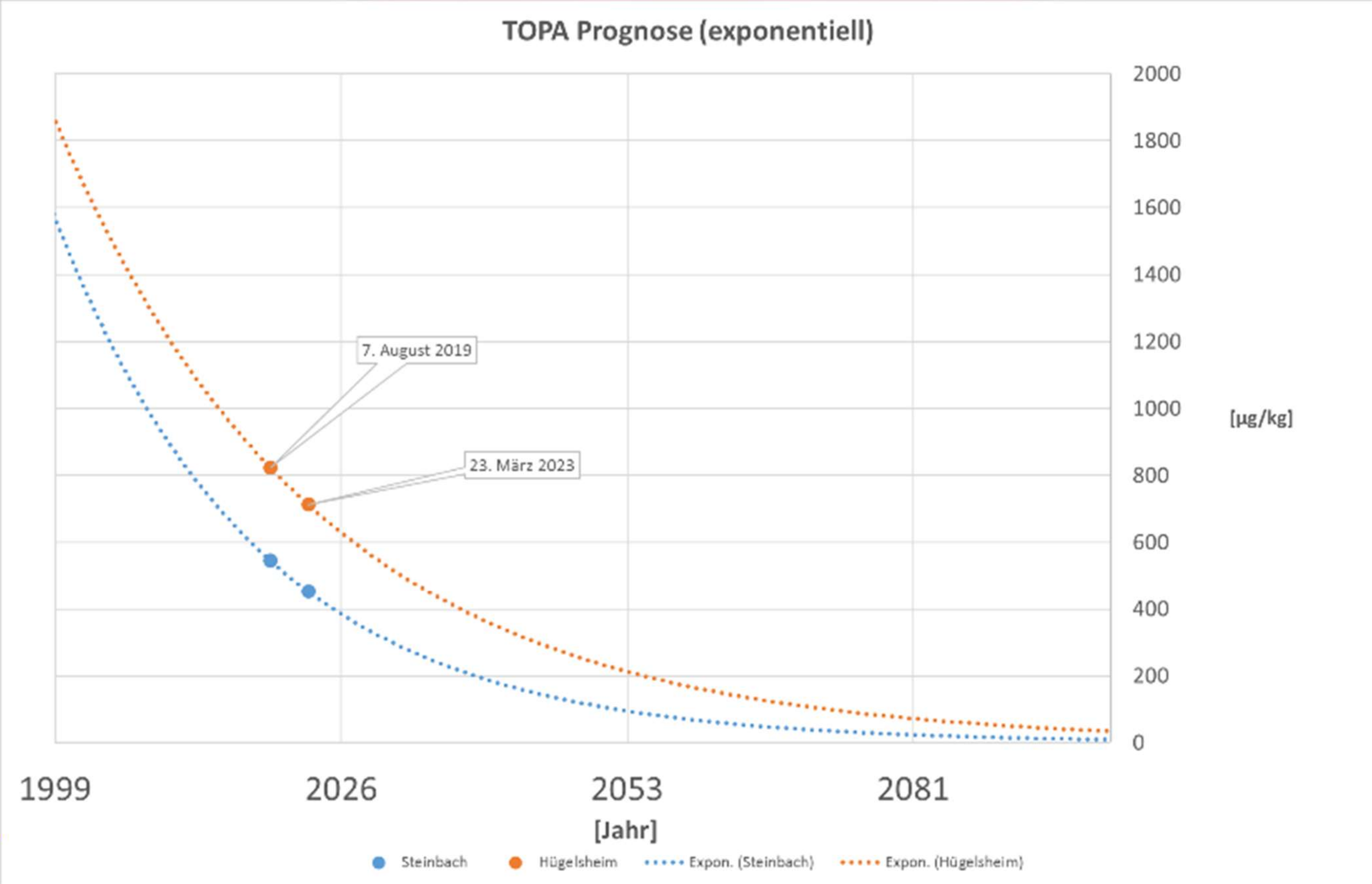
Source: Ergebnisse der PFC-Blutkontrolluntersuchung im Landkreis Rastatt 2020, Landesgesundheitsamt Baden-Württemberg, 2021

Costs

- Water suppliers > 25 million €
- Research, state and district > 13 million €
- Municipalities: several million €
- Private sector ?

- -> Lawsuits pending

Outlook



TOPA Prognose (exponentiell)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
[µg/kg]
7. August 2019
23. März 2023
1999
2026
2053
2081
[Jahr]
Steinbach
Hügelsheim
Expon. (Steinbach)
Expon. (Hügelsheim)

Health

Soil

Surfacewater

Groundwater

- **Protection of the population**
- Prevention cross-contamination

Thank you for your attention!

Further information:

PFAS-Newsletter: https://www.landkreis-rastatt.de/pfc_pfas

https://pfas-dilemma.info/

https://www.zdf.de/dokumentation/umwelt-crime/umwelt-crime-der-fall-rastatt-pfas-chemikalien-im-trinkwasser-100.html

Source: J. Walter

EU Green Week

PARTNER EVENT

ZeroPM Special Symposium on PFAS elimination from drinking water

Karlsruhe

12-13 June 2024

#WaterWiseEU

ZerOPM

UNIVERSITY OF THE AEGEAN

PFAS and sewage treatment plants: point sources and process modification

Nasos Stasinakis, Professor

University of the Aegean, UoA

Mytilene, Greece

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

EU Green Week
PARTNER EVENT
#WaterWiseEU

Contribution of UoA in ZeroPM project

Participation in **WP7**: Technical Solutions Method Development and Analysis

<u>Objectives</u>

- To study the fate of PFAS (and other PMT substances) during biological and thermal sewage sludge treatment
- To develop/improve technical solutions for removing PMT substances during sludge treatment

Structure of the presentation

- Occurrence and fate of PFAS in WWTPs

ZeroPM

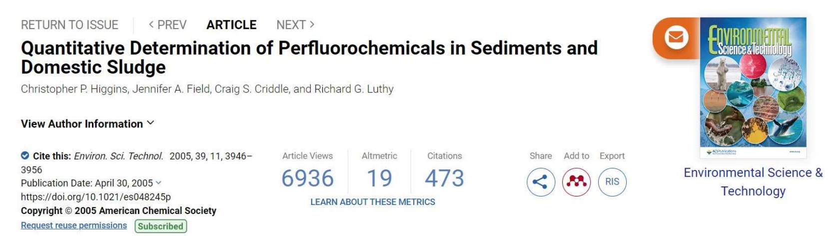
- Laboratory results on PFAS fate during sewage sludge treatment
- Planned research in the pilot-scale system

PFAS and me: first meeting

2005

Detection in Sewage Sludge (USA, SF)

- ✓ Digested and primary sludge from 11 WWTPs
- ✓ [PFOS] in sludge: 14-2610 ng/g
- ✓ [PFOS] in sediments: up to 3.8 ng/g
- ✓ Existence of PFOS precursors in sludge samples: N-MeFOSAA, N-EtFOSAA



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Quantitative Determination of Perfluorochemicals in Sediments and Domestic Sludge

Christopher P. Higgins, Jennifer A. Field, Craig S. Criddle, and Richard G. Luthy

View Author Information

Cite this: *Environ. Sci. Technol.* 2005, 39, 11, 3946–3956
Publication Date: April 30, 2005
https://doi.org/10.1021/es048245p
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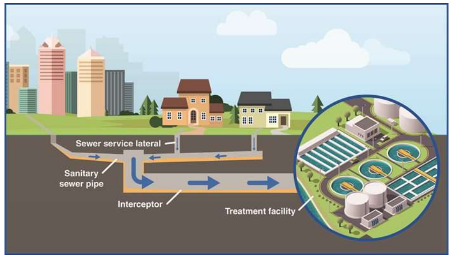
Environmental Science & Technology

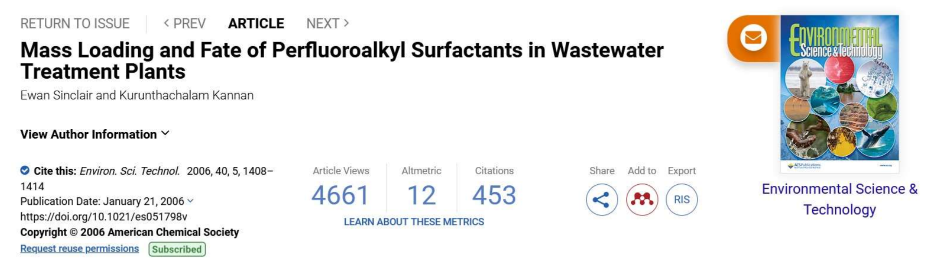
Higgins et al (2005)
https://doi.org/10.1021/es048245p

2006

Detection in domestic wastewater (USA, NY)



- ✓ Raw and treated WW from 6 WWTPs
- ✓ [PFOA] > [PFOS]
- ✓ [PFOA] in WW: 58-1050 ng/L



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Mass Loading and Fate of Perfluoroalkyl Surfactants in Wastewater Treatment Plants

Ewan Sinclair and Kurunthachalam Kannan

View Author Information

Cite this: *Environ. Sci. Technol.* 2006, 40, 5, 1408–1414
Publication Date: January 21, 2006
https://doi.org/10.1021/es051798v
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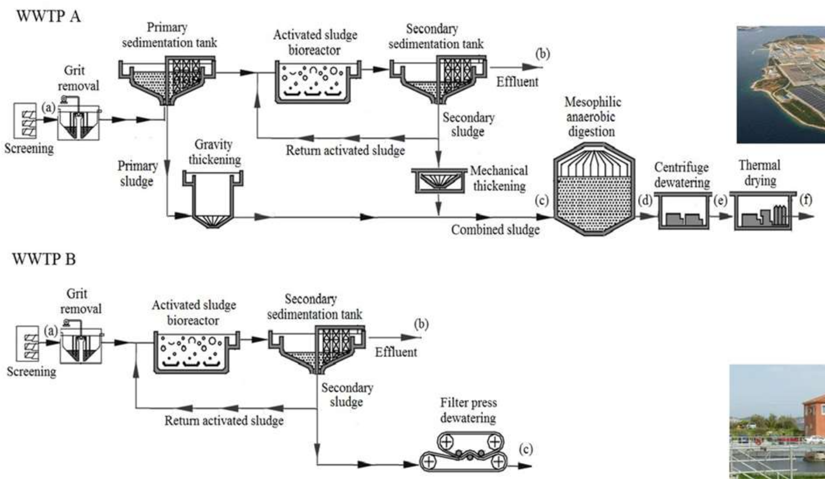
Environmental Science & Technology

Sinclair and Kannan (2006)
https://doi.org/10.1021/es051798v

PFAS in Greek WWTPs

2012 & 2013

Detection in Greek WWTPs

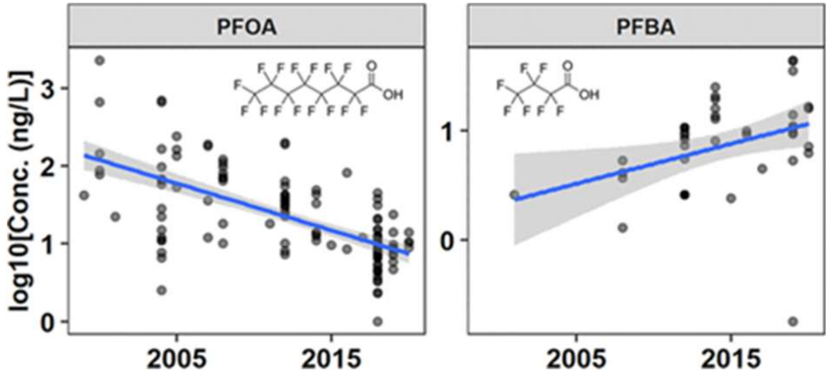


- Number of studied PFAS: 18
- Collected WW samples (in, out): 24 + 14
- Collected sludge samples: 21 + 17
- Dominant PFAS: PFPeA, PFOS, PFOA
- Range in WW: up to 209 ng/L
- Range in sludge: up to 45 ng/g (d.w)
- Differences in distribution between phases
- No effect of seasonality
- Higher concentrations in WWTP A

Arvaniti et al (2012)
https://doi.org/10.1016/j.jhazmat.2012.02.015

Stasinakis et al (2013)
https://doi.org/10.1016/j.scitotenv.2013.06.087

Trends in PFAS concentrations found in WWTPs (USA)



Correlations between log-transformed wastewater effluent PFOA and PFBA concentrations and sample year in the US without stated industrial sources.

Treated wastewater

- Declined [C] of long chain PFAS over time – Increased [C] of short chain PFAAS
- Average [PFOA] : 68.9 ng/L (data 1998-2020)
- Average [PFOA] : 12.8 ng/L (data 2013-2020)
- Higher concentrations in case that industrial WW are discharged to the WWTP

Sludge

- Average [PFOA] : 23.8 ng/g (data 1998-2020)
- Average [PFOS] : 233 ng/g (data 1998-2020)

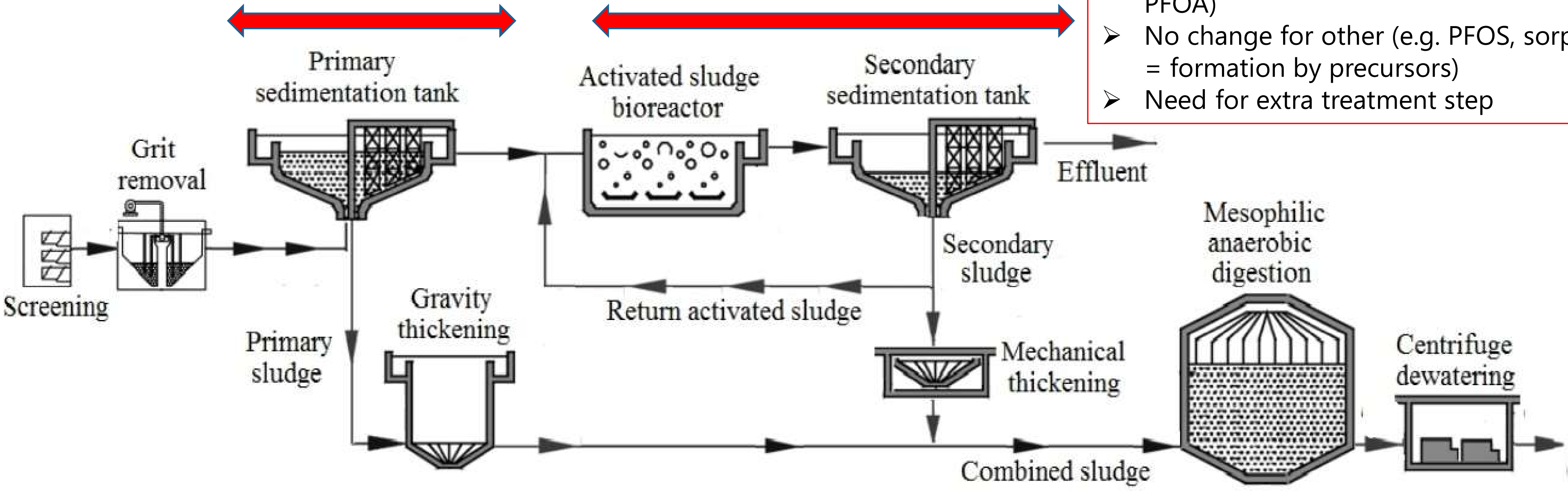
Thompson et al (2022)
https://doi.org/10.1021/acsestwater.1c00377

Fate of PFAS during wastewater treatment

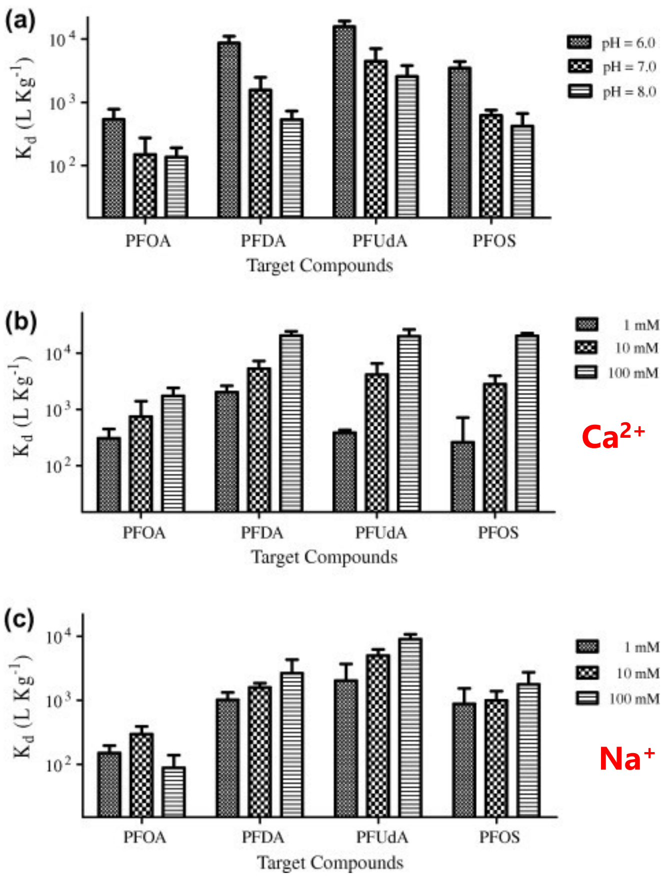
- Sorption to TSS
- Accumulation to PS

- Biotransformation of some precursors
- No biotransformation of known PFAS
- Sorption to activated sludge

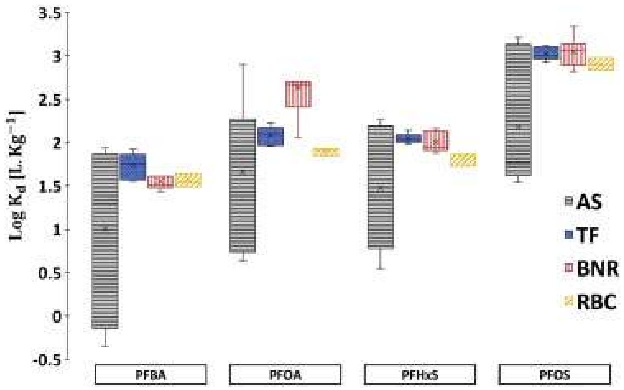
- Increased [C] for some compounds (e.g PFOA)
- No change for other (e.g. PFOS, sorption = formation by precursors)
- Need for extra treatment step



PFAS sorption to sludge



Arvaniti et al (2014)[1]
https://doi.org/10.1016/j.chemosphere.2014.03.087



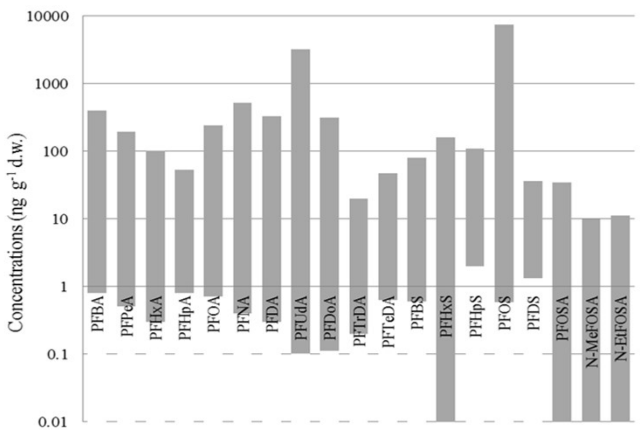
- Partitioning coefficients increase with increased fluoroalkyl chain length
- PFSA compounds had higher sorption capacities compared to PFCA compounds
- Lower pH and higher [Ca^{2+}] increased PFAS sorption
- Important differences on sorption coefficients according to the type of sludge, target compound, protocol used etc[1,2]

Ebrahimi et al (2021)[2]
https://doi.org/10.1016/j.chemosphere.2020.129530

Occurrence of PFAS in sewage sludge

2015[1]

- Number of PFAS detected in sludge: 19
- PFCAs (C4 to C18); PFSAs (C4 to C10); perfluoroalkyl sulfonamides, FASA
- [C]: few ng/g to some hundreds ng/g



[1]Arvaniti & Stasinakis (2015)
https://doi.org/10.1016/j.scitotenv.2015.04.023

2024[2]

- Number of PFAS detected in sludge: 178
- Ultrashort- (C<4); new generations PFAS (e.g. GenX); PFAS precursors
- Need for including them in future monitoring studies
- Lack data from specific countries/areas

[2]Arvaniti et al (2024) under preparation

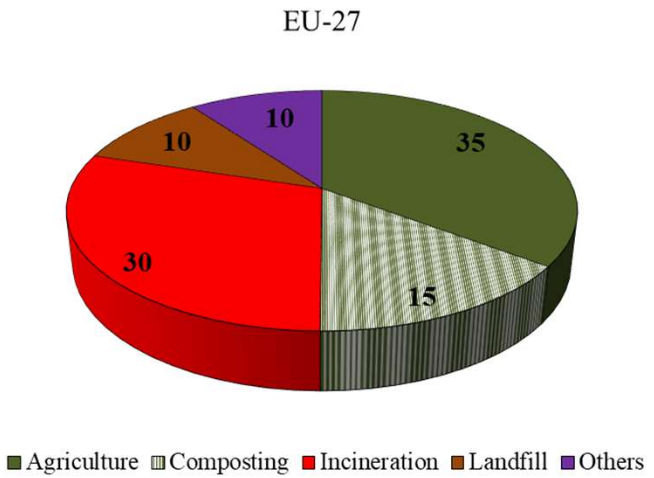
Sludge management and threats from PFAS detection

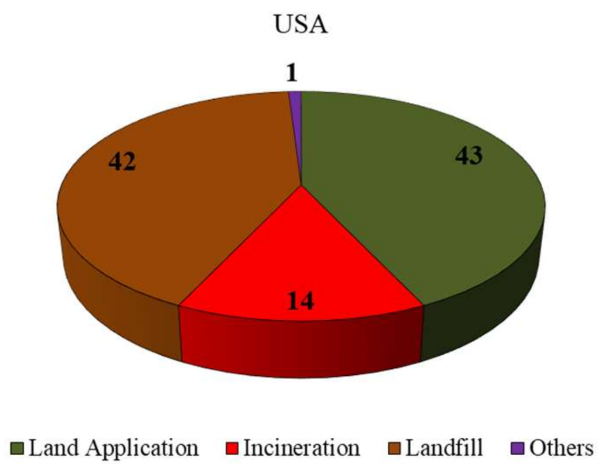
- 8300 kt/y of sewage sludge (as DS) are produced in EU
- In EU 50% of the produced sludge is disposed to soil (agriculture + composting)
- In US 43% of the produced sludge is disposed to soil

- Important amounts are also disposed to landfills

!

Increased risk due to the occurrence of micropollutants





Occurrence of PFAS in sludge amended soil

- **Few studies** concerning the agricultural land contamination with PFAS due to long-term application of biosolids
- Σ_{12}PFAS concentration up to 196 ng/g (d.w.) in soil (15 y of biosolids application)[4]
- PFOS and PFOA were the predominant compounds
- PFAS levels were correlated to sludge loadings
- **Limited knowledge** on the uptake of PFAS from sludge-amended soils to plants and on their leaching to groundwater
- Lack of long-term experiments

[4]Johnson (2022)
https://doi.org/10.1016/j.watres.2021.118035

Fate of PFAS during sludge anaerobic digestion

Limited information

Monitoring of full-scale anaerobic digesters shows[3]:

- Moderate decrease of ΣPFAS-F (10-38%) in some AD
- No clear trend for the removal of specific PFAS (increase up to 95% for some)[3]

Problems

- Monitoring of a small number of PFAS
- Presence of precursors
- Collection of grab samples

} No clear results on the ability of AD to remove (specific) PFAS

[3]Lakshminarasimman et al. (2021)
https://doi.org/10.1016/j.scitotenv.2020.142431

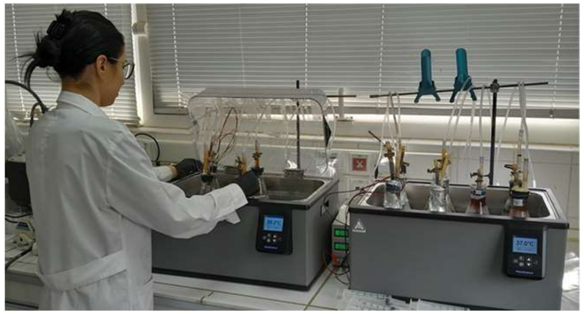
ZeroPM

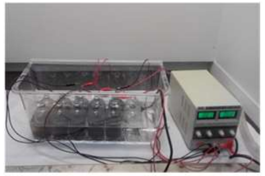
Laboratory results on PFAS fate during sludge treatment

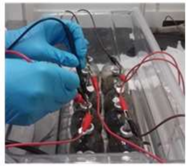
Studied Technology 1: Modified Anaerobic Digestion

Biomethane Potential Batch Experiments & Continuous-flow Experiments

- Fate of 7 PFAS during AD
- Modification of the process adding GAC, voltage
- Role sludge pretreatment (thermal, ultrasound)
- Role of T (° C) during AD (mesophilic, thermophilic)



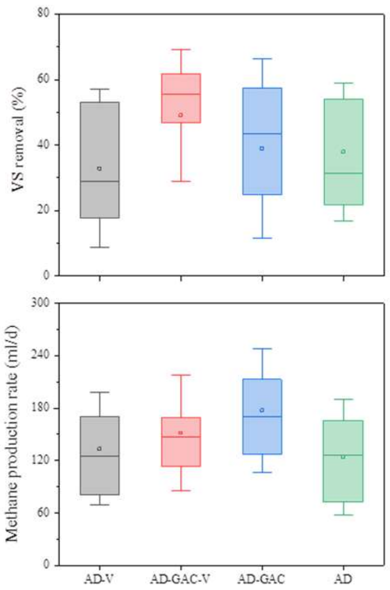


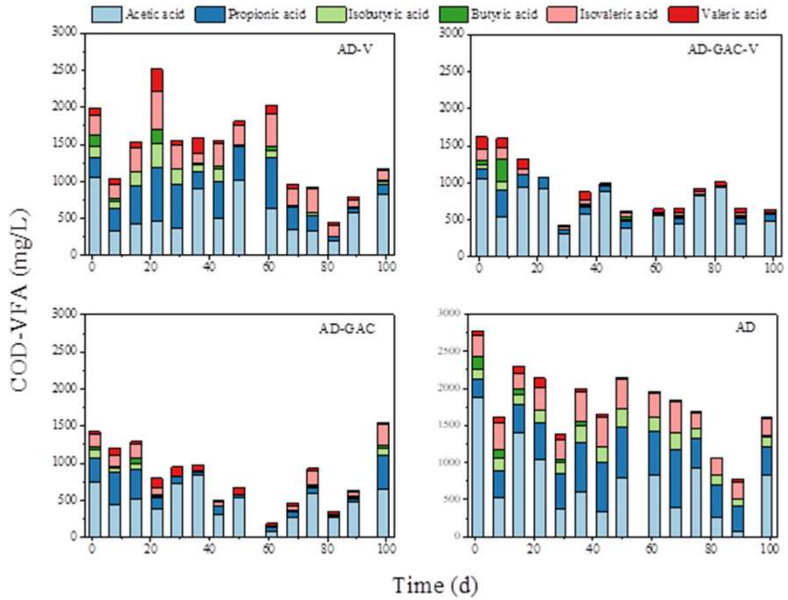


Studied Technology 1: Modified Anaerobic Digestion

Addition of GAC

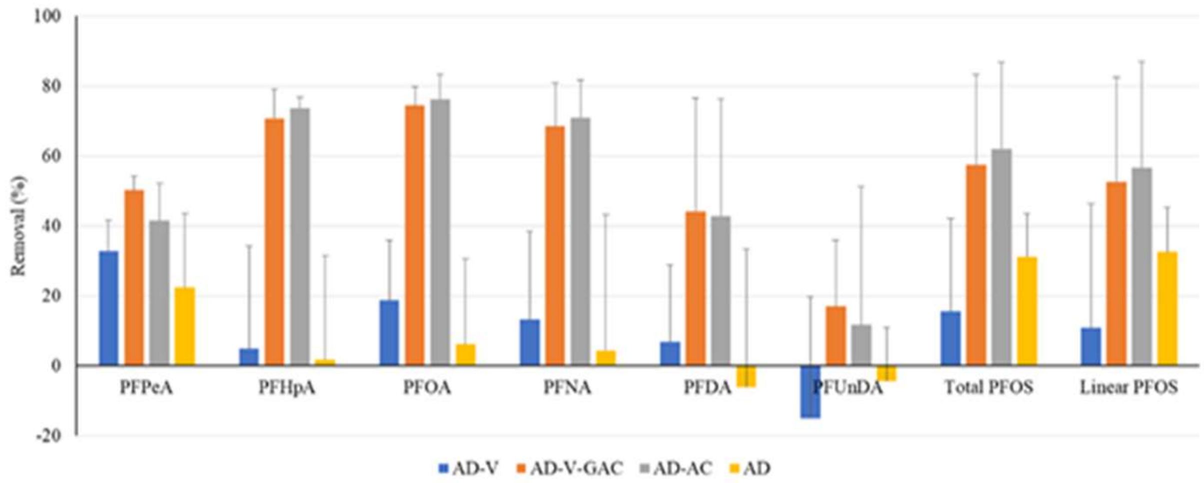
- Slightly higher removal of VS
- Reduced VFAs concentrations
- Higher methane production

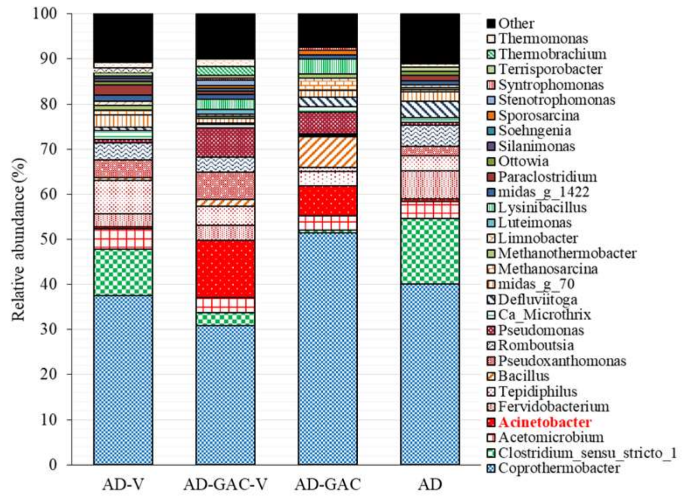




Studied Technology 1: Modified Anaerobic Digestion

- Conventional AD => no removal of target PFAS
- No important differences under mesophilic & thermophilic conditions
- Addition of GAC => increased removal PFAS



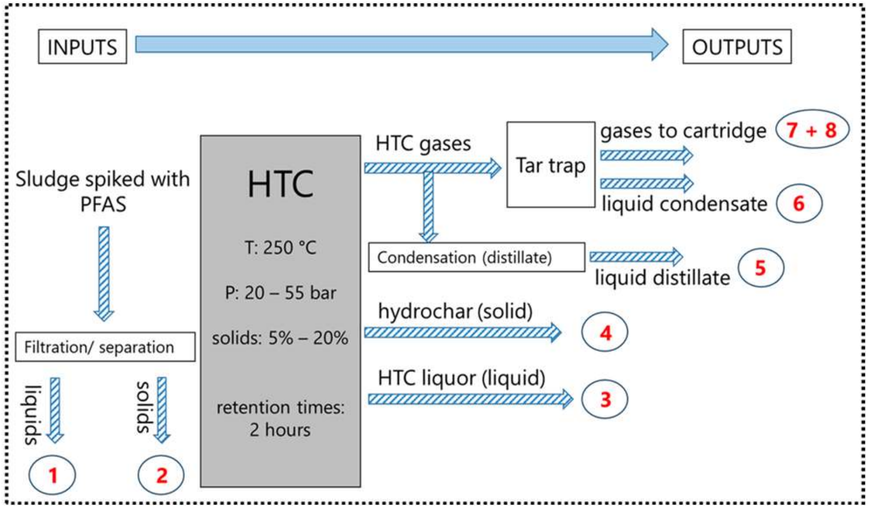


Removal based on analysis of dissolved & particulate phase and application of mass balance

Studied Technology 2: Hydrothermal carbonization

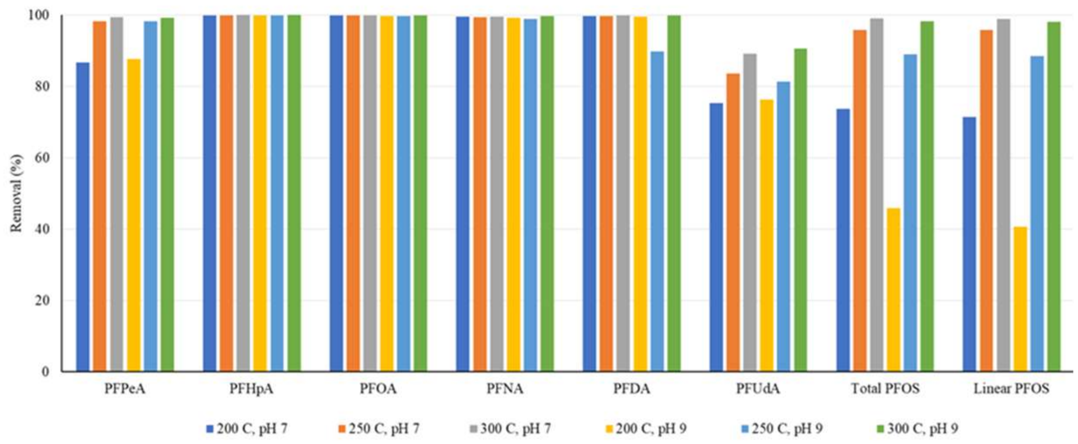
Identifying the role of:

- Applied pressure
- Applied temperature (°C)
- pH



Studied Technology 2: Hydrothermal Carbonization

- With exception of PFOS and PFUdA, high removal (>85%) of PFAS under all tested conditions
- Increase of T=> improved PFAS removal
- Detection of trace amounts of some PFAS in the gas phase

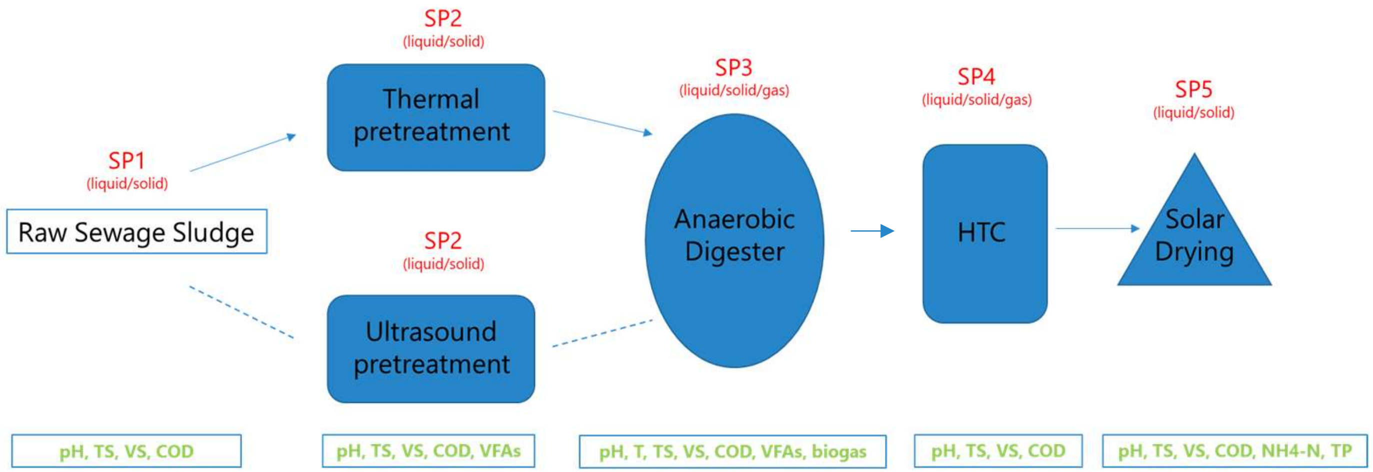


Removal based on analysis of dissolved & particulate phase and application of mass balance

Next Work: Operation of the sludge pilot system

Time Schedule

- Start-up: March 2024
- Monitoring for a period of 2 years



Conclusions

- Decreasing concentrations of long chain PFAS over time/increase of short chain PFAS
- No important removal during conventional WW treatment => need for advanced treatment
- Removal from WW via sorption vs Formation by precursors

- PFAS concentrations in sewage sludge up to some hundreds ng/g, expanding the list
- Their fate during AD is not clear, biotransformation seems to be possible for some compounds
- HTC seems to be a promising technology for removing them, need for long-term monitoring

u1

Thank you for your attention

Contact info

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Slide 22

u1 Nasos, 12/06/2024

PFAS destruction by electrochemical oxidation in drinking water

Symposium on PFAS, Rastatt, 12.-13.06.2024

Lara Stelmaszyk & Barbara Behrendt-Fryda, Heico Schell, Markus Hegel, Ronja Hesse, Rieke Neuber, Andreas Tiehm

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

Limitations of PFAS treatment methods

- **Advanced Oxidation Processes (AOPs) not effective** for removal from waste and drinking water[1]
- Removal by **activated carbon (AC)** with **efficiencies of 80 % for long chained PFAS** (less for short chained)[2]
- Good removal with **ion-exchangers (IEX)**[2], but **expensive**[3]
- Removal with **AC and IEX** results in **concentrates/regenerates** with **high PFAS concentrations**

→ **EAOP®** can overcome current limitations for drinking water treatment

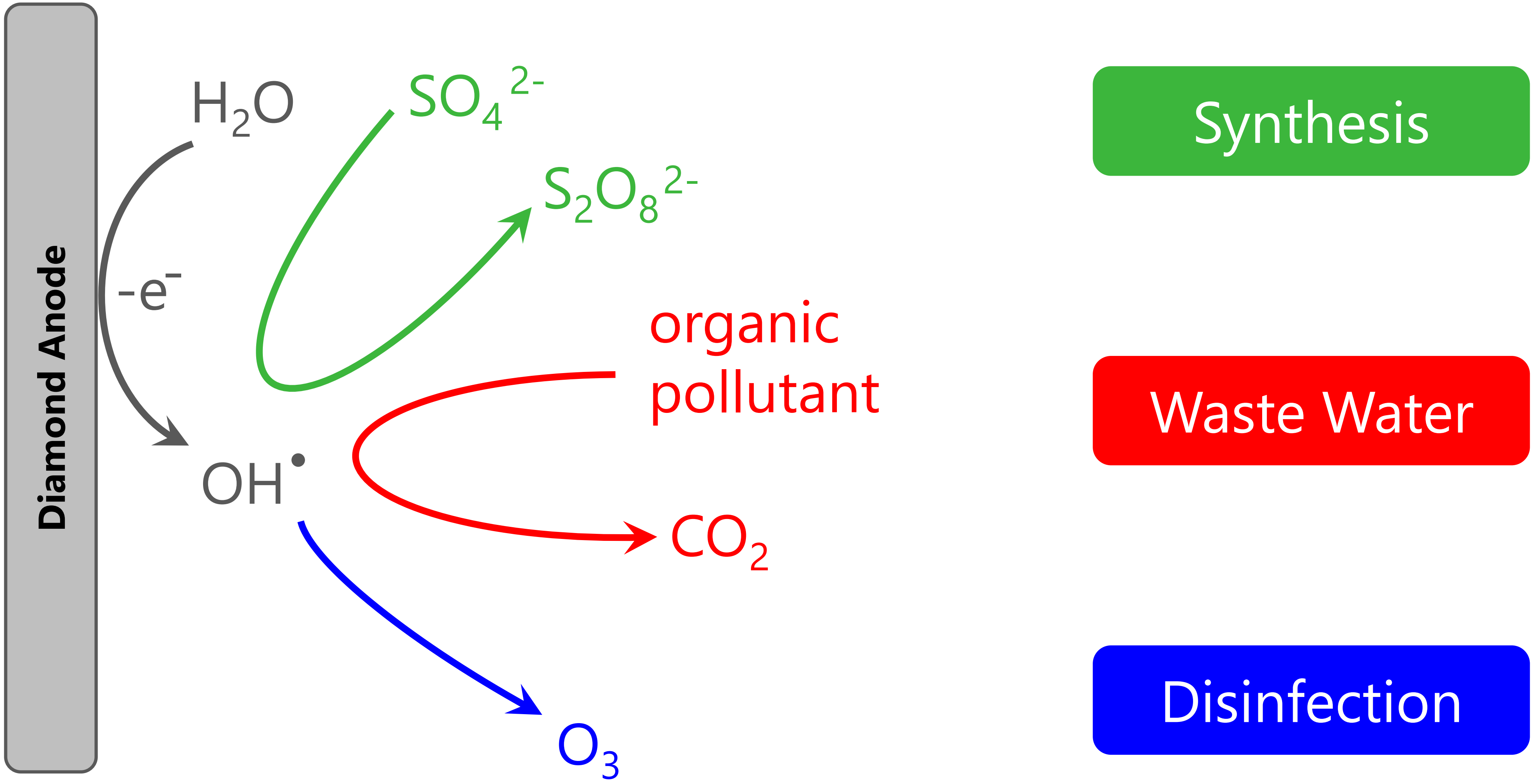
[1] Georgi and Mackenzie, 2022
[2] McCleaf et al., 2017
[3] Riegel et al., 2020

Diamond Coating with HF-CVD

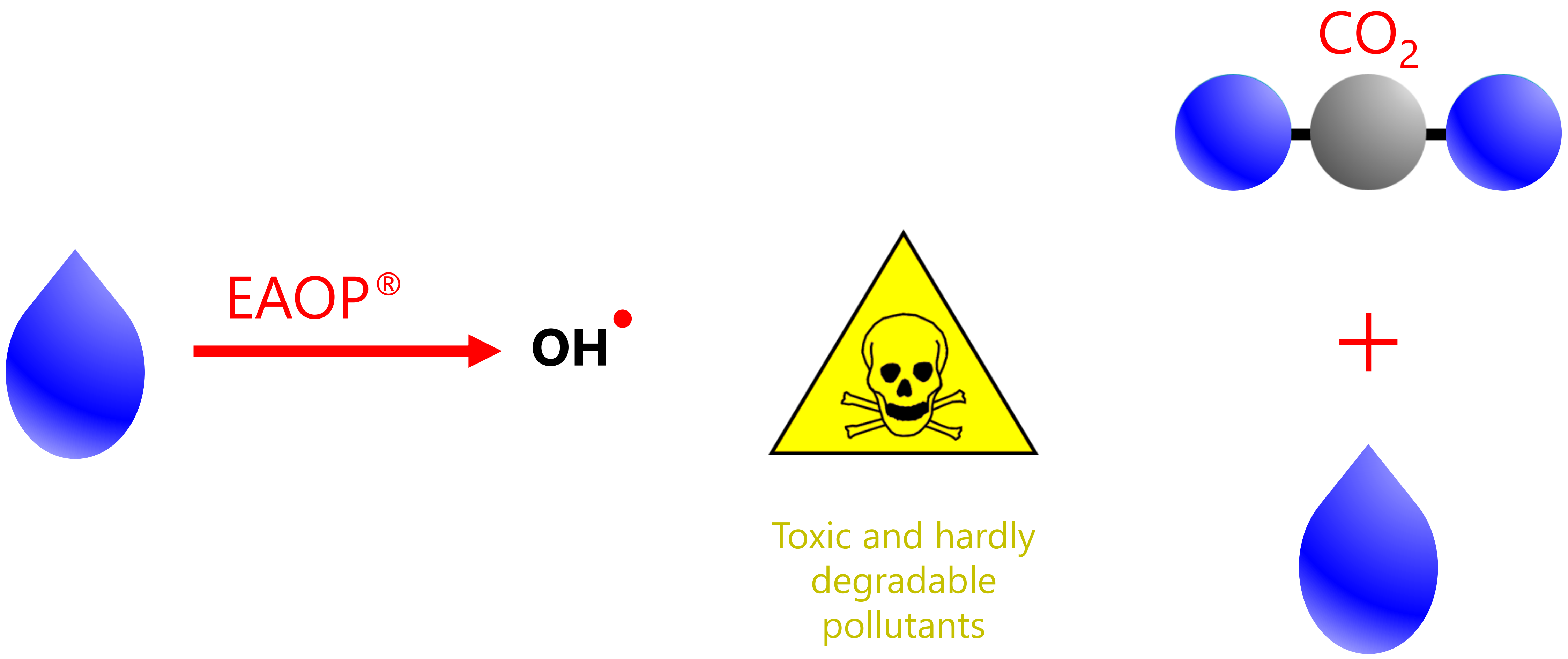
Diamond Coating with HF-CVD

Diamond Coating with HF-CVD

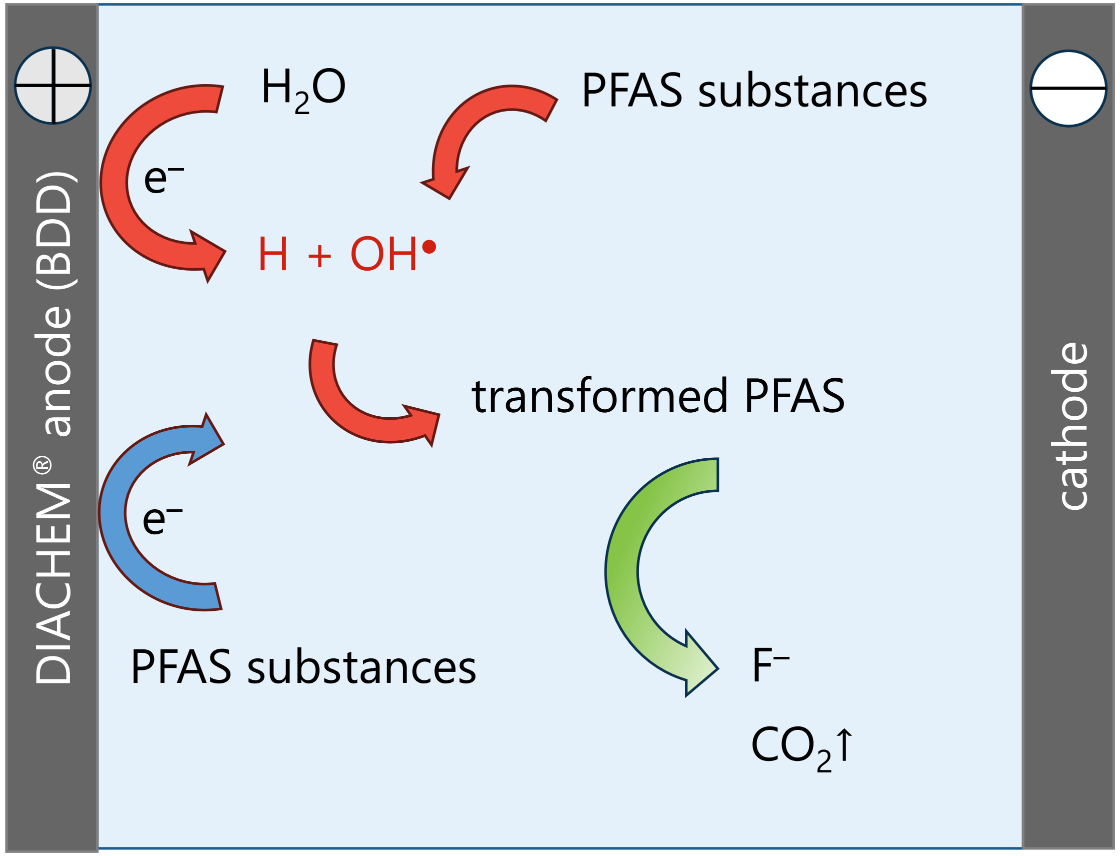
Electrochemical Advanced Oxidation Process – EAOP®



EAOP® Waste Water Treatment



PFAS destruction



Pathway 1:

Oxidation by hydroxyl radical

Pathway 2:

Direct destruction at BDD anode

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 · September 2008 https://doi.org/10.1021/es703273s

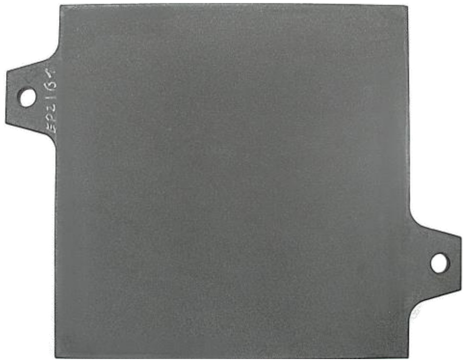
Electrochemical degradation of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in groundwater. Trautmann, A. M.; Schell, H.; Schmidt, K. R.; Mangold, K-M; Tiehm, A. in Water science and technology 71 (10), S. 1569–1575. 2015 https://doi.org/10.2166/wst.2015.143.

PFAS destruction – Equipment – Cell

Electrochemical Cell "CONDIACELL®
Cell Model SSZ-100" equipped with
DIACHEM® anode

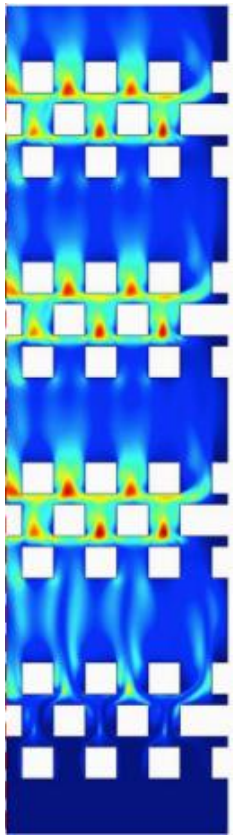
Electrochemical Cell "CONDIACELL®
Cell Model ECWP D20" equipped
with DIACHEM® anode

PFAS destruction – Equipment – Electrode



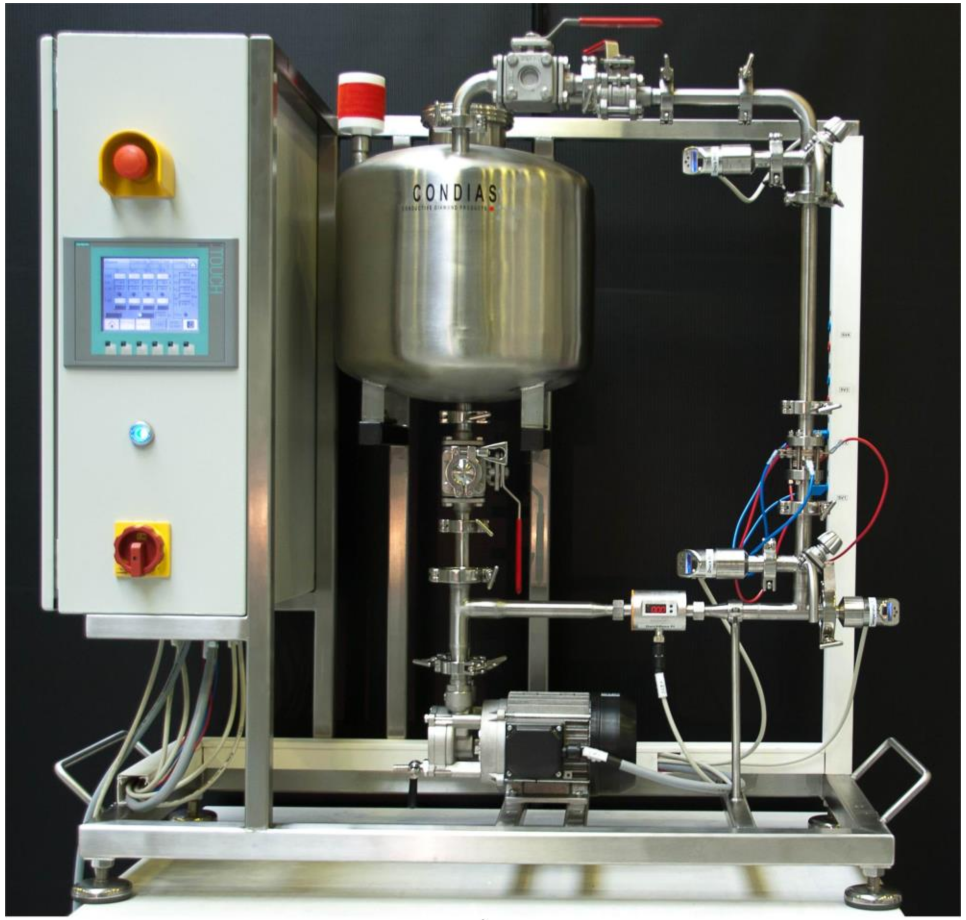
Laminar electrolyte flow for efficient degradation of organic concentrations (range: mg/L to g/L)

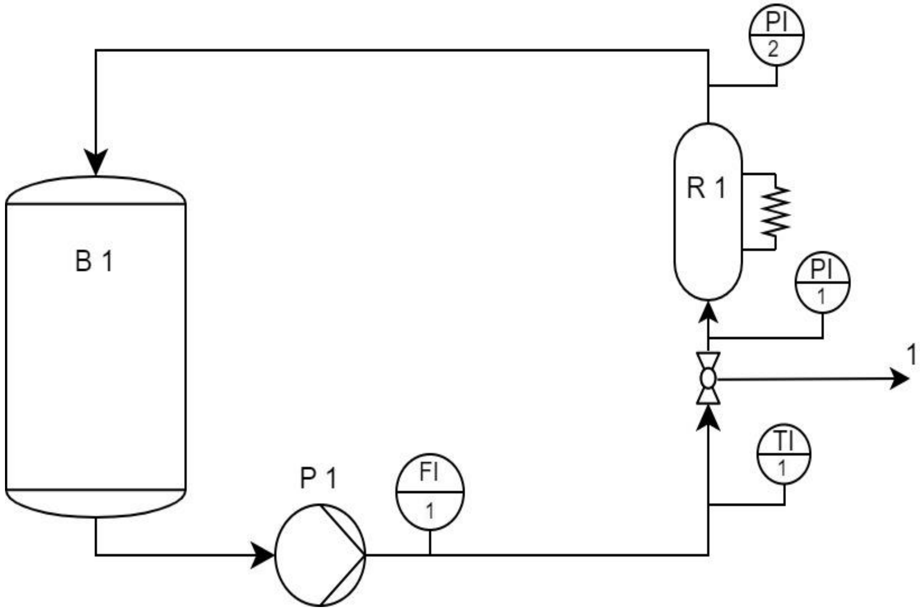
Turbulence electrolyte flow for efficient degradation of low organic concentrations (range: µg/L to mg/L)



K. Lindholm 2016, TUM; Characterisation and optimisation of hydrodynamics in a boron-doped diamond electrode reactor for the advanced oxidation of trace organic chemicals

PFAS destruction – Equipment – System

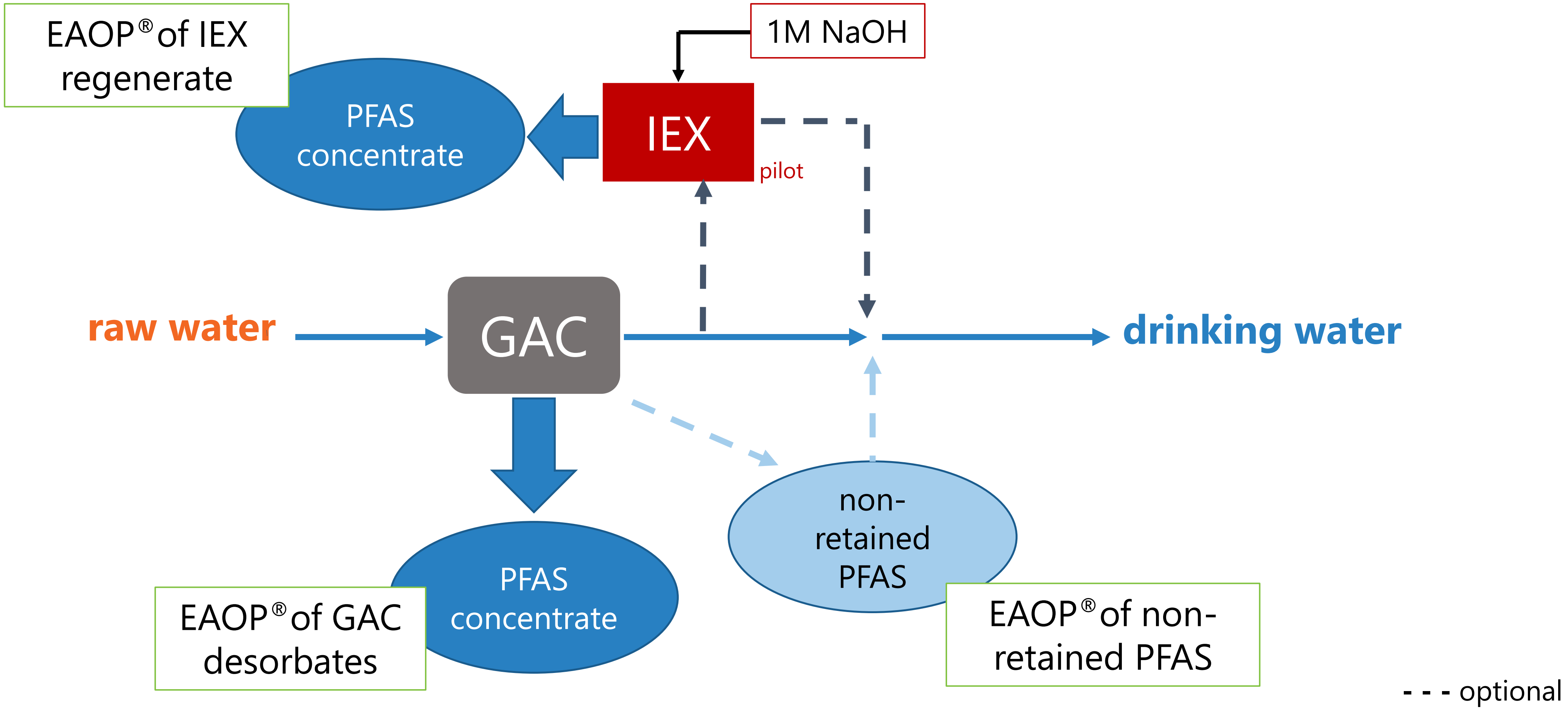




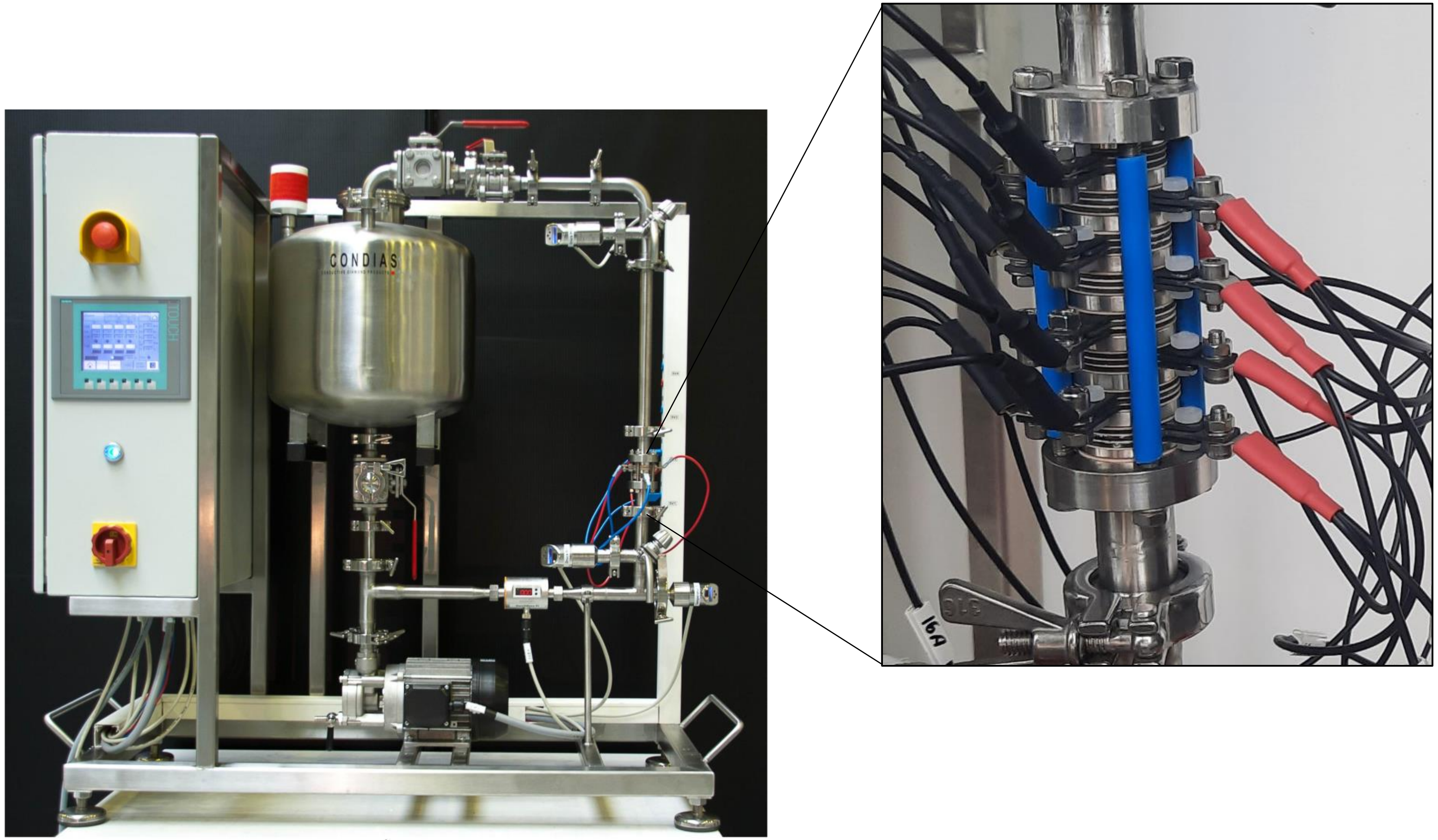
B 1	Storage tank
P 1	Pump
R 1	Reactor with 4 electrode packages
1	Ball valve for sampling
FI	Flow meter
PI	Pressure sensor
TI	Temperature sensor

Relevance of EAOP® processes for drinking water suppliers

e.g. WW Rastatt Rauental



Set up for 20 L scale electrochemical oxidation



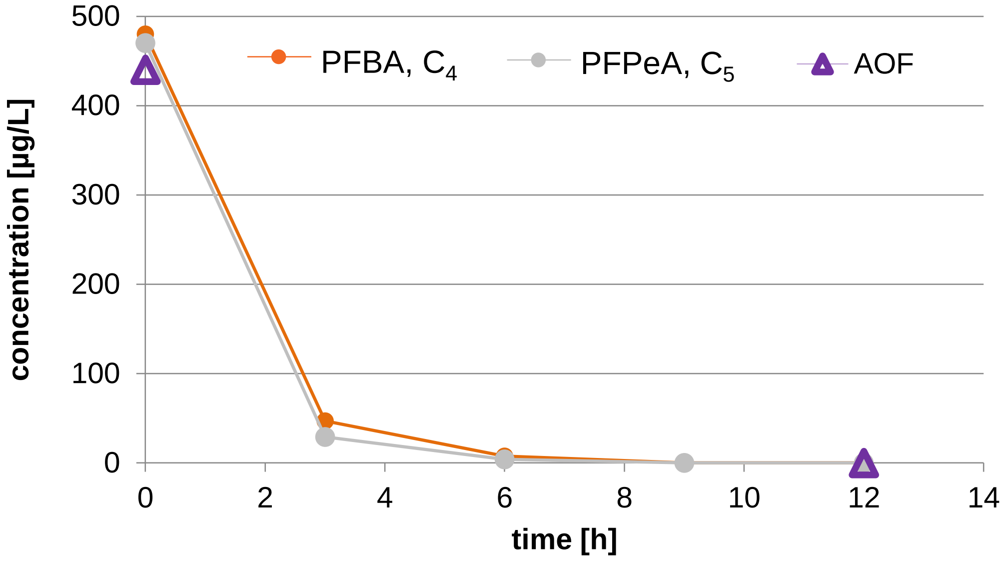
electrolysis plant: 20 L scale

- 10 L working volume
- ECWP with 8 electrode packages

Elimination of short chain PFAS in IEX regenerates

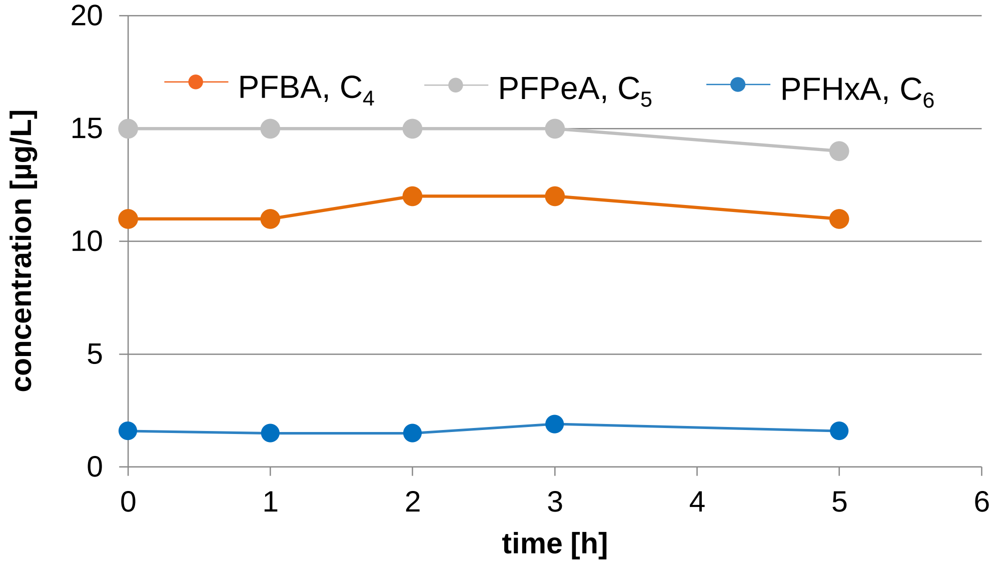
Synthetic regenerate 2 mM NaOH

cond. $\kappa \approx$ 470 µS/cm
scale: 10 L
I = 1.5 A

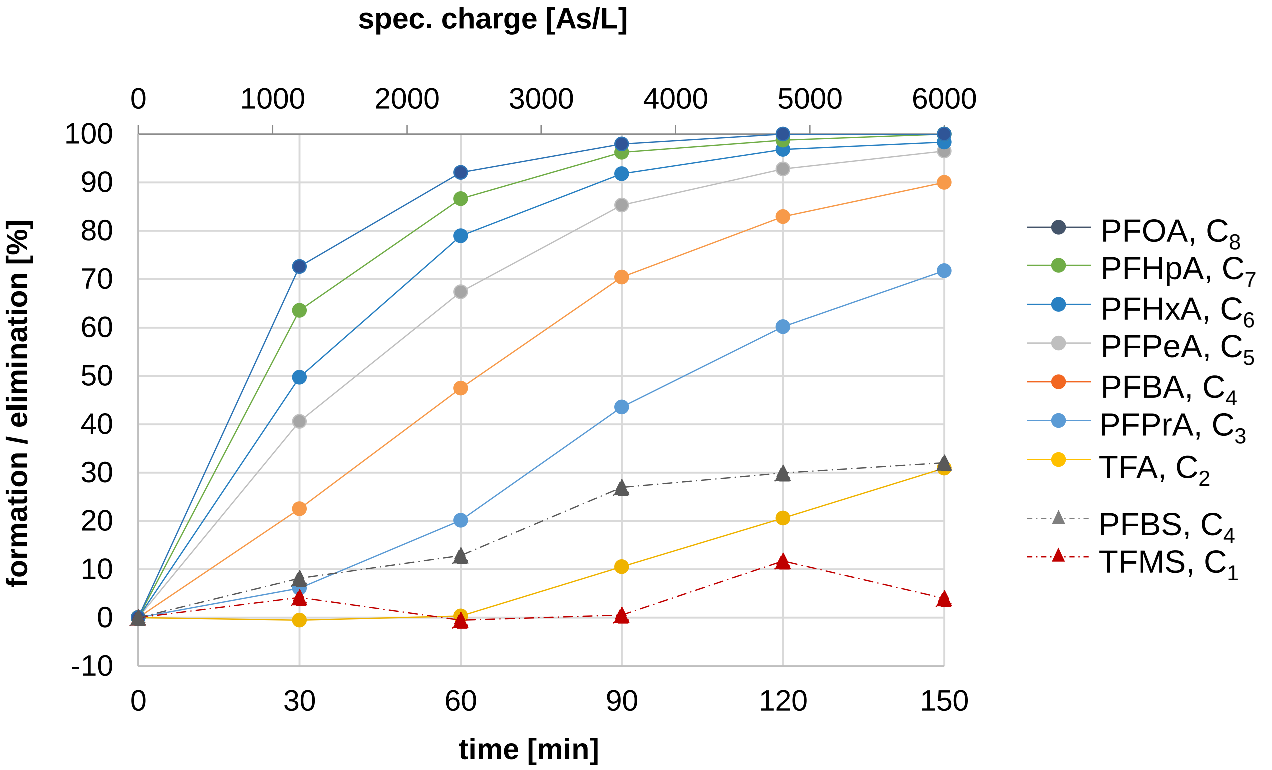


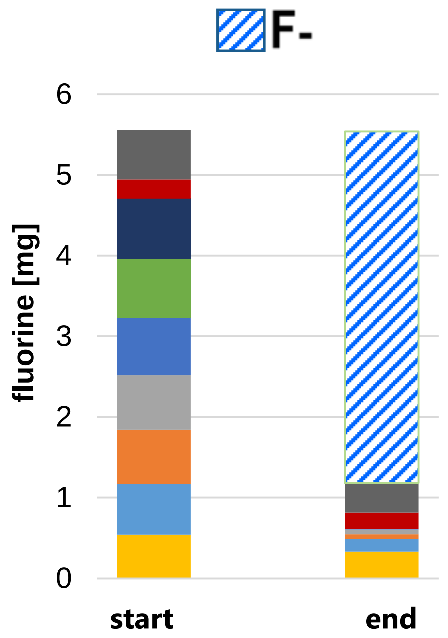
Regenerate IEX 0.8 - 1 M NaOH (pilot plant)

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



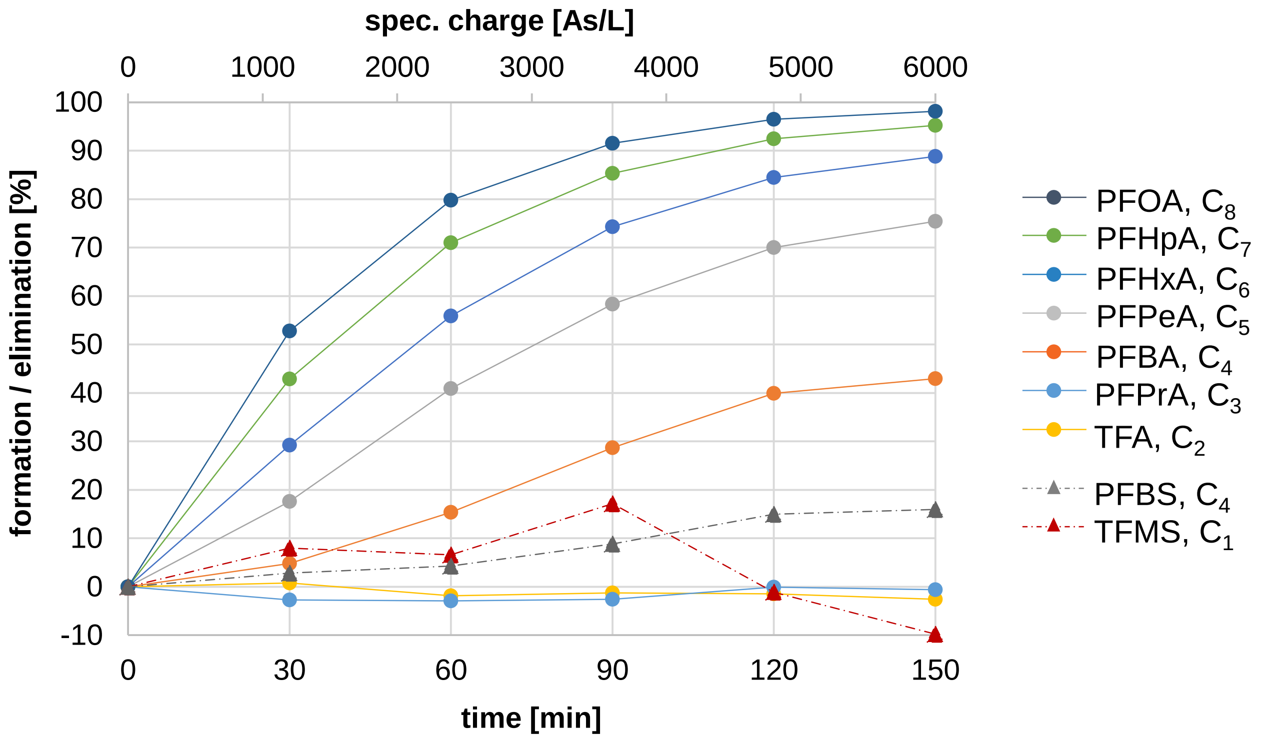
Elimination of short chain PFAS in *soft* drinking water matrix

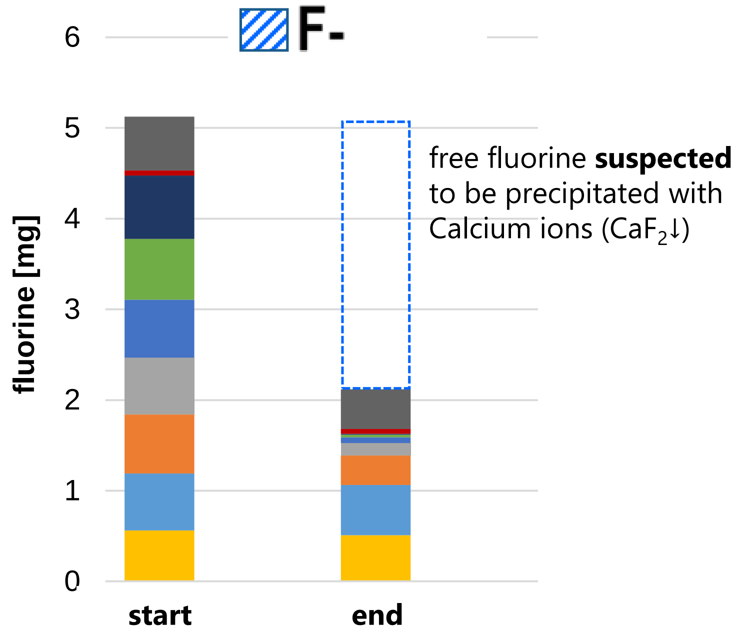




scale: 10 L
cond. soft drinking water κ ≈ 600 µS/cm
I = 1.5 A
initial PFAS conc.: 100 µg/L each

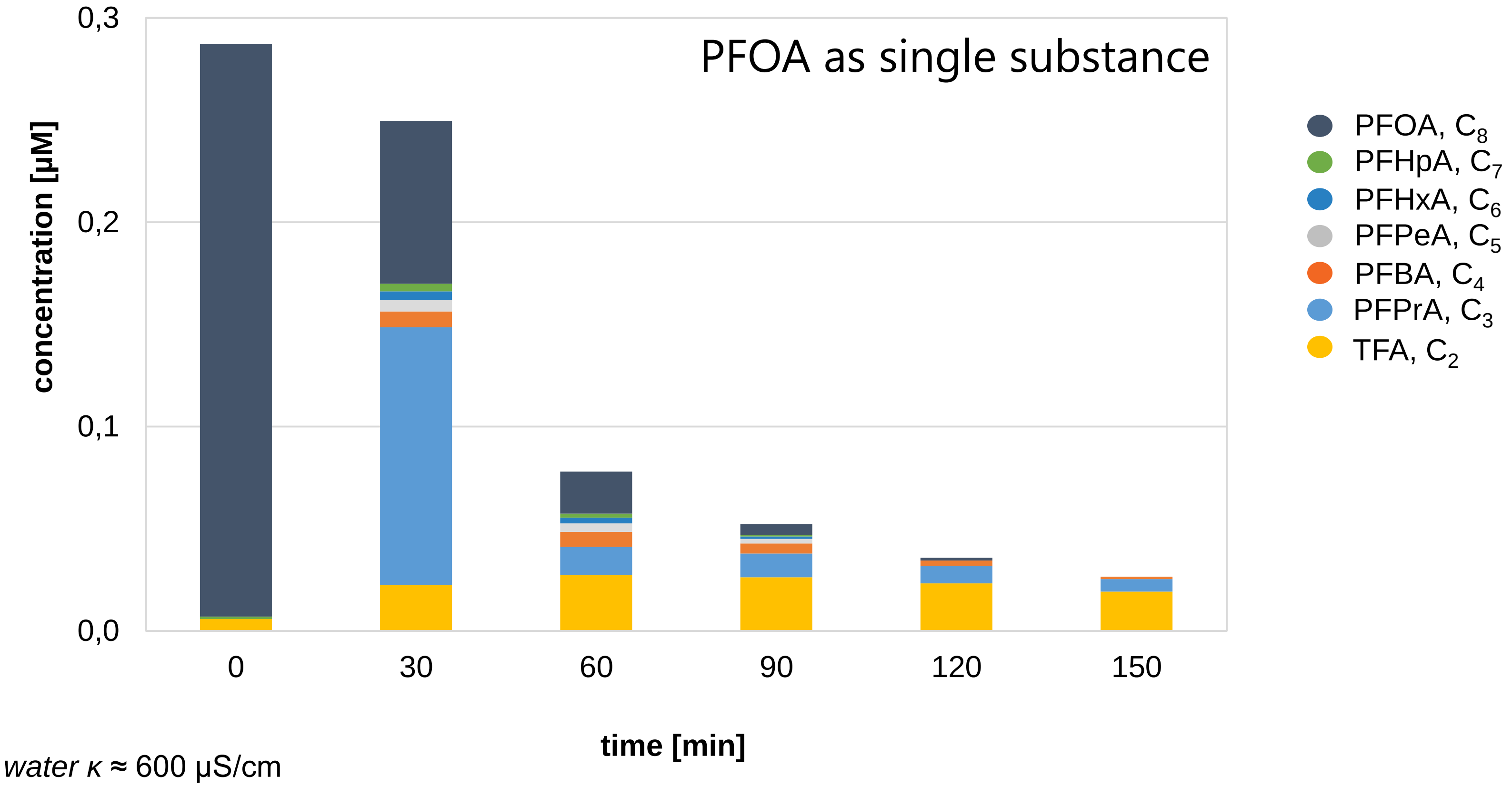
Elimination of short chain PFAS in *hard* drinking water matrix





scale: 10 L
cond. hard drinking water κ ≈ 1800 µS/cm
I = 1.5 A
initial PFAS conc.: 100 µg/L each

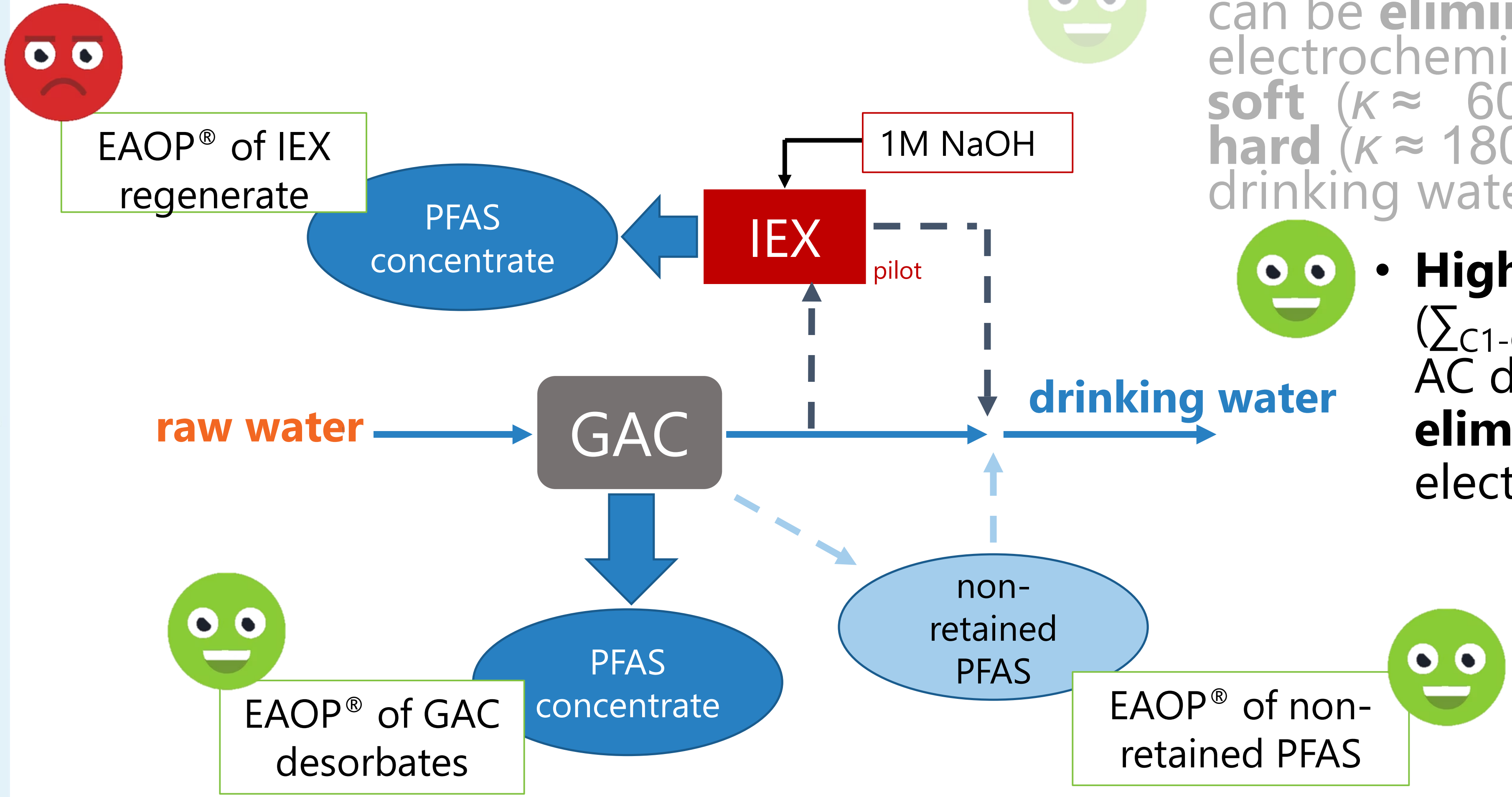
Transformation product formation



scale: 10 L
cond. soft drinking water κ ≈ 600 µS/cm
I = 1.5 A
initial PFAS conc.: 100 µg/L PFOA

Summary

- IEX regenerates (0.1-1 M NaOH) **cannot be treated so far** with electrochemical oxidation
- **Short chained PFAS (incl. TFA)** can be **eliminated** by electrochemical oxidation in **soft** ($\kappa \approx$ 600 µS/cm) and **hard** ($\kappa \approx$ 1800 µS/cm) drinking water matrices



- **High PFAS concentrations** ($\sum_{C1\text{-}C8} \approx$ 900 µg/L) in e.g. AC desorbates can be **eliminated** by electrochemical oxidation

Outlook

- Treatment of **raw water** from Rastatt
- Adjustment of operational parameters to **optimize** treatment efficiancies
- **combination** of AC desorption and electrochemical oxidation

ZeroPM

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chemsec
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NGI

DVGW TZW Technologiezentrum Wasser

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TG ENVIRONMENTAL RESEARCH

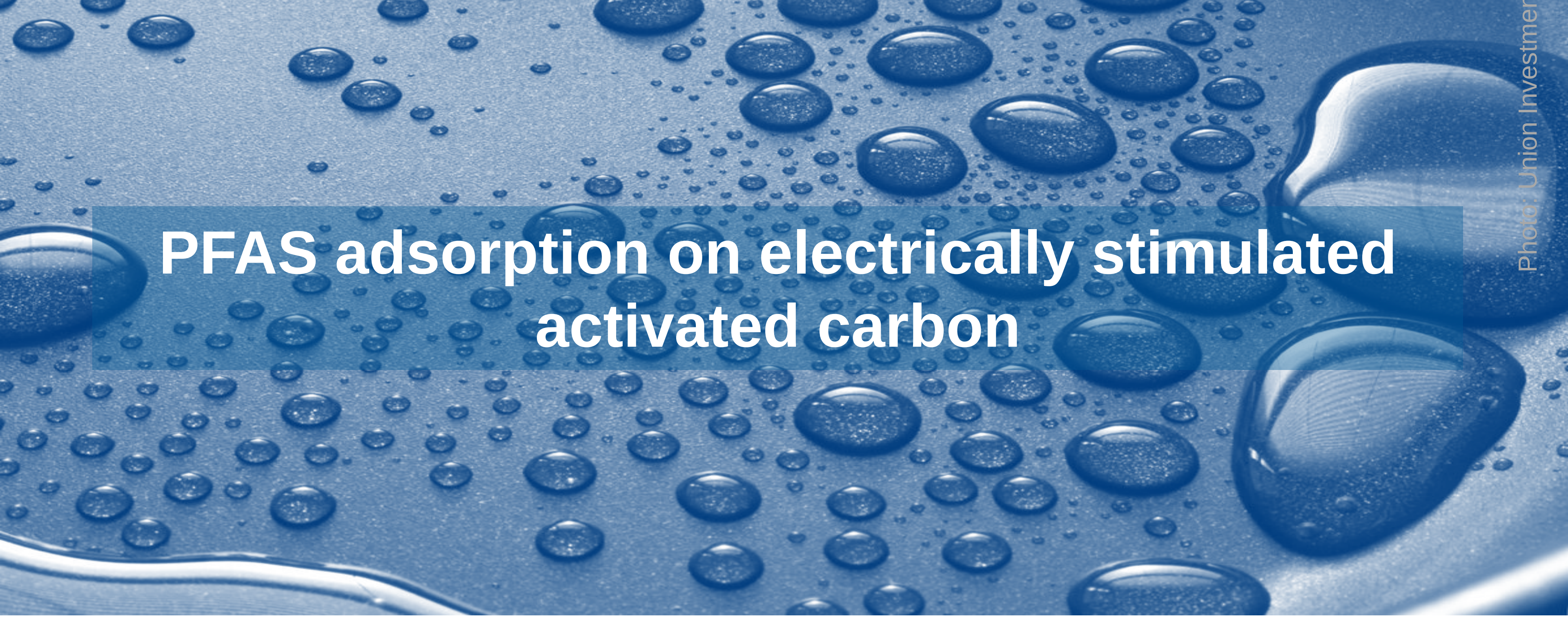
Stockholm University

universität wien

Umwelt Bundesamt

VU VRIJE UNIVERSITEIT AMSTERDAM

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



PFAS adsorption on electrically stimulated activated carbon

Anett Georgi, Navid Saeidi, Sarah Sühnholz, Robert Köhler, Katrin Mackenzie

Helmholtz-Center for Environmental Research – UFZ, Leipzig, Germany

Department of Technical Biogeochemistry

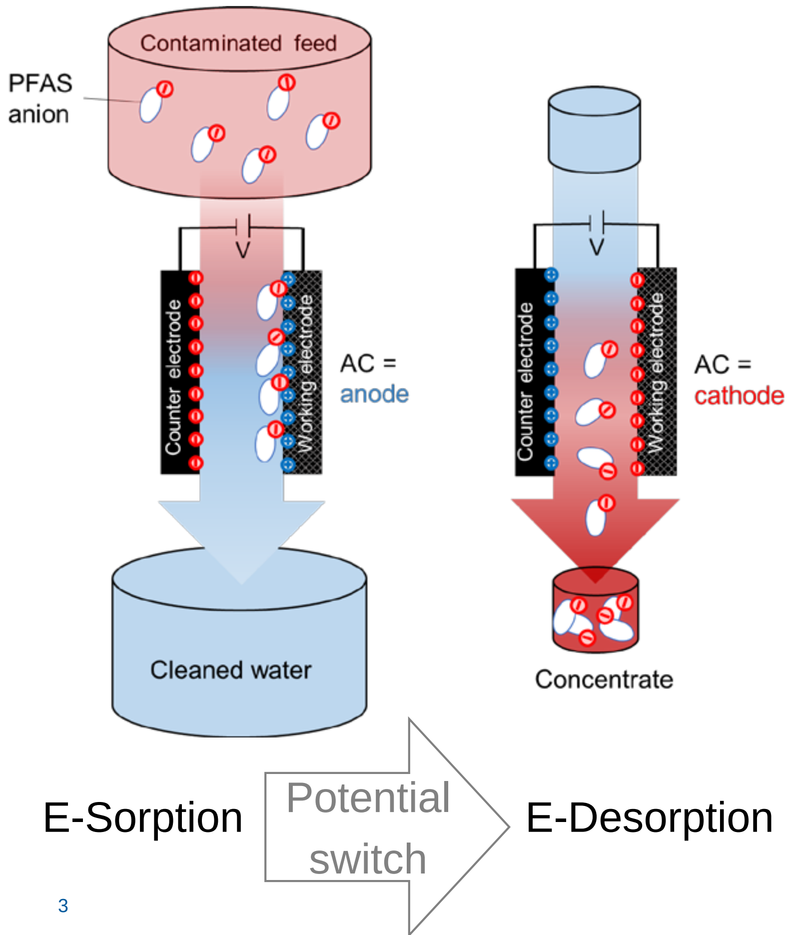
HELMHOLTZ Centre for Environmental Research

Activated carbon (AC) adsorption is widely applied – Never change a running system?

Problems:

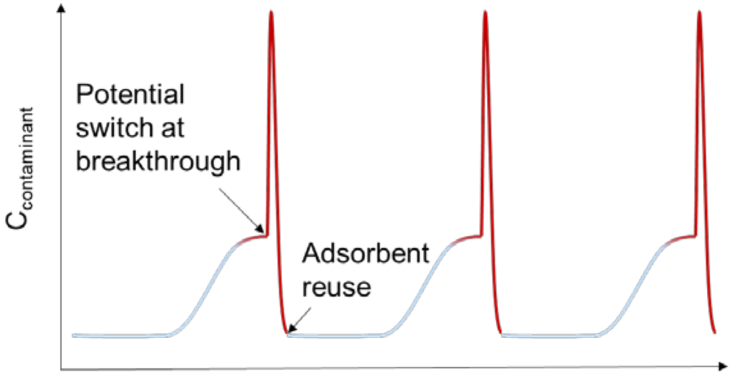
- Short-chain PFAS – frequent exchange of AC adsorbers
- AC main production in Asia from hard coal or coconut shell
- AC production and regeneration – high CO_2 footprint
- High T processes – fossil fuel dependent, not easily electrified

Concept of electrosorption

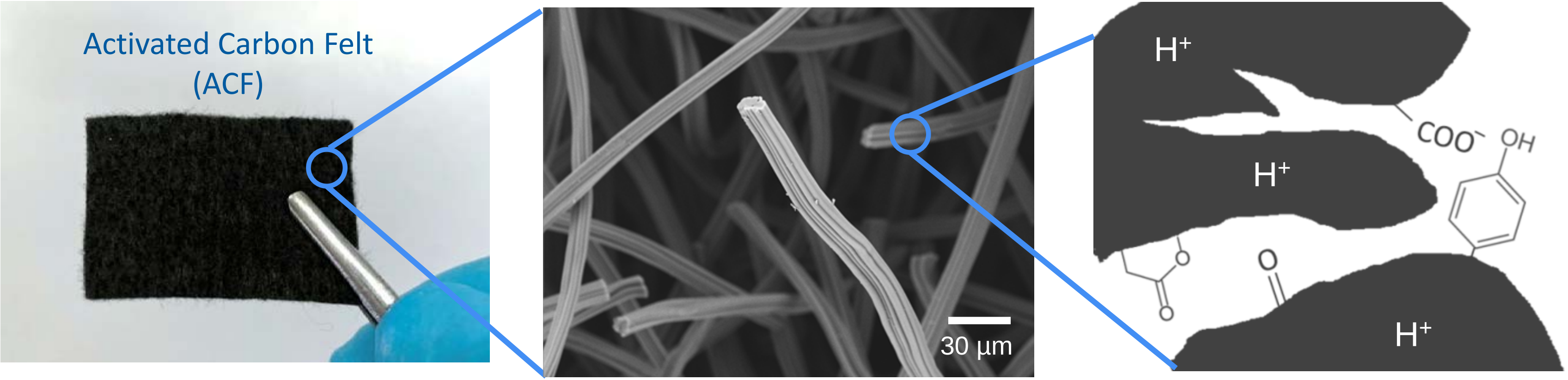


Solution:

- improve adsorption of hydrophilic short-chain PFAS anions by positive electric potential
- regenerate adsorbent with green electricity on-site by simple potential switch →
- desorb by negative electric potential



Adsorbent / Electrode material



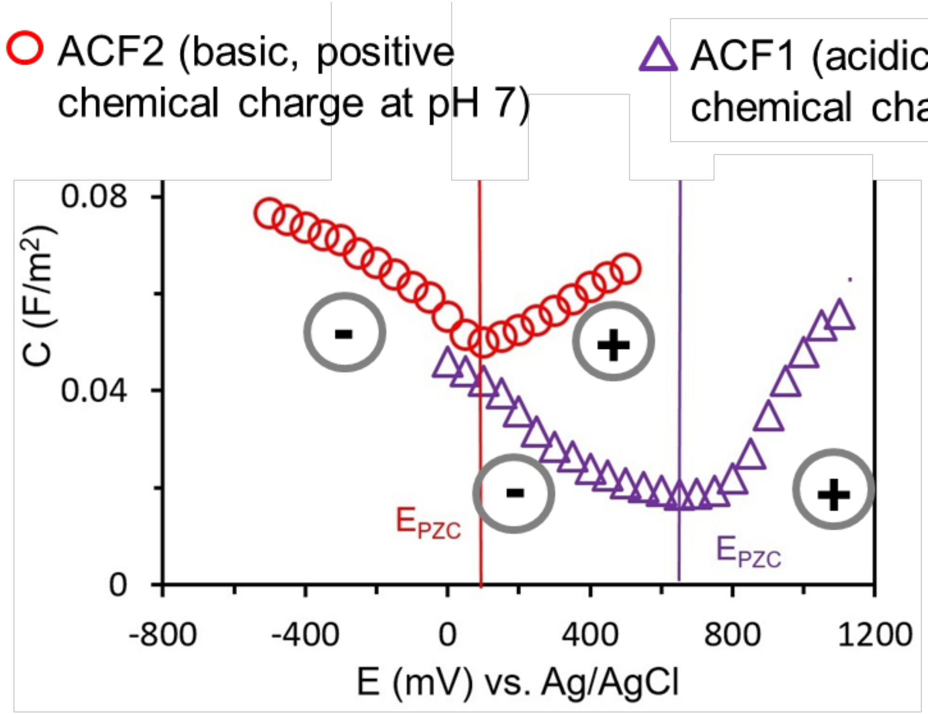
* Functional groups for illustration / not in the correct size scale

- ✓ Conductive → **electrosorption**
- ✓ Continuous structures → easy to operate
- ✓ **High specific surface area (SSA > 10^3 m^2/g)**
  → high sorption performance

Selection of carbon material – charging properties

When electric potential is applied to AC - chemical and electric charges superimpose.

For charge reversal E_{PZC}… potential of zero net charge must be crossed.



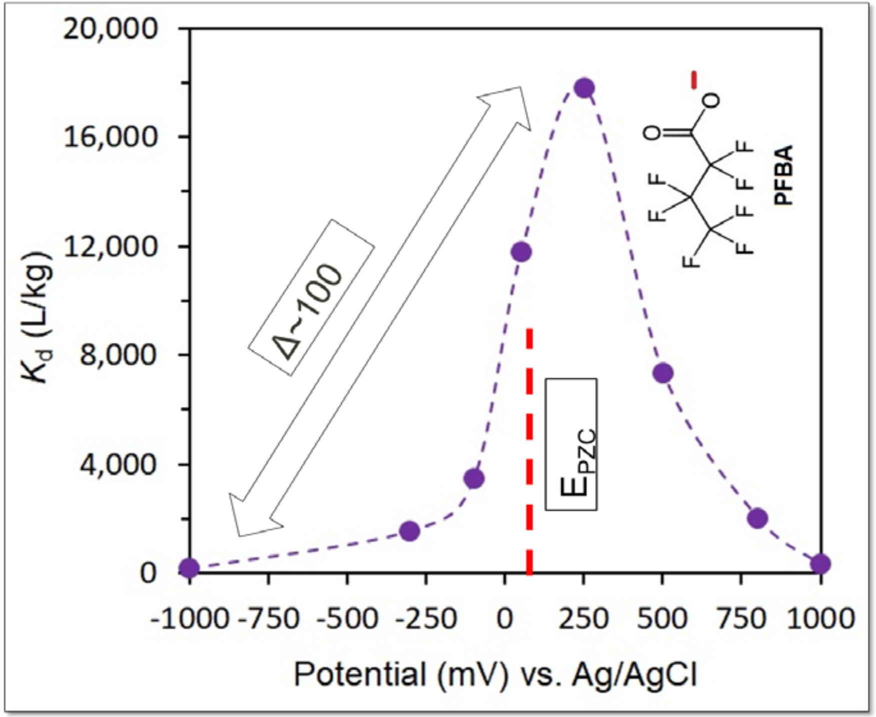
→ Higher positive potential needed to cross E_{PZC} for acidic ACF1

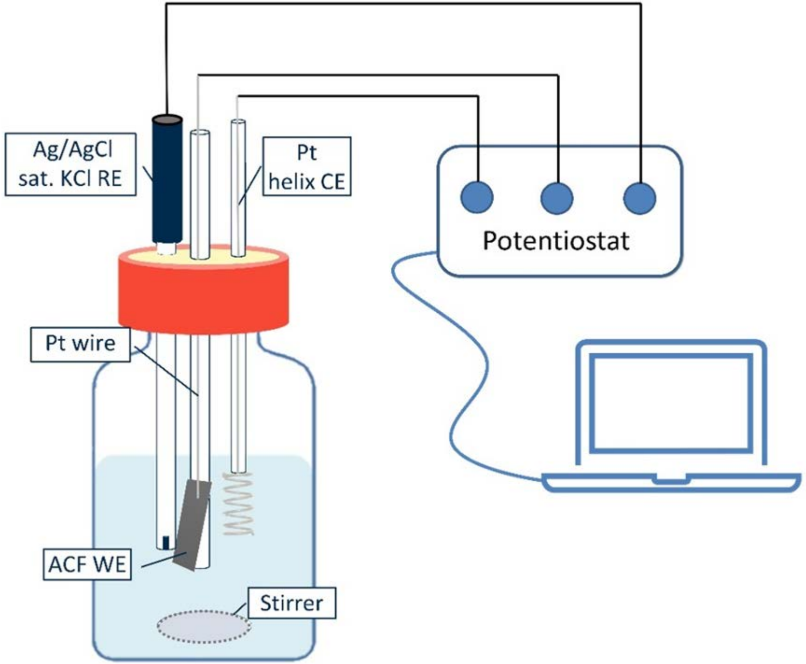
E_{PZC} determined as minimum in capacitance by Electrical Impedance Spectroscopy

Selection of suitable charging state – batch experiments

Sorption coefficients K_d of PFBA

(pH 6.5, 10 mM Na_2SO_4)



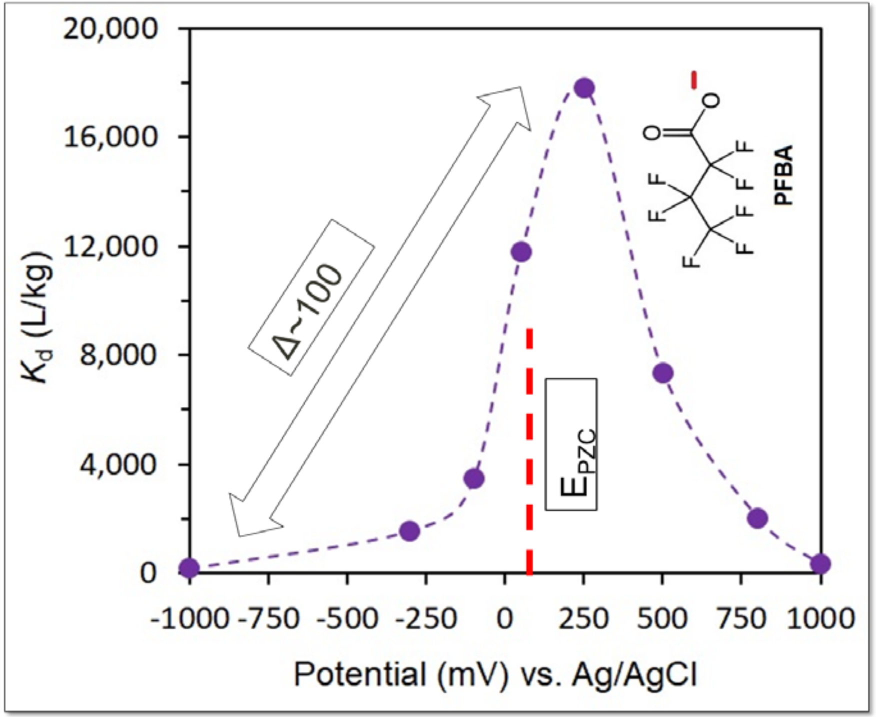


N. Saeidi, F.-D. Kopinke, A. Georgi, Chem. Eng. J. 416 (2021) 129070.

Selection of suitable charging state – batch experiments

Sorption coefficients K_d of PFBA

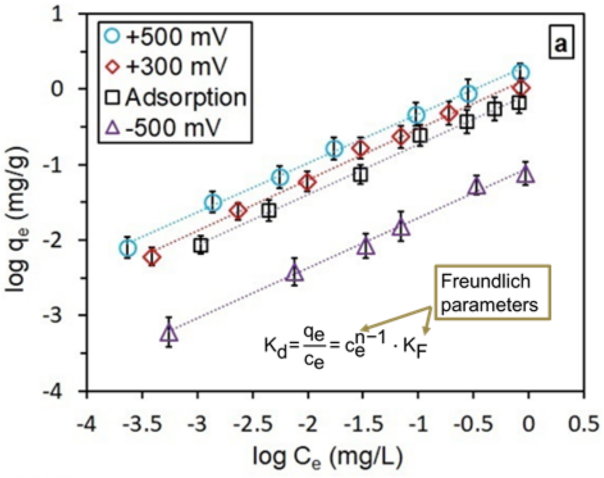
(pH 6.5, 10 mM Na_2SO_4)

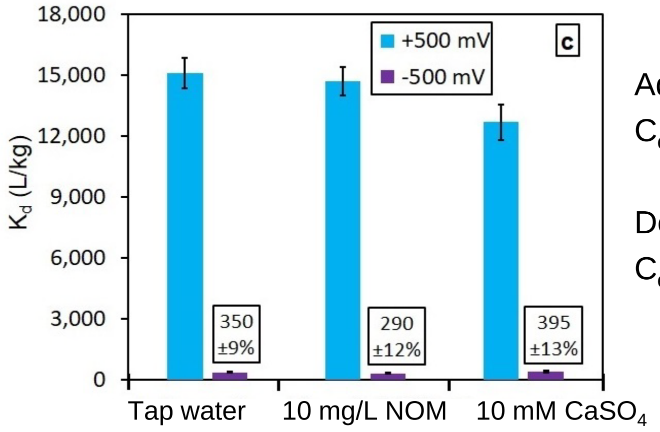


- optimum potential range
- optimum = superpostion of hydrophobic effect, VdW and electrostatic interactions
- below = electrostatic repulsion of PFBA dominates
- beyond = highly polar/charged surface → strong competition with water molecules

N. Saeidi, F.-D. Kopinke, A. Georgi, Chem. Eng. J. 416 (2021) 129070.

Batch experiments – isotherms and matrix effects





Adsorption:

$C_{e,PFBA}$ = 30 µg/L

Desorption:

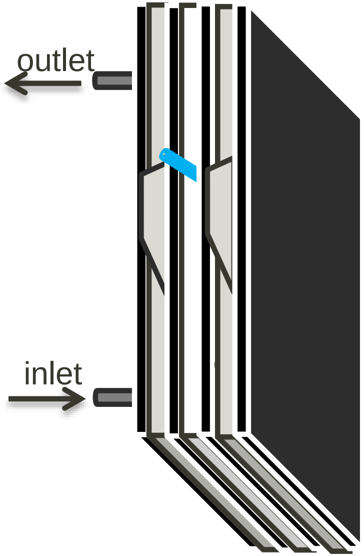
$C_{e,PFBA}$ = 1 mg/L

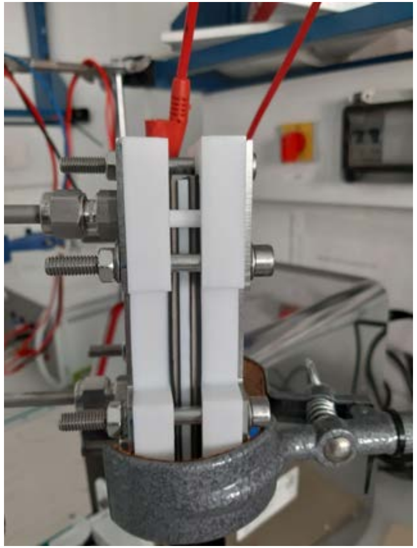
- Modulation of adsorption by electric potential works over wide concentration range and water matrix composition
- Prediction of concentration factors from Freundlich isotherm parameters

$$\frac{V_{ads}}{V_{des}} = \frac{c_{des}}{c_{in}} = c_{in}^{(n_{ads}/n_{des} - 1)} \times \left(\frac{K_{F,\,ads}}{K_{F,\,des}}\right)^{1/n_{des}}$$

N. Saeidi, F.-D. Kopinke, A. Georgi, Chem. Eng. J. 416 (2021) 129070.

Flow cell: setup





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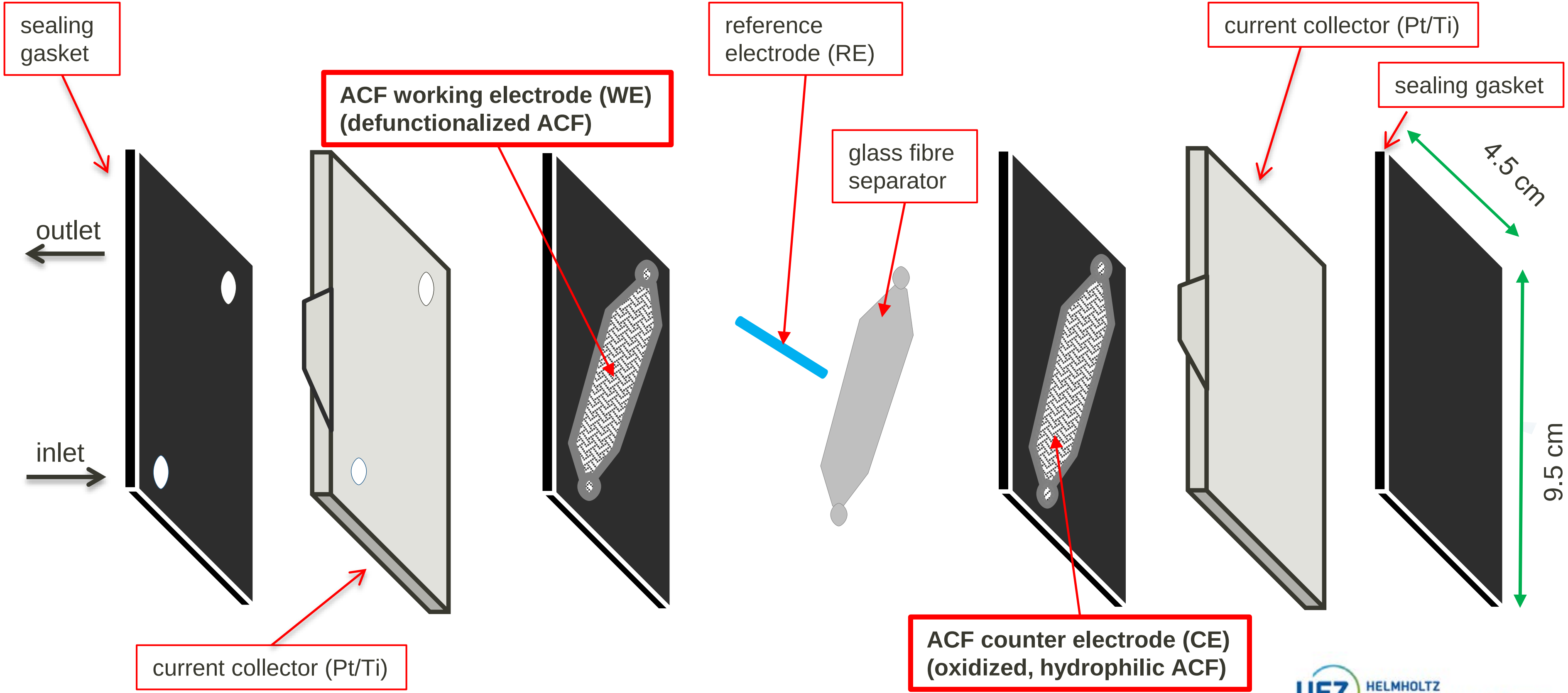
Flow cell: setup



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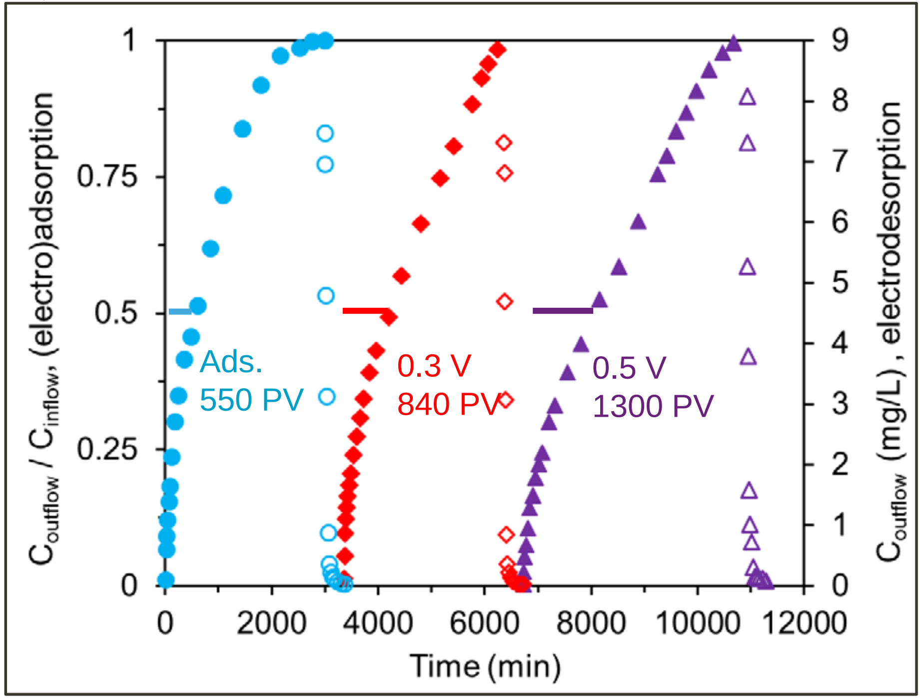
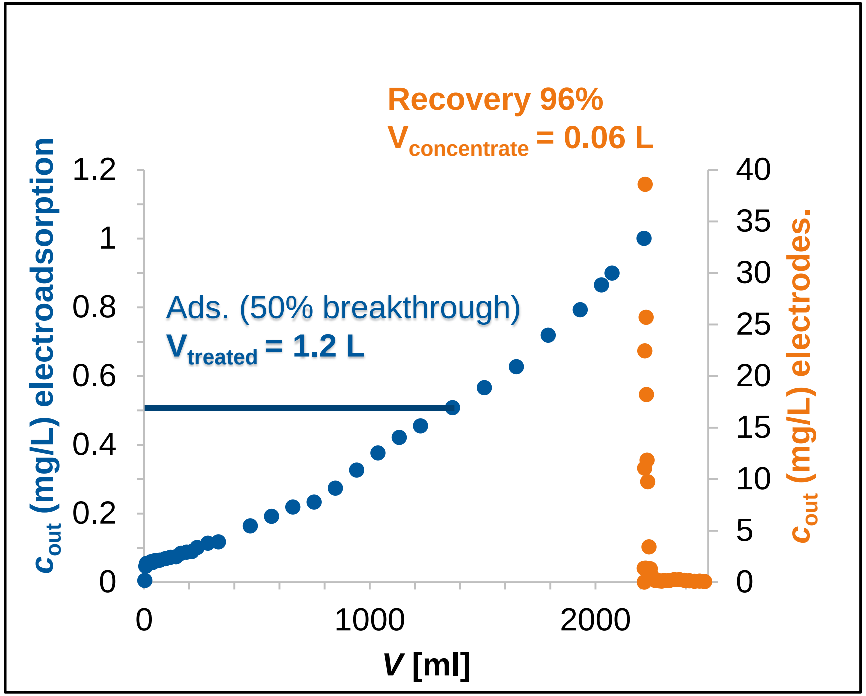
PFBA (electro)adsorption and -desorption experiments

$C_{0,PFBA}$ = 1 mg/L in tap water, potentials vs. Ag/AgCl





- **Stable performance over several cycles**
- **Positive WE potential increases adsorption performance**

- **Increasing concentration effect by fitting flow rate to desorption kinetics**
- **Predicted vs. achieved concentration factor: 42 vs. 16 (miniaturized system)**

BMBF-funded collaborative project FABEKO (2021-2024)
Soil washing and electrosorption modules for PFAS removal

FABEKO
SANIERUNG PFAS-HALTIGER BÖDEN & GRUNDWÄSSER

SENSATEC · UFZ HELMHOLTZ Centre for Environmental Research · GEOlogik Wilbers & Oeder GmbH · M&P Ingenieurgesellschaft

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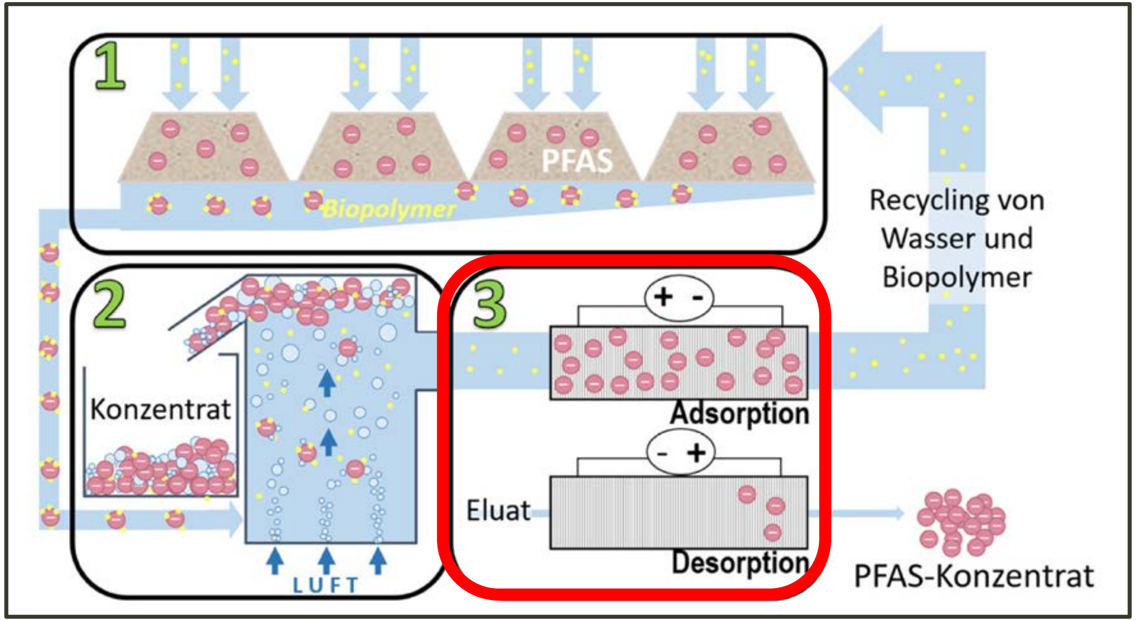
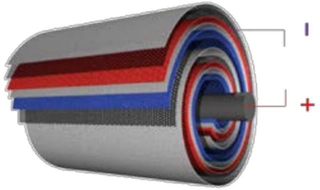
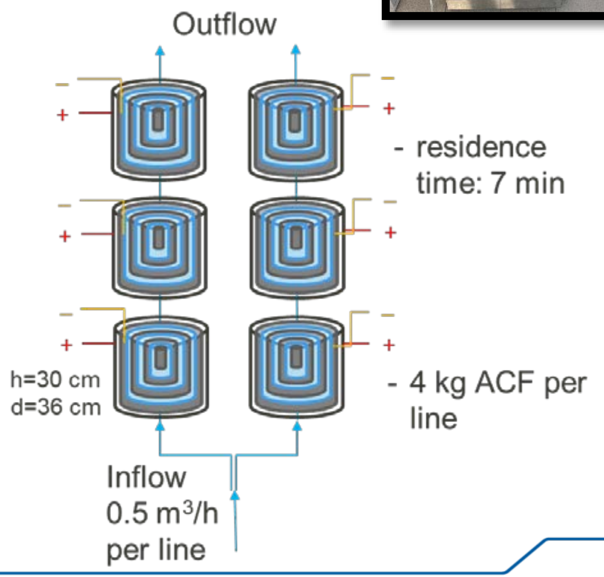




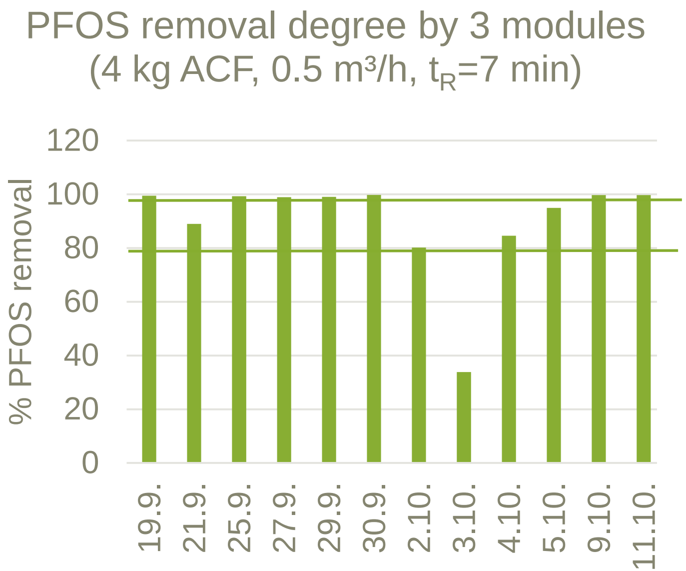
Electrode area: 6 m²

Swiss roll design



Pilot test results for electrosorption modules (PFOS)

FABEKO
SANIERUNG PFAS-HALTIGER BÖDEN & GRUNDWÄSSER

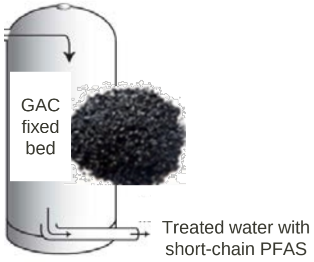


- Succesful upscaling of modules
- AFFF-contaminated site (PFOS dominating)
- 7 of 12 sampling events ≥ 99% removal degree, 11 of 12 events ≥ 80%
- 732 m³ soil washing water treated

→ Adsorption performance of modules is good

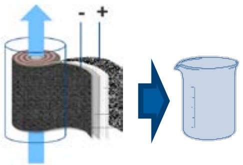
- Electro-Desorption stage: 2-4 V cell voltage → no water splitting, safe operation
- Pilot test allowed only 1.3 m³ for desorption → incomplete desorption
- PFOS prediction: treat > 4000 m³ and desorb into 130 m³ (conc. factor 30)
- PFOS not ideal application

Treatment trains: Separation/Concentration + Destruction



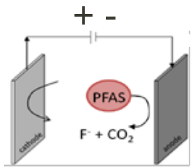
1. GAC adsorption

→ Efficient for **long-chain PFAS** removal



2. Electrosorption/-desorption

= **On-site regeneration and re-use**
→ Efficient for **short-chain PFAS**



(e.g. BDD or TiOx electrodes)

3. Electrooxidation

PFAS degradation in concentrate

UFZ HELMHOLTZ Centre for Environmental Research

Thank you for your attention!

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Helmholtz Centre for Environmental-Research - UFZ

Thanks to:
Navid Saeidi, Sarah Sühnholz, Robert Köhler, Katrin Mackenzie

See also Review:

Saeidi, et al., **Electrosorption of organic compounds: State of the art, challenges, performance, and perspectives**, Chem. Eng. J. 471 (2023) 144354.

Project partners:

SENSATEC
GEOlogik Wilbers & Oeder GmbH
M&P Ingenieurgesellschaft

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DAAD


EU Green Week
PARTNER EVENT
SCENARIOS
Rastatt, Germany
13 May 2024
#WaterWiseEU
SENSOIL
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FORTH
INSTITUTE OF CHEMICAL ENGINEERING SCIENCES
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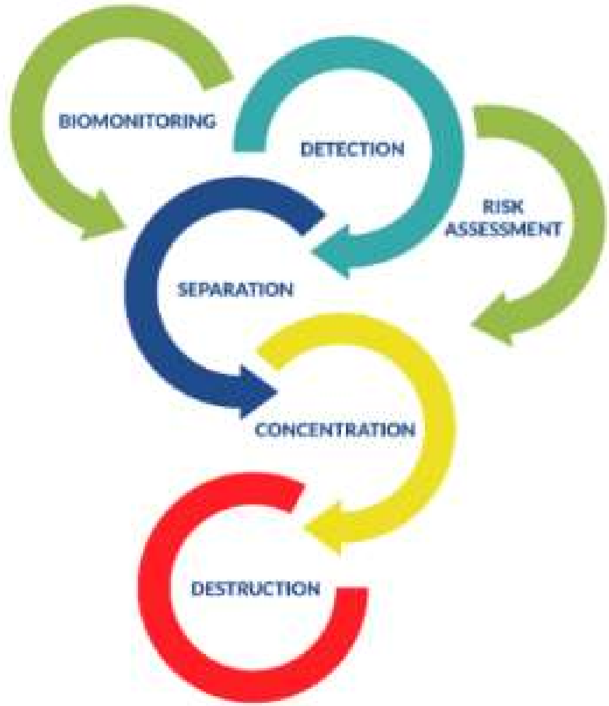
UNIVERSITÀ DEL PIEMONTE ORIENTALE
אוניברסיטת בן-גוריון בנגב
Ben-Gurion University of the Negev

e

SCENARIOS

VALUE CHAIN
PILLAR 1
PILLAR 2
PILLAR 3
Detection
Monitoring
Hazar and Risk assessment
Remediation
FORTH
UPO
AO AL
BfR
UPO
AO AL
LIST
FORTH
emytech
Water
Soil
Biota
Human
In vitro models, Advanced 3d in vitro models, Pbpk models,
in vivo models (fish) biota, Exposure, weight of evidence,
prioritization
Separation & concentration,
destruction, bio-adsorption
TECHNOLOGIES FOR PFAS
FIELD OF APPLICATION
Environmental monitoring
human biomonitoring
PILOT-DEMO 1
Public health
Policy and decision making
regulation legislation
PILOT-DEMO 2
Industry
Environmental remediation pollution control
drinking and waste water treatment agriculture
PILOT-DEMO 3
Drinking water
Health Assessment
AO AL
Exploitation
LOMARTOV
Environmental Assessment
Communication & Dissemination
comet



BIOMONITORING
DETECTION
RISK ASSESSMENT
SEPARATION
CONCENTRATION
DESTRUCTION

EU H2020, Scenarios WP7

SCENARIOS

Scope: To conduct demonstration activities for up scale remediation of PFAS at Technology Readiness Level 5/6 (TRL5 and 6) in ground water , leachate & drinking water applications

7.1: demonstrate SCENARIOS PILLAR 1 technologies for PFAS detection and monitoring at TRL 5/6.

7.2: demonstrate SCENARIOS PILLAR 2 technologies at TRL 5/6, i.e. Risk Assessment for PFAS, implemented as an open micro-server tool on the internet.

7.3: upscale systems and demonstrate SCENARIOS PILLAR 3 technologies for green and nearly zero energy PFAS remediation of groundwaterl leachate and drinking water applications

Tasks:

Task 7.1 Human biomonitoring program and Risk Assessment (DEMO1, Pillar 1 detection and Pillar 2 Risk Assessment). (M12-48) (Lead AOAL/ participen UPO BGU FORTH NTAU NovaM UoB)

Task 7.2 Design, construction and evaluation of upscaled units for demonstration purpose (M6-36) (Lead FORTH participant ENVYTECH SENSOIL IDP)

Task 7.3 Demonstration of remediation activity in groundwater and leachate (DEMO 2). (M24-48) (Lead ENVYTECH/ participant SENSOIL FORTH BGU Geo)

Task 7.4. Demonstration in a drinking water treatment plant (M24-48) (Lead IDP/ partecipant ENVYTECH FORTH)

envytech Miljö & teknik

FORTH INSTITUTE OF CHEMICAL ENGINEERING SCIENCES

IDP ingeniería · medio ambiente · arquitectura

SENSOIL

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Ben-Gurion University of the Negev

Geo

UPO UNIVERSITÀ DEL PIEMONTE ORIENTALE

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Talks about #pfas, #leachate, #horizon2020, and #watertreatment

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Talk Outline

- Short overview of available PFAS treatment options

- Presentation of SAFF – Surface Active Foam Fractionation, the first sustainable (?) PFAS removal technology

- Presentation of treatment results in H2020 Scenarios project:

  - Treatment of PFAS contaminated groundwater at AFFF training site using SAFF in combination with additives for long and short chain PFAS removal

  - Presentation of treatment results from SAFF landfill leachate treatment project in combination with additives and destruction technologies for "closed loop" treatment

Introduction:
A summary of treatment technologies for PFAS Contaminated Waters

Adsorption

- Activated Carbon
- Ion exchange mass
- New adsorption materials (!)

Concentration

- **SAFF – Surface Active Foam Fractionation**
- Flocculation Precipitation products
- Reverse Osmosis / Nano Filtration

Destruction

- **Electrochemical Oxidation**
- **Photoactivated Reductive Defluorination**
- SCWO – super critical water oxidation
- Thermal destruction
- HALT method
- **Cold Plasma** / Plasma



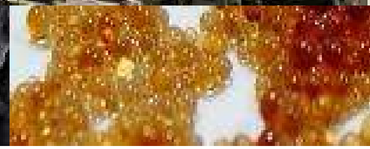

Adsorption – Filter Medias

Filter Media can be used for almost all organic contaminants as well as metals and “half” metals

- Dissolved PAH
- Petroleum Hydrocarbons
- Dissolved metals
- PFAS
- Nitrogen

It is however, important to know when and how to use filter medias as they are sensitive to:

- Particles
- pH
- Conductivity, salts, metal ions
- Cross-contaminants
- Other water chemistry , (ex BOD, DOC, COD TOC)



Adsorption – Filter Medias

But why do we have to know this ?
Filtermedias remove 99,9% of all PFAS, right ?

YES! 99,9% removal etc.
But To what cost – All and all, and for how long?

The cost does not only include the filter media it self, it also involves:

- Cost for rental / buy of pre treatment tech, vessels
- Chemicals for flocculation/precipitation
- Pre-filter medias
- Filter medias
- Service for pre treatment, backflushing etc
- Service for filtermedias exchange
- Cost for sludge handling system
- Cost of transport and deposition of sludge, WHERE?
- Cost of waste from used pre filter, incl Transport and deposition, WHERE?
- Cost of waste used filters, incl. Transport and deposition, WHERE?




Surface Active Foam Fractionation – SAFF

Developed by OPEC systems Australia as a result of a grant from Australian Defence

First full scale plant comissioned in May 2019 in Oakey, Australia

Envytech OPEC September 2019

First full scale mobile unit comissioned in Sweden February 2021

Chosen technology for EU grants Horizon2020 as well as EU LIFE

SCENARIOS

LIFE SOuRCE

Global deployment on three continents

Over 1 million m3 of PFAS contaminated water treated world wide

SAFF
Surface Active Foam Fractionation

– A concentration treatment

Perflourinated substances has
Hydrophilic head → Head loves water
Hydrophobic tail → Tail hates water

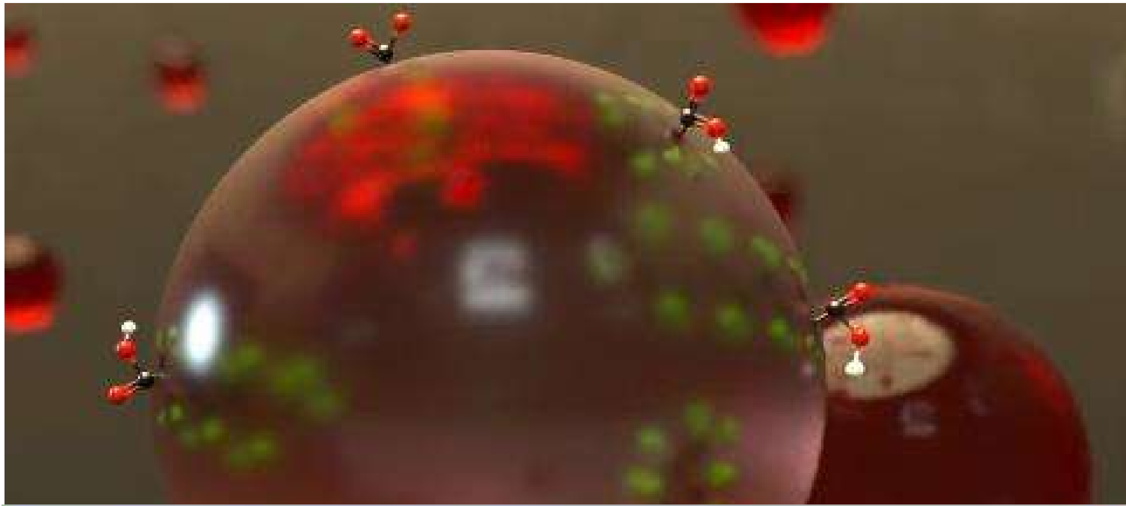
The bubble becomes the perfect environment C6 PFAS and above – tail sticks in the bubble, easy to remove.

Primary step: 10 x initial concentration

By ”top up push” stratified short chain PFAS can be removed to some extent

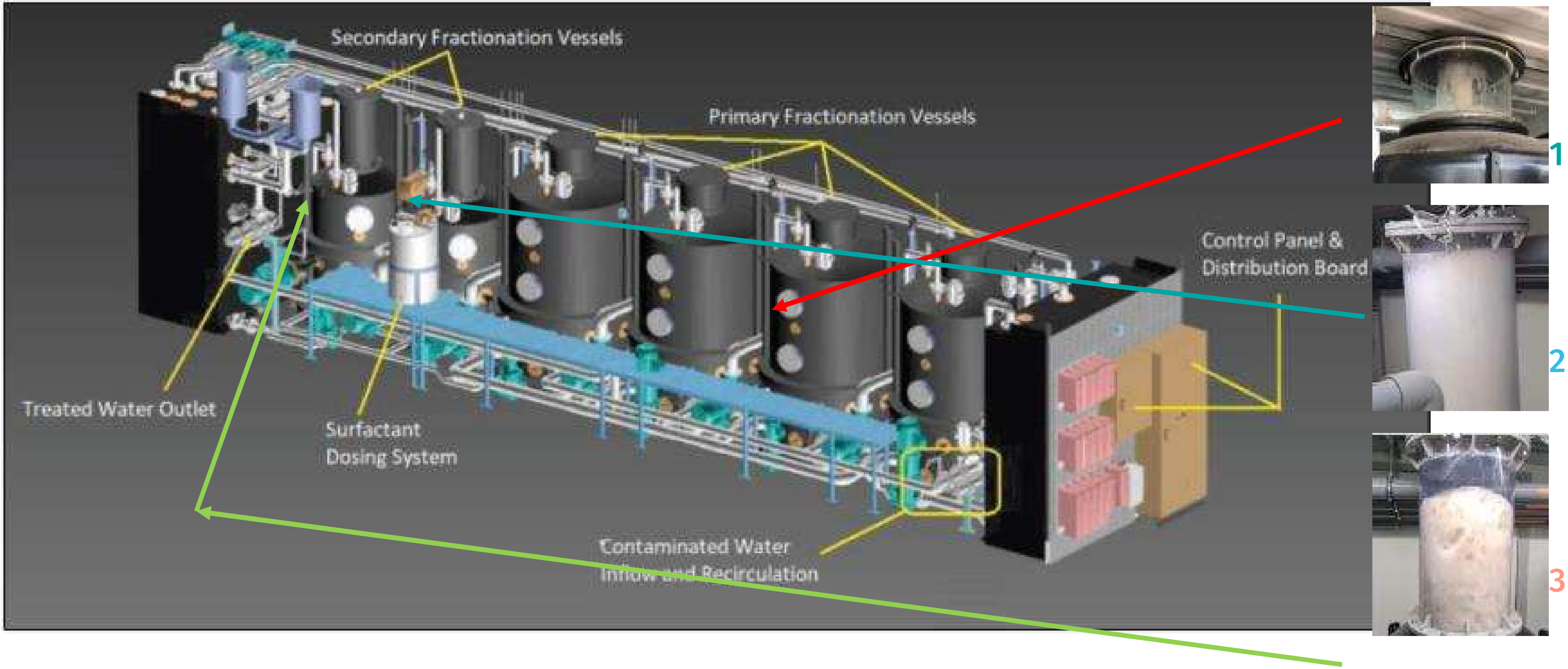
Secondary Step: 1500 x initial concentration

Tertiary Step: 50 000-2 000 000x initial concentration





EPOC SAFF40 containerised System



Full scale SAFF40 system treats flows up to 25 m3/h, using 0,7 kwh/m3 treated, generating less then 10 m3 waste per year

Concentration

SAFF – Surface Active Foam Fractionation
– Lets check it out

Primary Fractionation of raw leachate

Primary Fractionation of raw groundwater

Concentration

SAFF – Surface Active Foam Fractionation – Lets check it out

Secondary Fractionation

Tertiery Fractionation

And this is where the patent of this technology is situated, in large.
Treatment in series to minimize waste, and the use of vacuum

Mobile treatment, winter islotated

“Plug and play” installation procedure

Tuning after start up – needed because all waters are different, approx. 2 days

Remote surveillance, fine tuning, 24h / 7 day controlled

You can follow flow, status, electricity used, total volume and more via the app!

Every pump, valve and sensor, reports data continuously. We can see exactly when , what and where a problem has occurred and can usually fix it remotely straight away

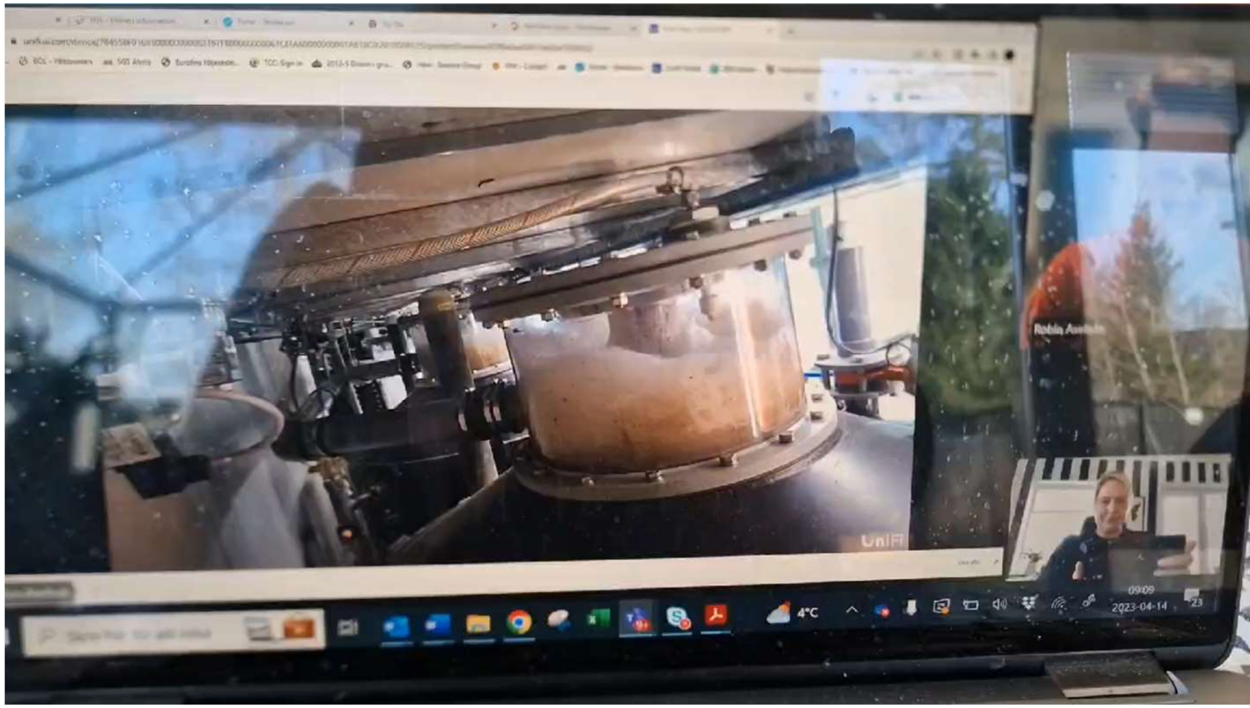
Treatment control

SAFF is remotely surveilanced by producers EPOC Enviro 24/7

Envytech staff can watch process, change settings for fine tuning of foam contro. Remotely

We train local staff at comissioning, so minimum cost will be spent on external service crew

Can ”live” guide local staff for service, sampling or questions on the performance or all else.



The system is completely automatic and have work health and safety measures for minimizing possible contact with PFAS aerosols

When and Why SAFF

SAFF is a very robust treatment option. PFAS removal efficiency is:

- ✓ NOT sensitive to PFAS levels (High/Low)
- ✓ NOT sensitive to pH
- ✓ NOT sensitive to Suspended particles DOM, DOC, Salinity
- ✓ Not sensitive to cross contaminants, (organics, metals, salts)

Further more

SAFF needs no pre treatment steps

(bagfilter 200 um)

Capable of removing PFAS4 and PFAS6 up to 99,9% using no consumables or additives

Produces minimal waste amounts

Uses only electricity, 0,7 kwh/m3 treated

Proven technology with over 500 000 m3 treated

Expected Removal Rates

Comparison of results of PFAS removal rates for Groundwater/ Leachate / Fire Fighting water / Surface water runoff at airport

Substance	OPEE GW Australia 150 000 m³	NSR Leachate 30 000 m³	Telge Leachate 250 000 m³	Löt Leachate 15 000 m³	Mjölbo Leachate 9000 m³	Swedish Airport 40 m³	Fire Fighting water Refinery 12 000 m³	EU LIFE SouRCe Groundwater	EU LIFE SouRCe Groundwater
PFDA	100%	100%	100%	100%	100%	100%	100%	96%	Up to 99,9%
PFNA	100%	100%	100%	100%	100%	100%	100%	Up to 99,9%	Up to 99,9%
6:2 FTS	100%	100%	100%	100%	100%	100%	99,5%	Up to 99,9%	Up to 99,9%
PFOA	100%	100%	100%	100%	99%	98%	99%	ND	Up to 99,9%
PFOS	100%	99%	98%	100%	100%	100%	100%	84%	98%
PFHxS	97%	100%	100%	99%	99%	79%	99,5%	51%	99%
PFHpA	67%	99%	98%	90%	92%	99%	95%	93%	Up to 99,9%
PFHxA	20%	54%	29%	35%	10%	0%	35%	42%	99%
PFPeA	24%	0%	3%	38%	7%	0%	0%	4%	98%
PFBA	21%	8%	1%	0%	0%	0%	0%	76%	99%
PFBS	22%	43%	10%	19%	8%	0%	52%	ND	Up to 99,9%
Total PFAS conc.	4000 ng/l	6000 ng/l	4000 ng/l	15 000 ng/l	4000 ng/l	4000 ng/l	100 000 ng/l	100 000 ng/l	2 000 000 ng/l

Perfect combination with Soil Washing

– Amongst other waters ☺

Soil wash water (soil for soil wash) contains >95% long chained PFAS
After 1,5 years, we see no accumulation of short chain PFAS

Soil wah plants recirculate process water => no outlet target criteria

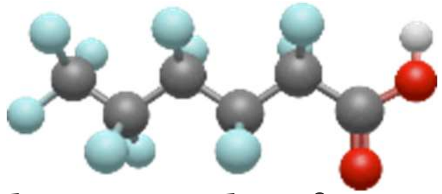
Only partial flow treatment needed to keep PFAS levels in water low enough for washing.
Full flow can be processed over night during plant stand down

Almost no waste – 25 m3/h ➔ < 5 m3 waste per year.

		TYP1		TYP1 L/S=2	TYP1 L/S=8
Ämne	Enhet	0,25-1	Enhet	0,25-1	0,25-1
Torrsubstans	%	90,3			
6:2 FTS (Fluortelomer sulfonat)	µg/kg Ts	3,9	ng/l	1900	97
PFBA (Perfluorbutansyra)	µg/kg Ts	0,33	ng/l	37	<10
PFBS (Perfluorbutansulfonsyra)	µg/kg Ts	<0,10	ng/l	33	<10
PFDA (Perfluordekansyra)	µg/kg Ts	0,53	ng/l	120	25
PFHpA (Perfluorheptansyra)	µg/kg Ts	0,25	ng/l	190	<10
PFHxA (Perfluorhexansyra)	µg/kg Ts	0,48	ng/l	240	12
PFHxS (Perfluorhexansulfonsyra)	µg/kg Ts	2,4	ng/l	330	41
PFNA (Perfluornonansyra)	µg/kg Ts	0,47	ng/l	140	12
PFOA (Perfluoroktansyra)	µg/kg Ts	2,2	ng/l	910	42
PFOS (Perfluoroktansulfonsyra)	µg/kg Ts	[illegible]	ng/l	[illegible]	11000
PFPeA (Perfluorpentansyra)	µg/kg Ts	0,88	ng/l	400	<10
PFOSA (Perfluoroktansulfonamid)	µg/kg Ts	13	ng/l	2000	720
Summa PFAS 11	µg/kg Ts	230	ng/l	85000	11000
Summa PFAS 28	µg/kg Ts	250	ng/l	88000	12000

SO,
A perfect match for SAFF !

But what about short chains – and can we further enhance the effect for long chains



Foam Fractionation works by attracting surface active PFAS compound to an air bubble. But the ability to attach to the bubble

Short chain PFAS are not as surface actie as long chain PFAS, but this can be changed / enhanced.

Research conducted by many suggests that adddition of amendments and/or surfactants can increase short chain uptake by bubble.

We work togehter with Allonnia (US) to develop and trial different additives for different waters to increase SAFF removal potential

Research and trial of additives is also ongoning within the Scenarios project

Immediate Application Possible

SAFF
Surface Active Foam Fractionation

– Ready for the future

All Full scale SAFF units are equipped with a Chemical dosing tank and pump system

Possibility to add of solvents / additives or other type of amendments to increase efficiency of the foam fractionation process

Injection is performed straigh tinto the Foam Fractionation process, no extra treatment steps or treatment system needed.

Figure 20: Dosing tank and pump

Scenarios H2020 Team Scenarios

Site 1 . Korsör AFFF Fire Fighting training site

Evaluation of Foam Fractionation method SAFF for long chain PFAS in combination with additives for enhanced short chain PFAS Removal

Site 2. Treatment of landfill leachate

Evaluation of potential of different destruction technologies as a sustainable, economic and effective SAFF waste tratment option creating a ”closed loop” / no waste option

Site 1
Treatment of AFFF contaminated groundwater at a fire fighting training site in Denmark

- Korsör FF School is Ground Zero for PFAS In Denmark
- Groundwater PFAS levels varies from
  20 000 - 100 000 ng/l
- PFAS 6 xx% , short chain PFAS xx%
- Low organic loading, none to low levels of TOC and other contaminants
- Performed trials:
  - Lab scale SAFF treatment using only SAFF
  - Full scale pilot treatment using only SAFF
  - Lan scale SAFF treatment using SAFF+Additives

Active SAFF20 plant treating highly contaminated groundwater, Korsör Brandskole, RESC, Denmark

Envytech miniSAFF

Bench scale testing unit

Situated at Envytech laboratory in Stockholm.
Clients can send water from all over Europe to perform treatability studies to evaluate effect of SAFF on site specific waters

Groundwater treatment at Korsör Fire Fighting training center

Step 1: Lab scale trial
Performance of lab scale trial using water from the site

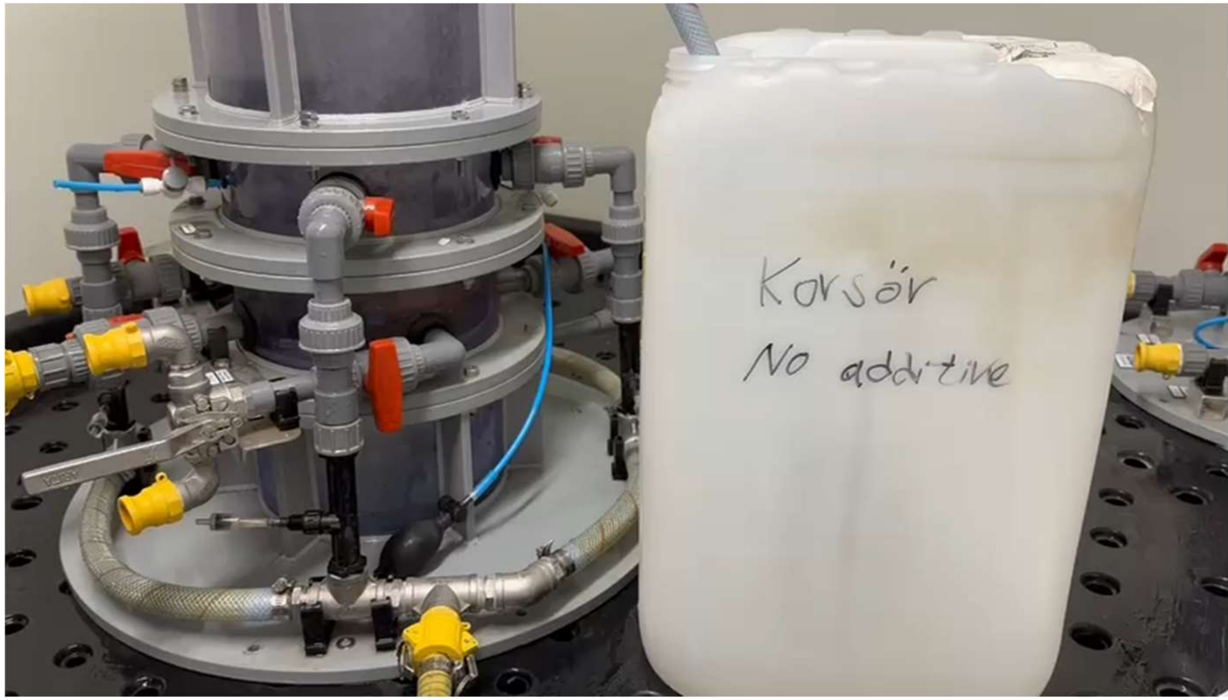
Test performed in miniSAFF lab scale model designed and produced by EPOC Enviro

Water was treated in a mini primary reactor build to mimic full scale SAFF plant. Unit isused to evaluate performance potential of SAFF on specific waters.

PFAS removed as foam is collected in separate vessel.

Treated water remains in the primary vessel

Sampling of treated water is carried out by collection of treated water from primary vessel
Untreated and treated water was analyzed by Eurofins Sweden



Groundwater treatment at Korsör Fire Fighting training center

Step 1: Lab scale trial
Results

Use of Envytech treatment pattern to enhance the PFAS removal without natural foaming

Results in miniSAFF show minimum of 99% removal of PFASnincluding PFOS, PFOA, 6:2 FTS and PFHpS.
Same effciency is expected for PFOSA, PFNA & PFDA

PFHxS removal efficemcy of 94% is expected to be higher in full scale.

Lower removal efficiency – as expected for short chain PFAS.

		MiniSAFF - Bench scale trial		
PFAS substance		Untreated	Treated	Removal rate (Treated - Untreated)
PFBA (Perfluorobutanoic acid)	ng/l	5600	5600	0%
PFPeA (Perfluoropentanoic acid)	ng/l	9000	9300	0%
PFBS (Perfluorobutanesulfonic acid)	ng/l	21000	20000	5%
PFHxA (Perfluorohexanoic acid)	ng/l	27000	24000	11%
PFPeS (Perfluoropentanesulfonic acid)	ng/l	19000	12000	37%
PFHpA (Perfluoroheptanoic acid)	ng/l	3800	1100	71%
PFHxS (Perfluorohexanesulfonic acid)	ng/l	18000	1100	94%
PFHpS (Perfluoroheptanesulfonic acid)	ng/l	100	<10	upp till 99,9%
PFOA (Perfluorooctanoic acid)	ng/l	1700	19	99%
PFOS (Perfluorooctane sulfonic acid)	ng/l	190	<10	upp till 99,9%
6:2 FTS (Fluorotelomer sulfonate)	ng/l	26	<10	upp till 99,9%
PFOSA (Perfluorooctanesulfonamide)	ng/l	<10	<10	ND
PFNA (Perfluorononanoic acid)	ng/l	<10	<10	ND
PFDA (Perfluorodecanoic acid)	ng/l	<10	<10	ND
Sum of 20 PFAS	**ng/l**	**110000**	**73000**	**34%**

Groundwater treatment at Korsör Fire Fighting training center

Step 2: Full scale trial
Results

	IN	OUT	Trial 1	IN	IN_TOP	OUT	Trial 2	In	Out	Trial 3
PFAS substance	Results	Results	Removal rate (OUT-IN)	Results	Results	Results	Removal rate (OUT-IN)	Results	Results	Removal rate (OUT-IN)
PFBA (Perfluorobutenoic acid)	840	710	15%	1 100	1 100	1 000	9%	1 400	1 400	0%
PFBS (Perfluorobutanesulfonic acid)	4 900	3 500	29%	6 200	6 800	5 800	6%	7 600	6 800	11%
PFPeA (Perfluoropentanoic acid)	1 400	1 200	14%	2 000	1 900	1 900	5%	2 100	2 100	0%
PFPeS (Perflucropentanesulfonic acid)	2 900	490	83%	3 600	4 600	1 700	53%	24 000	4 200	83%
PFHxA (Perfluorohexanoic acid)	4 800	3 100	35%	5 700	7 000	5 500	4%	13 000	8 100	38%
PFHxS (Perfluorohexanesulfonic acid)	10 000	25	100%	15 000	15 000	470	97%	13 000	370	97%
PFHpA (Perfluoroheptanoic acid)	830	14	98%	900	940	150	83%	1 500	70	95%
PFHpS (Perfluoroheptanesulfonic acid)	280	<10	upp till 99,9%	330	340	<10	upp till 99.9%	280	<10	upp till 99,9%
PFOA (Perfluorooctanoic acid)	1 100	<10	upp till 99,9%	950	990	21	98%	940	18	98%
PFOS (Perfluorooctane sulfonic acid)	2 100	<10	upp till 99,9%	2 800	2 600	41	99%	2 000	16	99%
6:2 FTS (Fluorotelomer sulfonate)	400	<10	upp till 99,9%	430	360	<10	upp till 99.9%	250	<10	upp till 99,9%
Sum of PFOA, PFOS, PFNA and PFHxS	**13000**	**25**	**99,8%**	**18750**	**18590**	**532**	**97%**	**15940**	**404**	**97%**
Sum of 20 PFAS	**30 000,00**	**9 000,00**	**70%**	**39 000,00**	**41 000,00**	**17 000,00**	**56%**	**66 000,00**	**23 000,00**	**65%**
PFOSA (Perfluorooctanesulfonamide)	<10	<10	ND	<10	<10	<10	ND	<10	<10	ND
PFNA (Perfluorononanoic acid)	<10	<10	ND	<10	<10	<10	ND	<10	<10	ND
PFNS (Perfluorononanesulfonic acid)	<10	<10	ND	<10	<10	<10	ND	<10	<10	ND
PFDA (Perfluorodecanoic acid)	<10	<10	ND	<10	<10	<10	ND	<10	<10	ND

High removal rates (>99%) for PFAS6. Full scale results show as expected higher efficiency then lab scale
As expected, lower removal rates for short chain PFAS

Lab scale trial groundwater
SAFF in combination with Allonnia Booster no1

Lab scale trial
SAFF in combination with Allonnia Booster no1
Results

envytech Miljö & teknik	Unit	Korsör IN_1	Korsör OUT_1	Korsör OUT dos 1	Korsör OUT_3_dos2	Korsör OUT_dos 4
			Inget additiv	Additive 1	Additive 2	Additive 3
PFDA (Perfluordekansyra)	ng/l	<10	<10	<0,30	<0,30	<0,30
8:2 FTS (Fluortelomer sulfonat)	ng/l	<20	<20	<0,30	<0,30	<0,30
4:2 FTS (Fluortelomer sulfonat)	ng/l	<10	<10	<0,30	<0,30	<0,30
PFNA (Perfluornonansyra)	ng/l	<10	<10	<0,30	<0,30	<0,30
6:2 FTS (Fluortelomer sulfonat)	ng/l	300	<10	<0,30	<0,30	<0,30
PFOA (Perfluoroktansyra)	ng/l	720	<10	<0,30	0,43	0,47
PFOSA (Perfluoroktansulfonamid)	ng/l	<10	<10	<0,30	<0,30	<0,30
PFHpS (Perfluorheptansulfonsyra)	ng/l	280	<10	<0,30	1,5	2,6
PFHpA (Perfluorheptansyra)	ng/l	670	94	<0,30	<0,30	<0,30
PFOS (Perfluoroktansulfonsyra)	ng/l	2100	<10	**3,9**	**31**	**33**
PFHxS (Perfluorhexansulfonsyra)	ng/l	11000	230	5,6	23	31
PFHxA (Perfluorhexansyra)	ng/l	4100	3300	19	2,7	1,2
PFBS (Perfluorbutansulfonsyra)	ng/l	4500	4100	57	5,2	2,4
PFPeA (Perfluorpentansyra)	ng/l	1500	1400	490	120	42
PFBA (Perfluorbutansyra)	ng/l	810	820	820	630	500
Summa PFAS 4	ng/l	**14000**	**230**	**9,5**	**54**	**64**
Summa PFAS 28	ng/l	**29000**	**11000**	**1400**	**820**	**620**

e

Lab scale trial
SAFF in combination with Allonnia Booster no1
Results

envytech Miljö & teknik	Unit	Removal % Bench scale test No additiv	Removal % Bench scale test Additive 1	Removal % Bench scale test Additive 2	Removal % Bench scale test Additive 3
PFDA (Perfluordekansyra)	ng/l	ND	ND	ND	ND
8:2 FTS (Fluortelomer sulfonat)	ng/l	ND	ND	ND	ND
4:2 FTS (Fluortelomer sulfonat)	ng/l	ND	ND	ND	ND
PFNA (Perfluornonansyra)	ng/l	ND	ND	ND	ND
6:2 FTS (Fluortelomer sulfonat)	ng/l	Up to 100%	Up to 100%	Up to 100%	Up to 100%
PFOA (Perfluoroktansyra)	ng/l	Up to 100%	Up to 100%	100%	100%
PFOSA (Perfluoroktansulfonamid)	ng/l	ND	ND	ND	ND
PFHpS (Perfluorheptansulfonsyra)	ng/l	Up to 100%	Up to 100%	99%	99%
PFHpA (Perfluorheptansyra)	ng/l	86%	Up to 100%	Up to 100%	Up to 100%
PFOS (Perfluoroktansulfonsyra)	ng/l	Up to 100%	99,9%	99%	98%
PFHxS (Perfluorhexansulfonsyra)	ng/l	98%	99,9%	100%	100%
PFHxA (Perfluorhexansyra)	ng/l	20%	99,5%	100%	100%
PFBS (Perfluorbutansulfonsyra)	ng/l	9%	99%	100%	100%
PFPeA (Perfluorpentansyra)	ng/l	7%	69%	92%	97%
PFBA (Perfluorbutansyra)	ng/l	-1%	2%	29%	40%
Summa PFAS 4	ng/l	**98%**	**99,9%**	**100%**	**100%**
Summa PFAS 28	ng/l	**62%**	**95%**	**97%**	**98%**

Lab scale trial
SAFF in combination with Allonnia Booster no1
Results

Analysing treated water in regards of residual surfactant components related to Booster additive.

Results show ND for all compounds proving removal of the added substances in the SAFF process

Dodecyldimetylbensylammonium	µg/L	<5.0	<5.0	<5.0
Tetradecyldimetylbensylammonium	µg/L	<5.0	<5.0	<5.0
Hexadecyldimetylbensylammonium	µg/L	<5.0	<5.0	<5.0
Oktadecyldimetylbensylammonium	µg/L	<5.0	<5.0	<5.0
Dodecyltrimetylammonium	µg/L	<5.0	<5.0	<5.0
Tetradecyltrimetylammonium	µg/L	<5.0	<5.0	<5.0
Hexadecyltrimetylammonium	µg/L	<5.0	<5.0	<5.0
Oktadecyltrimetylammonium	µg/L	<5.0	<5.0	<5.0
Didecyldimetylammonium	µg/L	<5.0	<5.0	<5.0
Didodecyldimetylammonium	µg/L	<5.0	<5.0	<5.0
Ditetradecyldimetylammonium	µg/L	<5.0 1)	<5.0 1)	<5.0 1)
Dihexadecyldimetylammonium	µg/L	<5.0 1)	<5.0 1)	<5.0 1)
Dioktadecyldimetylammonium	µg/L	<5.0 1)	<5.0 1)	<5.0 1)
Oktylfenoxietoxietyldimetylbensylammonium	µg/L	<5.0	<5.0	<5.0
Dodecylpyridinium	µg/L	<5.0	<5.0	<5.0
Hexadecylpyridinium	µg/L	<5.0	<5.0	2600
Dodecylisokinolinium	µg/L	<5.0	<5.0	<5.0
Katjonogena ytaktiva ämnen	µg/L	<65 2)	<65 2)	2600 2)

Site 2

Treatment of Raw PFAS contaminated Landfill Leachate, Sweden

- Landfill leachate collected at a lined landfill
  - PFAS levels varies of 12 000 ng/l
  - TOC 1400 mg/l
  - DOC 1400 mg/l

- Performed trials:
  - Lab scale SAFF treatment using only SAFF
  - Lab scale SAFF treatment using SAFF+Additives
  - Lab scale destruction trials using:
    - Electrochemcial oxidation (EO) by Aclarity
    - Photoactivated Reductive Defluorination (PRD)
    - Cold Plasma by FORTH, Scenarios H2020

envytech Miljö & teknik		Untreated
		2024-03-28
	Unit	
PFDA (Perfluordekansyra)	ng/l	<10
8:2 FTS (Fluortelomer sulfonat)	ng/l	<20
4:2 FTS (Fluortelomer sulfonat)	ng/l	<10
PFNA (Perfluornonansyra)	ng/l	14
6:2 FTS (Fluortelomer sulfonat)	ng/l	430
PFOA (Perfluoroktansyra)	ng/l	810
PFOS (Perfluoroktansulfonsyra)	ng/l	810
PFOSA (Perfluoroktansulfonamid)	ng/l	<10
PFHpS (Perfluorheptansulfonsyra)	ng/l	40
PFHxS (Perfluorhexansulfonsyra)	ng/l	1500
PFHpA (Perfluorheptansyra)	ng/l	600
PFHxA (Perfluorhexansyra)	ng/l	1900
PFPeA (Perfluorpentansyra)	ng/l	1600
PFBA (Perfluorbutansyra)	ng/l	1500
PFBS (Perfluorbutansulfonsyra)	ng/l	2000
Summa PFAS 4	ng/l	3100
Summa PFAS 28	ng/l	12000

Status report, Scenarios Project 2: Treatment of Landfill Leachate using Surface Active Foam Fractionation

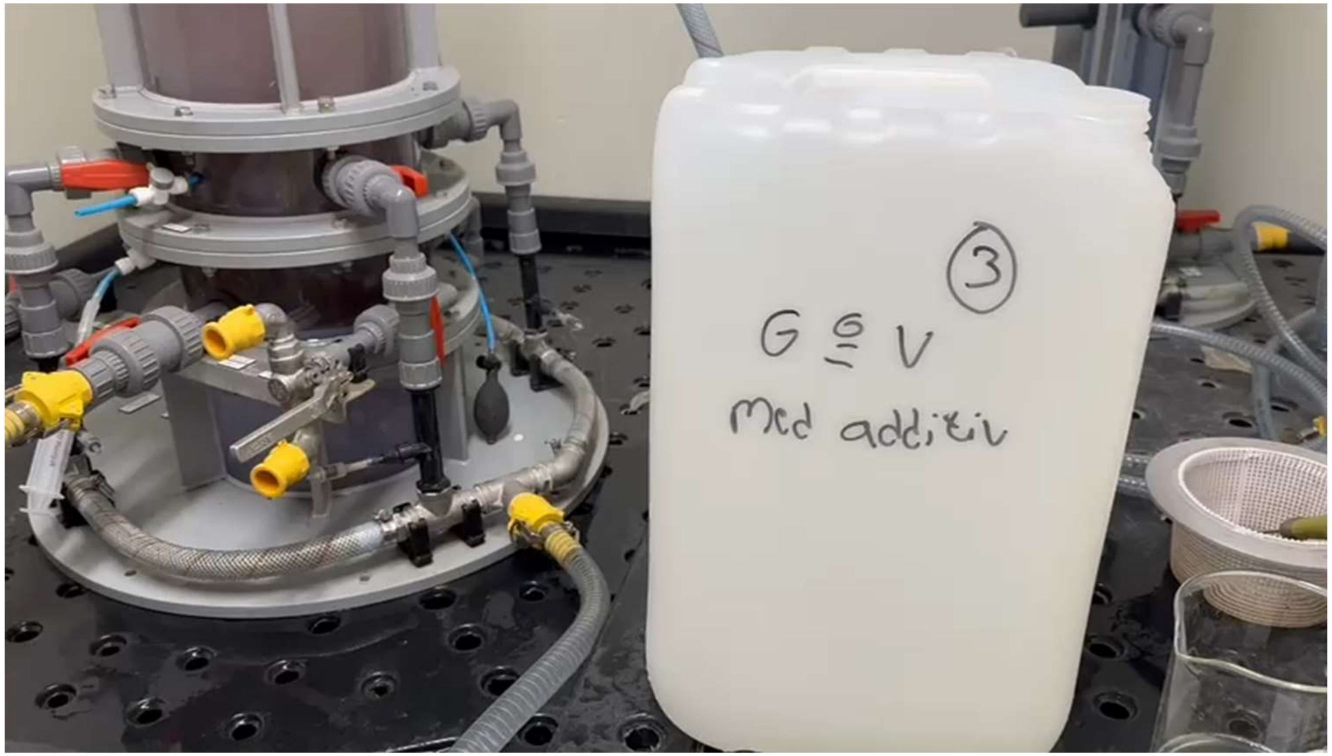
Step 1: Lab scale trial
Performance of lab scale trial using water from a Swedish Landfill

Trial using no additive

Status report, Scenarios Project 2: Treatment of Landfill Leachate using Surface Active Foam Fractionation

Step 1: Lab scale trial
Performance of lab scale trial
using water from
a Swedish Landfill

Trial using additive



Status report, Scenarios Project 2: Treatment of Landfill Leachate using Surface Active Foam Fractionation

Step 1:
Lab scale trial

- Only SAFF – no additive

- SAFF with additive

We see remarkable removal rates for PFBS and also also higher reduction rates for PFPeA and PFHxA

envytech Miljö & teknik		Untreated	Treated 1	Treated 2	Treated 3	Treated 4
			No additive	Booster 1 dose 1	Booster1 dose 2	Booster1 dose 3
		2024-03-28	2024-03-28	2024-03-28	2024-03-28	2024-03-28
	Unit					
PFDA (Perfluordekansyra)	ng/l	<10	<10	<10	<10	<10
8:2 FTS (Fluortelomer sulfonat)	ng/l	<20	<20	<20	<20	<20
4:2 FTS (Fluortelomer sulfonat)	ng/l	<10	<10	<10	<10	<10
PFNA (Perfluornonansyra)	ng/l	14	<10	<10	<10	<10
6:2 FTS (Fluortelomer sulfonat)	ng/l	430	<10	<10	<10	<10
PFOA (Perfluoroktansyra)	ng/l	810	<10	<10	<10	<10
PFOS (Perfluoroktansulfonsyra)	ng/l	810	<10	<10	<10	<10
PFOSA (Perfluoroktansulfonamid)	ng/l	<10	<10	<10	<10	<10
PFHpS (Perfluorheptansulfonsyra)	ng/l	40	<10	<10	<10	<10
PFHxS (Perfluorhexansulfonsyra)	ng/l	1500	<10	<10	<10	<10
PFHpA (Perfluorheptansyra)	ng/l	600	<10	<10	<10	<10
PFHxA (Perfluorhexansyra)	**ng/l**	**1900**	**580**	**14**	**<10**	**<10**
PFPeA (Perfluorpentansyra)	**ng/l**	**1600**	**1600**	**1100**	**520**	**520**
PFBA (Perfluorbutansyra)	ng/l	1500	1500	1500	1400	1400
PFBS (Perfluorbutansulfonsyra)	**ng/l**	**2000**	**1300**	**110**	**<10**	**<10**
Summa PFAS 4	ng/l	3100	ND	ND	ND	ND
Summa PFAS 28	ng/l	12000	5000	2700	1900	1900

Status report, Scenarios Project 2: Treatment of Landfill Leachate using Surface Active Foam Fractionation

Step 1:
Lab scale trial
Results, treatment efficency %

Results show remarkable removal rates for long chain PFAS using only air for such complex waters.

2 concentrations steps will be needed to minimize the large foam volumes.

Enhenced short chain removal Possible from 68% up to ND for PFBS and PFHxA

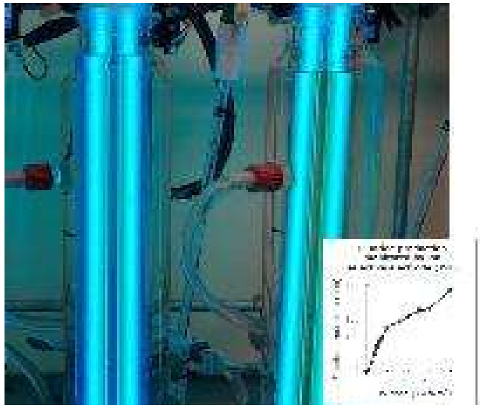
Possible increase for PFHxA from 68% to ND

envytech Miljö & teknik	Treated 1	Treated 2	Treated 3	Treated 4
	No Additive	Booster 1 dose 1	Booster1 dose 2	Booster1 dose 3
	Removal Rate	Removal Rate	Removal Rate	Removal Rate
	%	%	%	%
PFDA (Perfluordekansyra)	ND	ND	ND	ND
8:2 FTS (Fluortelomer sulfonat)	ND	ND	ND	ND
4:2 FTS (Fluortelomer sulfonat)	ND	ND	ND	ND
PFNA (Perfluornonansyra)	>99,9%	>99,9%	>99,9%	>99,9%
6:2 FTS (Fluortelomer sulfonat)	>99,9%	>99,9%	>99,9%	>99,9%
PFOA (Perfluoroktansyra)	>99,9%	>99,9%	>99,9%	>99,9%
PFOS (Perfluoroktansulfonsyra)	>99,9%	>99,9%	>99,9%	>99,9%
PFOSA (Perfluoroktansulfonamid)	ND	ND	ND	ND
PFHpS (Perfluorheptansulfonsyra)	>99,9%	>99,9%	>99,9%	>99,9%
PFHxS (Perfluorhexansulfonsyra)	>99,9%	>99,9%	>99,9%	>99,9%
PFHpA (Perfluorheptansyra)	>99,9%	>99,9%	>99,9%	>99,9%
PFHxA (Perfluorhexansyra)	**68%**	**97%**	**99%**	**>99,9%**
PFPeA (Perfluorpentansyra)	**-7%**	**13%**	**31%**	**68%**
PFBA (Perfluorbutansyra)	17%	17%	0%	7%
PFBS (Perfluorbutansulfonsyra)	**32%**	**67%**	**>99,9%**	**>99,9%**
Summa PFAS 4	>99,9%	>99,9%	>99,9%	>99,9%
Summa PFAS 28	55%	68%	78%	84%

But about the waste ?

- Many upcoming technologies and providers on the world market
- We have ongoing trials using HALT, SCWO, Cold Plasma, PRD and EO
- Trials have been performed on Full scale tertiery foam concentrate from landfill leachate
  and soil wash water SAFF concentrate
- Presentation of results and some costs (!!) of :
  - Cold Plasma
  - Electrochemical Oxidation
  - Photoactivated Reductive Defluorinatiom



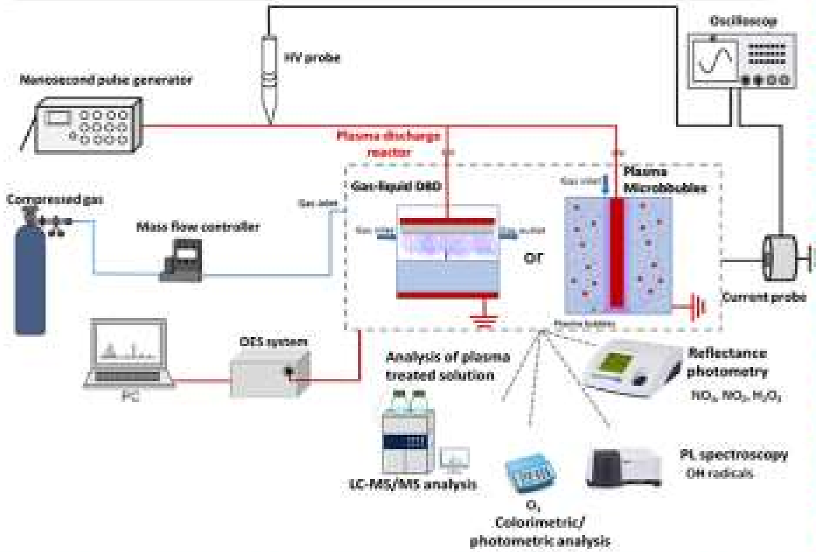



Destruction trial using Cold Plasma
Part of H2020 Scenarios project

Cold atmospheric plasma for PFAS destruction in water

Task 6.1

Experimental setup

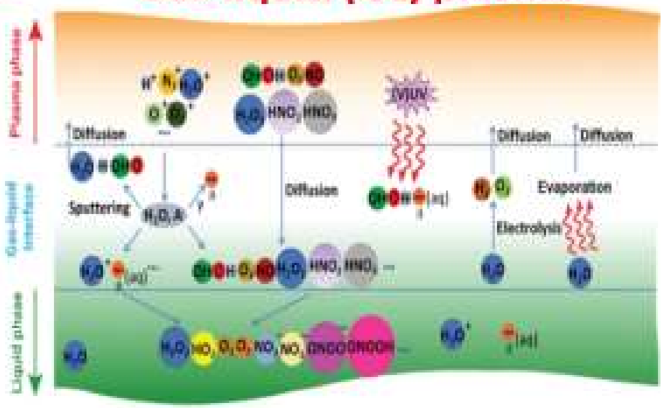


Plasma reactors

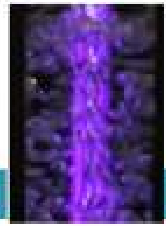
GL- Multi-pins Corona

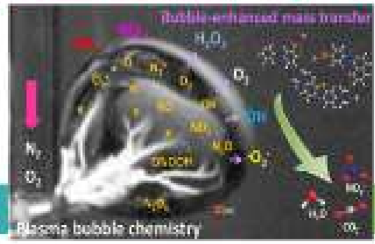
GL-DBD

Gas-liquid (GL) plasma

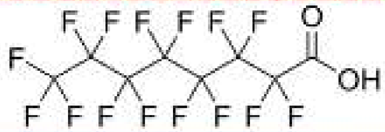


Underwater plasma microbubbles (PMB)





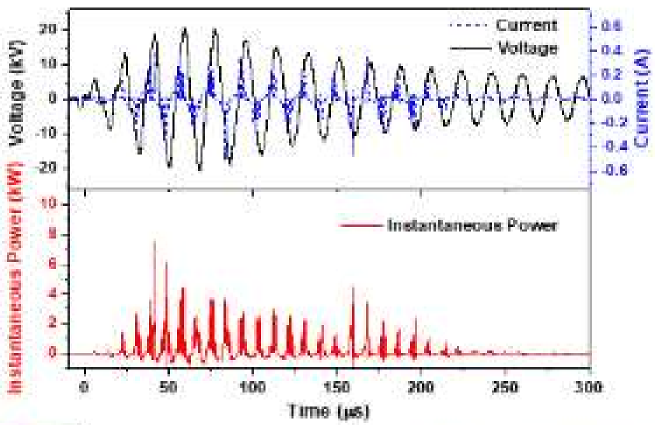
PFOA: $C_8HF_{15}O_2$



Electrical characterization of plasma reactors energized by different high voltage (HV) waveforms

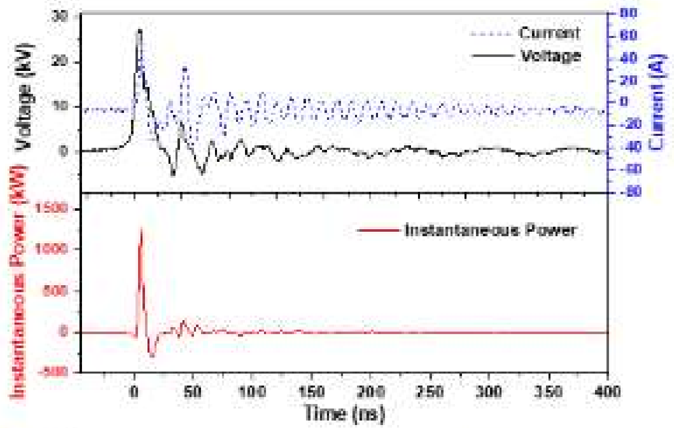
Task 6.1

HV micropulses (MSP)



$$P = f \int_{pulse} V(t) I(t) dt$$

HV nanopulses (NSP)



MSP-PMB:
Power: 36.9 W

MSP-GLDBD:
Power: 60.0 W

NSP-PMB:
Power: 0.5 W

NSP-GLDBD:
Power: 1.1 W

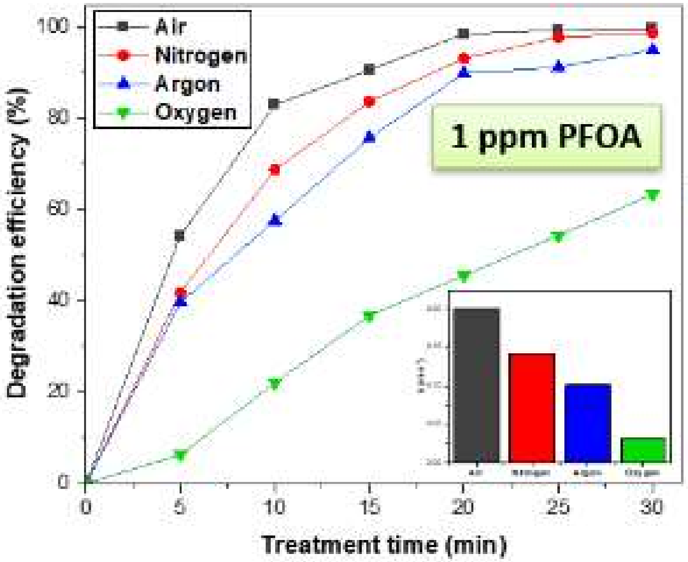
Cold atmospheric plasma for PFOA destruction in water

Task 6.1

INSTITUTE OF CHEMICAL ENGINEERING SCIENCES

Effect of plasma gas on PFOA degradation efficiency

Water matrix: **3DW**



Air > Nitrogen > Argon > Oxygen

Argon : ·OH and e⁻

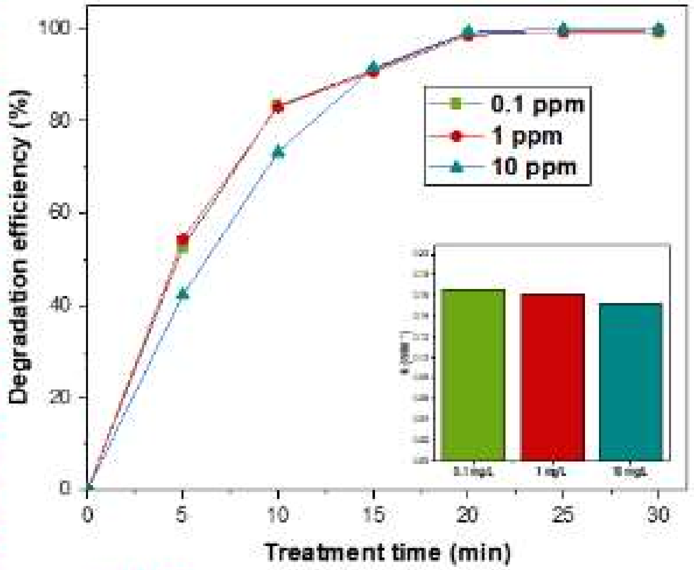
Air: ·OH and e⁻ (less than Ar) and RNS (NO_3^-, $ONOO^-$)

- Argon also very effective due to the action of hydrated e⁻
- **Air** seems to be very effective for PFOA degradation most probably due to e⁻ and high RNS like NO_3^- and $ONOO^-$

·OH, e⁻ and $ONOO^-$ contribute on degradation

Effect of PFOA initial concentration

Plasma gas: **Air**



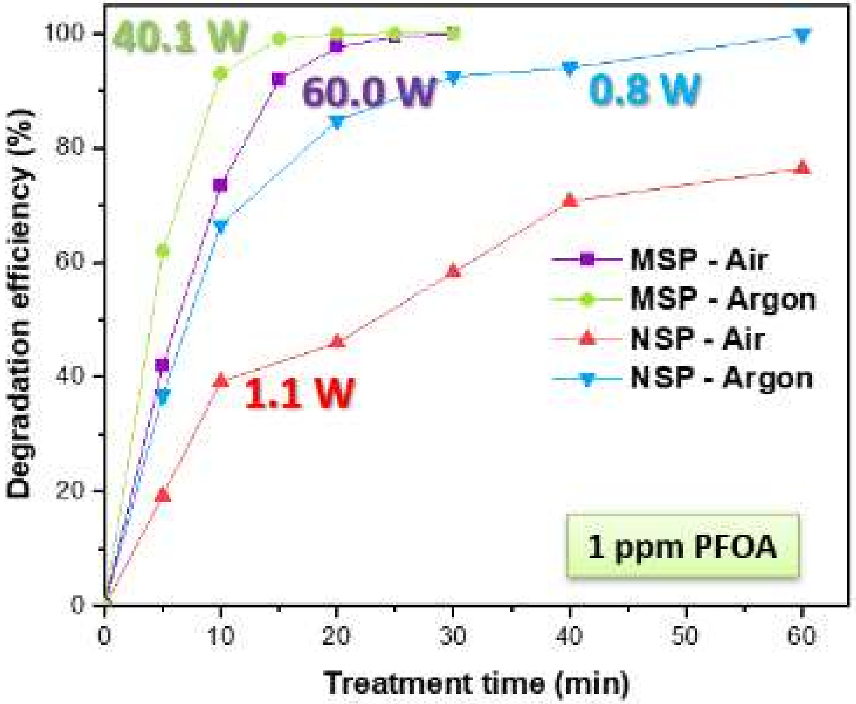
GLDBD is effective for PFOA degradation in the range 0.1-10 ppm

Cold atmospheric plasma for PFOA destruction in water

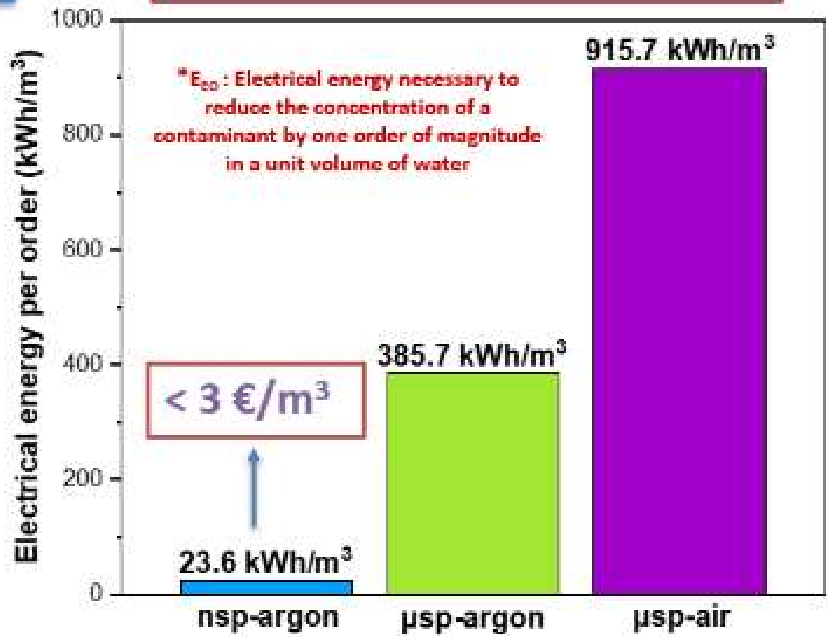
Task 6.1

Comparison between air and argon plasma under high voltage micropulses and nanopulses

Water matrix: TW



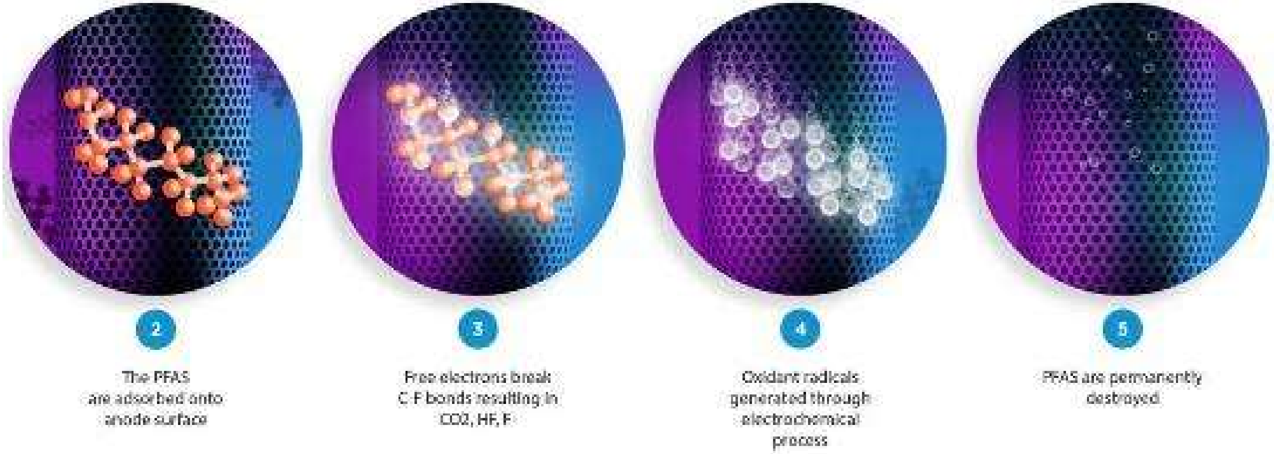
Electrical energy per order



NSP is more cost-effective compared to MSP

Aclarity

Electrochemical Destruction of PFAS in Foamate



But about the waste ?

Aclarity Electrochemical Destruction of PFAS in Foamate

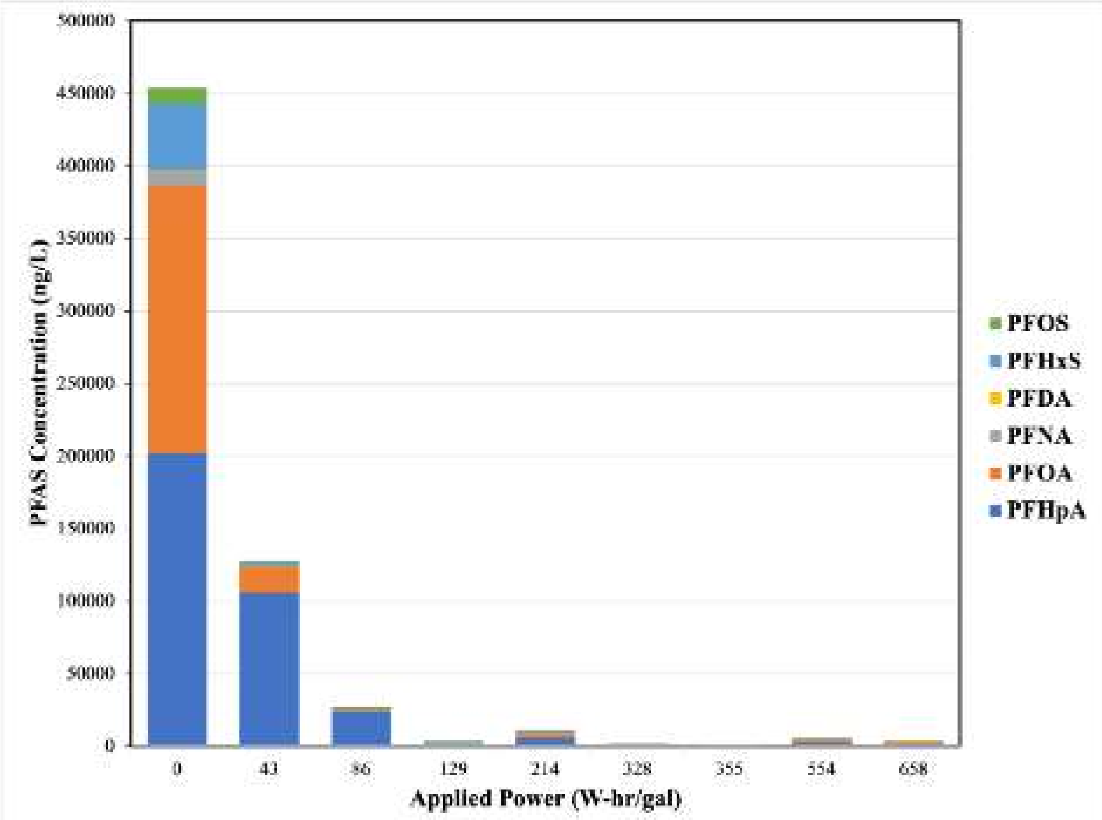


Table 1: Destruction of MA6 PFAS Compounds

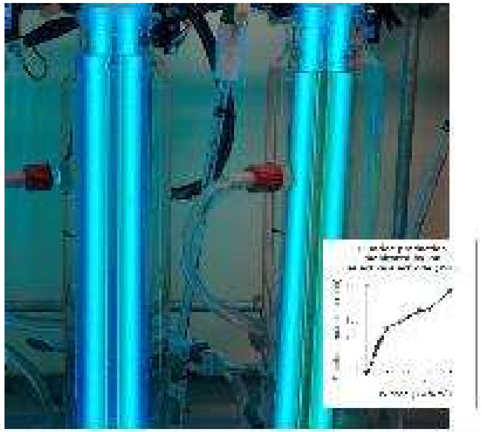
Compounds	Initial Concentration (ng/L)	Final Concentration (ng/L) at 129 W-hr/gal	% Destruction
PFHpA	202000	1200	99.4
PFOA	184000	321	99.8
PFNA	10700	301	97.2
PFDA	<381	<381	NA
PFHxS	45300	1030	97.7
PFOS	11700	704	94.0

Conclusion

Aclarity's SO-1 reactor demonstrated excellent destruction for PFAS compounds across a range of species including long chains (C8-C10) and shorter chains (C4-C7), with destruction of both carboxylic acids (PFOA, PFHpA) and sulfonic acids (PFOS, PFHxS). Aclarity's full-scale Octa™ system is 80x capacity of the SO-1, comprising 80 electrode pairs.

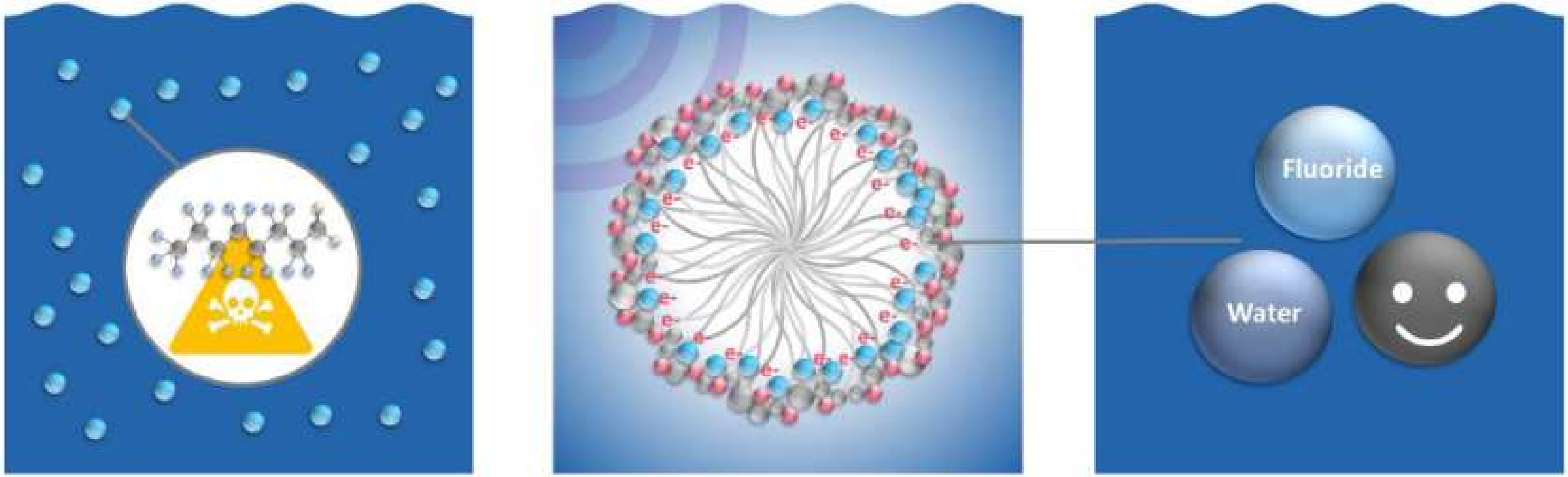
Based on the results of this testing, an electrical energy per order (EEO), or the amount of energy required to destroy 90% of a compound is 23.8 kW-hr/m^3/order.

Photoactivated Reductive Defluorination (PRD)



DoD & EPA
Award in 2021

Innovative Ways
to Destroy PFAS



Photoactivated Reductive Defluorination (PRD)

SAMPLE CHARACTERIZATION – HORIZON 2020 LANDFILL LEACHATE FOAM FRACTIONATION TERTIARY FOAMATE

Sample ID	Total [PFAS] (ppb)	Calculated [Organic fluorine] (ppb)	[Inorganic fluoride] (ppb)	pH	Total Dissolved Solids (TDS, ppm)	Transmission @ 254 nm
030A01	138,350	~86,468	286	7.2	6,600	0.4%

	UV Dose				
	0 kWh/m^3 (untreated)	600 kWh/m^3		2,400 kWh/m^3	
PFAS	µg/L	µg/L	% decrease from untreated	µg/L	% decrease from untreated
PFNA	1,700	100 U	>94.1%	100 U	>94.1%
PFOA	**41,000**	**11,000**	**73.2%**	**100 U**	**>99.8%**
PFOS	**100 U**	**100 U**	**n/a**	**100 U**	**n/a**
PFHxS	11,000	100 U	>99.0%	100 U	>99.0%
PFBS	1,000	100 U	>90.0%	100 U	>90.0%
HFPO-DA	200 U	200 U	n/a	200 U	n/a
Sum EPA MCL list PFAS	**54,700**	**11,000**	**79.9%**	**All ND**	**>99.8%**
PFHpA	49,000	20,000	59.2%	100 U	>99.8%
PFHxA	23,000	21,000	8.7%	4,800	79.1%
PFPeS	3,200	100 U	>96.9%	100 U	>96.9%
6:2 FTSA	5,900	250 U	>95.8%	250 U	>95.8%
Total PFAS	**135,800**	**52,000**	**61.7%**	**4,800**	**96.5%**

U = non-detected
Total PFAS = sum of all analytes excluding non-detected
EPA MCL list PFAS = PFNA, PFOA, PFOS, PFHxS, PFBS, HFPO-DA; sum excludes non-detected analytes

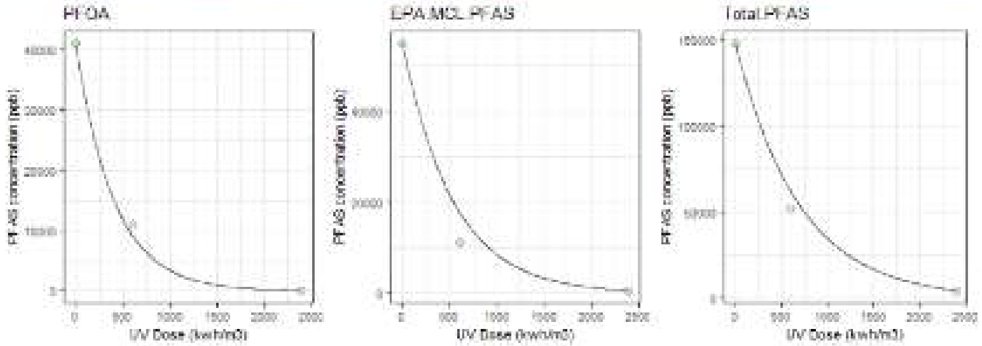
ENSPIRED SOLUTIONS

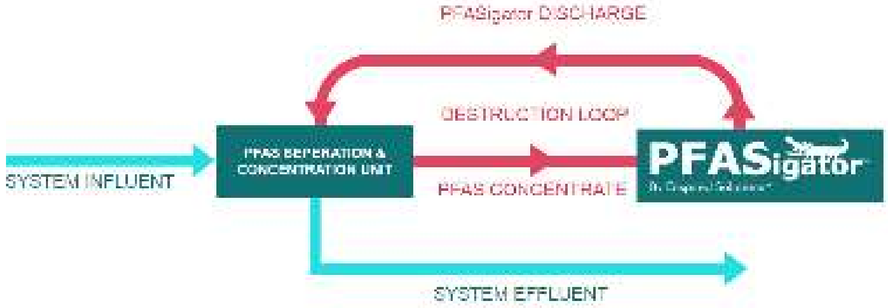
Photoactivated Reductive Defluorination (PRD)

TREATABILITY TEST RESULTS - HORIZON 2020 LANDFILL LEACHATE FOAM FRACTIONATION TERTIARY FOAMATE

- Foamate treated with PRD achieved a high degree of PFAS destruction
- Horizon 2020 landfill leachate foam fractionation tertiary foamate total PFAS concentration is much higher than landfill leachate foamate samples tested by Enspired from other sites

	EEO (Wh/L-order)	p value
Horizon 2020 Foamate PFOA	925	4.40E-04
Horizon 2020 Foamate Sum EPA MCL List PFAS	1,234	5.79E-03
Horizon 2020 Foamate Total PFAS	1,592	1.29E-03





	PFOA	EPA MCL List PFAS	Total PFAS
$/gallon[1] concentrate	$4.01	$7.20	$7.21
$/gallon CAPEX[2]	[illegible]	$2.48	[illegible]
$/gallon reagents	[illegible]	[illegible]	[illegible]
$/gallon energy use	$0.45	$2.62	[illegible]
$/gallon machine maintenance	[illegible]	[illegible]	[illegible]
$/gallon OPEX[3]	[illegible]	$2.72	[illegible]

[1]Cost includes both CAPEX and OPEX
[2]CAPEX and OPEX per gallon calculations assumes machine runs 24 hr, 7 days a week, for 15 years.
[3]OPEX is the sum of reagents, energy use and machine maintenance.

SAFF Economics

Wonderful results!
But how much does it cost ?

Rental or Buy:	Ask us for a quote
Capacity :	Up to 25 m^3/h, SAFF40 3 step fractionation, up tp 14 m^3/h SAFF20 2 step fractionation
Installation:	< 80 h operational staff, including fine tuning
Electricity:	0,7 kwh / m^3 treated
Service:	From 8h service technician per month – depending on water
Waste	From leachate: 0,2 - 6m^3 / 50 0000m^3 treated From GW: <0,1 (10 liters) per 50 000 m^3 treated

Possibility!
- Short chain removal using additives
- No waste – "Closed loop" possibility – Full scale, On-site, within 6-12 months.

This project has received funding from the European Union's H2020 programme under Grant Agreement No. 101037509

EU Green Week

PARTNER EVENT

Special Symposium on PFAS Eleimination from Drinking Water

Karlsruhe, Germany

13 June 2024

#WaterWiseEU

CHART WATER

Water consumers in the US wouldn't wait for the formal PFAS EPA regulation

Water consumers in the US wouldn’t wait for the formal PFAS EPA regulation

Ronit Erlitzki, PhD
ChartWater
Ronit.Erlitzki@chartIndustries.com

CHART WATER

ChartWater:

a global manufacturer and service provider of water treatment solutions with over 8,100 installations in 85 countries

Chart has over 10,000 experts in over 115 locations across the globe with assets installed in 169 countries

40+ *Service centres*

64 *Manufacturing sites*

CHART

BlueInGreen
A Chart Industries Company

AdEdge

Howden
A Chart Industries Company

Process	Biological Filtration		Adsorption					O/F	C/F	HMO	Ion Exchange								Membranes	Physical	Oxidation	Oxygenation Aeration	Acidification	Chemfeed
Technology or Media	biottta	NoMonia	AD74	E33	AD140	GAC	FS	AD26	ADGS+	ADGS+	AD88	AD92	ADBor	ADCr6	ADNO3	ADPx	ADSOF	ADTOC	RO/NF	Air Stripping & Filtration	HyDOZ	SDOX Turbo Compressors	CDOX	Inline
Ammonia		●			●												●		●					
Arsenic		●	●	●				●	●										●					
Boron													●						●					
BOD																						●		
Chromium VI	●													●					●					
Disinfection																					●			
Fluoride			●																●					
Gross Alpha										●	●	●							●					
Hardness																	●		●					
Iron		●						●	●	●											●			
Lead				●	●														●					
Manganese		●						●	●	●											●			
Nitrates	●														●				●					
Perchlorate	●											●												
PFAS						●	●									●			●					
pH control																							●	●
Radium										●	●								●					
Selenium	●											●							●					
Sulfides/ Odor						●		●	●										●			●		
TDS									●										●					
TSS									●											●				
TOC						●												●			●			
Turbidity									●											●				
Uranium												●							●					
VOCs	●					●																		

Awareness to PFAS contamination monitoring resulted in piloting programs and hundreds of systems installed

~65,000

Number of public water systems that will have to comply with US Environmental Protection Agency limits for PFOS & PFOA

$10.3 billion

Amount to be paid by 3M under a settlement of a lawsuit filed by public water utilities to support PFAS remediation (total >$17bn for potentially responsible parties PRP*)

715

US military sites that the Department of Defense is evaluating for potential contamination by PFAS

Nearly 12,000

Number of closed landfills in the US generating leachate containing PFAS

~3,000

Number of open landfills in the US generating leachate containing PFAS

https://cen.acs.org/environment/persistent-pollutants/Competition-destroy-forever-chemicals-heats/102/i7

Environmental Working Group
https://www.ewg.org/interactive-maps/pfas_contamination/map/

USEPA – Hotspots for PFAS interactive map

Showing only available water data from UCMR and state reported (Blue and yellow – above UNCR and HA, respectively). Not including spills, superfunds, federal site, industrial sites etc.
https://awsedap.epa.gov/public/extensions/PFAS_Tools/PFAS_Tools.html

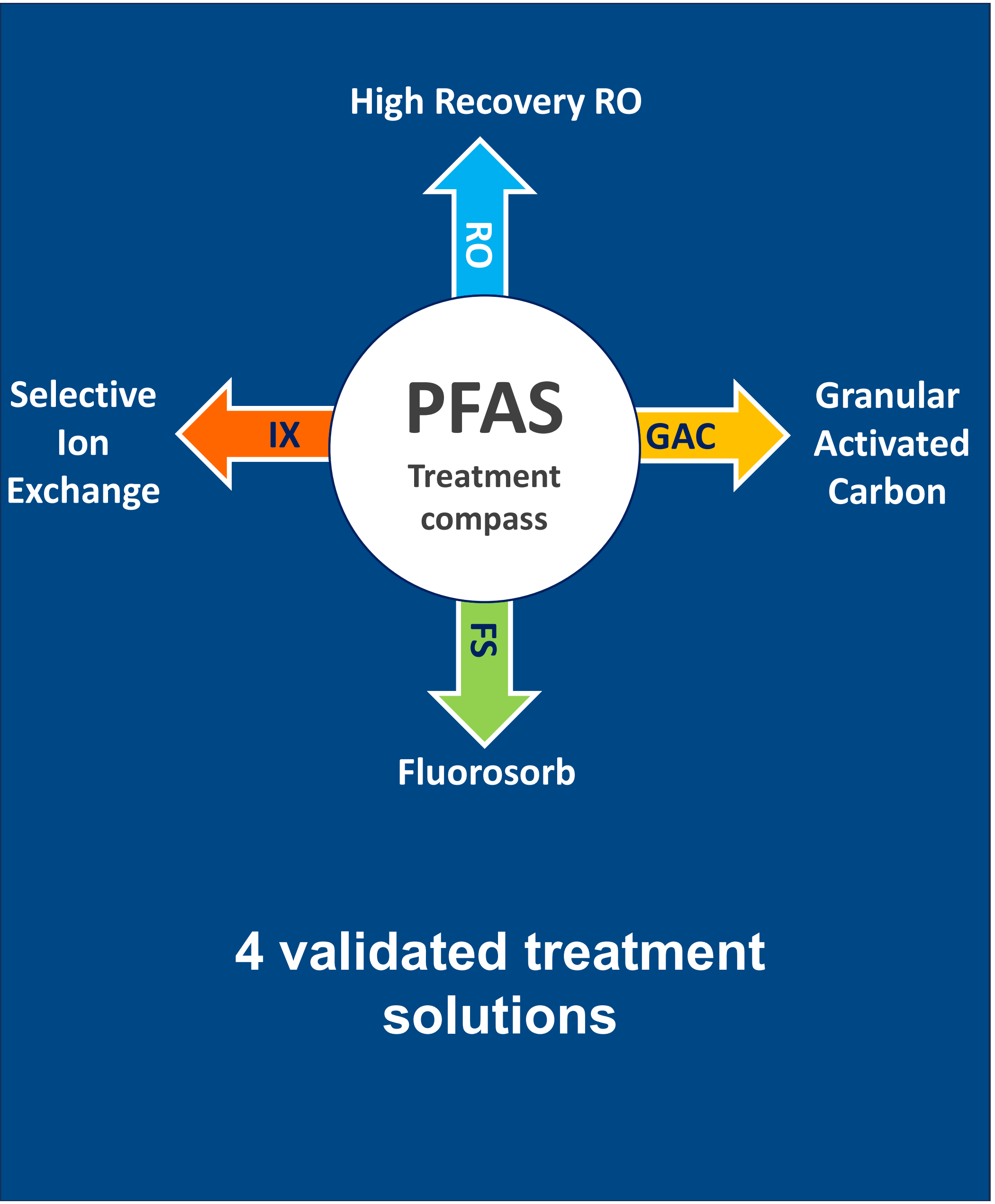
USEPA's Final Regulation (April 2024)

April 2024 Final Rule → **April 2027** Initial Monitoring Deadline → **April 2029** Compliance Deadline

PFAS Compound	MCL	PQL	Reporting Example based on Significant Figures
PFOA	**4.0**	4.0	RAA of 4.04 = round to 4.0 = **Compliant** RAA of 4.05 = round to 4.1 = **Exceedance**
PFOS	**4.0**	4.0	
PFNA	**10**	4.0	RAA of 14.9 = round to 10 = **Compliant** RAA of 15.0 = round to 20 = **Exceedance**
PFHxS	**10**	3.0	
GenX	**10**	5.0	
PFBS	**HI**	3.0	RAA of 1.49 = round to 1 = **Compliant** RAA of 1.50 = round to 2 = **Exceedance**
Hazard Index (mix) **PFNA, PFHxS, GenX, PFBS**	**1**		

*MCL is Maximum Contaminant Level in parts per trillion or nanograms per liter
*PQL is the Practical Quantification Limit in parts per trillion or nanograms per liter
*RAA - running annual average

$$HI\ MCL = \left(\frac{[HFPO\text{-}DA_{water}]}{[10\ ppt]}\right) + \left(\frac{[PFBS_{water}]}{[2000\ ppt]}\right) + \left(\frac{[PFNA_{water}]}{[10\ ppt]}\right) + \left(\frac{[PFHxS_{water}]}{[10\ ppt]}\right) = 1$$



PFAS Treatment buzz words

- Long chains, short chains
- Sulfonic acids vs. Carboxylic acids
- EBCT, Bed volume
- Footprint, CAPEX, OPEX
- Adsorption vs. destruction
- Acid-rinse GAC
- IX – Macro vs. Gel
- Media replacement and disposal
- Hydraulic Loading Rate (HLR)

CAPEX & Footprint depend on media selection

158 M3/hrs (1 MGD)

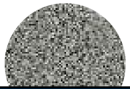
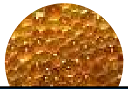
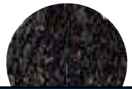
GAC
10 min EBCT
Lead-Lag

12ft Vessel
~ 1,187 cuft ea. vessel

IX or Fluorosorb®
3min EBCT
Lead-Lag

10ft Vessels
~275 cuft ea. vessel

Media Comparison
is there a single critical selection parameter?

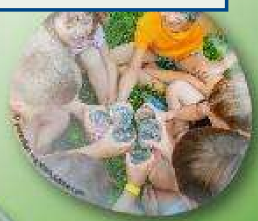
= Similar media characteristics	FLUORO-SORB ® (FS)	ION EXCHANGE (IX)	GAC
Media type	**Surface modified organo-clay (Quaternary amines) - mined**	**Gel-type, Buffered Product**	**Bituminous, can be Acid Rinsed**
EBCT	<3 min	<3 min	~10 min
TOC impact on media life	Minimal	Significant	Significant
Free Chlorine	Continuous tolerant up to 1 mg/L	No Continuous Tolerance	Consumed through GAC
TDS / Anions impact on media life	No Impact	Possibly reduced	No Impact
VOC / T&O	Not treated	Not treated	VOC / T&O = Treated by GAC
Bag Filter Pre-Treatment	Required, 5 micron	Required, 5 micron	Not Required, Recommended
Start-Up	• Initial backwash required for fines removal • Short Forward Flow	• No backwash required • Forward Rinse for NSF Compliance – 20BV • Non-buffered resin may require >150 BV for equilibrium • Buffered/Pre-Rinsed Product Available for 0 start-up waste	Initial BW Required for Fines Removal, 20 BV Forward Rinse for NSF, may required Forward Rinse for arsenic reduction before service
Backwashing (once in service)	Only if Required	None	Only if Required
Leaching	None	None / Unknown	None / Unknown
Manufacturing sites	USA	Europe, China, or India	USA
Media Unit Cost	Moderate	Higher	Lower

LifeCycle Cost Comparison using OCWD Phase 1 Pilot Data

https://onlinelibrary.wiley.com/doi/10.1002/wer.11035

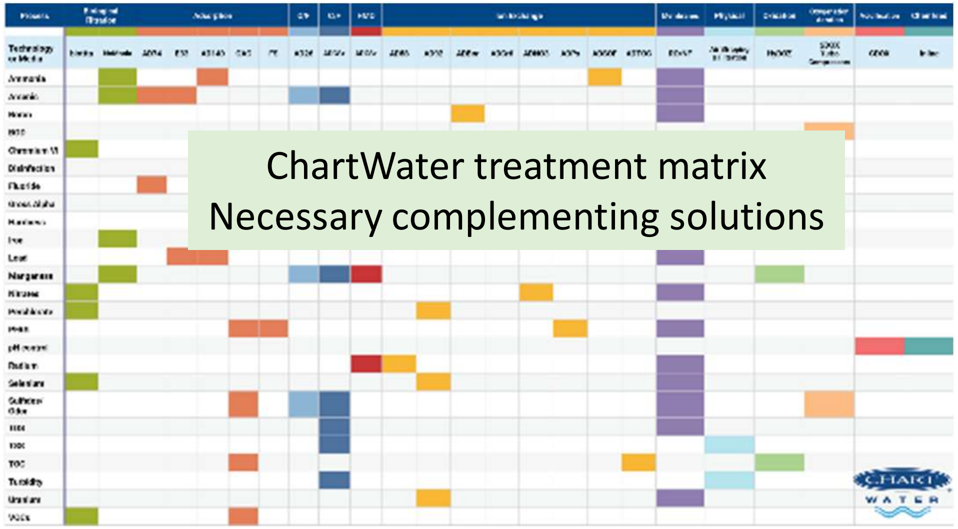
	GAC	IX	FLUORO-SORB
FLOW	694 gpm (1 MGD)		
EBCT (per vessel)	12.8 min	3.0 min	3.0 min
VESSELS	1 x 12ft Pair	1 x 10ft Pair	1 x 10ft Pair
EQUIPMENT COST	$500,000	$400,000	$400,000
TOTAL MEDIA QTY	2,374 cuft	550 cuft	550 cuft
MEDIA COST	$125 / cuft	$395 / cuft	$221 / cuft
TOTAL MEDIA COST	$296,750	$217,250	$121,550
MEDIA LIFE (mths)	14	20	24
10 YR O&M COST (media only)	$1,271,786	$651,750	$303,875
10 YR LIFE CYCLE COST	**$2,068,536**	**$1,269,000**	**$825,425**

- O&M assumes breakthrough out of lead vessel.
- GAC system design assumes 40,000 lbs per vessel.
- GAC pricing assumes rinsed product. IX pricing assumes buffered and pre-rinsed product.
- Turnkey media replacement services and disposal not included.
- Specific water quality and co-contaminants will influence the results
- Footprint and operator preferences will influence the results (e.g., multiple sites standardization)



2020 - Ramsey, NJ

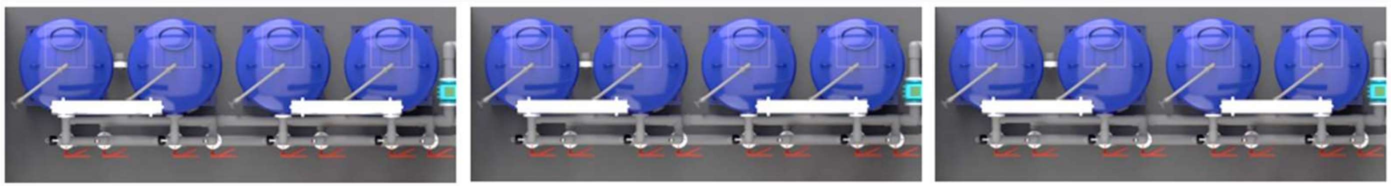
- **Multi-contaminant**
- **Rapid deployment**
- PFOA (15ppt) & Arsenic (7ppb)
- 6 wells – containerized systems
- ~170gpm (~39 M^3/hrs.)
- Limited footprint
- Used 3 types of resin
- Lead-Lag configuration
- The process included chlorination



Selecting IX:
GAC footprint was too big + no BW option, resulting in

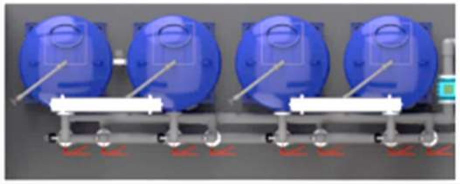
Optimized design in a 53 ft. container

GAC option



6 x 42” Dia. x 60” SSH
EBCT 10min

IX Option



Room for Arsenic treatment & Aux equipment

2 x 42” Dia. x 60” SSH
EBCT 3min

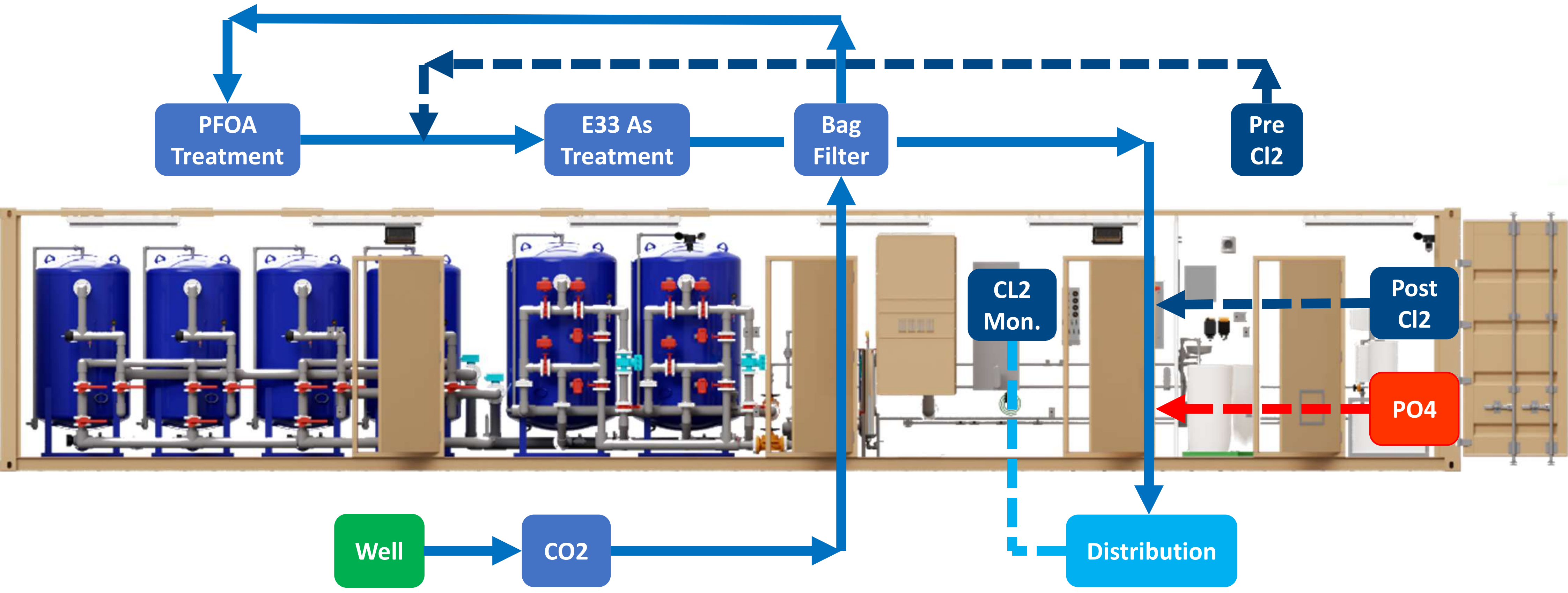
Sizing without space restriction:

GAC 96” Dia. x 96” SSH (x1)

IX 60” Dia. x 72” SSH (x1)

3 different types of IX media

A customized approach for an optimized solution

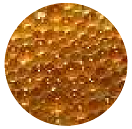


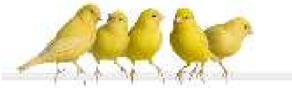
Installed Arsenic + PFOA Treatment system



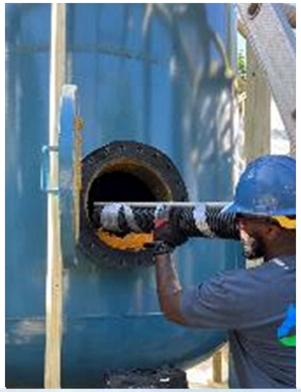



2022 - Essex Fells, NJ





- **Emergency 24 months rental and still running (TaaS)**
- 600gpm (136M^3/hrs.)
- PFOA, PFAS, PFHxA, PFPeA 40-50 ppt
- **Treated water is blended with other wells to reach <13ppt MCL, so treatment goal was 2ppt PFOA**
- Buffered IX (no BW option, footprint limitation)
- Single 120” tank (~3 M)
- Monitoring performance via PFHxA breakthrough (unregulated)
- NJ MCL
  - PFNA - 13 ppt (2018)
  - PFOA 14 ppt (2020)
  - PFOS 13 ppt (2020)


Using the non-regulated PFHxA compound to forecast PFOA breakthrough

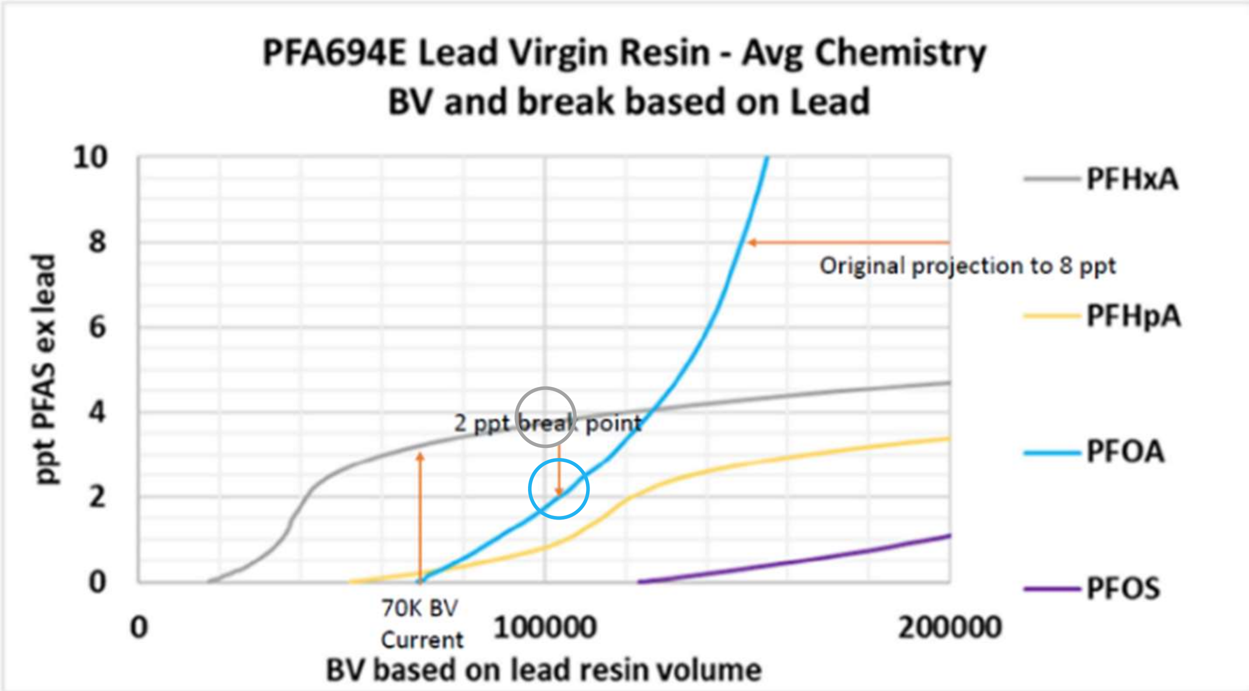
The canary in the coal mine strategy

- Close monitoring to prepare for media replacement when reaching **4ppt PFHxA and 2ppt PFOA**
  - System installed in January 2022
  - 2.78 ppt November 2022
  - 3.32 ppt February 2023

- Media change in Spring 2023 and in June 2024 (proactive)

- Projection to meet < 8 ppt from a single vessel = 120,000 bed volumes (270 million gallons)

Projection

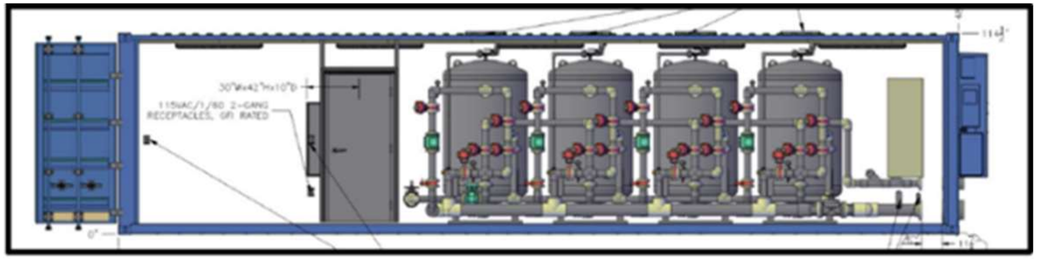


2023 – Yarmouth, MA

- **Multi-contaminants, ideal for Fluorosorb®**
- Fe, Mn, and PFAS 6
- The system was approved as a full scale pilot permit to meet growing water demand
- 550gpm (125M^3/hrs.)
- Containerized system

PFAS 6:
- PFOS
- PFOA
- PFHxS
- PFNA
- PFHpA
- PFDA

Accelerated Schedule and Permitting via a Full-Scale pilot



Early 2024 – Non detect PFAS6 concentrations

Design considerations:

- 2 wells
- 2 separate trains (potential mobility)
- Fe & Mn pretreatment with ADG (Sorption/ filtration)

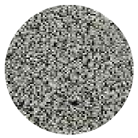
Media selection considerations:

GAC – Footprint limitation

IX – added complexity due to chlorination for the Fe & Mn removal

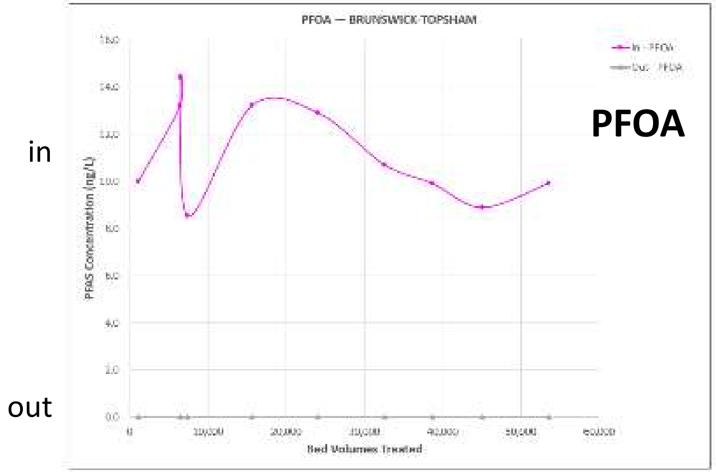
Fluorosorb® - can tolerate a 1 ppm residual chlorine level continuously without impacting PFAS removal capacity

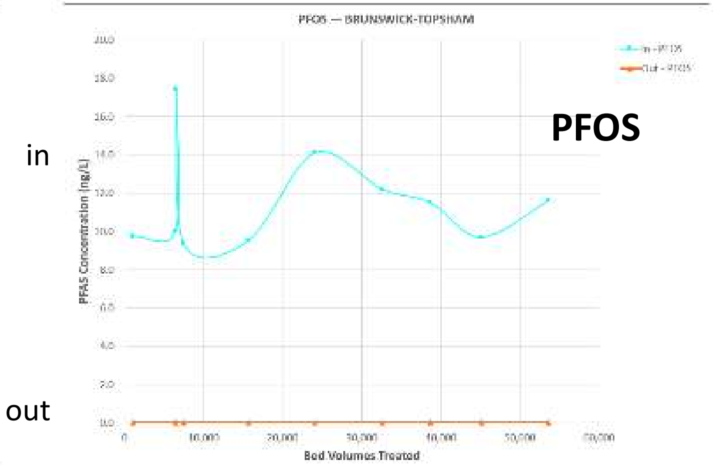
2022 - Brunswick-Topsham, ME

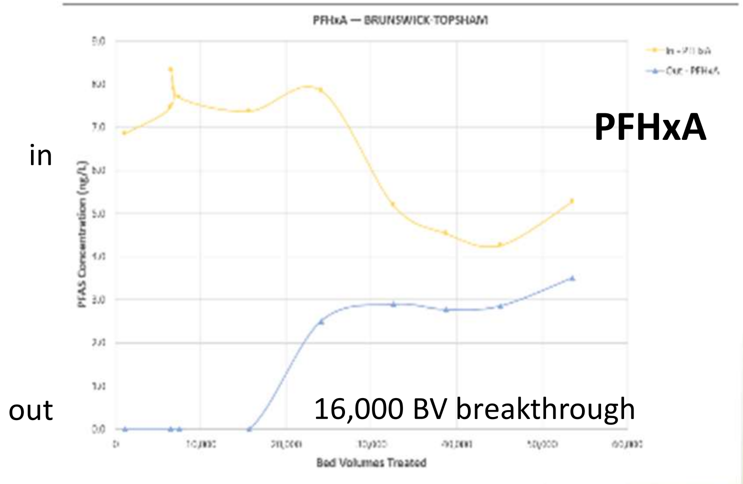


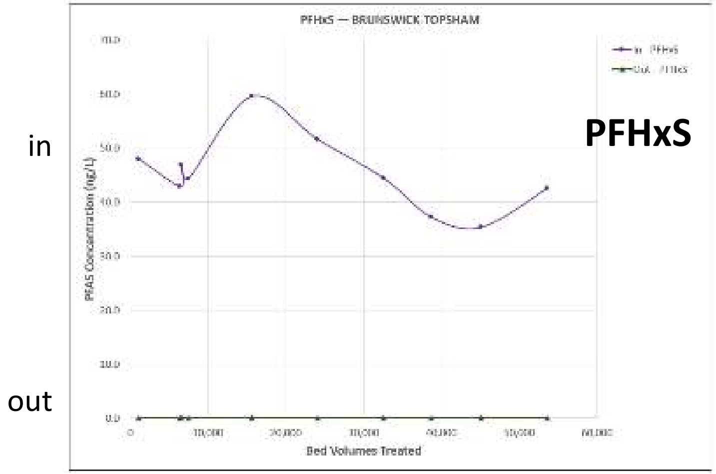
- **Controlling a PFAS plume to protect a nearby well field**
- **Location: near a Naval base**
- Media: FluoroSorb® - footprint, disinfection with chlorine during shutdown
- 250gpm, a single vessel
- All **PFAS-6** compounds have been effectively removed to non-detect
- Treated water is discharged to the aquifer
- Rapid delivery
- Intermittent operation (summer only) due to utilization and limited land application during the winter
- Simple, manual operation, no power excluding well pump
- Re-bedding in April 2024 due to customer decision (no DP)

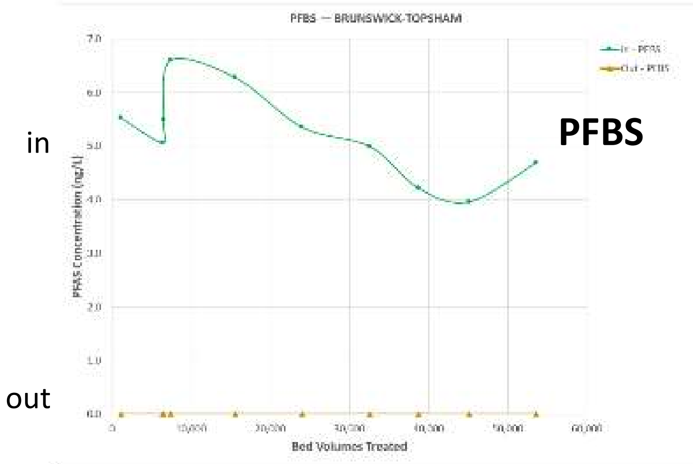
Brunswick-Topsham Data at 53,000BV
PFHxA early breakthrough







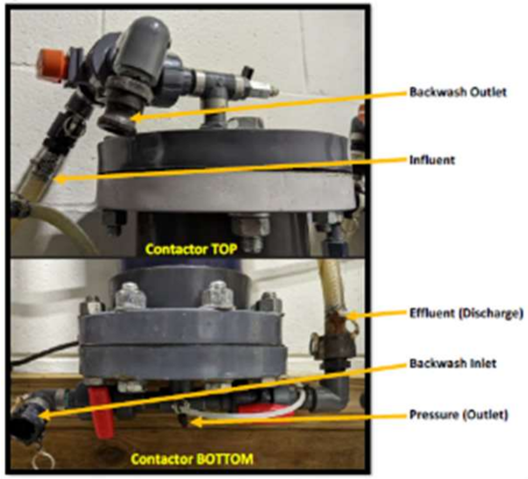




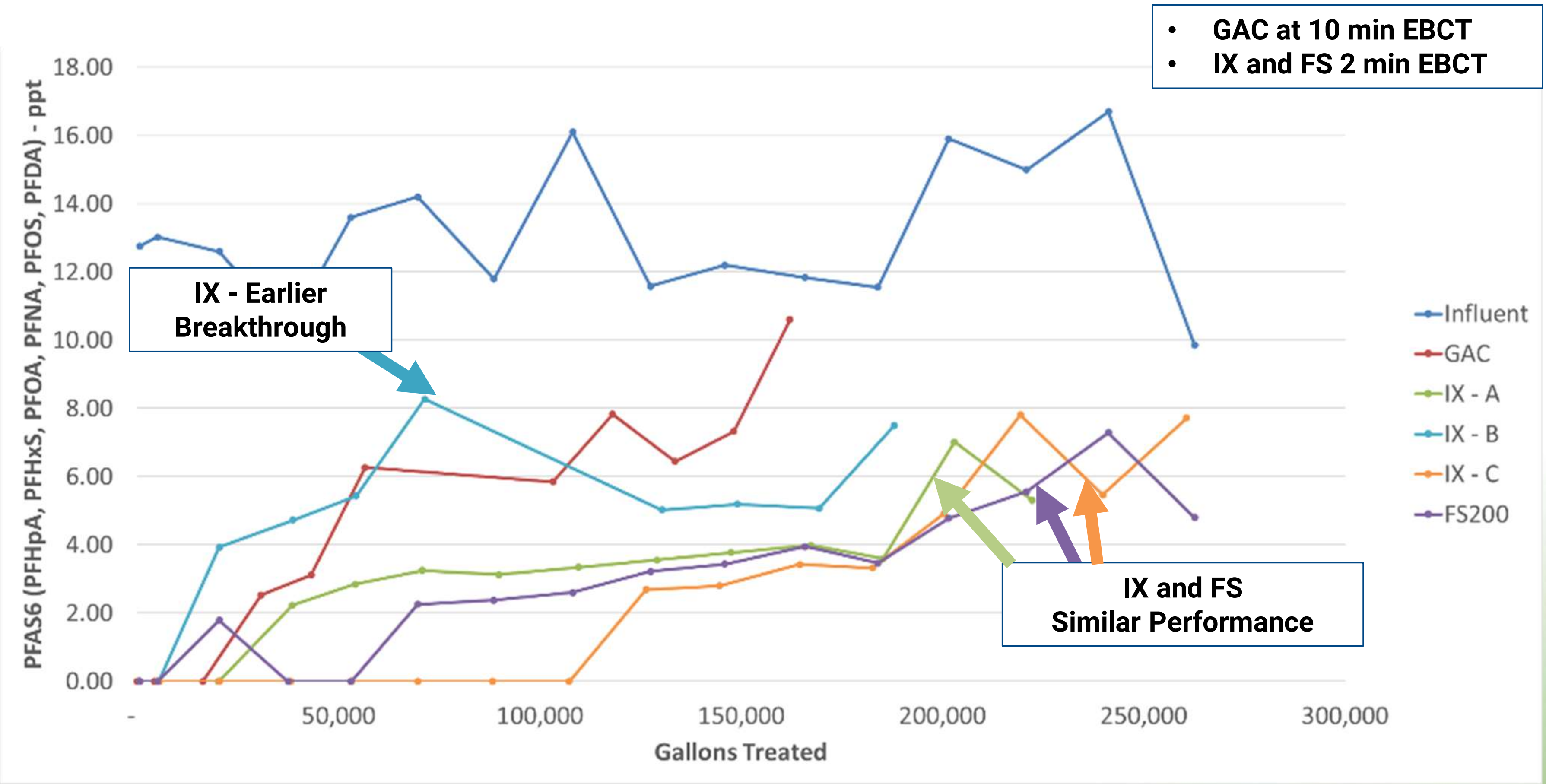
Projection:
274,215 bed volumes (524 days)
Proactive media change

2019 - Shrewsbury, MA – Pilot Testing

- **The City hired T&H for a 18-months pilot (ended in 2023)**
- **Target of < 20 ng/L "PFAS6":** PFOS, PFOA, PFHxS, PFNA, PFHpA, PFDA
- Comparison between different media types in preparation for adding 2 new wells (total 7.87MGD / 30000 M^3/day)
- Validated the hydraulics of FS - long term differential pressure at the design loading rate.
- No BW was required for duration of pilot
- FS is used as the basis of design



Shrewsbury, MA Pilot
Similar Performance for IX & FS



2022 - Hopatcong, NJ

- **A simple 70 gpm (16 M3/hrs.)**
- PFOS, PFOA removal (29ppt, 22ppt respectively)
- Both IX and GAC were offered, but GAC enabled rapid permitting
- BW frequency – 6 months

Full Scale Reference List

Project Name	Location	Contaminants	Solution	Flow Rate
Aqu: en Well	PA	PFAS	IX	160 gpm
Mou	NJ	PFAS	FS200	200 gpm
Ho H	NJ	PFAS	IX	339 gpm
Ho H	NJ	PFAS	IX	339 gpm
Ho H	NJ	PFAS	IX	339 gpm
Wes	MA	PFAS	FS200	450 gpm
Yarn istrict	MA	PFAS	FS200	600 gpm
Ho H	NJ	PFAS	IX	603 gpm
Hop: n Well 8	NJ	PFAS	GAC	70 gpm
Hop: n Well 12	NJ	PFAS	GAC	70 gpm
Hop: on Well 5	NJ	PFAS	GAC	70 gpm
Mah	NJ	PFAS	IX	832 gpm
Pete	MA	PFAS	GAC	10 gpm
Hop:	NJ	PFAS	GAC	100 gpm
Hop:	NJ	PFAS	GAC	150 gpm
Brun n	ME	PFAS	FS200	250 gpm
Aqu: akwood	CT	PFAS	GAC	30 gpm
Aqu: enda	CT	PFAS	GAC	30 gpm
Tusc	AZ	PFAS	IX	340 gpm
Dove ict	NY	PFAS	IX	40 gpm
Liber keer	NY	PFAS	GAC	41 gpm
Aqu: lls	PA	PFAS	IX	475 gpm
Esse	NJ	PFAS	IX	600 gpm
Hop: Well	NJ	PFAS	GAC	75 gpm
Aqu: ggs	CT	PFAS	GAC	9 gpm
Aqu:	NC	PFAS	IX	93 gpm
Aqu:	NJ	PFAS	IX	25 gpm
Hop: tyx	NJ	PFAS	GAC	75 gpm
Ram	NJ	PFAS	IX	130 gpm
Ram	NJ	PFAS	IX	170 gpm

- More than 30 installations (GAC, IX, FLUORO-SORB)
- Size: 10 gpm - 600 gpm
- Experience with Calgon Carbon F400 (and F400 AR+)
- Experience with all key resin manufacturers (Purolite, Lanxess, ResinTech)
- Official channel partner and application specialist for CETCO for FLUORO-SORB for the drinking water market