Treatment of PFAS in industrial wastewater by advanced reduction process and electro-oxidation

Baptiste MATHON (Treewater), Myriam KELLOU (GEPEA/Treewater), Muhammad USMAN (ENSCR), Hélène METIVIER (INSA Lyon), Gerald THOUAND (GEPEA), Khalil HANNA (ENSCR), Bruno CEDAT (Treewater), Emmanuel MOUSSET (GEPEA)

treewater KEEPING ON THE CYCLE®

INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON

deep

cnrs

GEPEA UMR CNRS 6144

Nantes Université

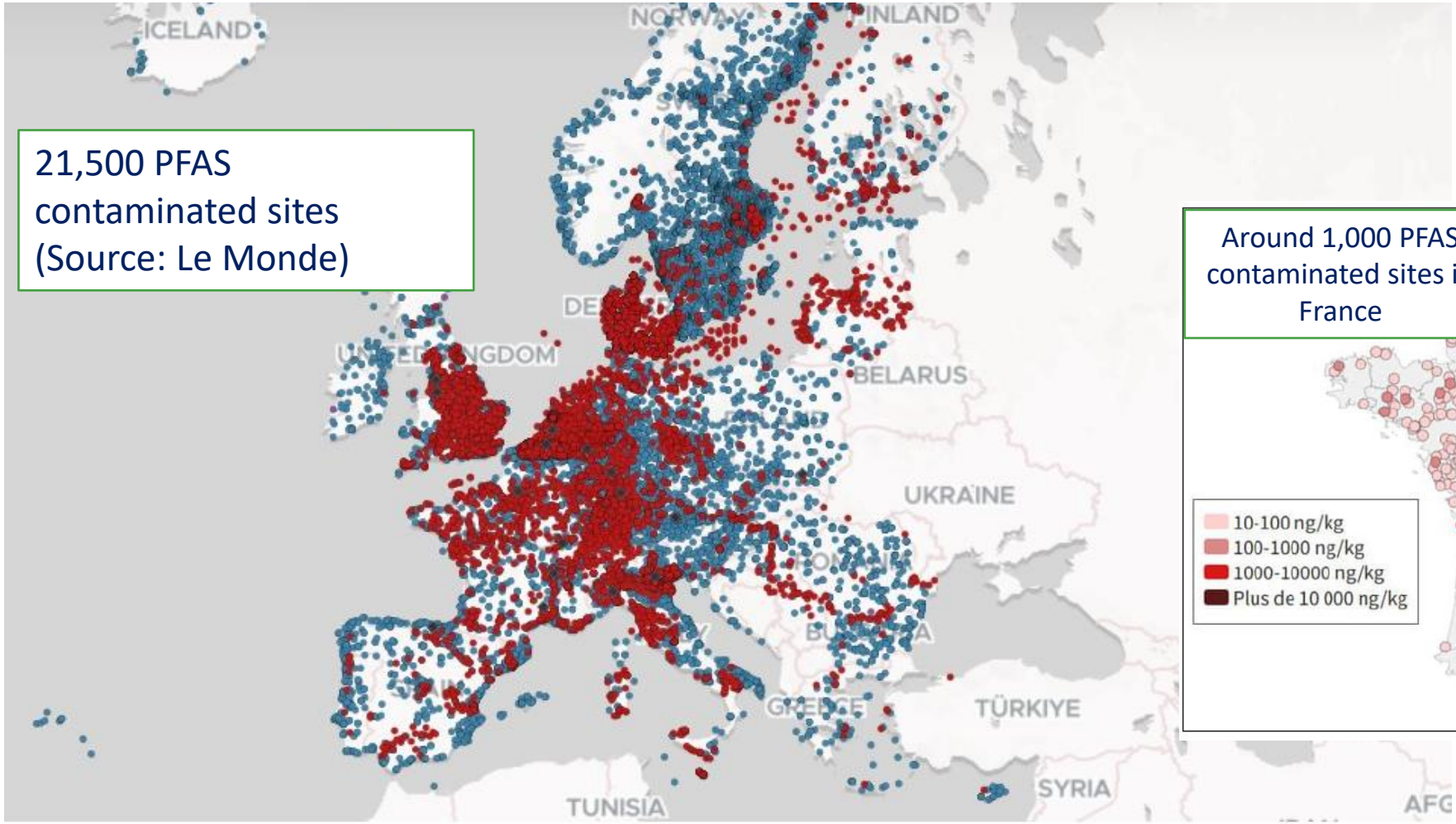
Ecole Nationale Supérieure de Chimie de Rennes

Per- and polyfluoroalkyl substances (PFAS)

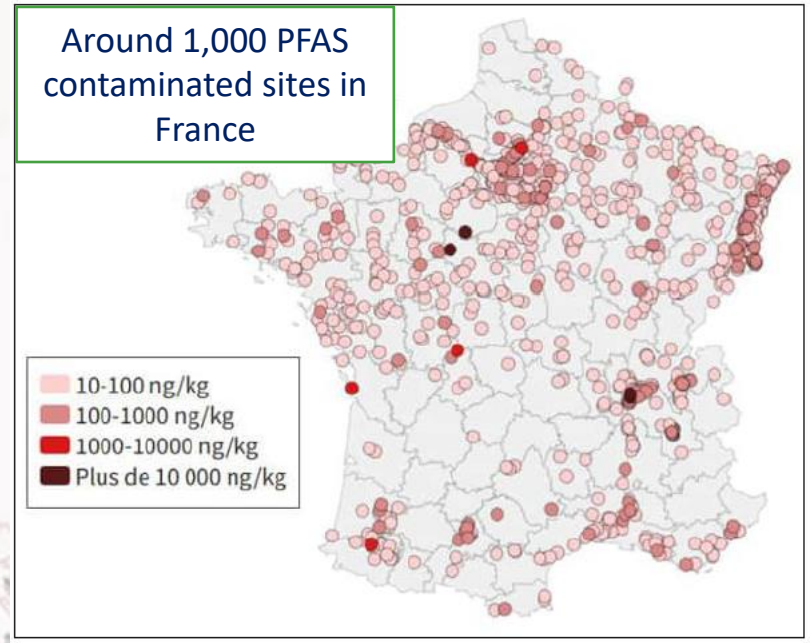
- Per- and polyfluoroalkyl substances, also known as PFAS, are a large family of more than 4,000 chemical compounds.
- Non-stick, water-repellent, and resistant to high temperatures, PFAS have been widely used since the 1950s in various industrial sectors and everyday consumer products.
- Their strong carbon-fluorine bonds make them extremely persistent in the environment and in living organisms, earning them the nickname 'forever chemicals'. As a result, they have become an emerging concern for human health and environmental safety.

Environmental emissions - widespread contamination in Europe

21,500 PFAS contaminated sites (Source: Le Monde)

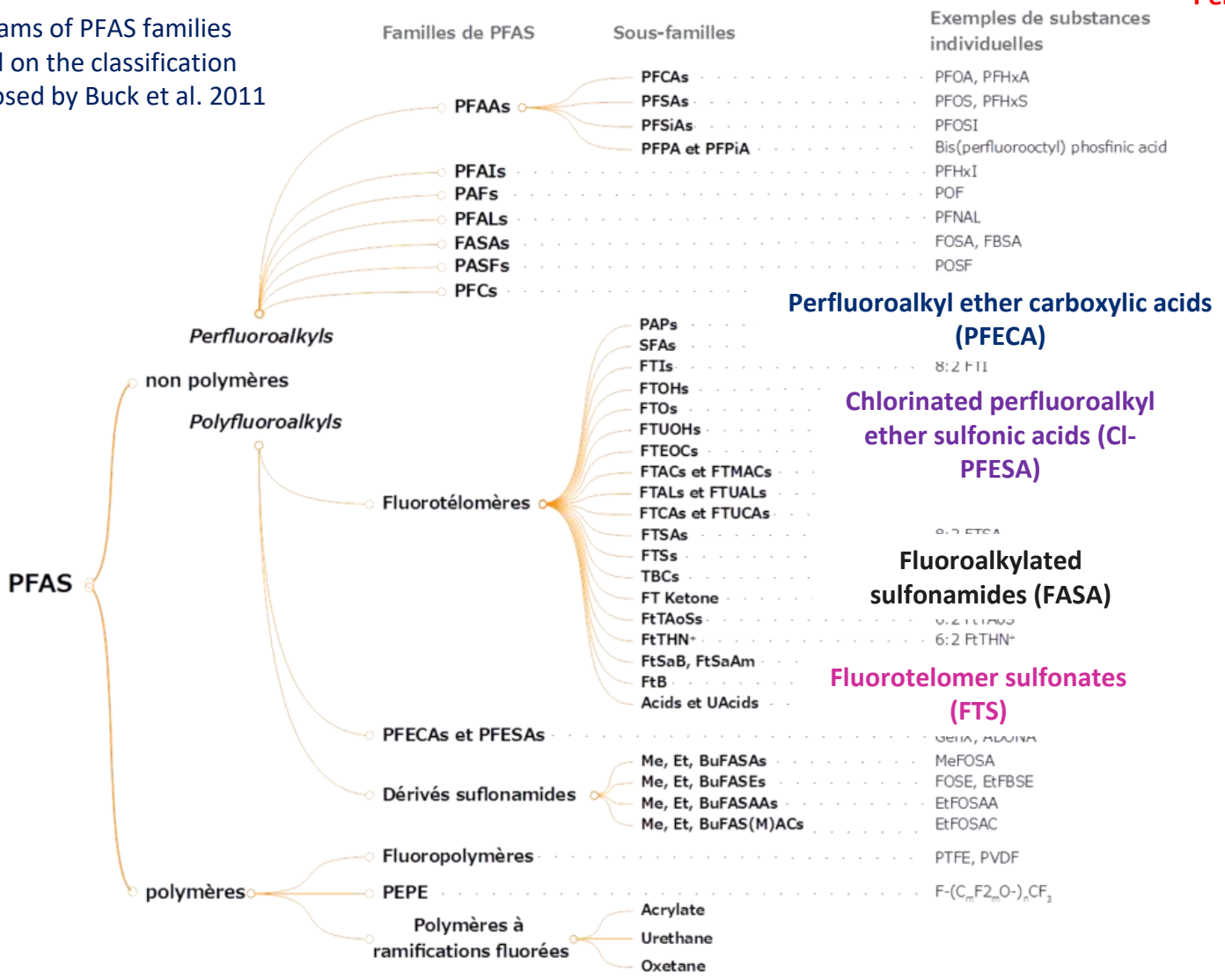


Around 1,000 PFAS contaminated sites in France

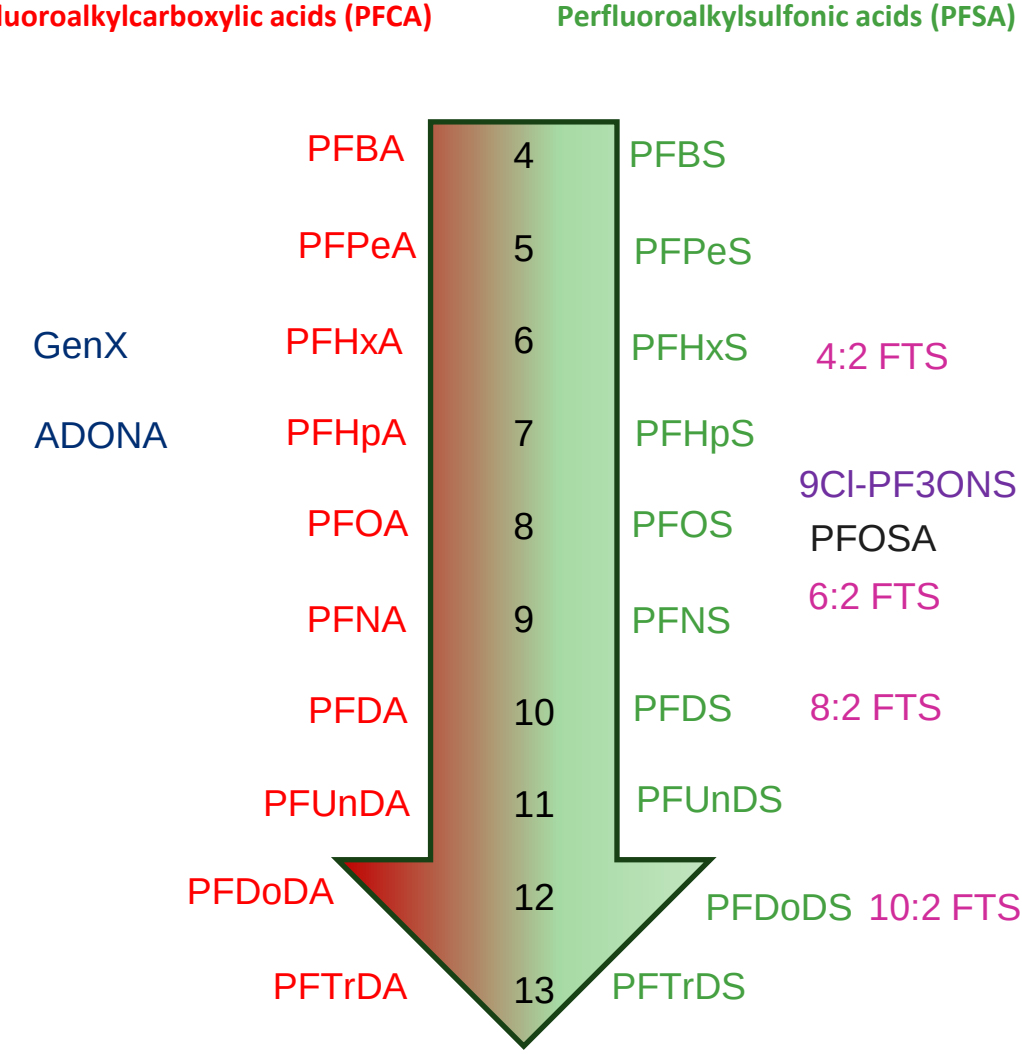


PFAS monitored and regulated

Diagrams of PFAS families based on the classification proposed by Buck et al. 2011

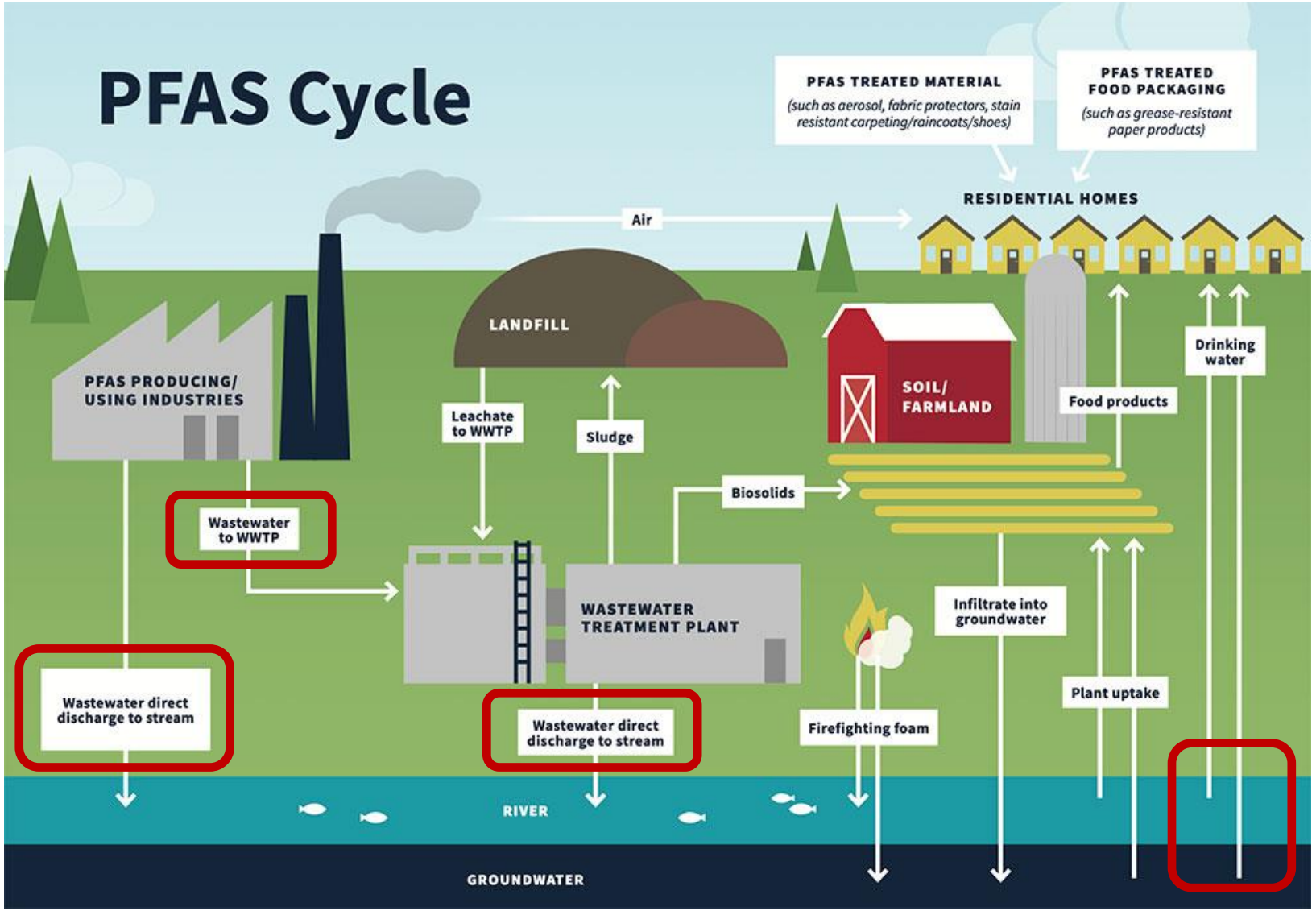


Ultra-short chains <4 (ex: TFA) ?



20 PFAS from the European Drinking Water Directive (Directive (EU) 2020/2184)

Environmental emissions - water to be treated



- Where do PFAS treatment solutions come into play?

- Treatment of industrial effluents at source, prior to discharge into the environment or WWTPs

- Treatment of contaminated groundwater prior to use in industrial processes or for drinking water purification

- In-situ treatment of wash water to extract contaminated soil

treewater®

KEEPING ON THE CYCLE

Treatment and Recycling of Industrial Effluents

Expert in advanced oxidation technologies

2 patents issued
2 patents in preparation

Industrial and commercial deployment underway

Our strategy:

Offer manufacturers a targeted solution at controlled cost.

Scientific partners, setting up development programs with French and European organizations

Facilities in operation for more than 3 years

European Commission · LES AGENCES DE L'EAU · INSA Institut National des Sciences Appliquées Lyon · Ecole Nationale Supérieure de Chimie de Rennes

The project

Existing Treatments:

- Membrane (concentrate management)
- Activated carbon (low loading rates, particularly for short chains)
- Ion exchange resins (complex regeneration -> incineration)

Significant challenges for the development of a **destructive treatment** capable of **reaching regulatory thresholds** imposed on industries

This **project** aims to develop a treatment solution for PFAS in complex industrial effluents:

- Advanced Reduction Process (ARP)
- Electrochemical Advanced Oxidation Process (EAOP)
- Case study : ARP and EAOP applications in real groundwater and industrial wastewater (raw effluent and concentrate)

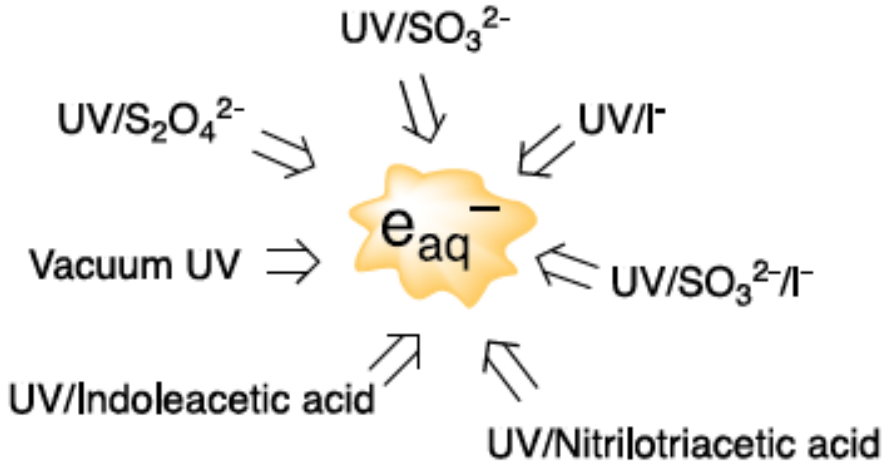
Advanced Reduction Process (ARP)

ARP based on the production of reducing species: **hydrated electrons** (e^-_{aq}).

There are several methods to generate these species: **UV**, ultrasound, electron beam, microwave.

Production by adding a **reducing agent** (iodide, thiosulfate, sulfite, etc.).

Highly reactive reducing species easily **scavenged by the matrix** of an effluent (dissolved O_2, H^+, nitrates, nitrites, halides, etc.).

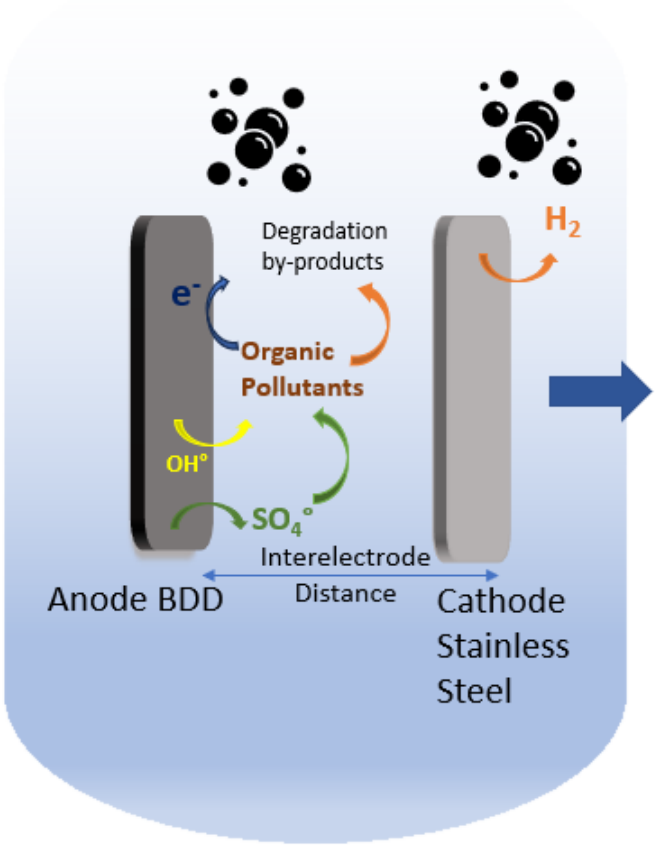


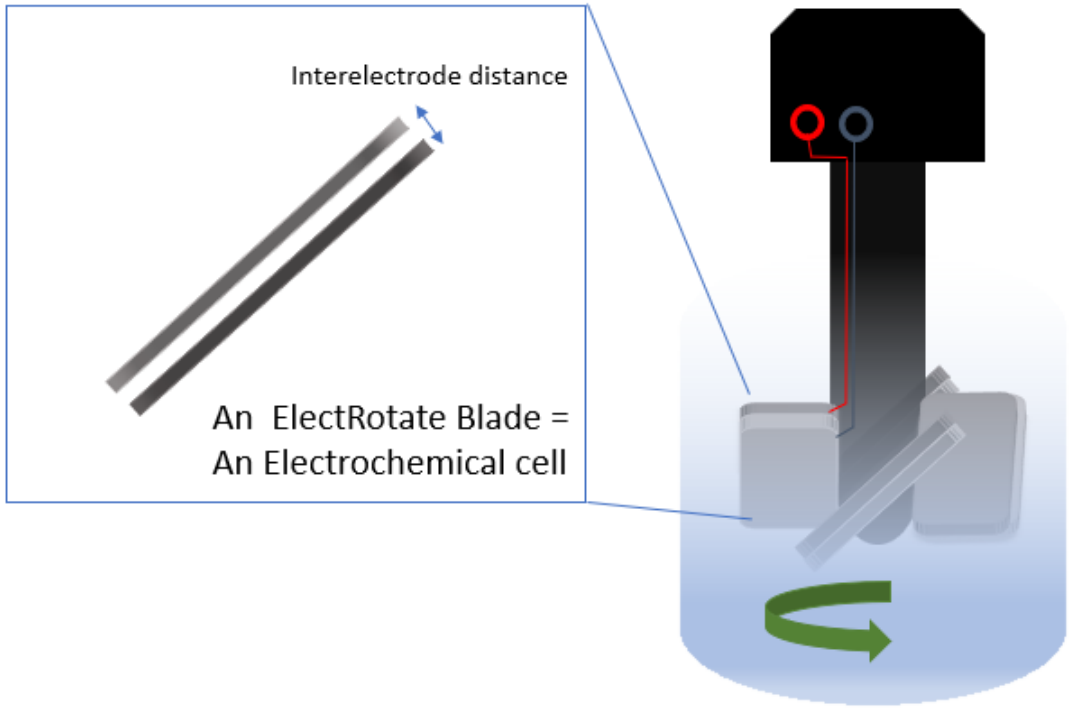
Electrochemical Advanced Oxidation Process (EAOP) & ElectRotate

EAOP allows to oxidate organic pollutants to CO_2 and H_2O.

EAOP is based on 3 mechanisms :

- **direct oxidation,**
- production of **Hydroxyl radicals,**
- and production of **other radicals and oxidants.**



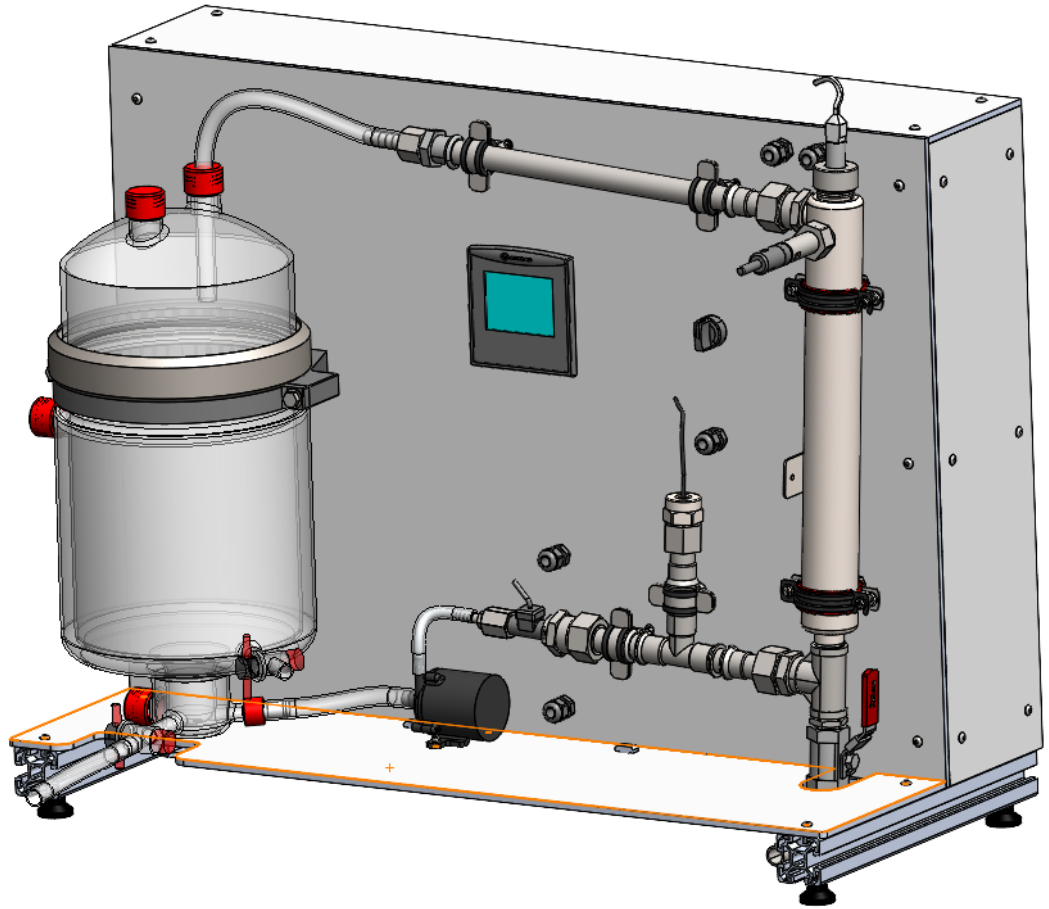


Treatment by ARP

Methodology:

- Goal: formation of $e^-_{(aq)}$
- Laboratory pilot tests (2L)
- Low-Pressure UVc Lamp, 24 W
- Treatment Parameters

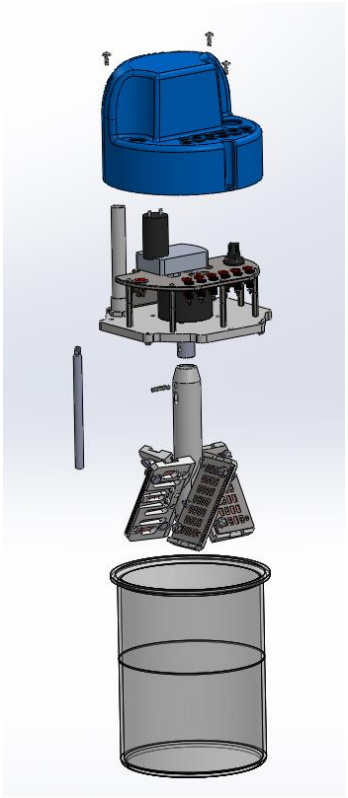
- No pH change
- [Sulfites] = 20 mM
- Cumulative UV dose
- two case studies:
  - groundwater contaminated with PFAS
  - TFA in industrial wastewater



Treatment by ElectRotate

Methodology:

Parameter	Value
Cathode	Stainless steel
Anode	Boron-doped diamond (BDD)
Current	5 A
Rotation speed	15 rpm
Inter-electrode distance	1 mm
Number of blades	4
Volume	5 L
Duration	12 h



1st Case Study: groundwater impacted by PFAS

Context :

- Presence of PFAS related to firefighting foam

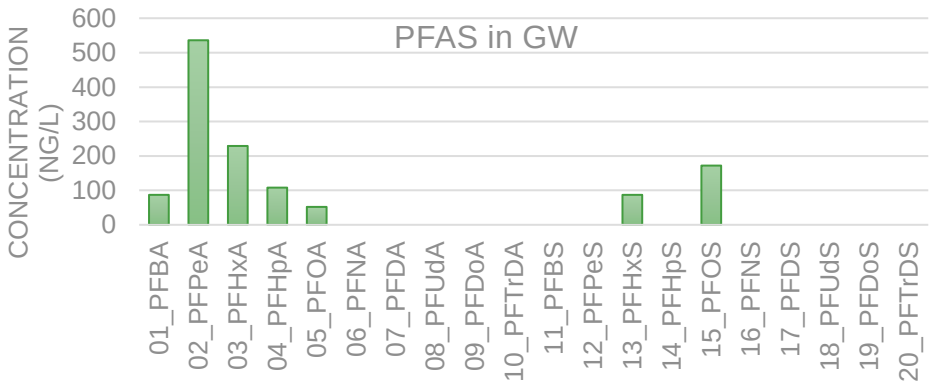
Physico-chemical parameters:

- **High UV transmittance:** promotes the penetration of UVc radiation
- **pH 8:** H^+ is a scavenger of $e^-(aq)$
- **Significant Impact of nitrates**: $k_{PFOA,e\text{-}aq}=5,1.\ 10^7\ M^{-1}\ s^{-1}$ vs $k_{nitrate,e\text{-}aq}=9,7.\ 10^9\ M^{-1}\ s^{-1}$

Monitoring of 20 PFAS

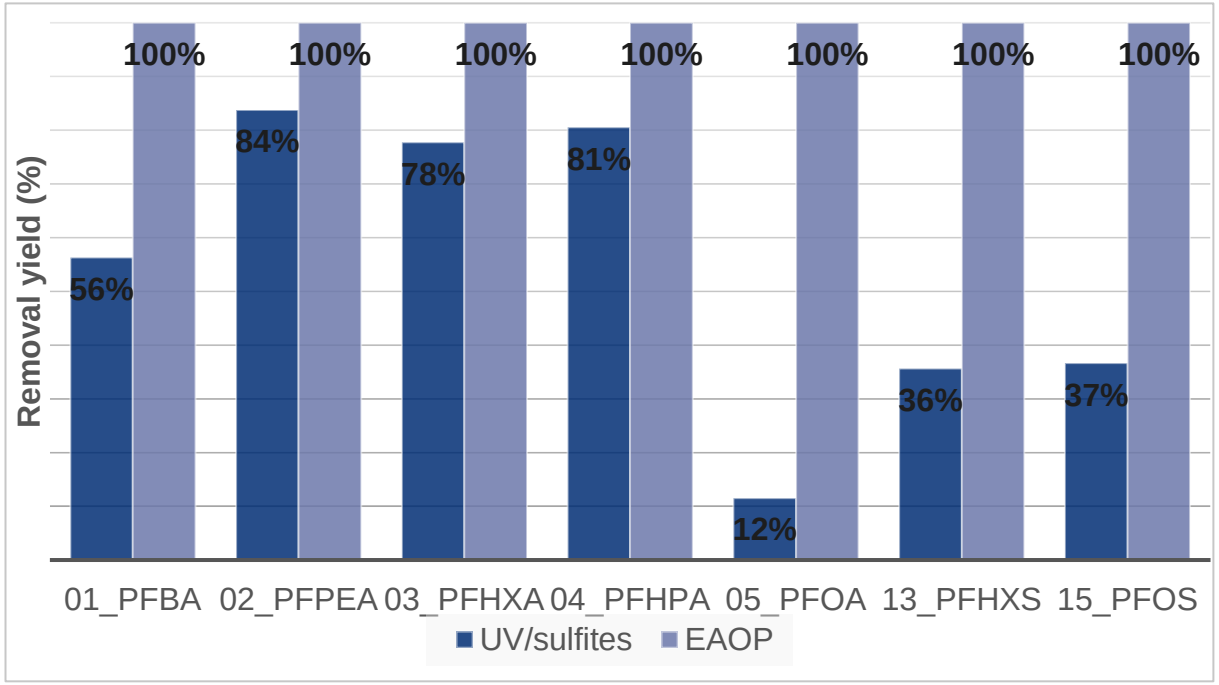
	Units	Groundwater
pH	/	8,11
Conductivity	mS/cm	1,094
COD	mgO_2/L	<15
UV Trans	%	92
Mg^{2+}	mg/L	2,62
Ca^{2+}	mg/L	54,9
Fluoride (F^-)	mg/L	0,286
Chloride (Cl^-)		346
Nitrates (NO_3^-)		0,741
Nitrites (NO_2^-)		<0,015
Bromide (Br^-)		<0,03
Phosphate (PO_4^{3-})		<0,6
Sulphates (SO_4^{2-})		55,4

1st Case Study: Results



- **7/20 PFAS quantified**: 5 perfluorocarboxylic acids (PFCA) and 2 perfluorosulfonic acids (PFSA).
- **Optimal conditions** identified in ultrapure water applied in groundwater: ARP and EAOP

- **ARP Efficiency**
  - Effective for perfluorocarboxylic acids with 60-80% reduction.
  - Challenges include potential formation of PFBA and PFOA?
- **Limitations**
  - ARP shows limited effectiveness for perfluorosulfonic acids.
  - Achieving optimal conditions necessitates the use of pre-oxidation
- **EAOP Solution**
  - EAOP enables total removal but may produce chlorinated degradation by-products.

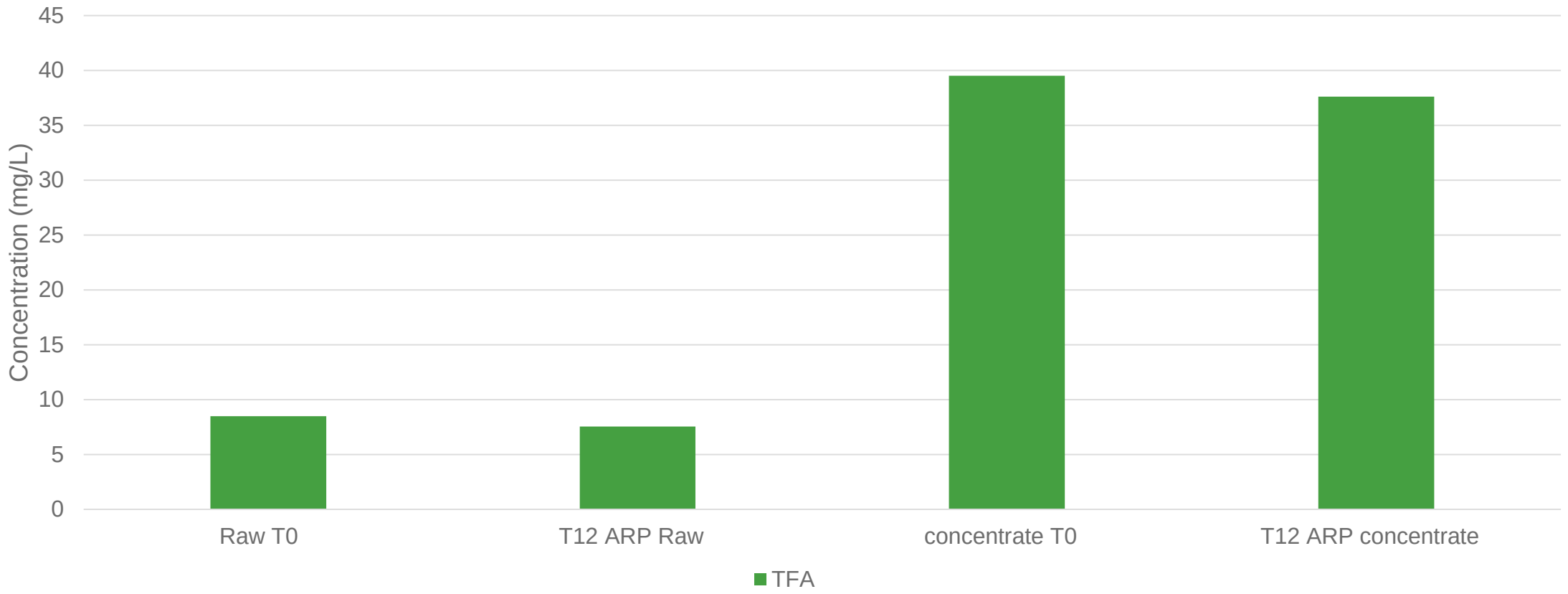


2nd Case Study: TFA in industrial wastaewater

- **Potential by-products:**
- Gaseous: CO_2 from acid mineralization and HF under acidic conditions (Mohamed Gar Alalm et al., 2022); Cl_2 from anodic oxidation of Cl^- (T. Arai et al., 2022)
- Dissolved : HF/F^- (pKa = 3.17); ClO_3^-/ClO_4^- from Cl^- oxidation (Xu et al., 2024)
- Precipitated: CaF_2 and MgF_2 during defluorination; $Ca(OH)_2$ and $Mg(OH)_2$ in basic conditions

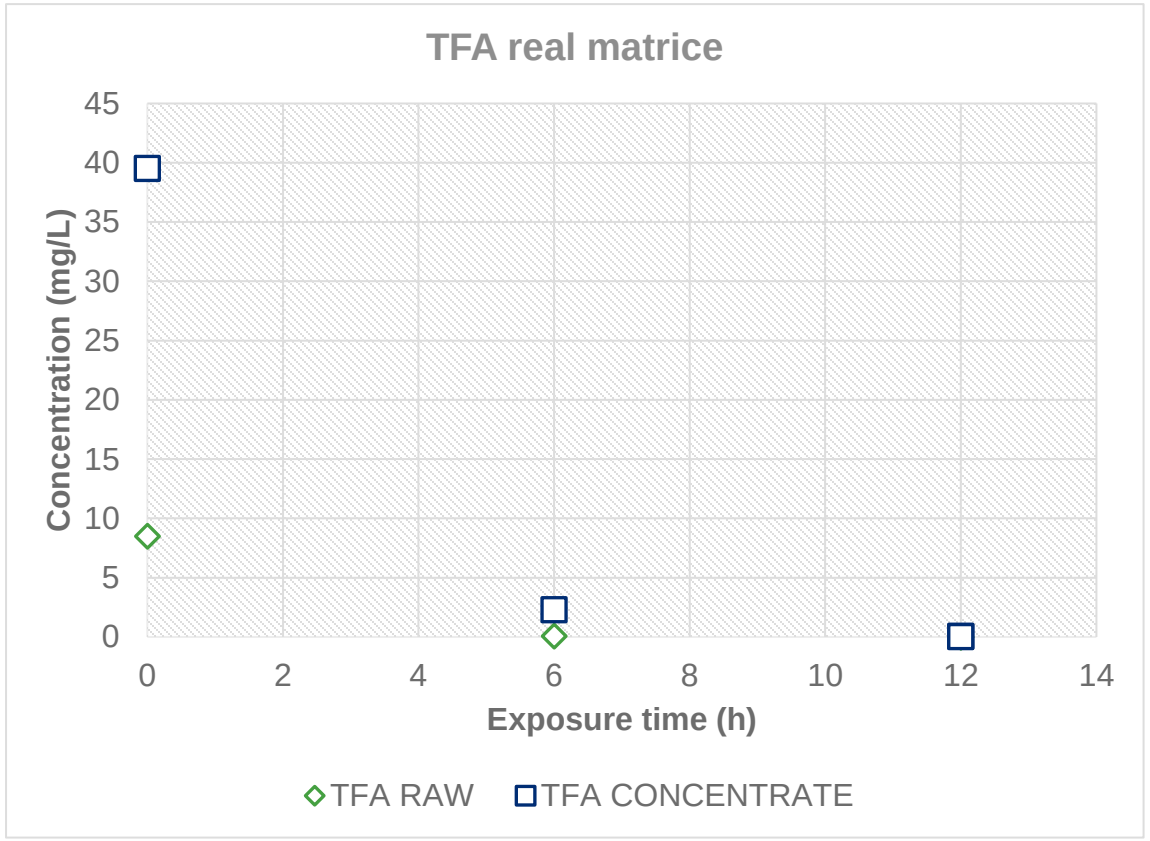
Parameters	Raw T0 (mg/L)	Concentrate T0 (mg/L)
pH	11,1	11,3
TFA	8,487	39,518
SO_4^{2-}	2 700	14 000
F^-	5,4	27
Cl^-	420	2 000
ClO_3^-	<400	2,4
ClO_4^-	<400	4
Ca^{2+}	460	640
Mg^{2+}	34	170

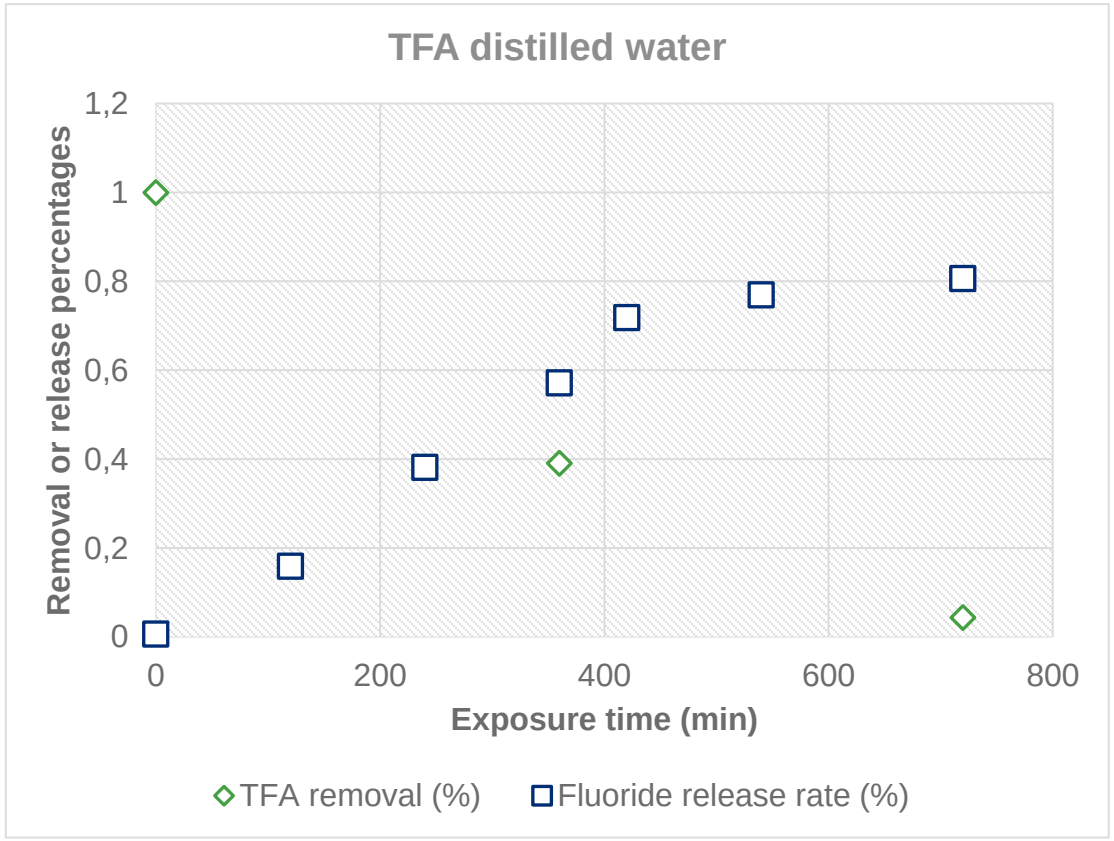
2nd Case Study: Results ARP



- **ARP proved ineffective for TFA removal—only 11 % reduction in the raw effluent and 5 % in the concentrate—so this treatment option was discarded based on these results**

2nd Case Study: EAOP results showed up to 99.99% removal efficiency!





- TFA removal >94% after 6 hours and > 99,9% after 12h
- Faster kinetics on real matrix: presence of ions promoting current flow
- Under identical operating conditions in distilled water, complete removal of TFA was achieved with a fluoride release rate of 80% - Fluoride gas emission?

Conclusions

The ARP, based on the generation of hydrated electrons (e^-_aq), showed good efficiency for PFCA degradation (60–80%) but limited performance on PFSA, complementary oxidation is required

The EAOP enables complete mineralization of PFAS with up to 99.99% removal efficiency.

Wastewater contaminated with TFA: ARP was ineffective for TFA, but EAOP showed high efficiency in after effluent concentration

EAOP appears to be a promising technology for treating PFAS-rich concentrates, making it a strong candidate for hybrid treatment strategies combining separation and destructive processes

Next steps include the deployment of a in-situ pilot (industrial site to be identified)

Thank you for you attention!

bmathon@treewater.fr

https://www.treewater.fr/

tree water®
KEEPING ON THE CYCLE

INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON

deep

cnrs

GEPEA UMR CNRS 6144

Nantes Université

Ecole Nationale Supérieure de Chimie de Rennes