CAPTURE

# Photoelectrocatalytic Advanced Oxidation Processes for the degradation of fluorinated organic pollutants in AFFF-contaminated water and groundwater

Silvia Franz, Alessandro Pietro Tucci – Politecnico di Milano

Paolo Ronco – VIACQUA spa

Life

SLU iFLUX ABO CONSULTANCY POLITECNICO MILANO 1863 GREENSOIL Group Sustainable Soil Remediation VIACQUA SGS UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA

# CAPTURE

## Combining novel Analytical Protocols for PFAS contamination with Technologies for sUstainable REmediation

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# 5 main objectives...

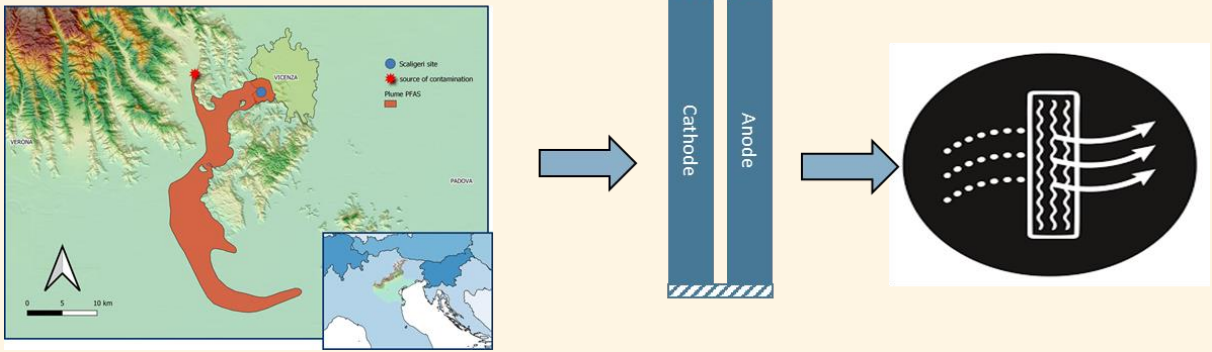
- **1** – Development of robust sampling and analytical protocols and techniques to evaluate any type of PFAS contamination (quantify the total amount of PFAS)
- **2** – to develop monitoring methods and transport models in soil, groundwater and sediment
- **3** - to design and test in 4 different sites innovative remediation technologies that have shown promising results at a smaller scale
- **4** – to develop methods for quantitative risk assessments
- **5** - to develop a code of practice/guidelines on PFAS remediation and to provide a replication and transfer plan

# ...to be achieved in 5 years (2022-27)

# Experimental PEC

## WP3, Task 3.2 RISK MITIGATION FOR GROUNDWATER

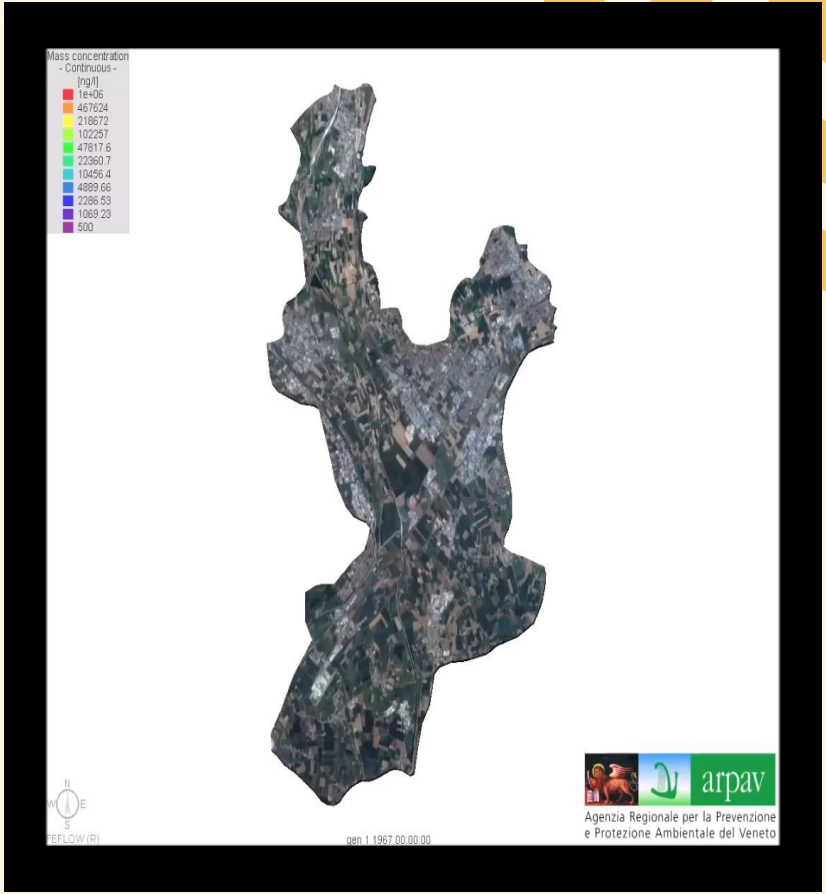
- to design and develop a TRL6 pilot based on PhotoElectrocatalytic Oxidation process and test it with PFAS contaminated groundwater at the Veneto case study



# The PFAS Contamination in Veneto Region (2013- n.a)

## MAIN FIGURES

- Source identified in 2013: MITENI spa (PFAS producer)
- source max concentration as Sum PFAS: 250-750 µg/l
- plume longitudinal length: > 40 km
- plume transversal width: 4-5 km
- plume vertical depth: > 100 m
- plume area (Sum PFAS> 0,5 ppb): 150 km2
- static water volume polluted : > 100 M m3
- drinking water demand : 30-40 M m3/y
- plume age: > 50 y
- observation period: 11 y (2013 - 2024)
- number of lab analysis: > 150.000
- exposed population (red zone): 140.000
- economic cost for corrective >> 110 M EUR
- time for remediation of the source site: > 10 y
- time for reasonable natural attenuation: > 50 y
- time for complete recovery from pollution: n.a




VIACQUA

# The PFAS Contamination in Veneto Region (2013- n.a)

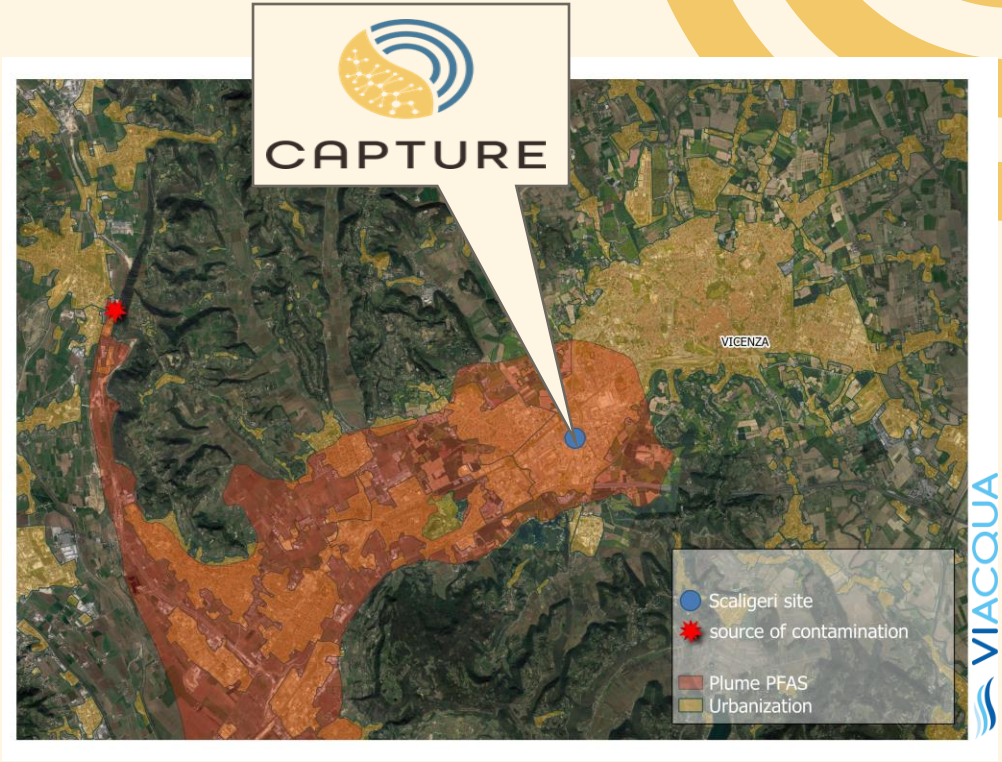
- RISK MITIGATION UNDERTAKINGS (from the drinking water point of view)

**At the source of contamination site**

- Plug-in of the Pump&Treat system
- Removal of contaminated industrial waste at the river's banks (2016)

**Drinking water supplies**

- Closure of contaminated boreholes
- Set up of new GAC units
- Interconnections with alternative sources
- Enviromental monitoring and characterization

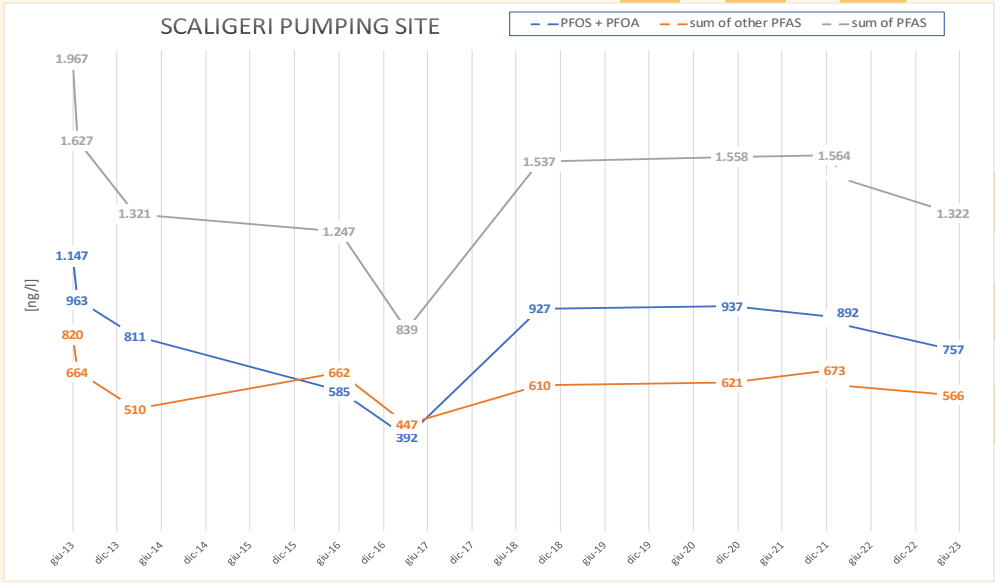


# LIFE CAPTURE in Veneto

## Current undertakings :

- Revamping of borehole (close since 2013)
- Q = 1,5 l/s (from 70 l/s)
- Testing of pre-treatment (RO?) to concentrate the contaminated water
- Design and installation of combined tratement :

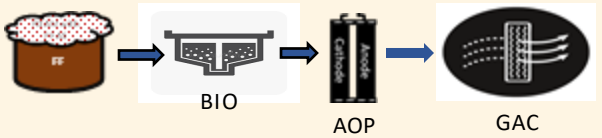
  **RO + PEC + GAC/Resins filters**




# Experimental:
# LIFE CAPTURE PROJECT

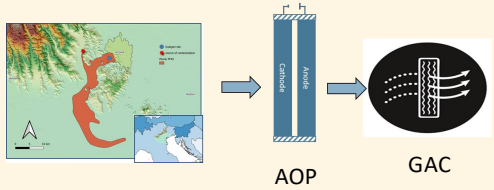
## WP3, Task 3.1: RISK MITIGATION FOR POLLUTED SOIL

- Soil foam fractionation (to extract ~ 90% of PFAS)
- Treatment train for the resulting foams



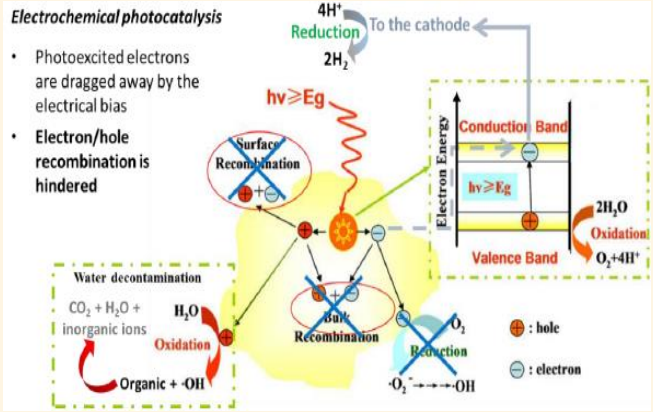

## WP3, Task 3.2 RISK MITIGATION FOR GROUNDWATER

- AOP based on Photoelectrocatalytic Oxidation
- Filtration on granular activated carbon



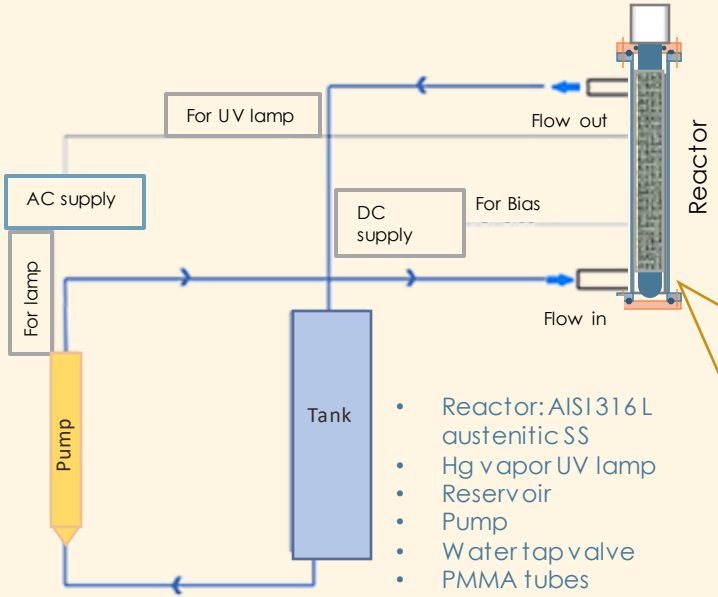
# Photoelectrocatalytic treatment of contaminated water

## Photoelectrocatalysis (PEC)

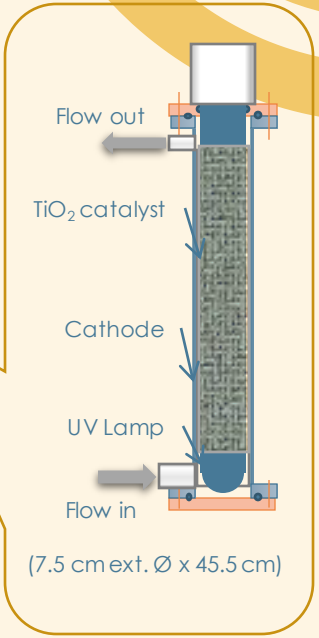



- Photoexcited electrons are **dragged away** by the **electrical bias**
- Electron/hole **recombination** is **hindered**

## Semi-batch System




- Reactor: AISI 316 L austenitic SS
- Hg vapor UV lamp
- Reservoir
- Pump
- Water tap valve
- PMMA tubes



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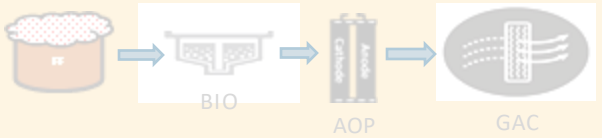


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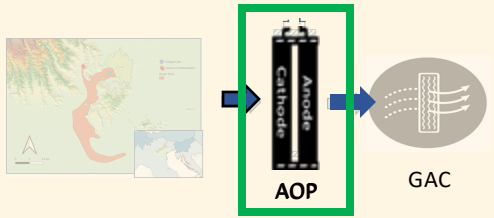
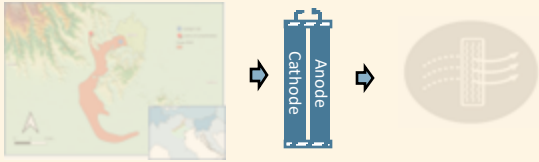
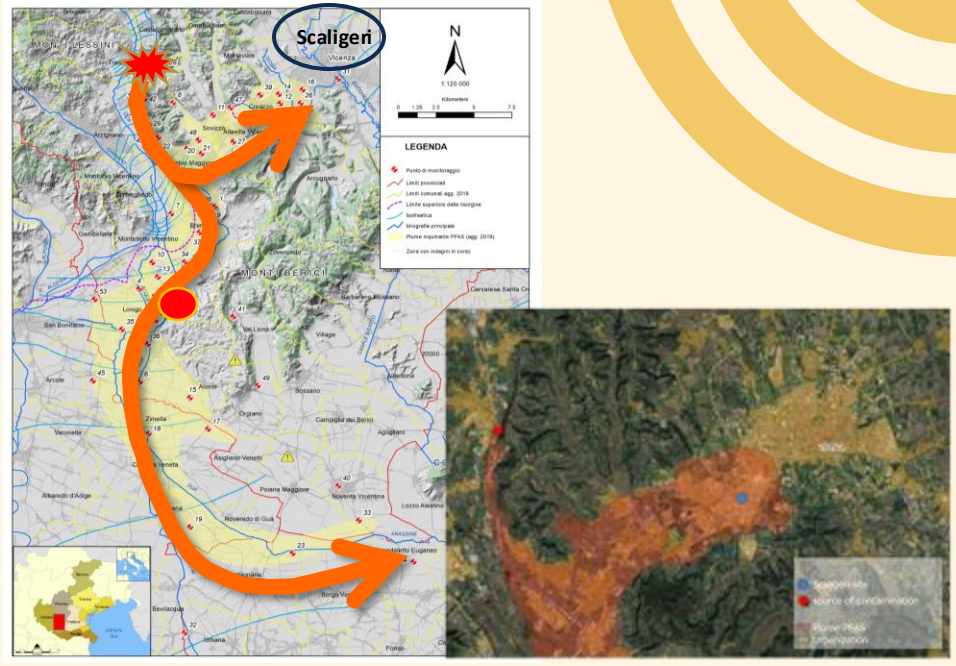


# WP3 – Groundwater from Veneto region




| | Chemicals | Acronym | Concentration (ng/L) | Detection limit (ng/L) |
|---|---|---|---|---|
| Perfluorocarboxylic Acids (PFCA) | Perfluorobutanoic Acid | PFBA | 124 | 20 |
| | Perfluoropentanoic Acid | PFPeA | 73 | 20 |
| | Perfluoroesanoic Acid | PFHxA | 65 | 20 |
| | Perfluoroeptanoic Acid | PFHpA | 0 | 20 |
| | Perfluoroottanoic Acid | PFOA | 430 | 20 |
| | Trifluoroacetic Acid | TFA | 1850 | 1000 |
| Perfluorosulfonic Acids (PFSA) | Perfluorobutsulfonic Acid | PFBS | 157 | 20 |
| | Perfluoroottsulfonic Acid | PFOS | 24 | 20 |

PFAS analyzed by HPLC-MS (ISO17025)




- **Total PFAS** concentration: **873 ng/L (2723 ng/L considering TFA)**
- Presence of untargeted **fluorinated or non-fluorinated compounds**

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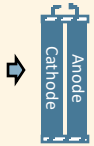
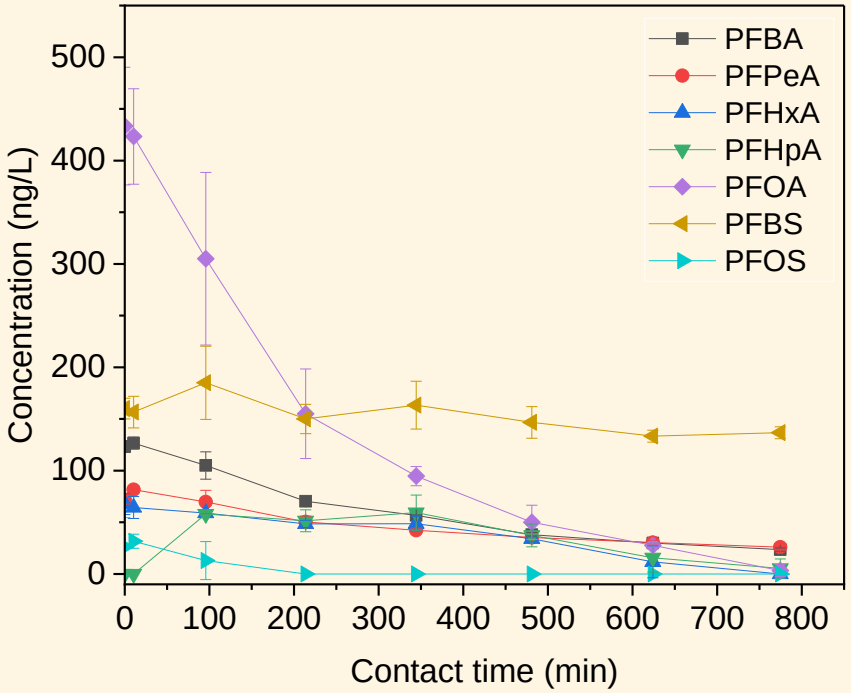
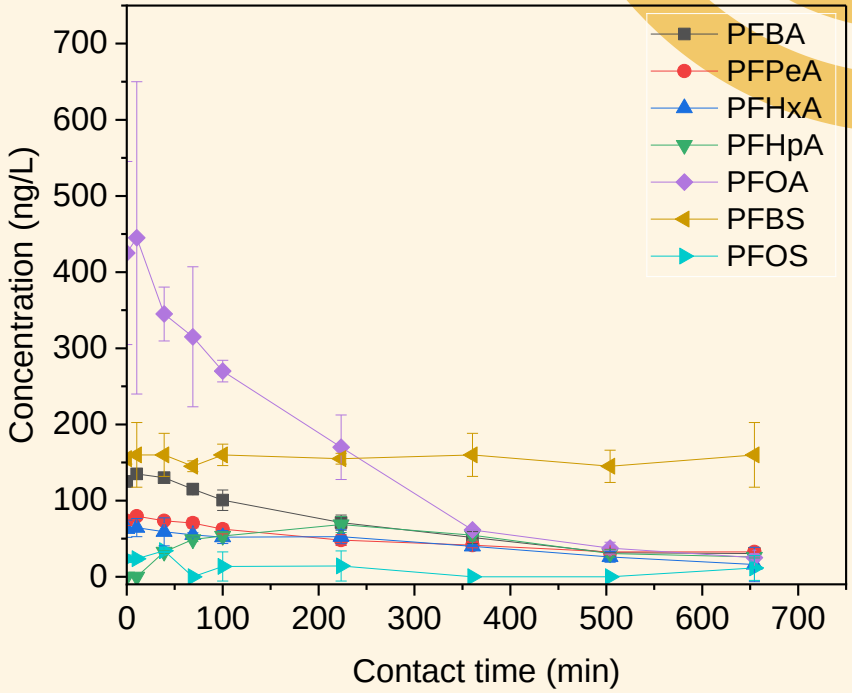





PEC $P_1$




PEC $P_2$ (< $P_1$)



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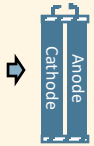
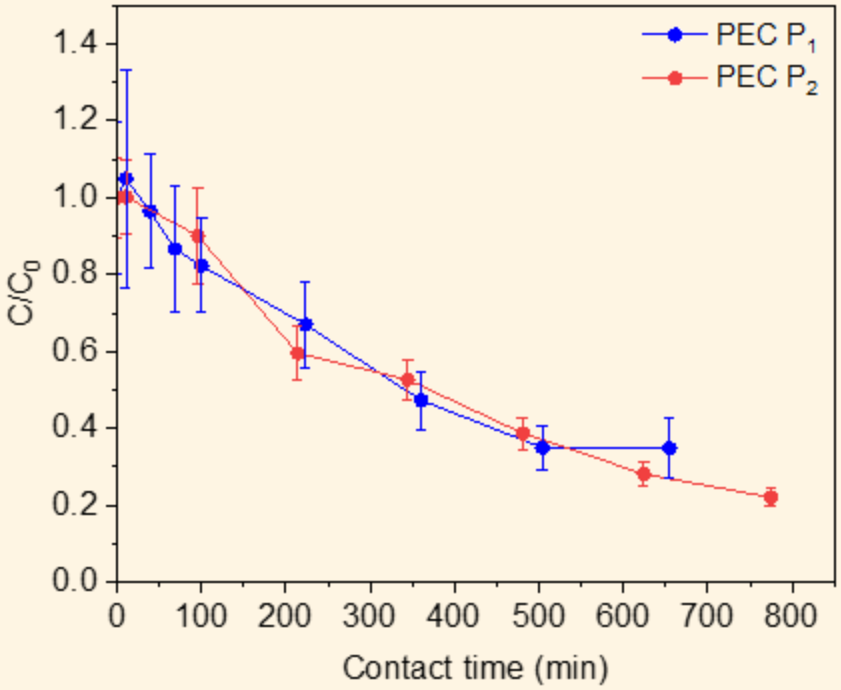
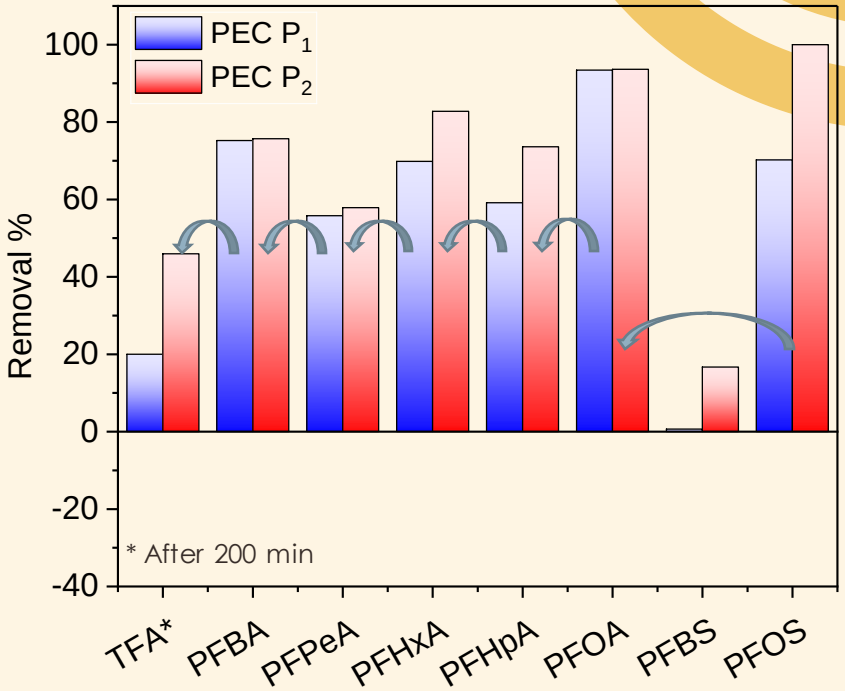





## Perfluoroalkyl subsatnces (PFAS) Degradation




## PFAS Removal% (600 min)



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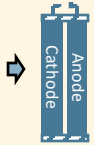
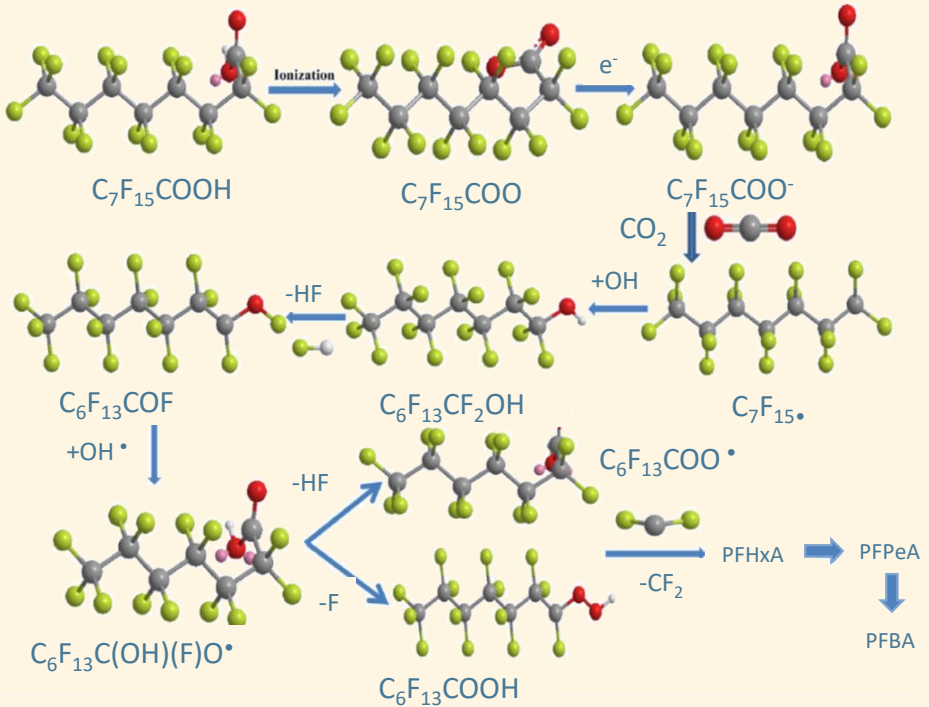
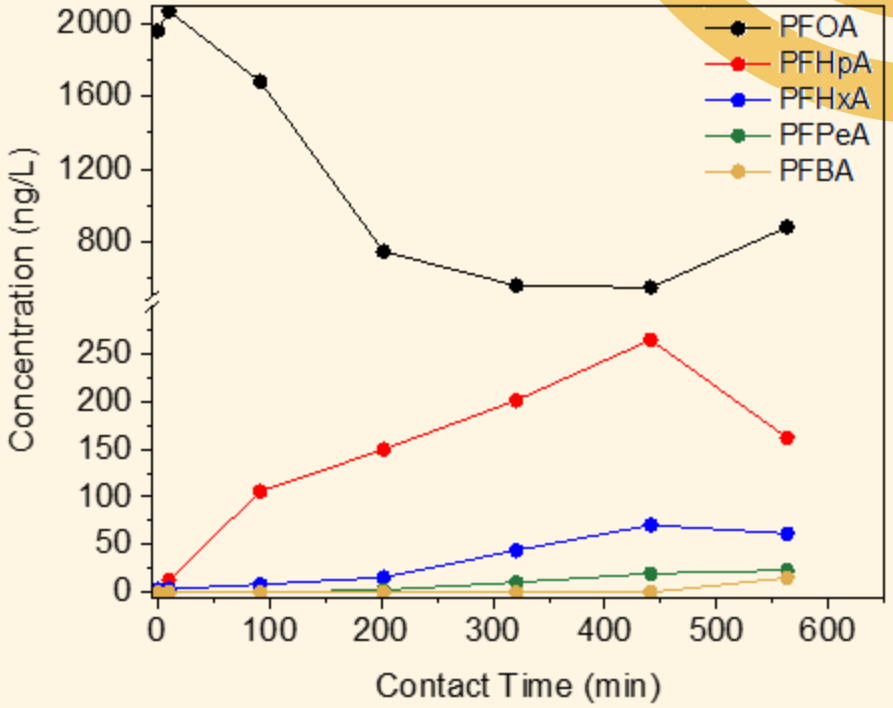





*Y.P. Peng, H. Chen, C.P. Huang, Appl Catal B. 209 (2017) 437–446. https://doi.org/10.1016/j.apcatb.2017.02.084.*




2 µg/L PFOA



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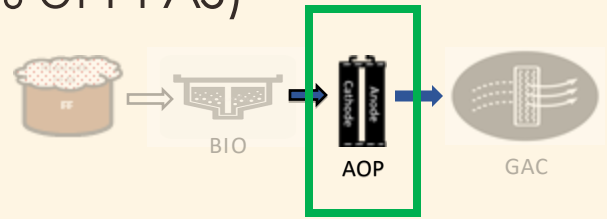


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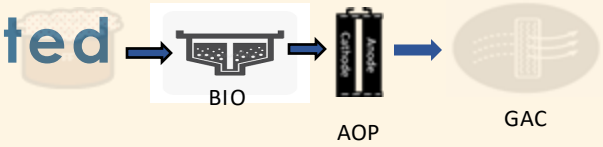
# WP3 – AFFF-contaminated process water




Influent: AFFF (10 mL/L) spiked municipal water after biological treatment, withdrawal of supernatant and filtration

COD: 41.6 ± 10.47 mg/L

N° of target fluorinated species: 50

Influent composition in PEC reactor

| Chemicals | PEC $P_1$ Concentration (µg/L) | PEC $P_2$ Concentration (µg/L) |
|---|---|---|
| PFBA | 0.355 | 0.445 |
| PFPeA | 0.18 | 0.24 |
| PFHxA | 1.35 | 1.7 |
| PFHpA | 0.108 | 0.265 |
| HPFO-DA | 0.035 | 0.0065 |
| 4:2 FTS | 0.11 | 0.13 |
| 6:2 FTS | 32.5 | 44.5 |

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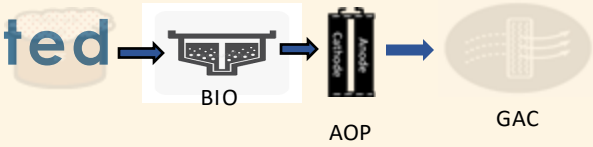


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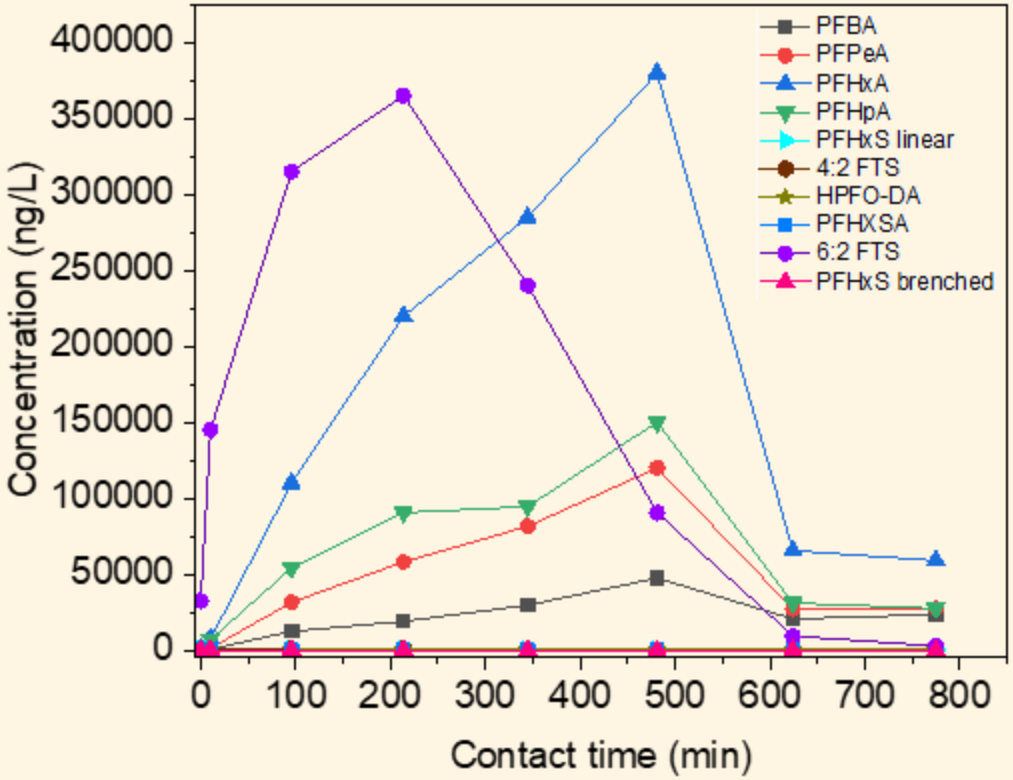

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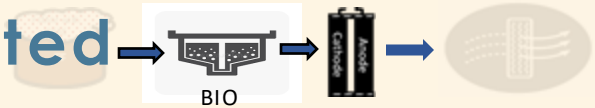
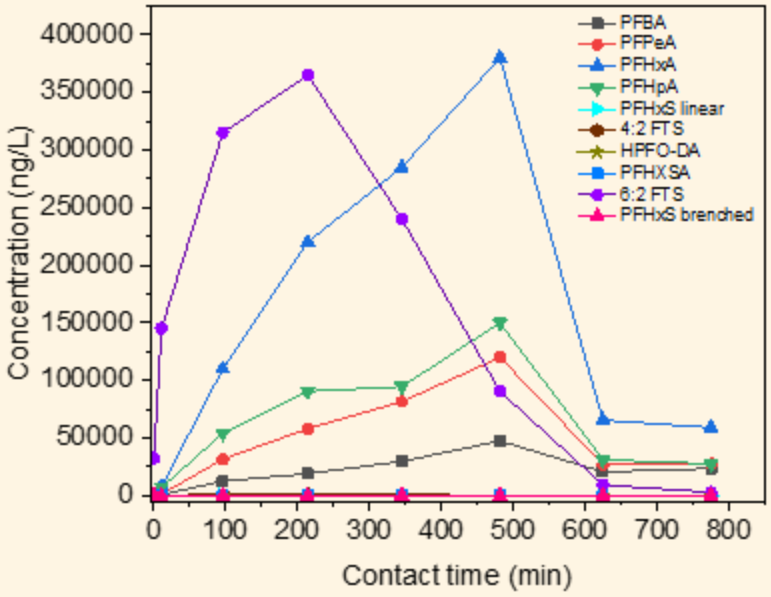
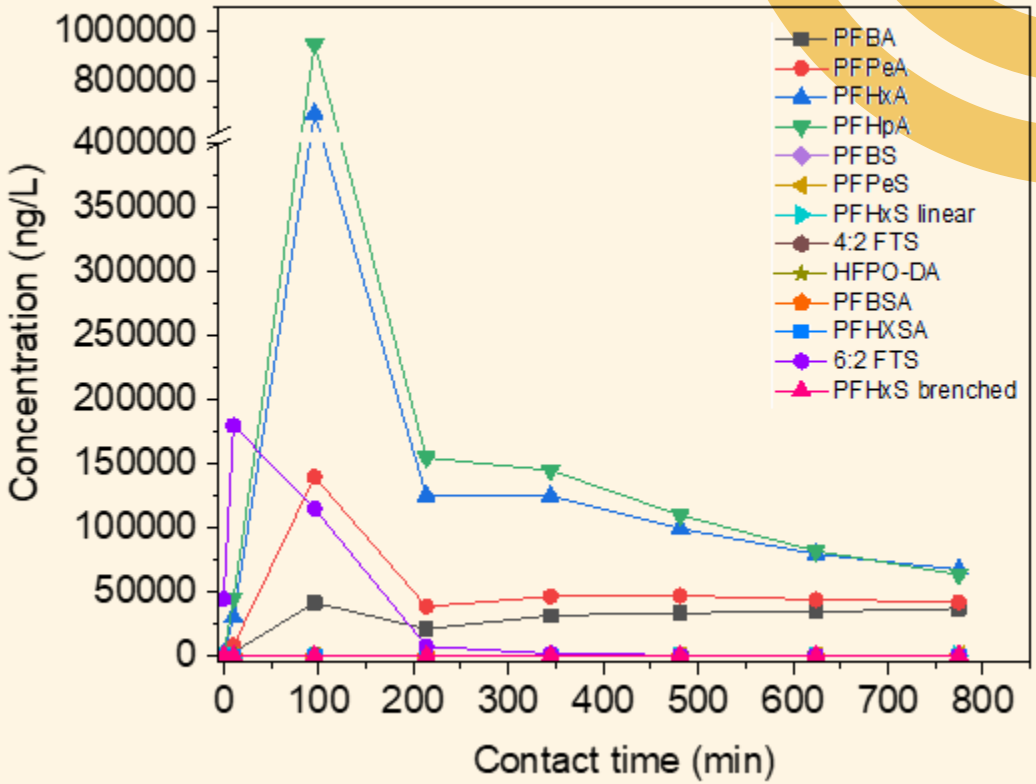



PEC $P_1$




PEC $P_2$ (< $P_1$)



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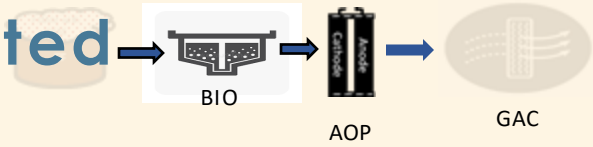
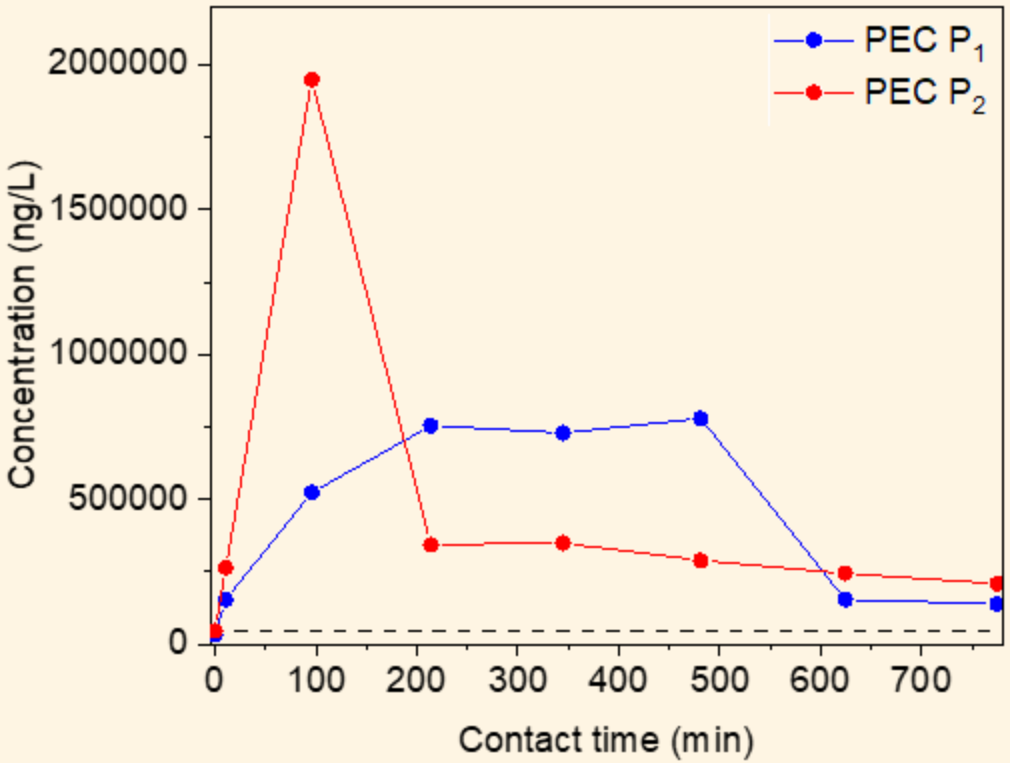
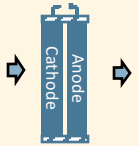



Total PFAS concentration ($P_1 > P_2$)




How many non-targeted PFASs are present in the foam?

# WP3 – Groundwater from Veneto region



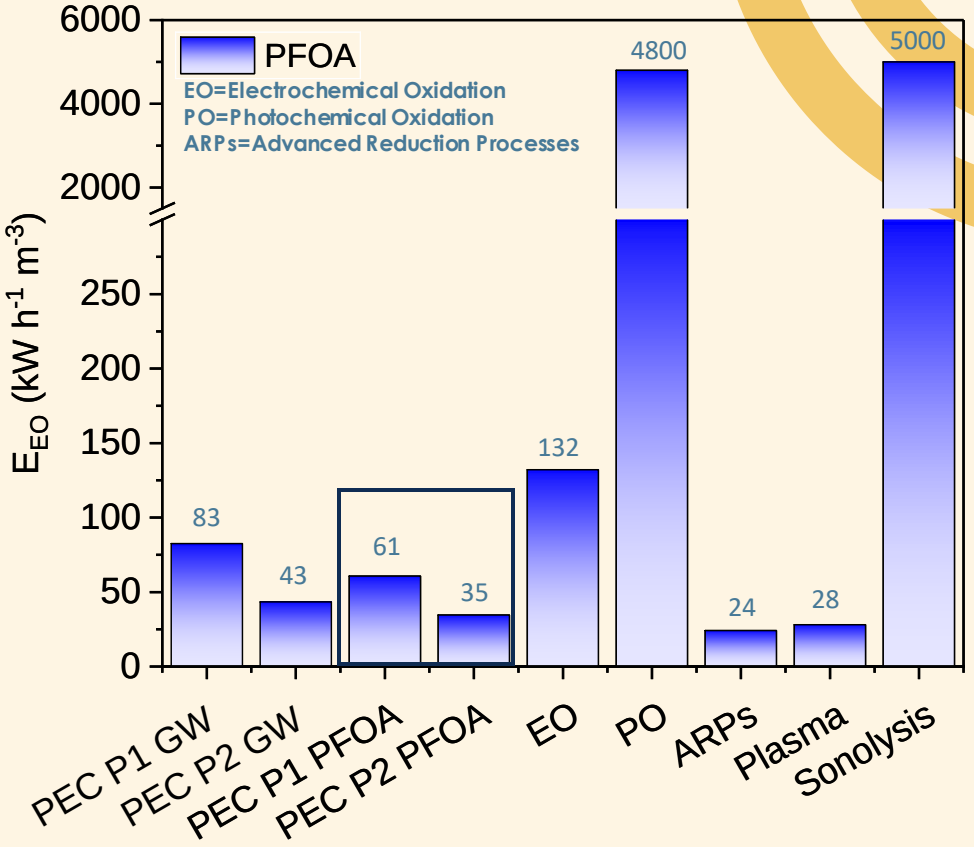



Mainly consists in UV source

$$E_{EO} = \frac{P_{elec} \cdot t \cdot 1000}{V \cdot 60 \cdot log\frac{c_i}{c_0}}$$

=

Electric energy [kWh]
required for the degradation of a contaminant
by one order of magnitude
(90% removal)
in a unit volume of contaminated water
(IUPAC)



# WP3 – Conclusions

## Conclusions

- PEC allows degradation of PFASs.
- Reaction mechanism: transient formation of shorter-chain PFASs.
- Degradation efficacy depending on the nature and quantity of PFASs.
- Process water: indirect evidence of high levels untarget PFASs.
- Preliminary OPEX (lab scale) comparable to the most efficient techniques for PFAS degradation.
- PEC suitable as quaternary/polishing step in WWTPs and GWTPs.

# WP3 – Outlook

## Outlook

- Engineering of PEC reactor & building of pilot plant
- (2-5 $m^3/h$, >50%removal)
- Integration with the other technologies (FF, bio, GAC/resisns)
- Travel all around Europe to test different water matrices

# THANK YOU FOR YOUR ATTENTION

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