PROMISCES

Preventing Recalcitrant Organic Mobile Industrial chemicalS for Circular Economy in the Soil-sediment-water system

PhD: Development of a chemical treatment process for perfluoroalkylated and polyfluoroalkylated substances (PFAS): determination of degradation mechanisms and kinetics

29/03/2024

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The PROMISCES project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 101036449

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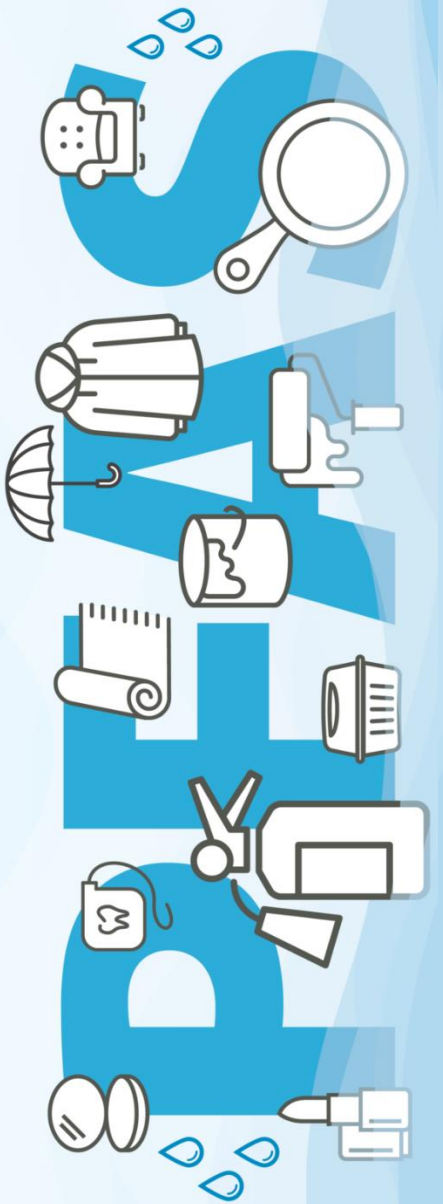
Summary:

I. Context: European project “PROMISCES” and issues associated with PFAS

II. PFOA removal with DMSO and NaOH mixture: principle and analyses

III. Results and short discussion

IV. Conclusions



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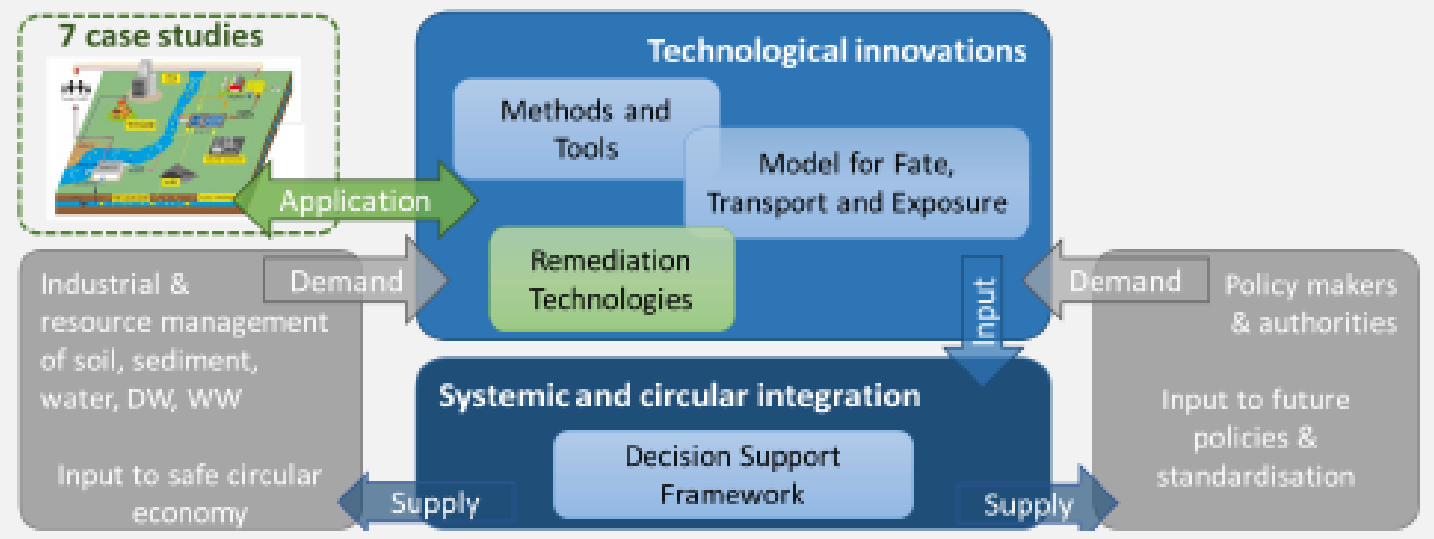
I. Context: European project "PROMISCES"

- ***Objectives of PROMISCES project:***
  - ✓ Contribute to a circular and sustainable economy
  - ✓ Improve the protection of human health and the environment
  - ✓ Overcoming the obstacles posed by the presence of highly persistent, mobile and potentially toxic substances in the soil-sediment-water system.



- ***Organisation in severals work package (WP) :***

❖ WP1: Development and implementation of analytical and toxicological methods and derived monitoring strategies

❖ WP2: Fate, transport and exposure of PM(T) in the environment

❖ WP3: Demonstrating solutions for zero pollution for material cycles and soil-groundwater continuum

❖ WP4: Demonstrating solutions for zero pollution water cycles

❖ WP5: Decision Support Framework for risk management of PM(T) in a circular economy

❖ WP6: Communication, Dissemination and Exploitation

❖ WP7: Project Management and coordination

❖ WP8: Ethics requirements

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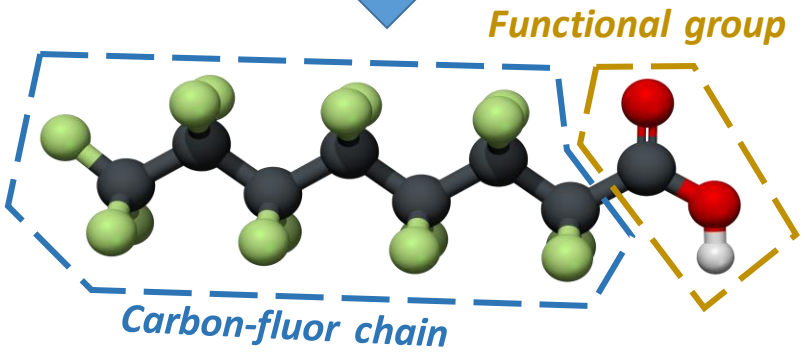
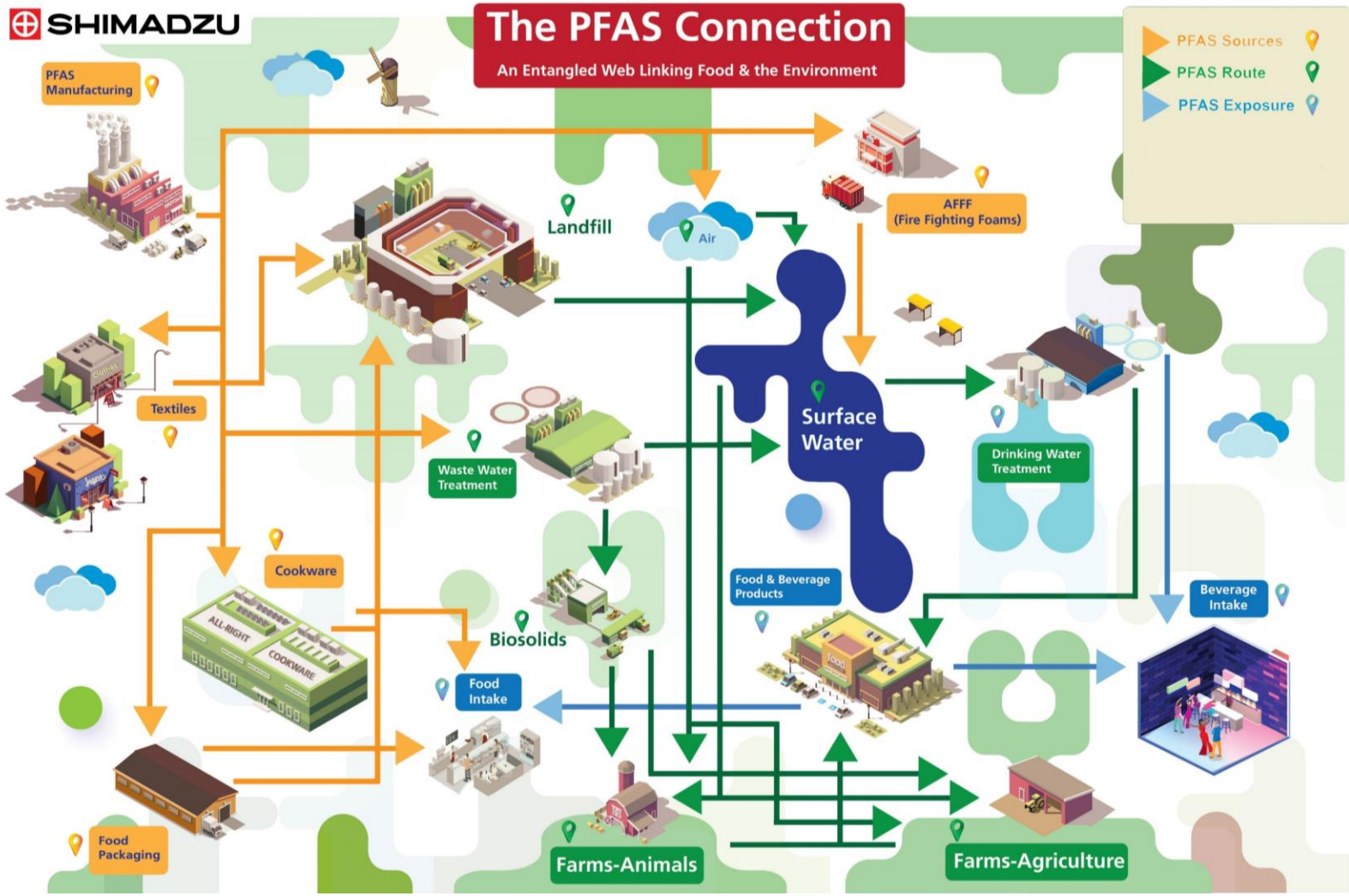
I. Context: issues associated with PFAS

***PFASs*: fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom**



Today, more than 5000 PFAS CAS number

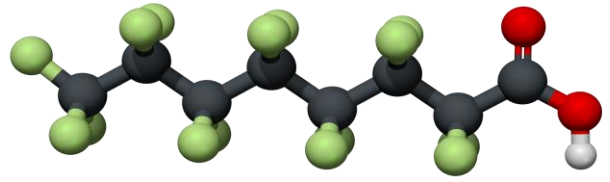


✓ **Principals properties**

- *Hydrophobic (molecule tail)*
- *Hydrophilic (head group)*
- *Thermally stable*

Targeted PFAS:

PFOA ($C_8HF_{15}O_2$)



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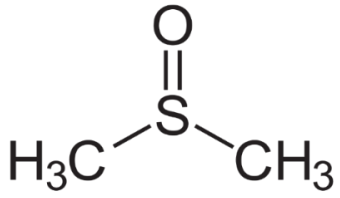
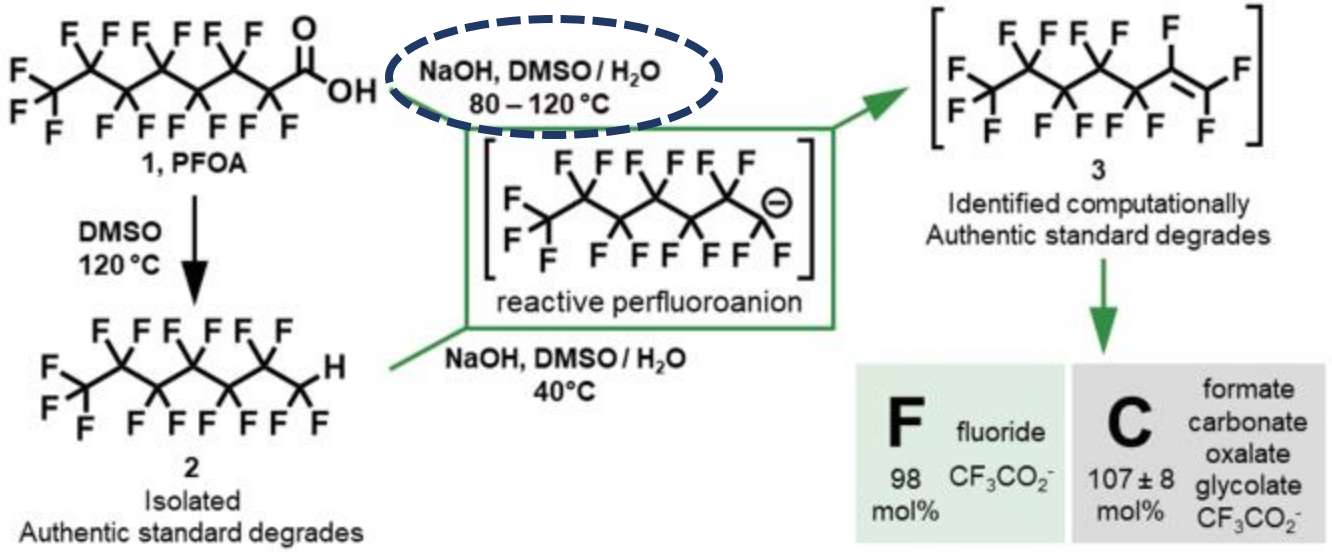
II. PFOA removal with DMSO and NaOH mixture: principle

- ✓ Progressive defluorination of PFOA using a DMSO/NaOH mixture (Trang, B. et al., Science, 2022).
- ✓ DMSO/NaOH ratio (8/1 v/v)
- ✓ NaOH/PFOA ratio (3/1 mol/mol)
- ✓ Temperature activation
  ⇒ breaks the carbon-functional group bond
- ✓ OH^- is responsible for the progressive defluorination of PFOA until trifluoroacetate CF_3COO^- or TFA is obtained

***DMSO*:**
polar aprotic solvent



Basic pH - polar aprotic solvent
OH^- ⇒ nucleophile



*Simplified degradation mechanism of PFOA in a DMSO/NaOH mixture (*Trang, B. et al., 2022)

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II. PFOA removal with DMSO and NaOH mixture: analysis

➢ Analytical procedure

Experimental conditions:

Vials of 20 mL:

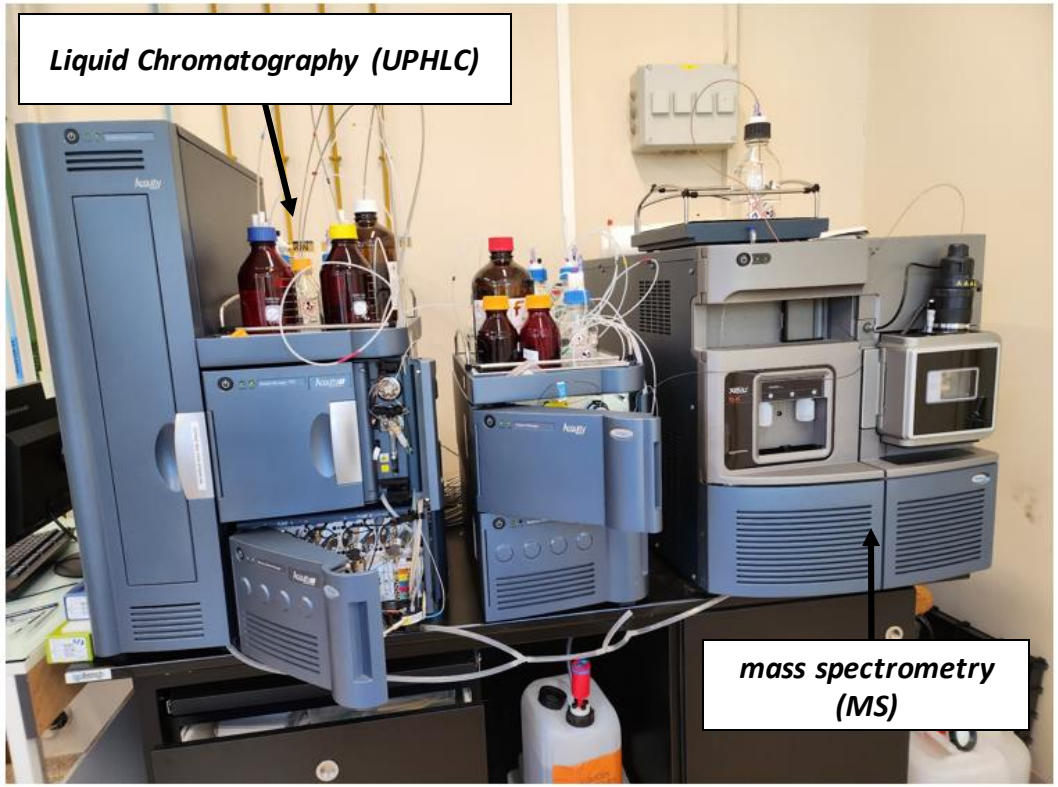
- Solution volume: 5,6 mL
- DMSO/NaOH (25g/L) ratio: 8/1 (v/v)
- PFOA concentration: 900 mg/L
- NaOH/PFOA molar ratio: 3/1
- Moles of F : $8{,}21.10^{-6}$ M
- **Total F: 580 mg/L**

Temperatures:

- 90°C
- 120°C

Reaction time: 144 hours

Liquid Chromatography-mass spectrometry (UPHLC-MS) for the determination of PFOA removal and PFOA degradation by-products



Liquid chromatography equipment with an ultra-high pressure chain coupled to a mass spectrometer (UPLC-MS)

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II. PFOA removal with DMSO and NaOH mixture: analysis

➢ Analytical procedure

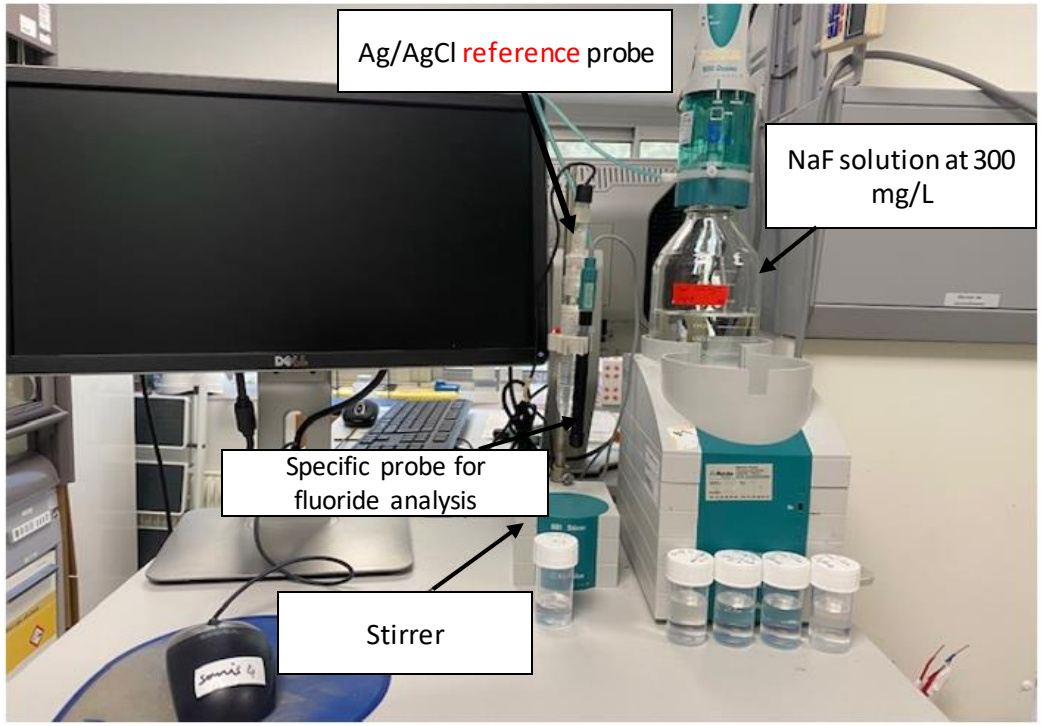
Protocol:

- Dilution (35 times) and pH adjustments (HNO_3 4%; Tisab 4)
- Analysis with a specific F^- electrode after calibration using the dosing addition method
- **F^- measurement range: 5 - 50 mg/L**

Utility of Tisab 4 :

✓ Preserve the pH of the analyte
✓ Decomplex fluoride

Fluoride measurement by potentiometric titration



Potentiometric titrator for fluoride ions

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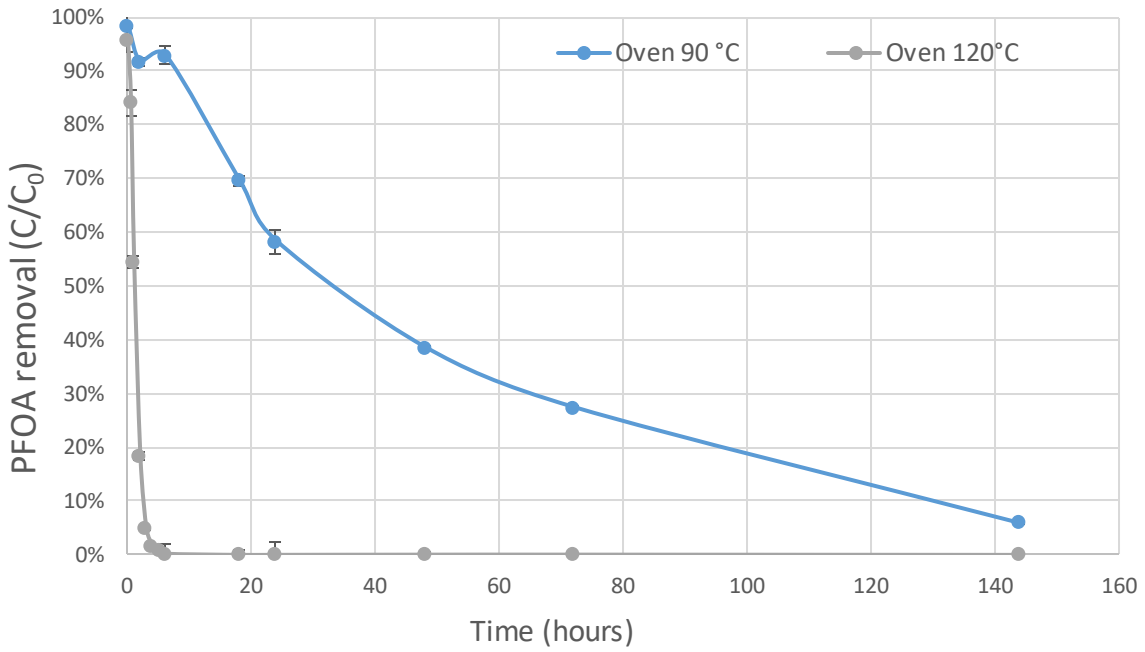
III. Results and short discussion

➢ PFOA removal with DMSO/NaOH

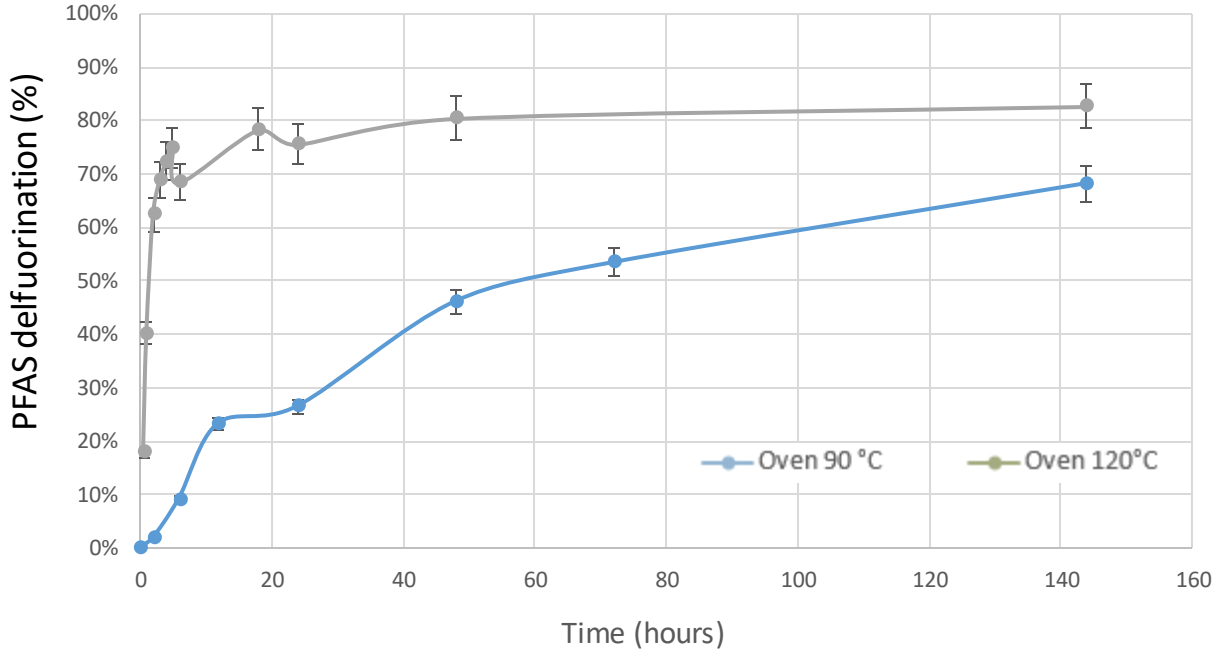
Evolution of PFOA removal versus time (hours)



- ✓ 80% of defluorination (PFOA and by-products) at 120°C after 18h
- ✓ 70% of defluorination at 90°C (oven) after 144h

➢ PFAS defluorination with DMSO/NaOH

PFOA and by-products defluorination versus time (hours)



- ✓ Defluorination of PFOA and by-products validated
- ✓ Occurrence of a persistent degradation by-product, possibly CF_3COO^- according to Trang, B. et al., Science, 2022

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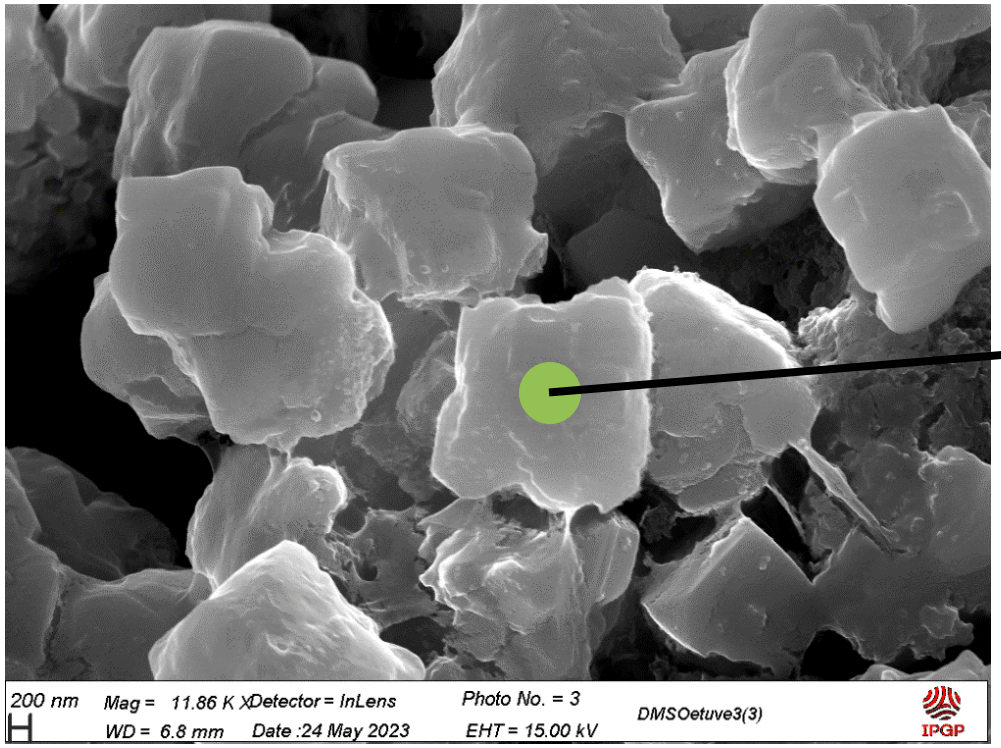
III. Results and short discussion

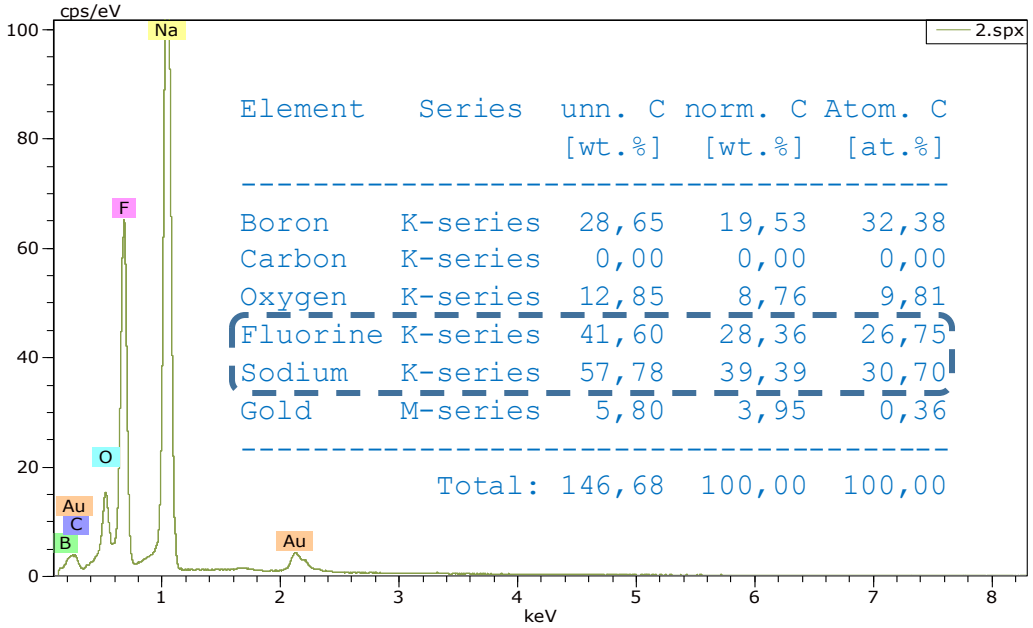
➢ PFAS defluorination with DMSO/NaOH

SEM photograph of sodium fluoride (NaF) crystals

20 µL of dried PFOA/DMSO/NaOH mixture after interaction at 120°C for 144 hours



EDS analysis on the face-centred cubic solid



Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
Boron	K-series	28,65	19,53	32,38
Carbon	K-series	0,00	0,00	0,00
Oxygen	K-series	12,85	8,76	9,81
Fluorine	K-series	41,60	28,36	26,75
Sodium	K-series	57,78	39,39	30,70
Gold	M-series	5,80	3,95	0,36
Total:		146,68	100,00	100,00

- ✓ Observation of NaF crystals
- ✓ Defluorination process of PFOA validated

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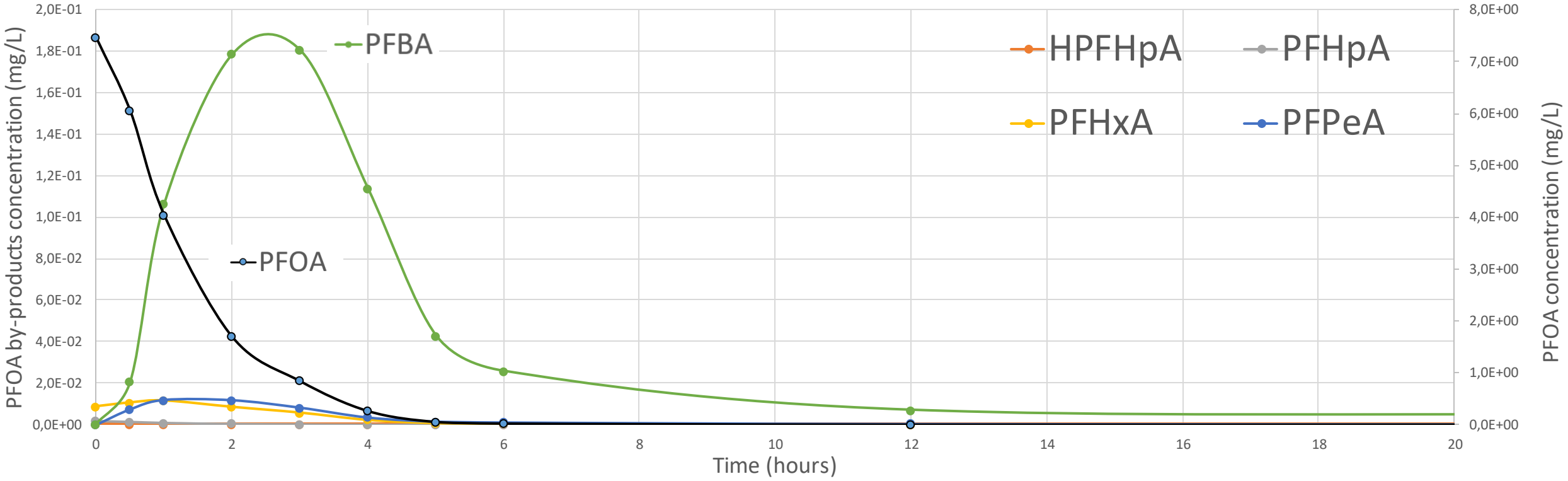
III. Results and short discussion

➢ **PFOA removal test with DMSO/NaOH : *investigation of PFOA by-products***

PFOA and by-products defluorination versus time (hours) for 120°C kinetic



✓ Presence of PFBA quantified by MS analysis (only 2% or 3% of initial PFOA concentration) between 30 min and 12 hours of reaction at 120°C

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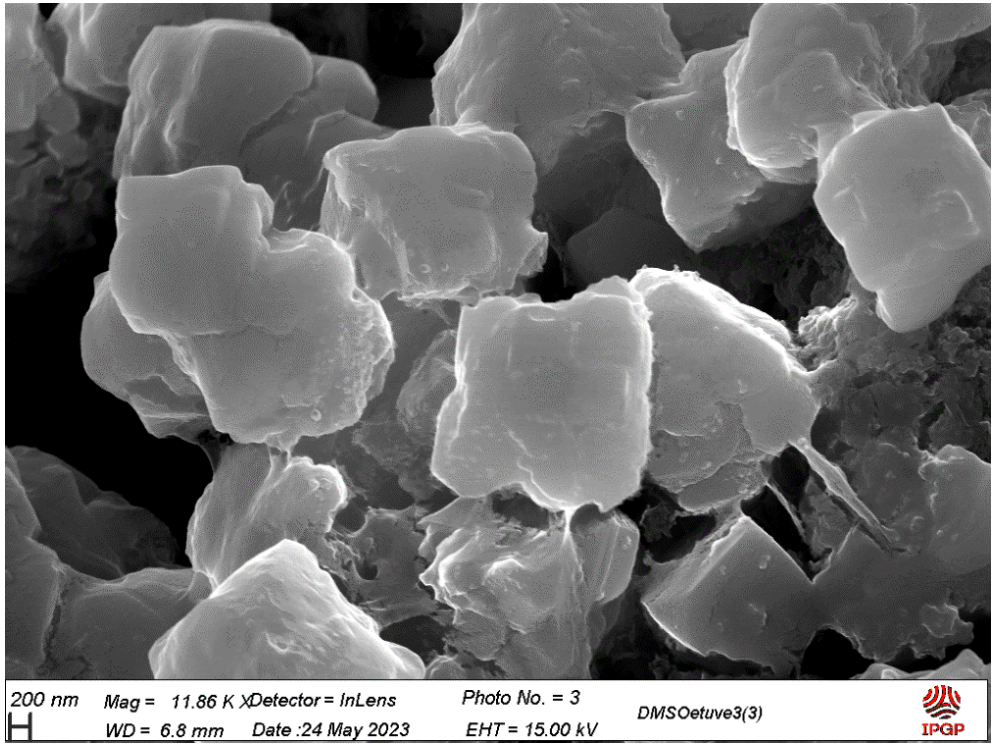
IV. Conclusions

SEM photograph of sodium fluoride (NaF) crystals



PFOA degradation in DMSO/NaOH:

- ✓ Total PFOA removal at 120°C in only 6 hours
- ✓ Not complete PFOA removal after 144 hours at 90°C (92%)

- ✓ Defluorination process:
  - ✓ SEM-EDS analyses
  - ✓ Potentiometric titration of F^-: 80% of PFOA defluorination at 120°C after 18h
  - ✓ UPHLC-MS: PFOA and by-products defluorination versus time (hours)
    - ✓ Quantified : PFBA with 2% or 3% of initial PFOA concentration

- ✓ **Need further analytical investigation for the molecular identification and the quantification of PFOA by-products**

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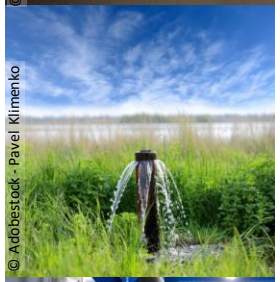

Thank you for your attention

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Thanks to

- the BRGM project manager : J. Lions

- the BRGM analysis team: Anne Berrehouc, Anne Togola, Sébastien Bristeau, and Emeline Coisy

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Full title: Preventing Recalcitrant Organic Mobile Industrial chemicalS for Circular Economy in the soil-sediment-water System

Coordinator: Philippe Negrel (BRGM)
Deputy Coordinator: Julie Lions (BRGM)
Communication Leader: Nicole Heine (DECHEMA)
Beneficiaries: 27 partners
Type of Action: RIA
EU contribution: 12M€
Duration: 01/11/2021 - 30/04/2025

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