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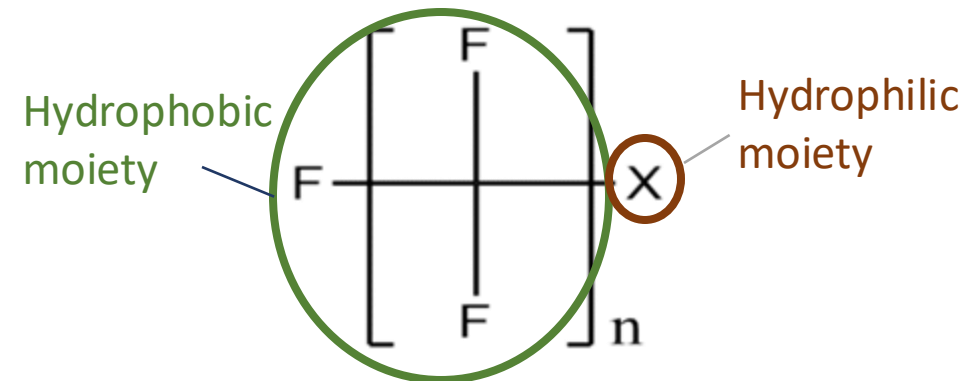
EAU
GRAND SUD-OUEST
AGENCE DE L'EAU ADOUR-GARONNE

Introduction to per- and polyfluoroalkyl compound (PFAS):

PFAS chemistry:

PFAS are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-\text{CF}_3$) or a perfluorinated methylene group ($-\text{CF}_2-$) is a PFAS. (OECD, 2021)

Those molecules are constituted of a hydrophobic alkyl chain and a hydrophilic moiety $\rightarrow$ Amphiphilic molecules (Buck *et al.*, 2011)



With X =

- $-\text{COOH}$ $\rightarrow$ Perfluoroalkyl carboxylic acid (PFCA, $n=1$ to 17)
- $-\text{SO}_2\text{OH}$ $\rightarrow$ Perfluoroalkyl sulfonic acid (PFSA, $n=1$ to 12)
- $-(\text{CH}_2)_2-\text{SO}_2\text{OH}$ $\rightarrow$ Fluorotelomer sulfonate (FTSA, $n=4,6,8,10$)
- And many others...

PFAS properties:

- High mechanical strength
- High thermal and chemical stability
- Lubricating
- Surfactant
- Etc.

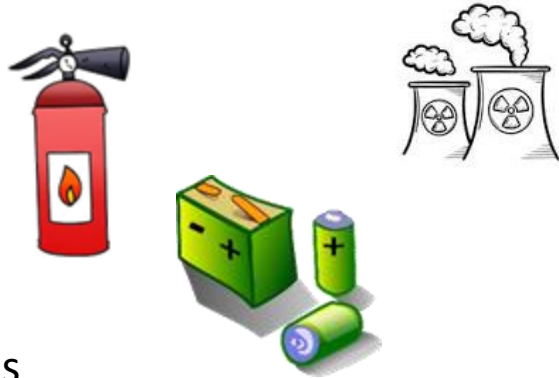
> 15 000 different compounds

Introduction to per- and polyfluoroalkyl compound (PFAS):

PFAS uses:

They are more than 200 uses for PFAS, in industrial field but also in daily life (Glüge *et al.*, 2020) :

- Fire-fighting foams
- Energy sector (e.g., nuclear)
- Biotechnology
- Cosmetics
- Cook- and baking ware
- Textile production
- Coatings, paints and varnishes
- Etc.



Environmental concern:

- Some PFAS have been proven to be toxic
- Presence of perfluorinated acids precursors (pre-PFAAs), unattributed and attributed, which can be transformed into perfluorinated acids on the long term (i.e. secondary source of PFAAs)
- Persistent, mobile and can biomagnify
- Less than 100 compounds are routinely analysed

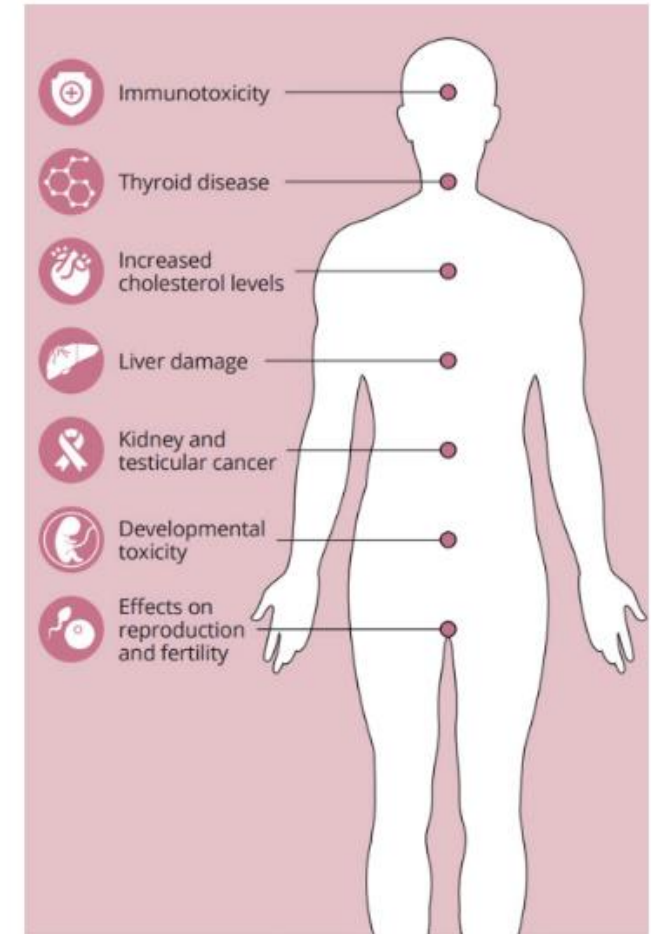


Illustration of reported effects of PFAS on humans
(from Brunn *et al.*, 2023)

GARBURE Project:

The Garonne River:

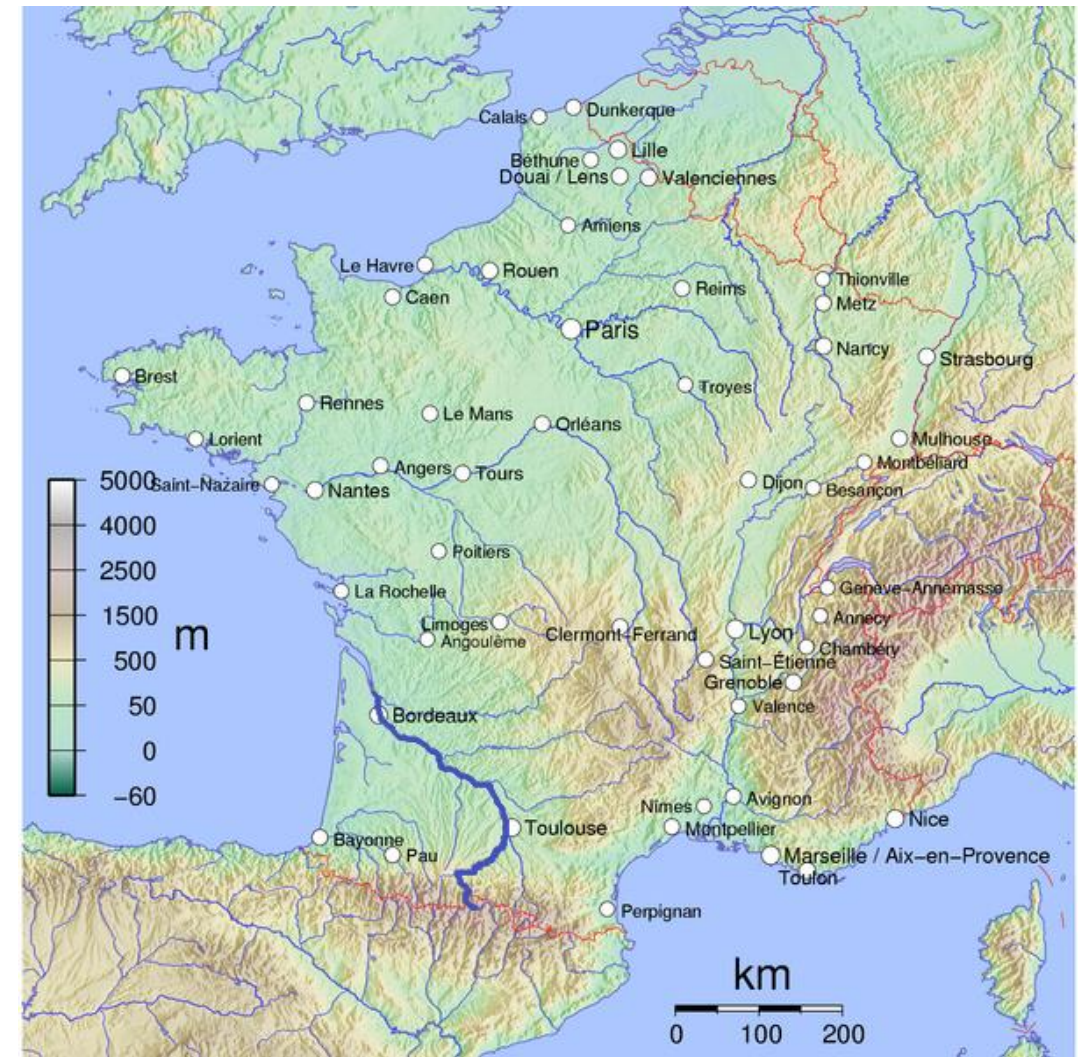
- 529km long from Spain to the Atlantic ocean
- 55 000 km² of watershed
- Meet with Dordogne to form the Gironde estuary

The Garonne River is subject to human activities; the watershed is home to millions of people, with cities such as Toulouse, Agen, and Bordeaux, and their activities with :

- Nuclear plants
- Airport
- Urban areas
- Industries (paper, pharmaceuticals, etc.)

The becoming of PFAS in the Garonne is known for only **8 compounds**. In this context the GARBURE project have 3 goals:

1. Estimate the concentration of 47 PFAS in the sediments and the water of the Garonne and their environmental behavior.
2. Studied the transfer of PFAS to the biofilm, the first link to the food chain.
3. Estimate the concentration of unknown pre-PFAAs using alternative methods.



Material and methods:

Sampling strategy:

- 2 sampling campaign (C1: September 2024, C2: March 2025)
- 21 sites were selected on the Garonne River and its tributaries
- Sediments, water and biofilm were sampled on each site

Sample treatment:

Upon arrival at the laboratory, sediment and biofilm samples were freeze-dried, finely ground, sieved at 2mm and stored at room temperature in an amber glass jar prior to extraction.

Water was store at 4°C and send at the UMR LEGOS for the analysis. LOD ranged from 0.01-0.3ng/g dw.



Micro-wave extraction
(MeOH+50mM
ammonium acetate)

Purification on graphite
cartridge (Envi-Carb)

HPLC-MS/MS analysis

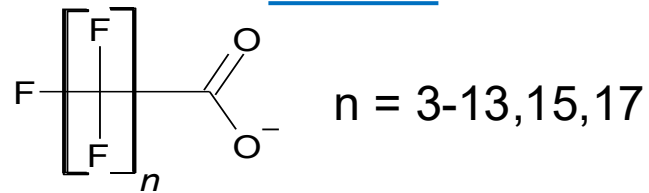


Map of the sampling sites on the Garonne River and its tributaries

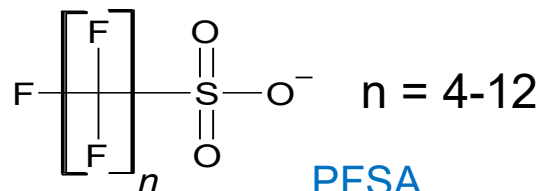
Material and methods:

Molecules analysed:

23 PFAA

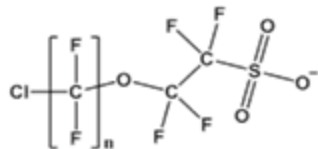


PFCA

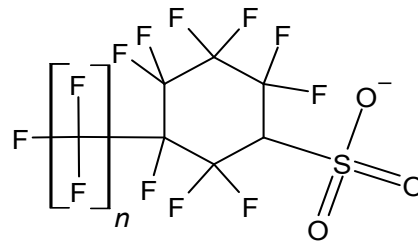


PFSA

8 PFAA alternative

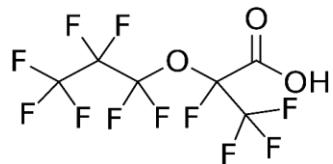
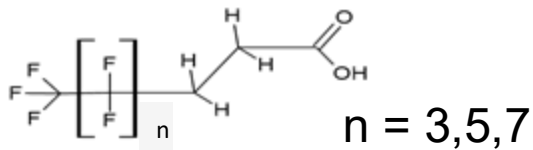


F-53B (major and minor)

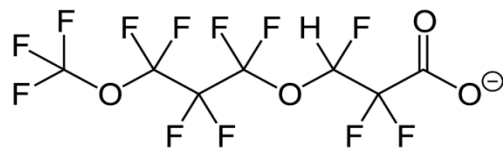


PFECHS

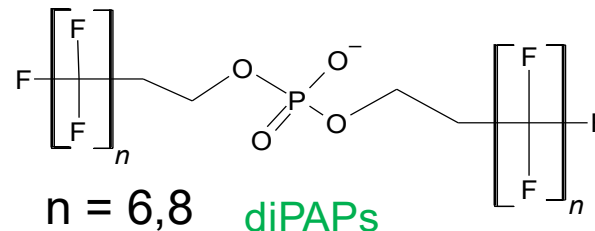
FTCA



GenX

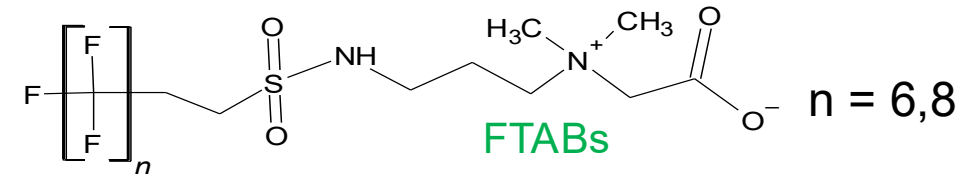


ADONA

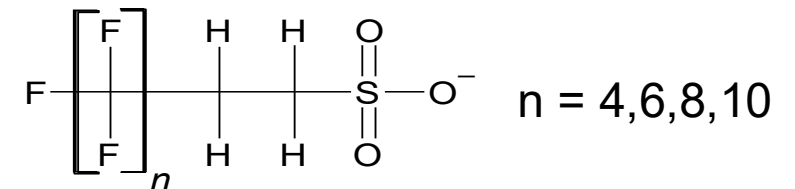


diPAPs

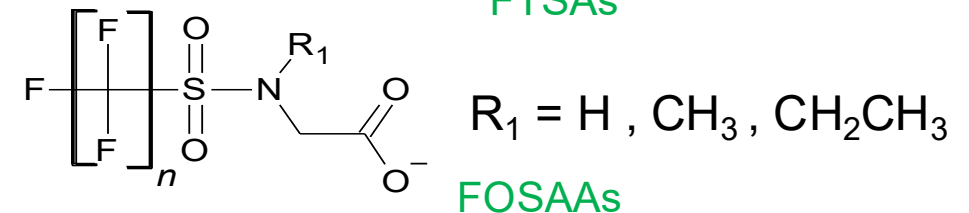
14 (pre-PFAA)



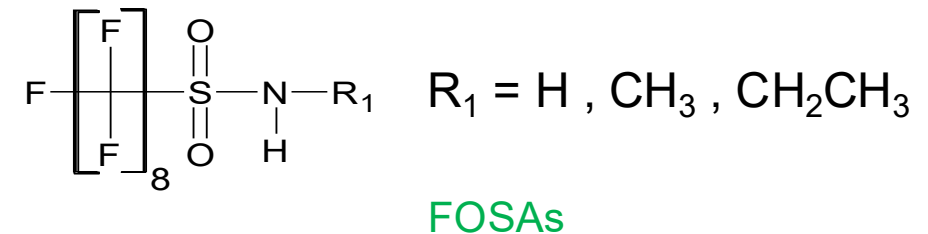
FTABs



FTSAs



FOSAAs



FOSAs

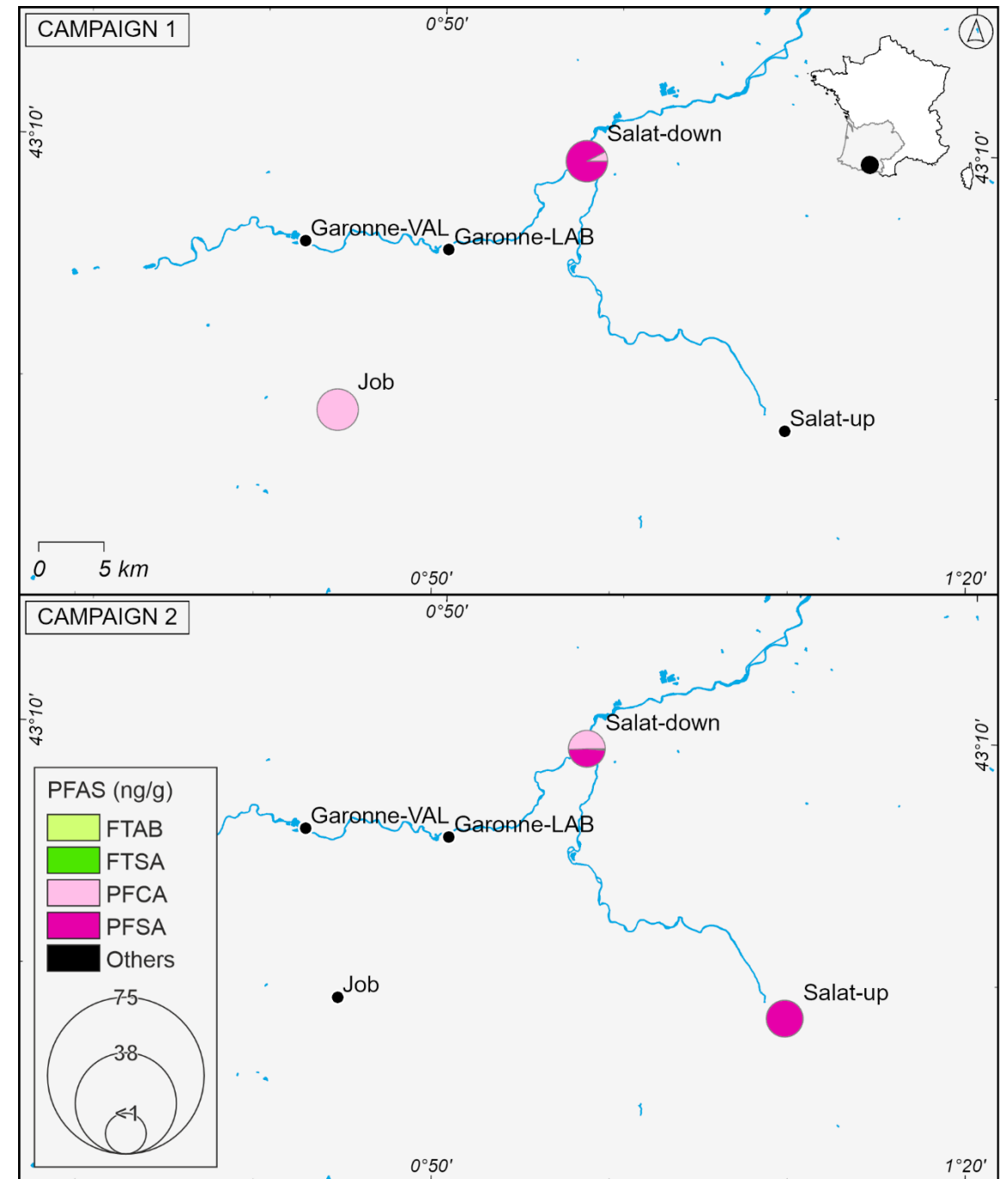
Results and discussion:

Watershed Head results:

- Detection of PFAS on 40% of the sites on both campaigns
- Low contamination levels on both campaigns ($<1\text{ng/g,dw}$)
- Max $[\text{PFAS}]_{\text{tot}} = 0.9\text{ng/g, dw}$, at the Salat down tributaries
- Molecular profile dominated by PFCA and PFSA with a threshold effect (*e.g.*, $[\text{PFNA}] = 0.025\text{ ng/g dw}$ and $\text{PFNA LOD} = 0.02\text{ ng/g dw}$ at Job-C1)
- PFHxA is the major compound with concentration up to 0.25ng/g, dw , followed by PFOS up to 0.15ng/g, dw

Rural fingerprint:

- Low level of contamination
- No industrial plant in the direct vicinity of the Garonne River or its tributaries
- Presence of PFAA only from either degradation of pre-PFAA, residual contamination or atmospheric deposition



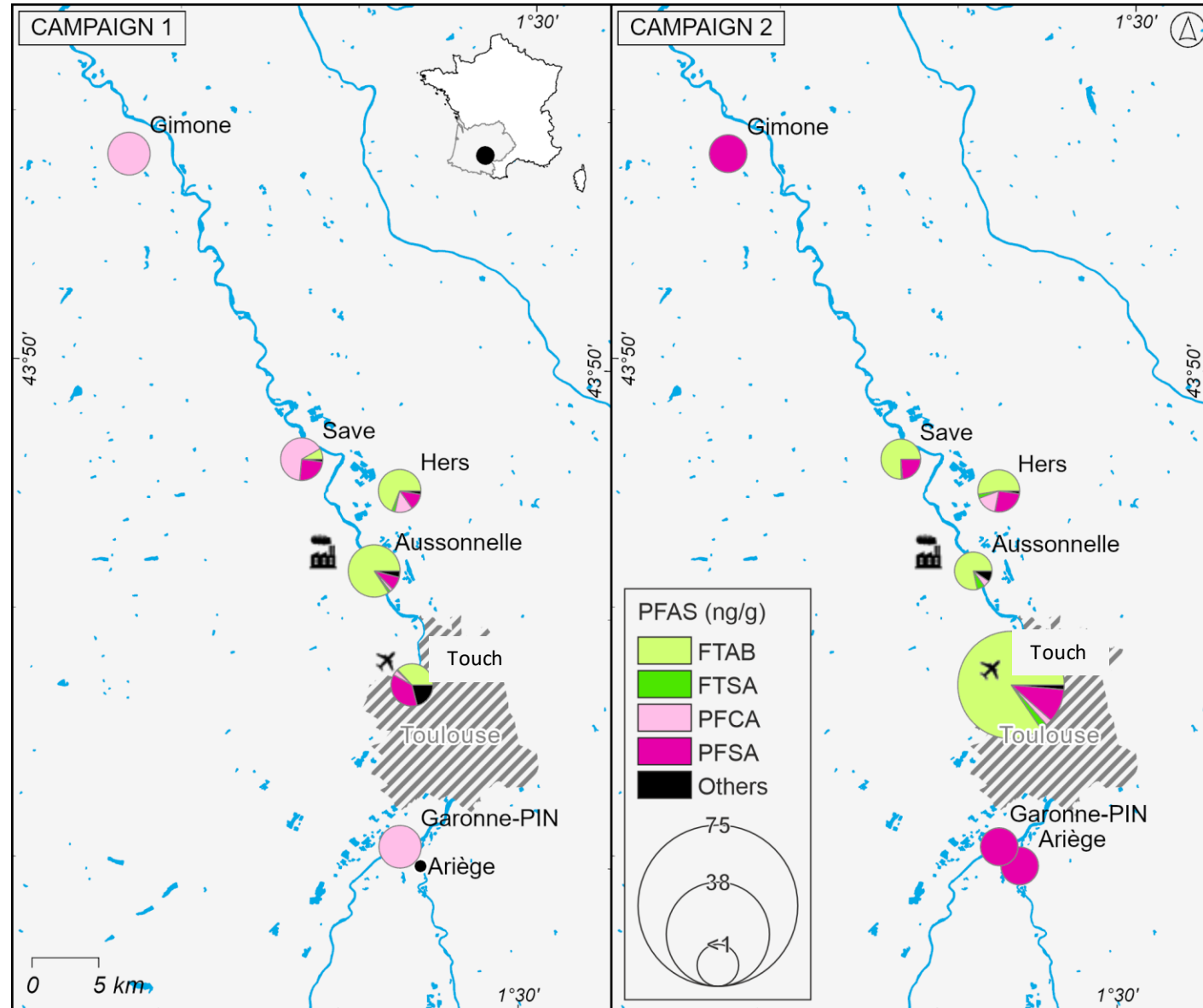
Results and discussion:

The Garonne River around Toulouse:

- Detection of PFAS on 85% of the sites for C1 and on all sites for C2
- Contamination levels range from 0.05 ng/g (Gimone) up to 14 ng/g (Aussonnelle) in C1 and from 0.03 ng/g (Gimone) up to 36 ng/g (Touch) in C2
- Molecular profiles dominated by 6:2 FTAB (<0,09-31 ng/g dw) and PFOS (<0.02-4 ng/g dw)
- Decrease in the total concentration on C2 except for the Touch, may be due to soil leaching.

Industrial fingerprint:

- Important level of contamination
- Profiles dominated by PFAS emitted by human activities (e.g., airport with fire fighting foam)
- Presence of pre-PFAA at high concentrations



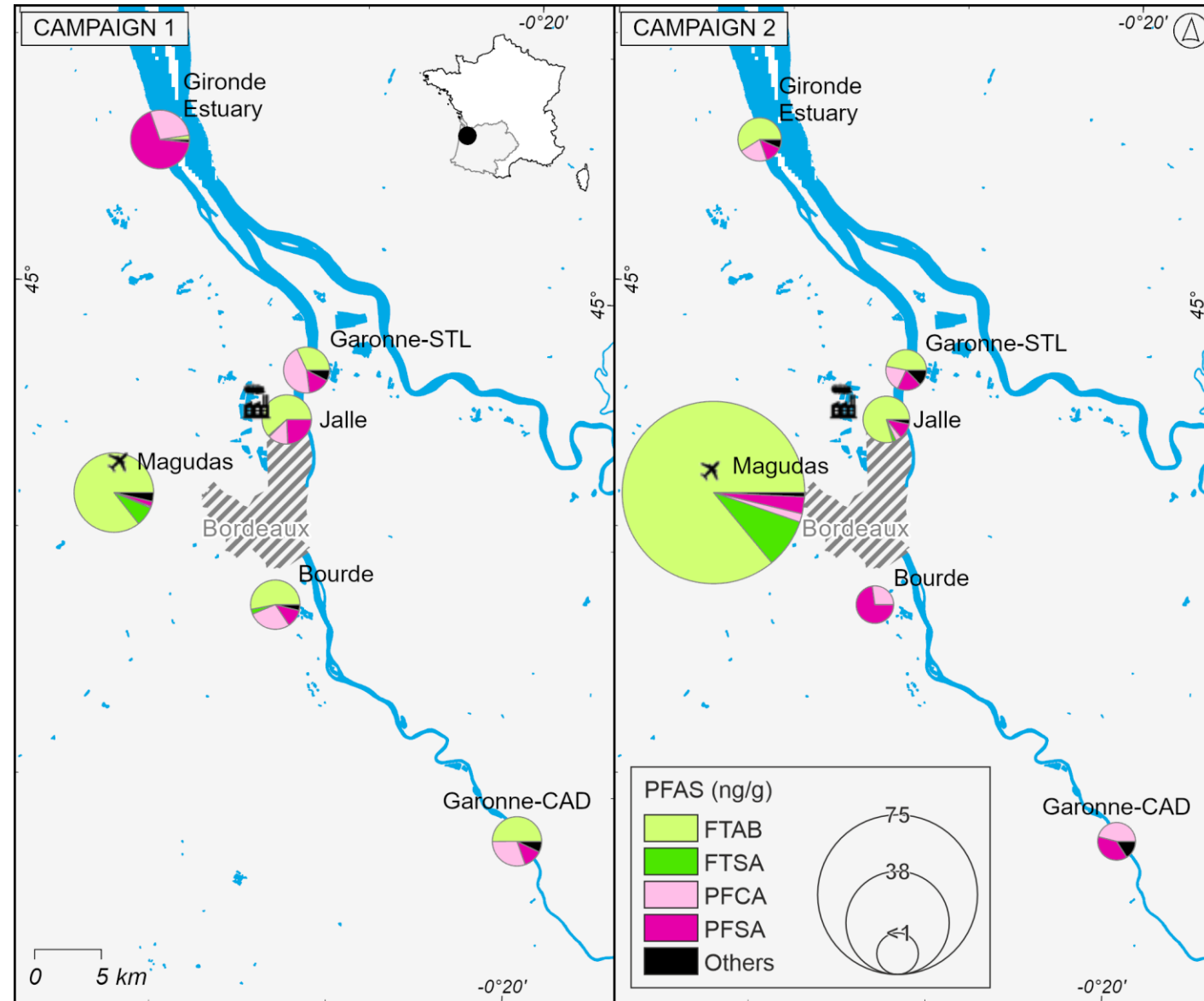
Results and discussion:

The Garonne River in the Gironde estuary:

- Detection of PFAS on 100% of the sites for both campaign
- Contamination levels range from 3.1 ng/g (Garonne-STL) up to 22 ng/g (Magudas) in C1 and from 0.1 ng/g (Bourde) up to 75 ng/g (Magudas) in C2
- Molecular profiles dominated by 6:2 FTAB (<0,09-60 ng/g dw), PFOS (<0.02-6 ng/g dw) and 6:2 FTSA (<0.2-6.3 ng/g dw)
- $[PFAS]_{tot}$ is homogenous on the Garonne River samples

Industrial fingerprint:

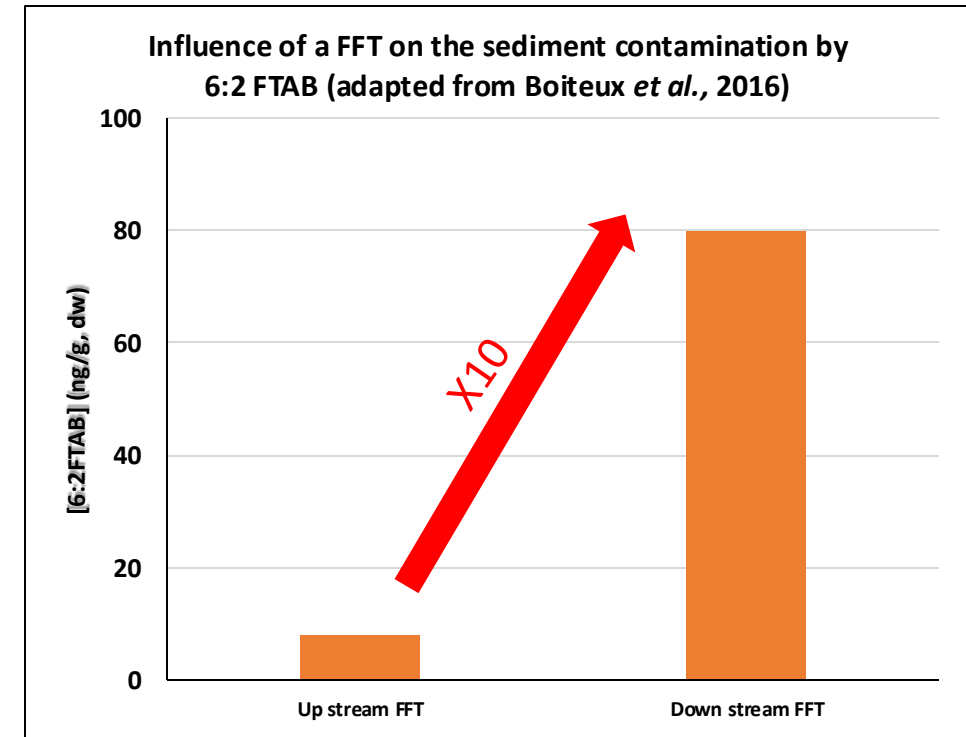
- Important level of contamination
- Profiles dominated by PFAS emitted by human activities (e.g., airport with fire fighting foam)
- Presence of pre-PFAA at high concentrations



Results and discussion:

Global information:

- PFAS were detected on **93%** of the samples for C1 and **88%** for C2, similar as Macorps *et al.*, 2023 (86%) and Campo *et al.*, 2016 (100%)
- **9 compounds** were not detected at all : PFNS, PFTrDS, 4:2FTSA, 8:2 diPAP, FPrPA, 9Cl-PFONS, 11Cl-PFOUdS, HFPO-DA and NaDONA
- **L-PFOS** and **PFDODA** have the highest detection frequency (80% and 76.5% respectively), similar as in Macorps *et al.*, 2023
- **L-PFOS** and **6:2 FTAB** represents **24.7%** and **23.2%**, on average of $\Sigma\text{PFAS}_{\text{tot}}$ and 6:2 FTAB represent **73 $\pm$ 17%** of the targeted pre-PFAA
- 6:2 FTAB is the main compound uses in the AFFF since 2010 (BRGM. 2024)
- Airport and fire-fighting training areas (FFT) are well known to be **major sources of PFAS contamination** across the world which is consistent with literature¹



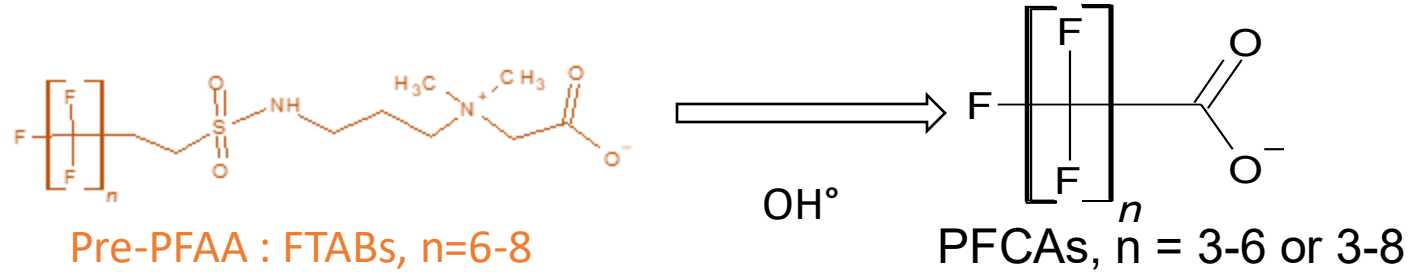
1:
Houtz *et al.*, 2013: <https://doi.org/10.1021/es4018877>
Filipovic *et al.*, 2015: <https://doi.org/10.1016/j.chemosphere.2014.09.005>
Nickerson *et al.*, 2021: <https://doi.org/10.1021/acs.est.0c00792>

Results and discussion:

Estimation of unattributed pre-PFAA using Total Oxidisable Precursor assay (TOP assay):

Principle:

- (1) $\text{S}_2\text{O}_8^{2-} + \text{heat} \rightarrow 2\text{SO}_4^{\cdot-}$
- (2) $\text{SO}_4^{\cdot-} + \text{OH}^- \rightarrow \text{OH}^\circ + \text{SO}_4^{2-}$
- (3) $\text{Pre-PFAA} + \text{OH}^\circ \rightarrow \text{PFCA}$



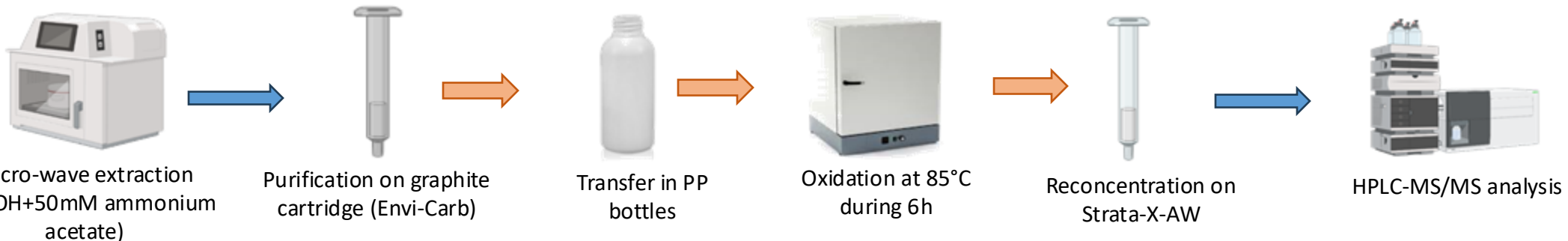
Δ PFCA:

$\Delta\text{PFCAs} = \sum n\text{PFCAs}_{\text{after oxidation}} - \sum n\text{PFCAs}_{\text{before oxidation}} \Longrightarrow$ Amount of PFCAs formed upon oxidation, i.e proxy of the amount of pre-PFAAs oxidised in the extract

n pre-PFAA_{unattributed}:

$n \text{ pre-PFAAs}_{\text{unattributed}} = \Delta\text{PFCAs} - n \text{ pre-PFAAs}_{\text{targeted}} \Longrightarrow$ Estimation of the amount of pre-PFAAs_{unattributed} in the extract

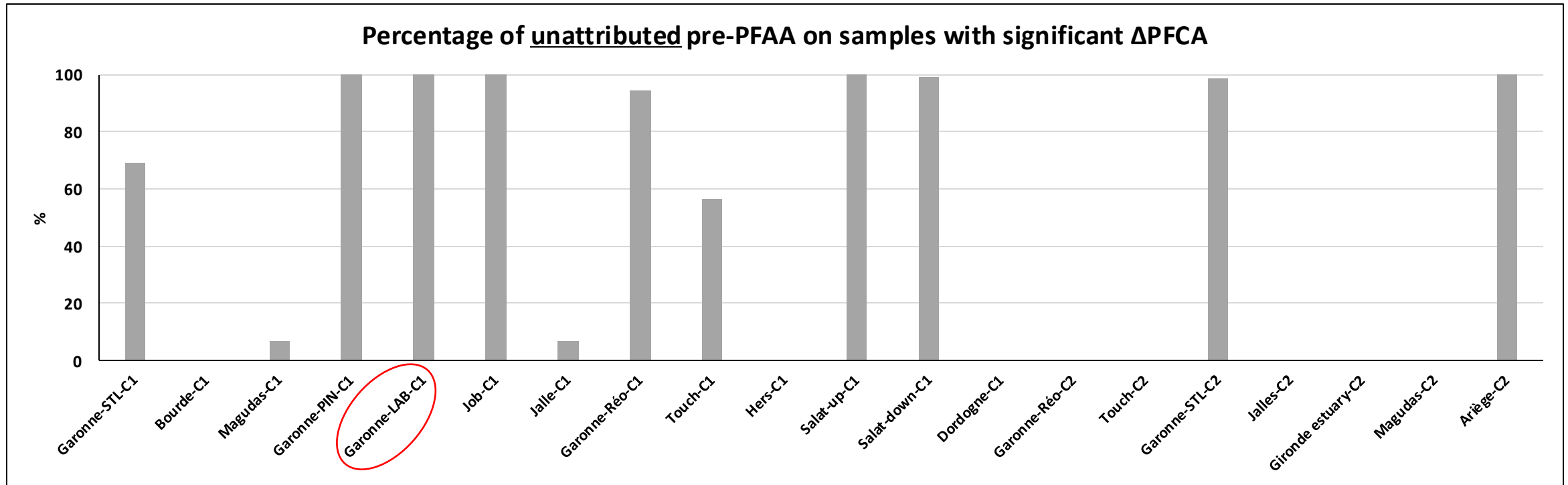
Protocol:



Results and discussion:

TOP assay results:

- 80% of the samples have a significant Δ PFCA values (**Δ PFCA =0.01-0.32 nmol/g**)
- 1 site which displayed Σ PFAS < LOD using targeted analysis showed a significant Δ PFCA values indicating the presence of unattributed pre-PFAA
- Unattributed pre-PFAA have a median contribution of 57% in PFCAs formed

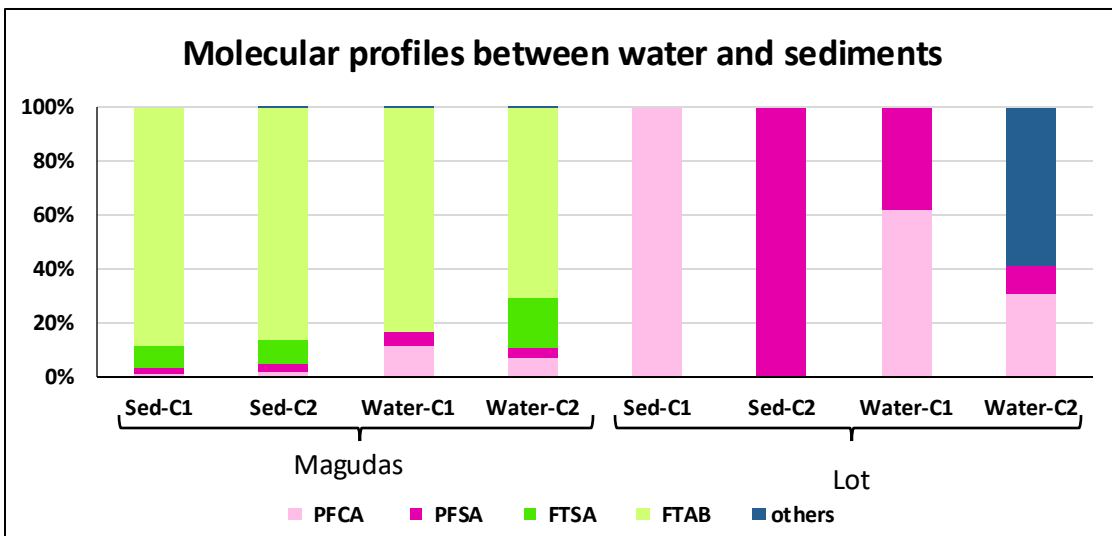


There is a hidden contamination on some sites, which emphasis the need to use alternatives methods in the characterisation of PFAS contamination in the environment.

Results and discussion:

Comparison with water results:

- PFAS were detected in 98% of the water samples with $[PFAS]_{tot}$ ranging from <LOD-1 400 ng/L (Garonne-STL and Magudas) for C1 and from 0.6-5 200 ng/L (Salat-up and Magudas) for C2
- 6:2 FTAB is the PFAS with the highest concentrations, up to 3 000 ng/L, followed by PFPeA with concentrations up to 800 ng/L



- Molecular profiles tend to be similar between water and sediments in urban areas and rural areas
- Distribution within a compound family differs between the matrices, for example: short chain PFCAs (C3-C6) represent 80% of the $[PFCAs]_{tot}$ in water but only 22% in sediments

→ Analysis of different abiotic matrices provides a better overview of the PFAS

Estimated log Kd:

Log Kd	6:2 FTAB	PFOS	PFNA
This study	1.8±0.5	2.1±0.8	1.77 ±0.9
Boiteux <i>et al.</i> , 2016	0.65	0.94	/
Chen <i>et al.</i> , 2020	1.7±0.7	1.65±0.7	1.6
D'agostino <i>et al.</i> , 2017	1.1	2.0±0.4	/
Chevreuil et Labadie, 2011	/	2.4±0.2	1.5±0.1

The Log Kd determined in this study are in the same range as other studies.

Results and discussion:

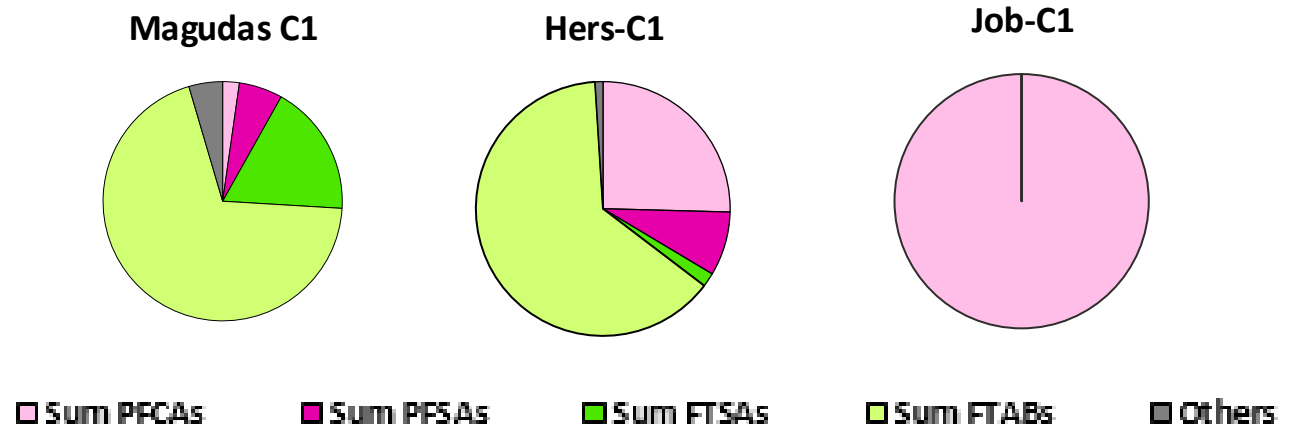
Biofilm results:

- PFAS were detected in 98% of biofilm samples with $[\text{PFAS}]_{\text{tot}}$ ranging from <LOD-392 ng/g dw
- $[\text{PFAS}]_{\text{tot}}$ is generally higher in biofilm than in sediment (Table 1)
- The 6:2 FTAB is the predominant PFAS with concentrations up to 350 ng/g dw, followed by 8:2 FTAB (80 ng/g dw) and PFOS (40 ng/g dw)

Site	$\frac{[\text{PFAS}]_{\text{tot biofilm}}}{[\text{PFAS}]_{\text{tot sediment}}}$
Magudas-C1	5,7
Magudas-C2	3,6
Touch-C1	4,1
Touch-C2	10,9
Bourde-C1	2,7
Bourde-C2	124,2
Save-C1	12
Save-C2	1,4
Hers-C1	217
Hers-C2	1,1
Salat-down-C1	0,02
Salat-down-C2	0,1
Garonne-STL-C1	1,8
Garonne-STL-C2	0,9

Table 1: Bioconcentration factors from sediment to biofilm

Molecular profiles are the same as in the sediment:



Total [PFAS] in biofilm is up to 217 times higher than in sediment, suggesting a preferential accumulation of these compounds from the environment

Conclusions:

PFAS are **ubiquitous**, they have been detected in all the matrices analysed in this study. The levels and profiles of contamination in sediment, water and biofilm reflect the human activities in the area of the Garonne river, with higher $[\text{PFAS}]_{\text{tot}}$ at the cities of Toulouse (31 ng/g dw) and Bordeaux (75 ng/g dw).

The use of the TOP assay **reveals a hidden contamination of unattributed pre-PFAA**. To have a better understanding of the PFAS contamination, targeted analysis are not sufficient and alternatives techniques should be used such as TOP and HRMS.

Next step:

Using data of the TOC to normalise the concentration and highlight the influence of the organic matter on the retention and adsorption of PFAS.

Performing statistical analyses to identify significant trends and correlations in the dataset.
Exploring the sites typology (*e.g.*, rural/urban/airports...).

Acknowledgments:

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The Environmental Science department of the University of Bordeaux for the congress funding.



The SedNet organisation, for giving me the opportunity to make an oral presentation.



Thank you for your attention !

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