ENVIRONMENTAL METROLOGY CHALLENGES FOR A BETTER UNDERSTANDING OF THE SOURCES AND TRANSFER OF PFAS IN THE ENVIRONMENT

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Géosciences pour une Terre durable
brgm

What are the challenges facing environmental monitoring?

✓ Over 10,000 compounds: which ones to track?

Source-specific compounds

Poor information (industrial secrecy / user ignorance)

Temporal evolution of uses (regulatory restrictions + technological developments)

✓ Different pathways of degradation/transfer depending compartments

Need to know degradation pathways

Specificity of different compartments (soil/surface water/groundwater)

To answer which questions? Occurrence?, Risk? Management?

These questions determine **what** to track, **where, how** and associated **analytical performances to reach**.

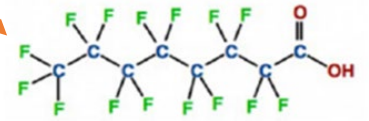
PFOA example..

End of production 2011 / end of use 2023

aqueous film-forming foam (AFFF)

Used in

degradation

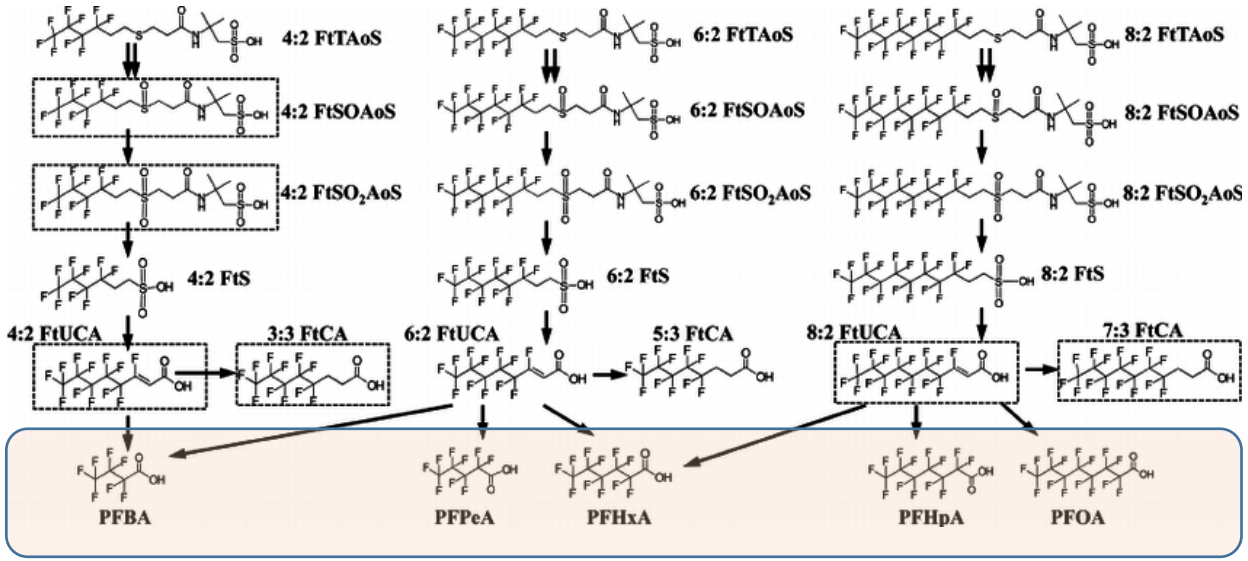


Used in → Polymers PVDF, PTFE

Used in → Pesticides ?

- Same compound as source and degradation by product :

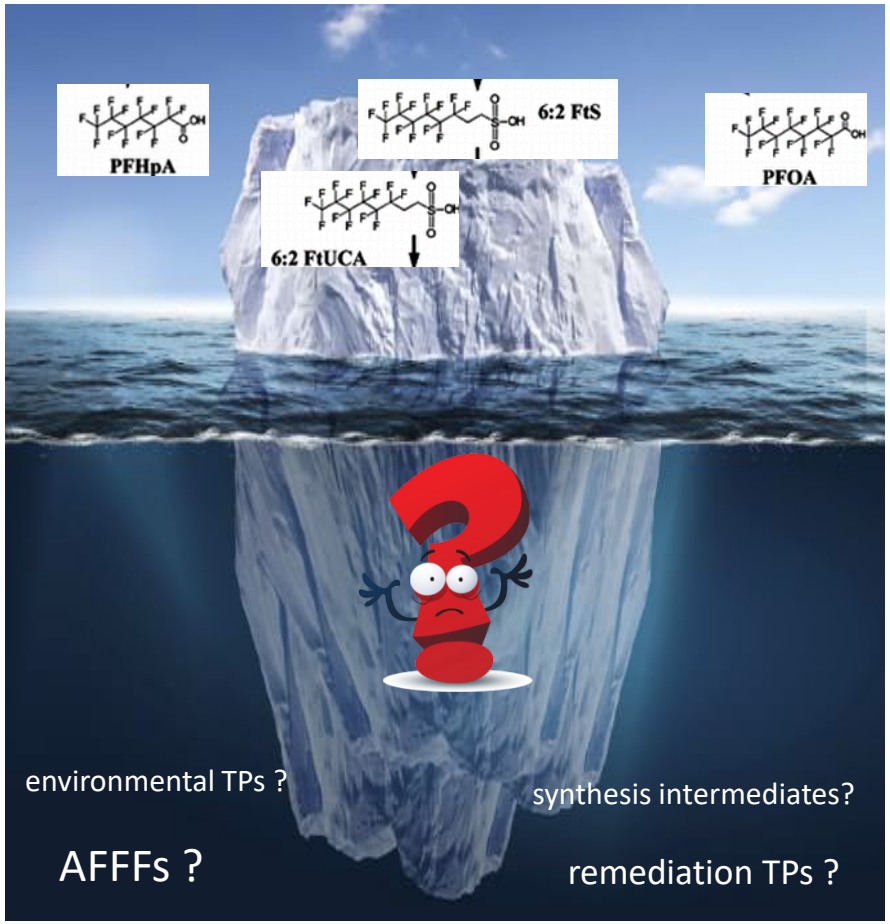
⇨ need to identify precursors and degradation pathways ..



The PFAS Universe

Less than 200 compounds :

- Identified
- with analytical standards
- with adapted methods



Expectation for PFAS

Most « relevant compounds »

PFAS to identify the source of pollution
PFAS to be remediate
PFAS to monitor in drinking water
…

At low concentrations levels
In all matrix of interest
…

An overview of stackeholder expectations…

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What were the main challenges in making steps towards foreseen advancement beyond the state of the art (related to Ambition1)

Methods developed depending on the objectives to reach

sediment

suppression of high matrix effects
Purification/dilution

Low cost
Quick and few sample prep

surface water

Others..

sludge

PFSA

PFCA

High/variable concentration
Large linear range

Heterogeneity of matrix
= robustness

FOSAs

Low LOQ
sensitivity

Large panel of compounds to consider
In the same method =
making compromise

Liquid waste

landfill

FTSAs

Drinking water

PFECA

FOSAAs

waste water

PAPs

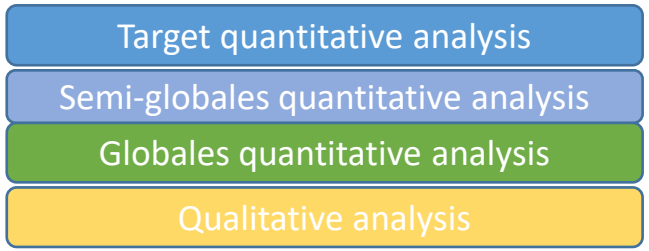
biota

process water

What are the challenges facing environmental monitoring?

knowledge challenges :

- New PFAS of interest ?
- Precursor's fate ?
- PFAS pattern related to specific sources ?
- Degradation by-products during remediation ?
- …



Objectives; : Propose and distinguish:

- Methods fit for purpose for research needs ?
- Method fit for purpose for regulation, management ..

Regulatory issues

List of few PFAS (20-28)

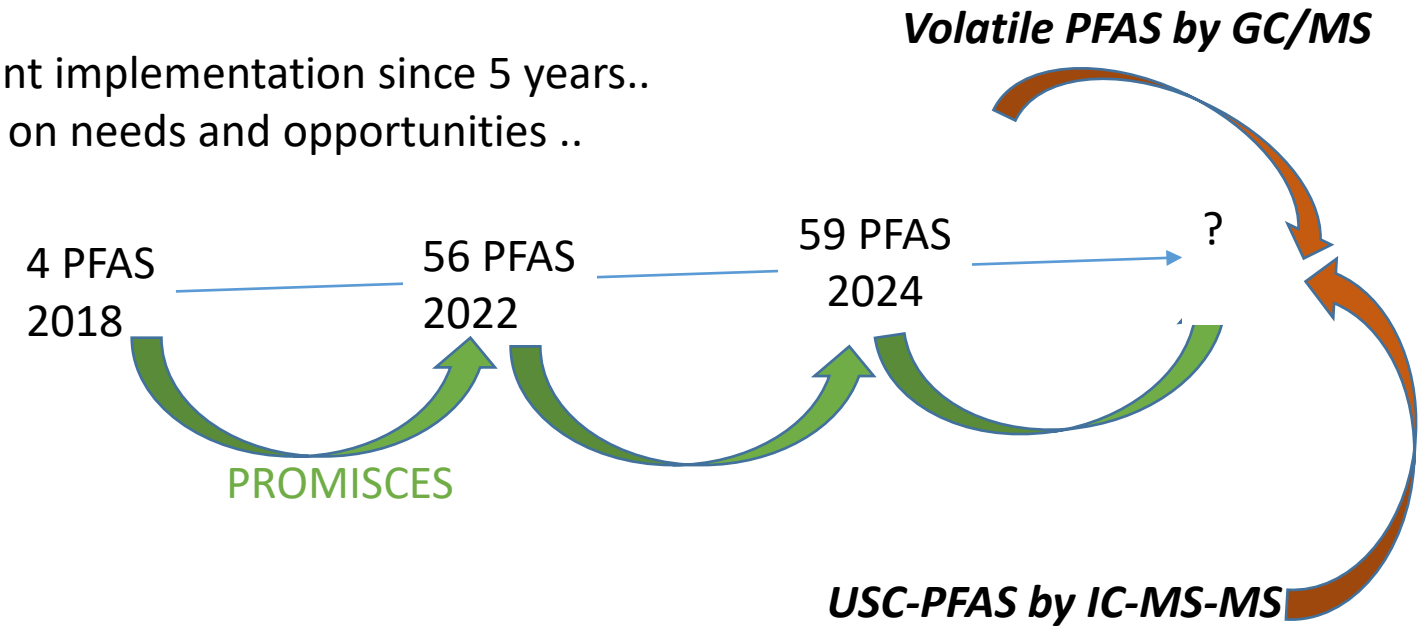
Need of low analytical performance (ng/L sub ng/L)

Other methods fit for purpose ??

Approaches implemented at BRGM

Target quantitative analysis

Constant implementation since 5 years..
based on needs and opportunities ..



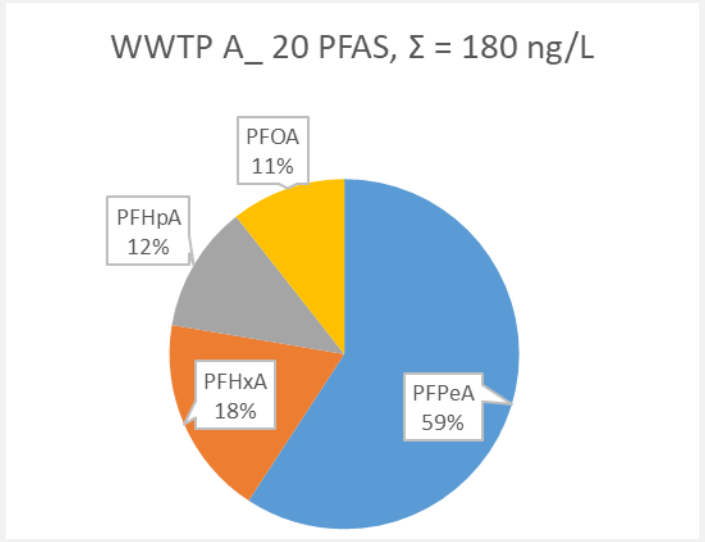

Acquity I-Class Waters® UPLC chain coupled to a Xevo TQD Waters® tandem mass spectrometer.

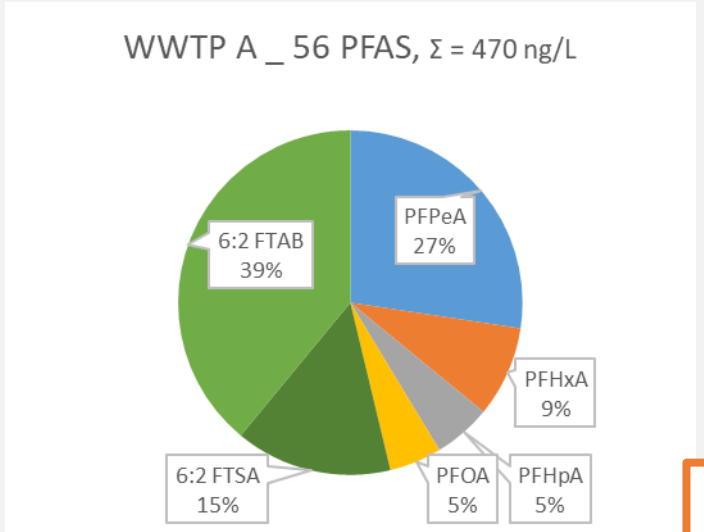
\+ Robust and reliables methods

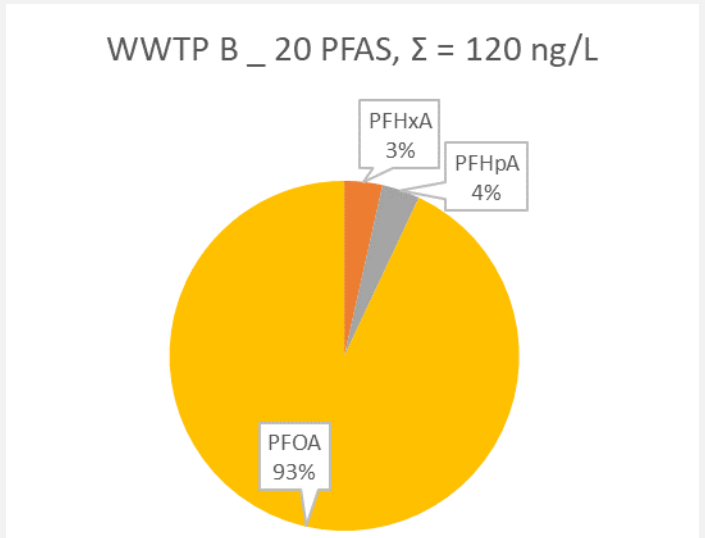
\- Limitation based on available standards

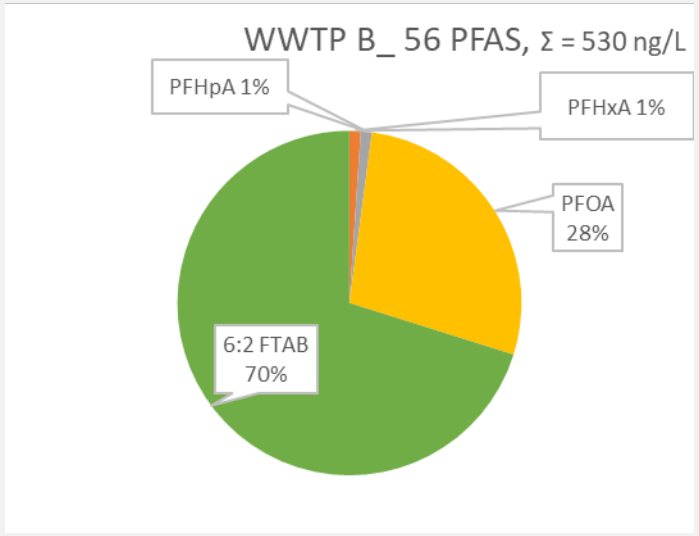
- Need of several analysis to cover different needs :
  from LC/MS/MS to IC/MS/MS and GC/MS/MS

Impact of the targeted list of compounds on data understanding





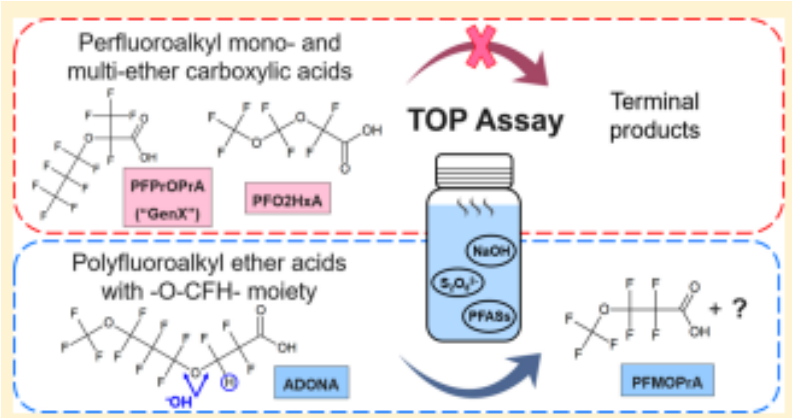




2 urban WWTP on the same areas (5 km)
Different PFAS fingerprints with the PFAS-20
but highly underestimated without 2 compounds..

Semi-globales quantitative analysis
Total oxidizable precursors « TOP »

- To have a better picture about the PFAS content
- Considering that main PFAS can be oxidized in a restricted list of PFAS



Zhang et al, EST Letters, 2019

+ More complete picture

+ Assesment of the potential of the « PFAS contamination » to be degraded in « persistant PFAS »

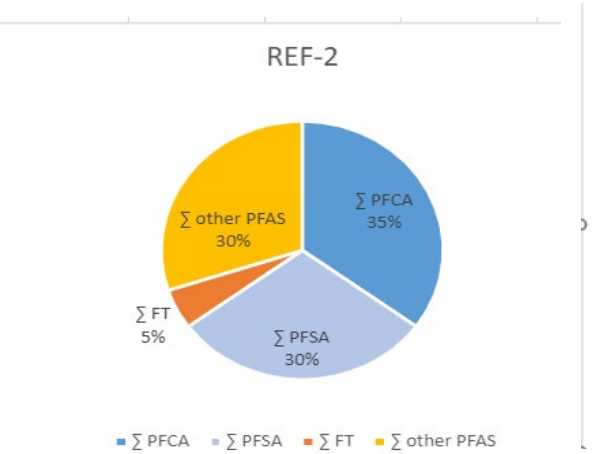
- Method should be better defined (lack of robustness , list of compounds analyzed, need of data on oxidability of some precursors..)

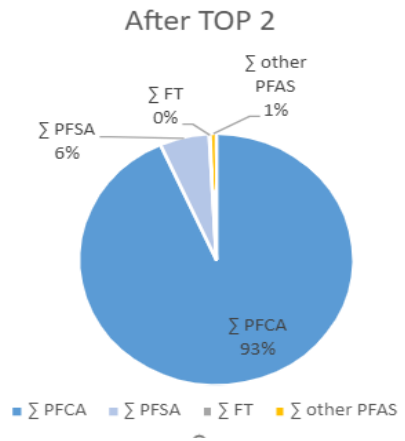
- No information on PFAS pattern

- should be used in association with targeted analysis

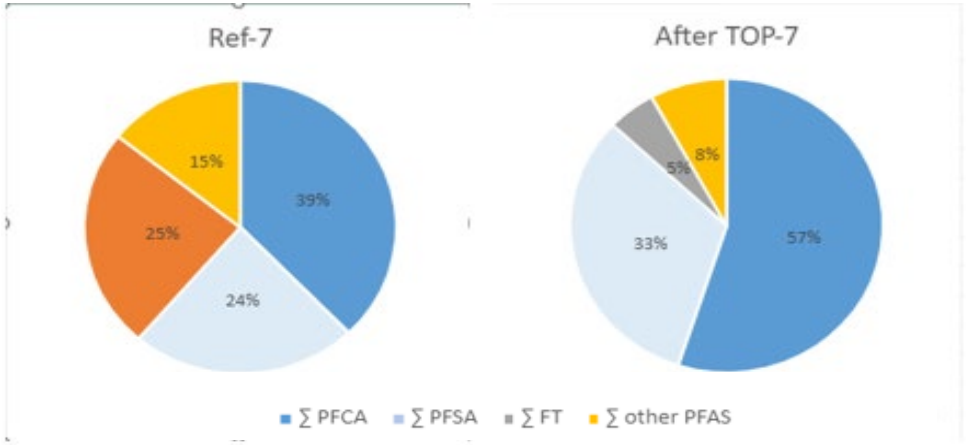
Some examples..

Blue : PFCA/PFSA « 20 DWD »
Orange : other PFAS oxidisable
Yellow : other PFAS partially oxidisable ..





TOP assay give a simplified view … based on short list of compounds



BUT : some compounds are not oxidisable..
or not completly ..

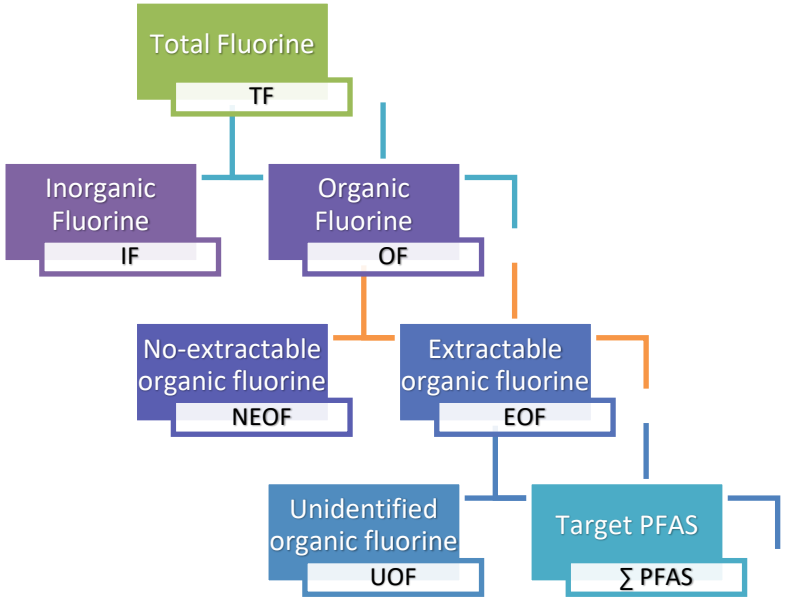
Interesting method:
Easier way to have a better overview

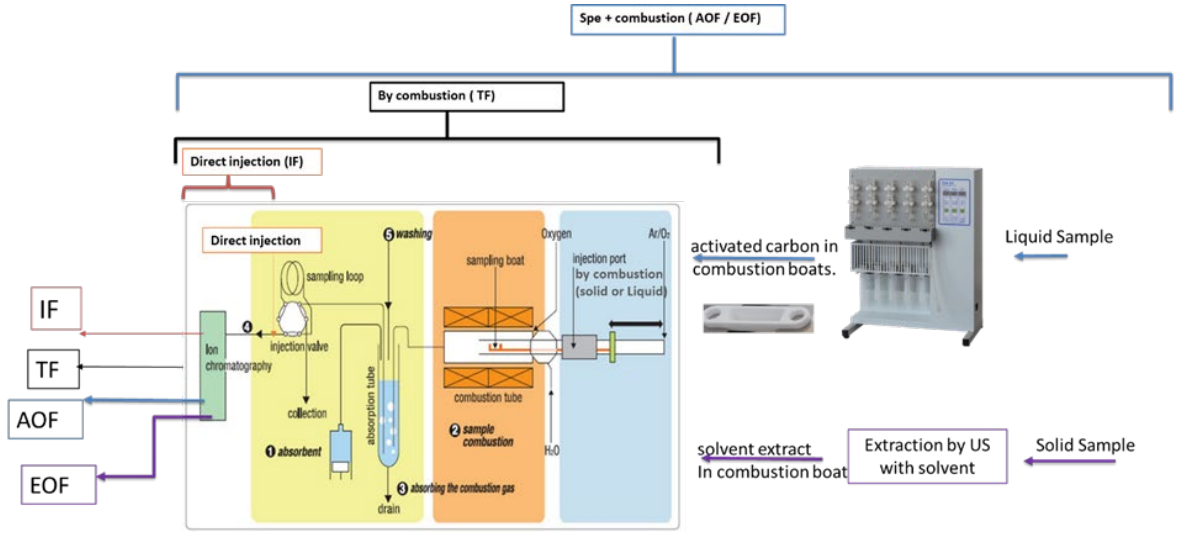
But need more robustness and QA/QC methods

	concentration ng/L		
	before TOP	after TOP	6:2 FTS oxidation efficiency
WWTP	1285	126	90%
WWTP	391		100%
Indus WWTP	1092	229	79%
Indus WWTP	24624	136	99%
Indus WWTP	1062367	1572	100%

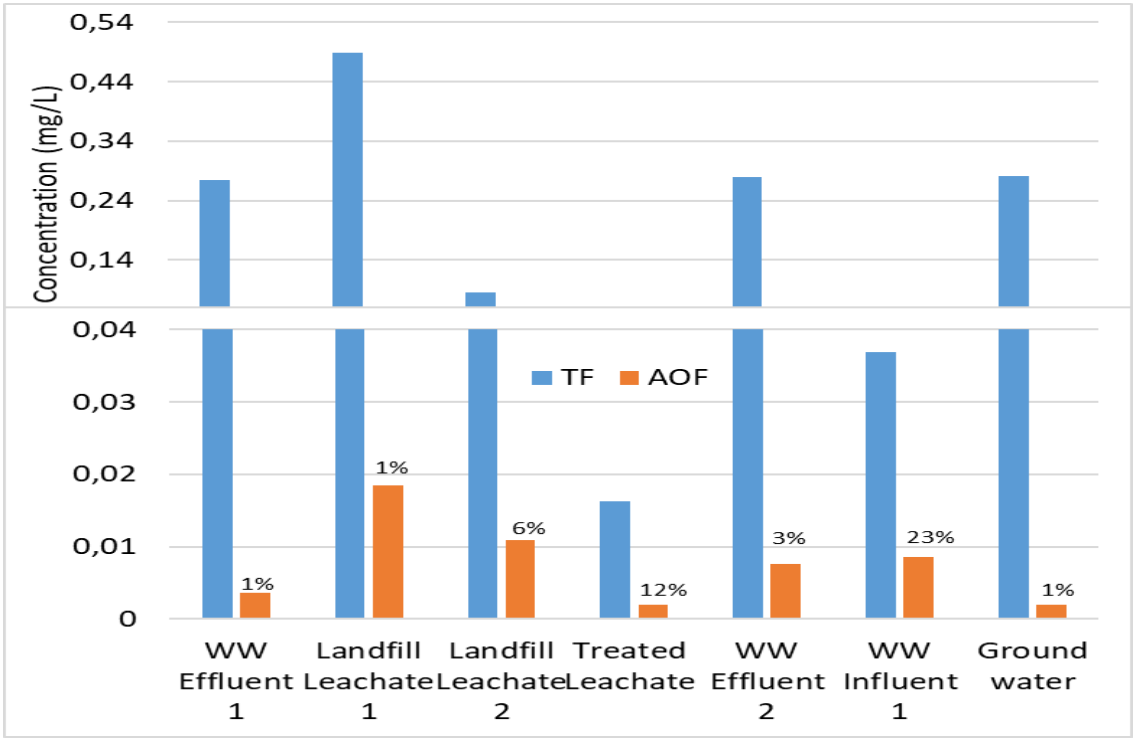
Global quantitative analysis

- Global analysis of fluorine compounds



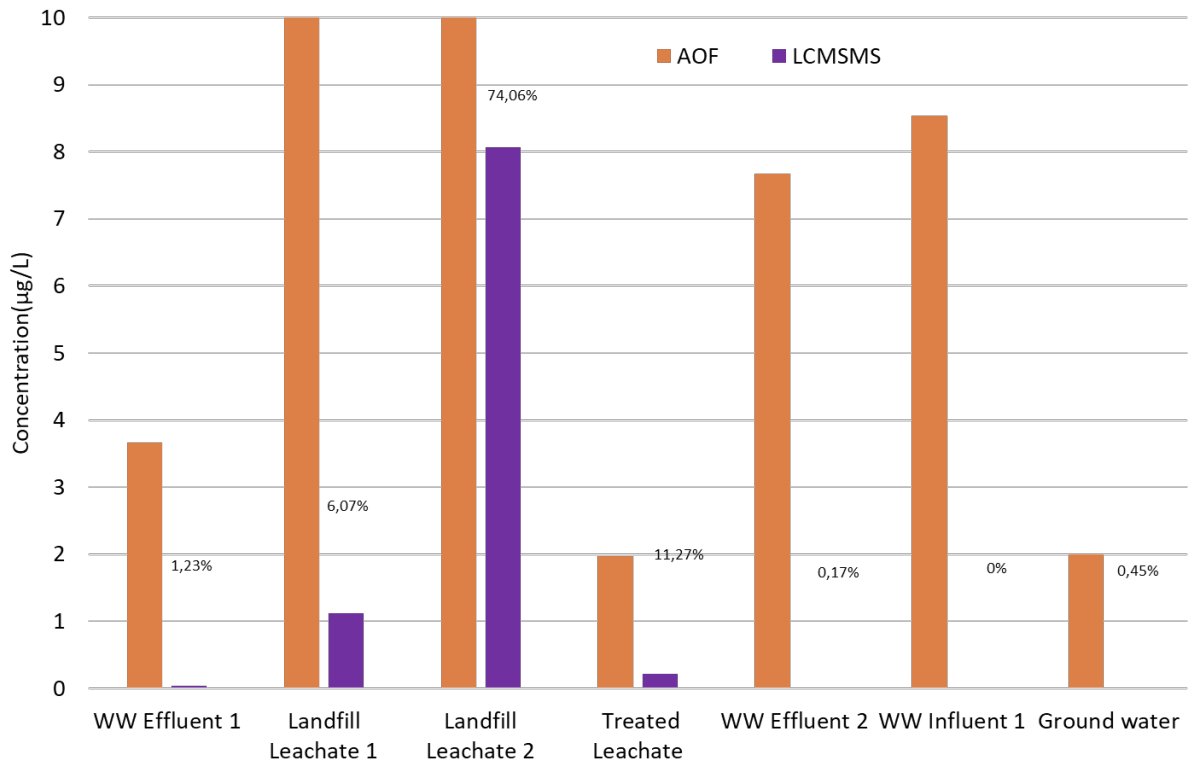


Comparison AOF and TF



- AOF method can explain 1 to and 23% of the TF.
- Results depend on samples.
- AOF seems not representative of the fluorinated compounds concentration in the environment.

Comparison AOF and Target analysis



- Only a very small fraction (<10%) of AOF is explained by targeted LCMSMS analysis (56 PFAS). Except for one sample where LCMSMS was able to explain 74% of the fluorine in the AOF.
- This value is very low compared to TF.

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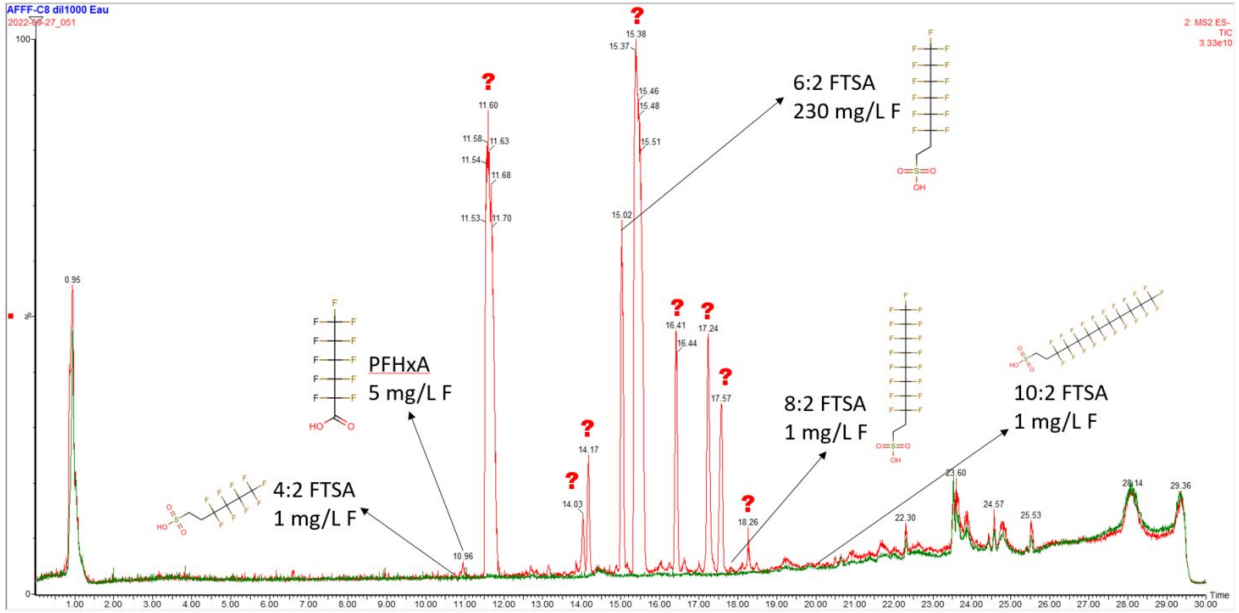
Qualitative analysis

Which PFAS in AFFF ?

Targeted analysis (56)
identification of 20% of the TF (PFAS)
Up to 18 unkowns ..
Biblio review = 1 candidate
80 % identification (PFAS-57)
And now PFAS 58 ?

But time consuming.. And so many unknown..
And dependant on standard availability ..



Qualitative analysis with HRMS

2024 -2025

In 2018 a database of digital samples (NTS fingerprint) of 85 surface waters has been built

Suspect screening applied :
Are a list of compounds (56 PFAS) in my samples?
Comparison of mass fingerprints in samples with « reference compounds fingerprints » in internal database

No QA/QC focused on PFAS in 2018 : risk of sample contamination
Are the extraction /analytical methods adapted to PFAS ?

- Recovery test (20- 60% recovery)
- Control of field blanks (only background level)
- Control of analytical blanks

Caution in data interpretation due to analytical uncertainties, but :

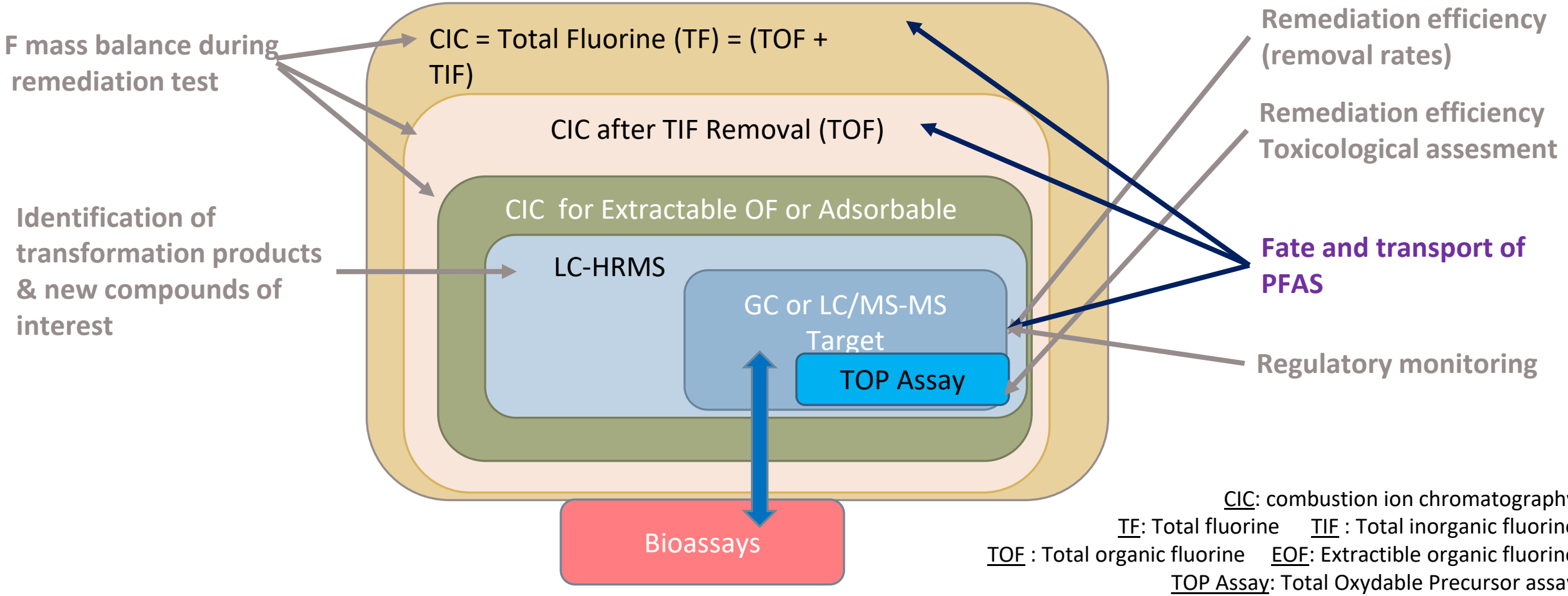
- 27 PFAS detected (list of 56..)
- 6:2 FTAB detected in 55% of the water sample with a high level of confidence, PFOS in 5% and PFBS in 15%

- More than 10 different PFAS detected in 10% of the samples

- Qualitative information !!
- retrospective quantification is not robust

- **Upcoming actions:**
  - identification of potential sources in correlation with the hot spots
  - Confirmation by new sampling campaign should be planned
  - Complementary approach using other PFAS databases to search for more compounds
  - Implementation of a new database based on real products (eg AFFF)

A lot of challenges for the PFAS monitoring
A lot of available tools..



CIC: combustion ion chromatography
TF: Total fluorine TIF : Total inorganic fluorine
TOF : Total organic fluorine EOF: Extractible organic fluorine
TOP Assay: Total Oxydable Precursor assay

But also a lot of needs :

The need to acquire knowledge while making progress on management and regulations
The need to communicate despite scientific uncertainty
The Need to regulate while waiting for new knowledges

= not the same tools / not the same players / not the same barriers!
Need for consultation, transparency on advantages/disadvantages/uncertainties on what we know ... and on what we don't know

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AQUAREF
Consortium scientifique et technique
BRGM, IFREMER, Ineris, INRAE et LNE

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