



Better Food. Better Health. Better World.



Targeted and Non targeted Screening of PFAS as water contaminants

Sylvain Mourard / Séverine Martinie



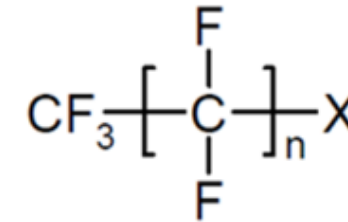
PFAS: emerging contaminants

Per- and polyfluoroalkyl substances (PFAS):

- Family of **THOUSANDS** of **synthetic chemicals**
- **Persistent contaminants**, also called «forever contaminants»
- **Emerging contaminants dangerous to environment and human health**
(suspected endocrine disruptors, carcinogens and affecting the immune system)

Diet is considered the main source of exposure to PFASs for humans.

EFSA: Tolerable Weekly Intake (TWI) of 4.4 ng/kg body weight per week for the sum of PFOS, PFOA, PFNA and PFHxS

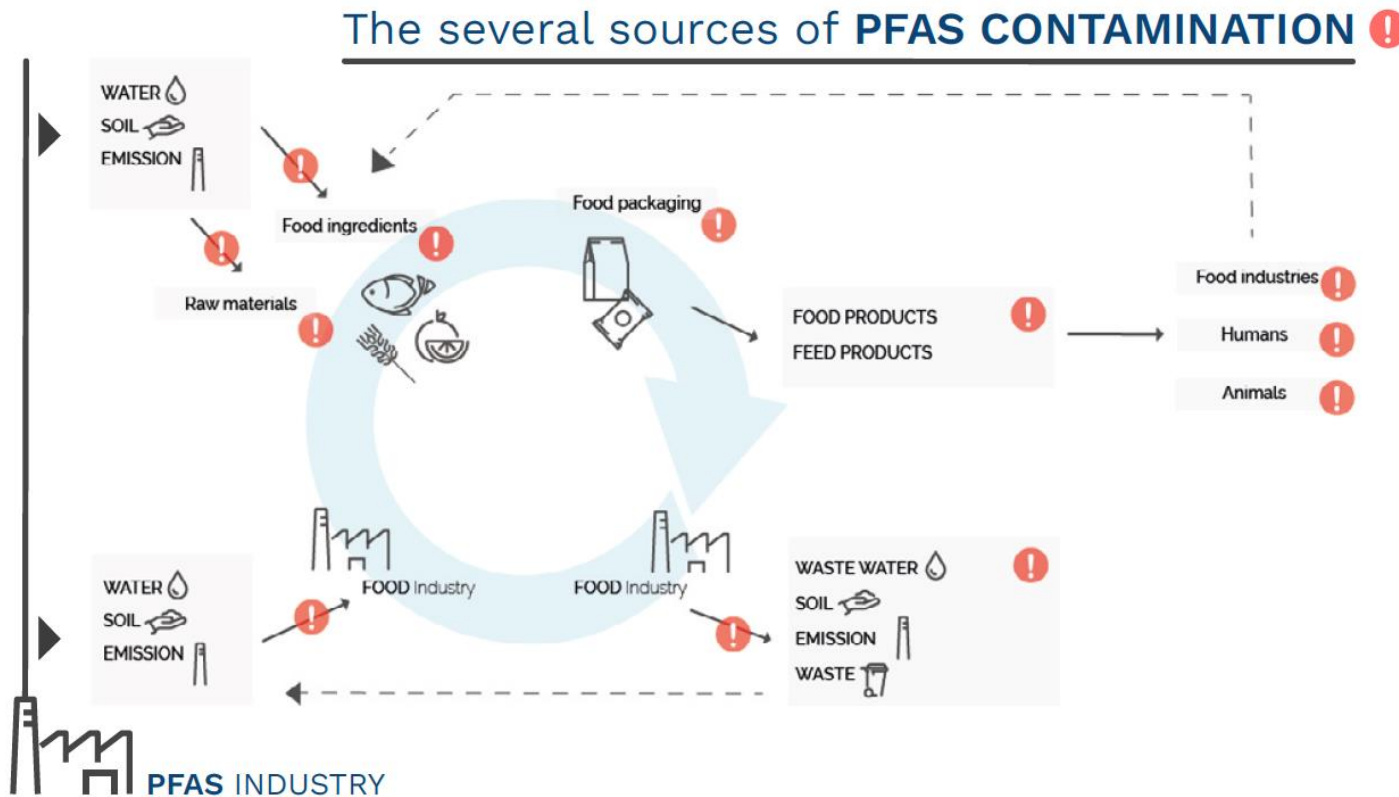


INTENTIONALLY ADDED FOR THEIR PROPERTIES

- Excellent **surfactants**
- **Strong C-F bond**
- **Applied everywhere** in society (household, industry, automotive, medical etc)



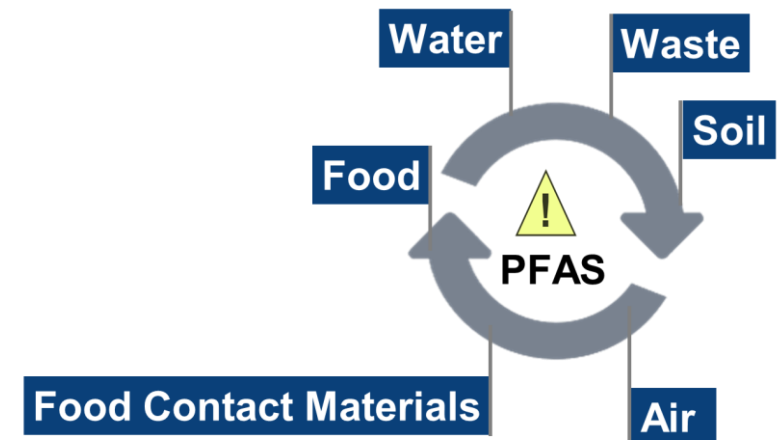
Sources of contamination and concerned matrices



- Domestic, civil and industrial contamination → **strongly present in water environment**, also because of their mobility
- **Conventional treatment do not eliminate this contaminants** either from drinking or waste water

BIOACCUMULATION IN FOOD CHAIN

Concerned matrices



PFAS in water

The road to the new directive EU 2020/2184

In ancient times

The requirements for describing water were sensory ones:

- Waters had to be **clear, odourless, colourless and of pleasant taste**
- Malodorous or **turbid water was considered contaminated**
- Recognised as **sources of contamination: droppings, metals, algae**
- Few or **no analytical methods**



Pont du Gard
Roman aqueduct

Nowadays

The scientific approach has greatly developed:

- Quality requirements with parameters, frequencies of analysis, analytical methods
- **Emerging contaminants monitoring**
- **Regulation open to future scientific and technical development**



European
Regulations

The importance of the new Directive

UE DIRECTIVE 2020/2184
on the quality of water
intended for human
consumption

Member States have to introduce it in national law



It substitutes EU Directive
83/1998

In many States it will be the
new **National reference for
water for human
consumption**

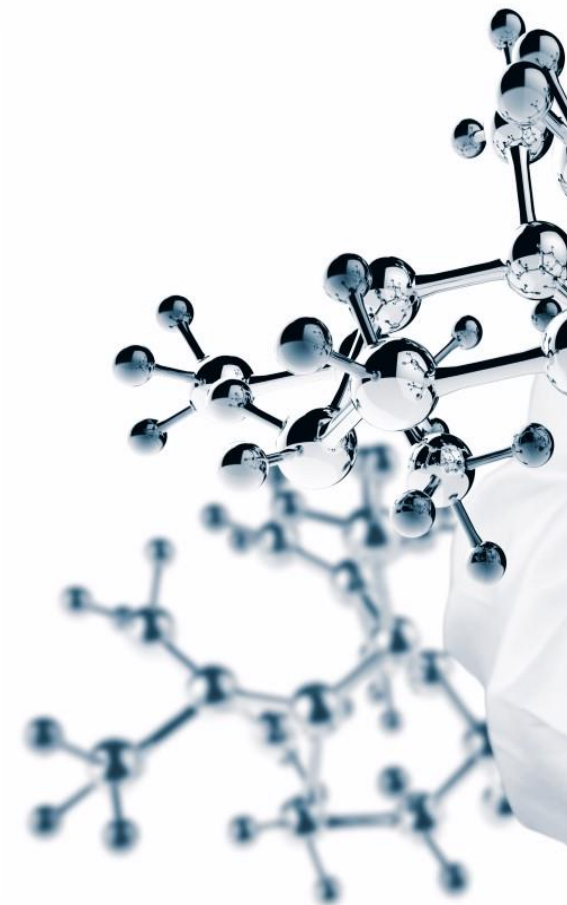
MAIN CHANGES

- **new parameters**
- redefinition of **scope**
- approach to safety based on **risk analysis**
- minimum hygiene requirements for **materials in contact with water** for human use
- minimum requirements for **chemical products and filtering materials** used for water treatment
- control parameters and **frequencies depending on the amount of water used**
- search for the method of **analysis for microplastics**

EU DIRECTIVE 2020/2184 on PFAS

PFAS Total	0,50	µg/l	<p>'PFAS Total' means the totality of per- and polyfluoroalkyl substances.</p> <p>This parametric value shall only apply once technical guidelines for monitoring this parameter are developed in accordance with Article 13(7). Member States may then decide to use either one or both of the parameters 'PFAS Total' or 'Sum of PFAS'.</p>
Sum of PFAS	0,10	µg/l	<p>'Sum of PFAS' means the sum of per- and polyfluoroalkyl substances considered a concern as regards water intended for human consumption listed in point 3 of Part B of Annex III. This is a subset of 'PFAS Total' substances that contain a perfluoroalkyl moiety with three or more carbons (i.e. $-C_nF_{2n}-$, $n \geq 3$) or a perfluoroalkylether moiety with two or more carbons (i.e. $-C_nF_{2n}OC_mF_{2m}-$, $n \text{ and } m \geq 1$).</p>

- Perfluorobutanoic acid (PFBA)
- Perfluoropentanoic acid (PFPA)
- Perfluorohexanoic acid (PFHxA)
- Perfluoroheptanoic acid (PFHpA)
- Perfluorooctanoic acid (PFOA)
- Perfluorononanoic acid (PFNA)
- Perfluorodecanoic acid (PFDA)
- Perfluoroundecanoic acid (PFUnDA)
- Perfluorododecanoic acid (PFDoDA)
- Perfluorotridecanoic acid (PFTrDA)
- Perfluorobutane sulfonic acid (PFBS)
- Perfluoropentane sulfonic acid (PFPS)
- Perfluorohexane sulfonic acid (PFHxS)
- Perfluoroheptane sulfonic acid (PFHpS)
- Perfluorooctane sulfonic acid (PFOS)
- Perfluorononane sulfonic acid (PFNS)
- Perfluorodecane sulfonic acid (PFDS)
- Perfluoroundecane sulfonic acid
- Perfluorododecane sulfonic acid
- Perfluorotridecane sulfonic acid



Possible answers?

Reference methods for waters

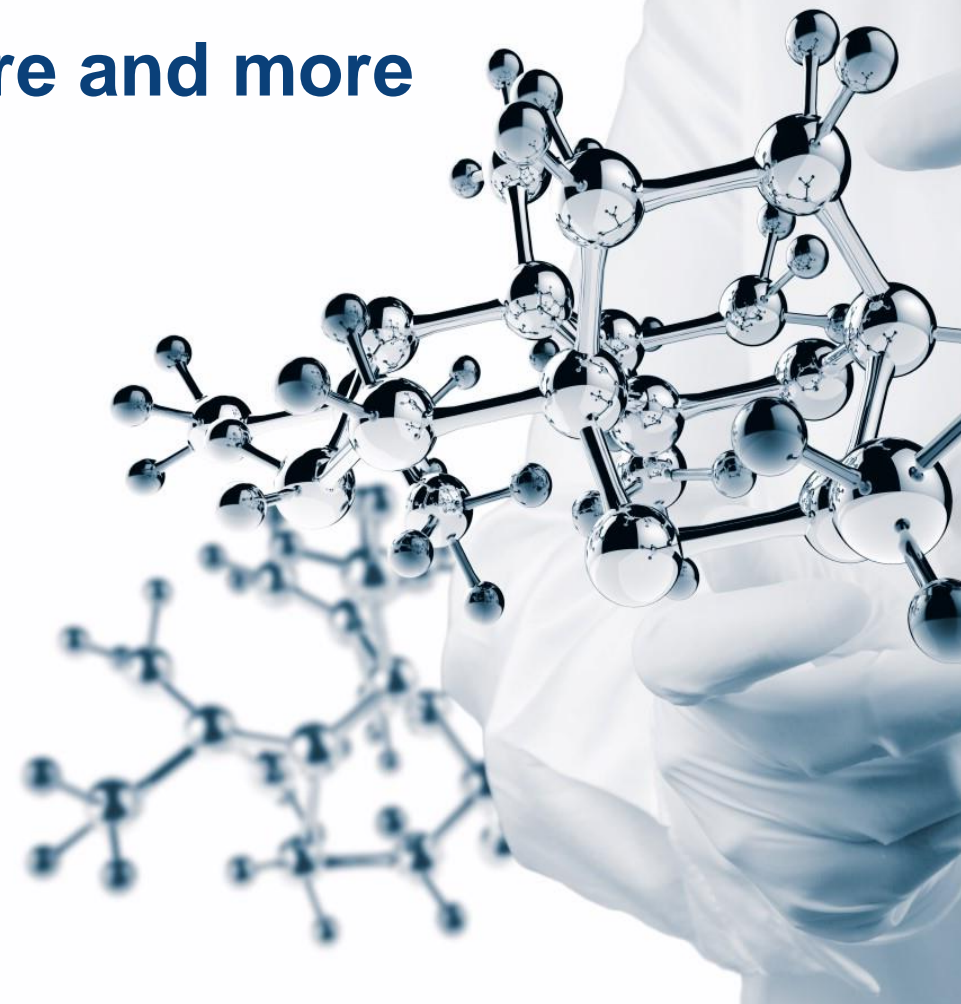
METHOD	Lab LOQ
EPA 537.1:2020 Drinking Water Ground water (clean waters)	0,01 µg/l
ISO 25101:2009 Drinking Water	0,001 µg/l for PFOA and PFOS 0,005 µg/l for others
ASTM D7979-20 Waste water	0,05-0,1 µg/l for all PFAS Except PFOS 0,01 µg/l
ISO 21675:2019 drinking water, fresh water and sea water containing less than 2 g/l solid particulate material	2,5 ng/l for all PFAS Except PFOA e PFOS 0,50 ng/l

Which PFAS has to be monitored?

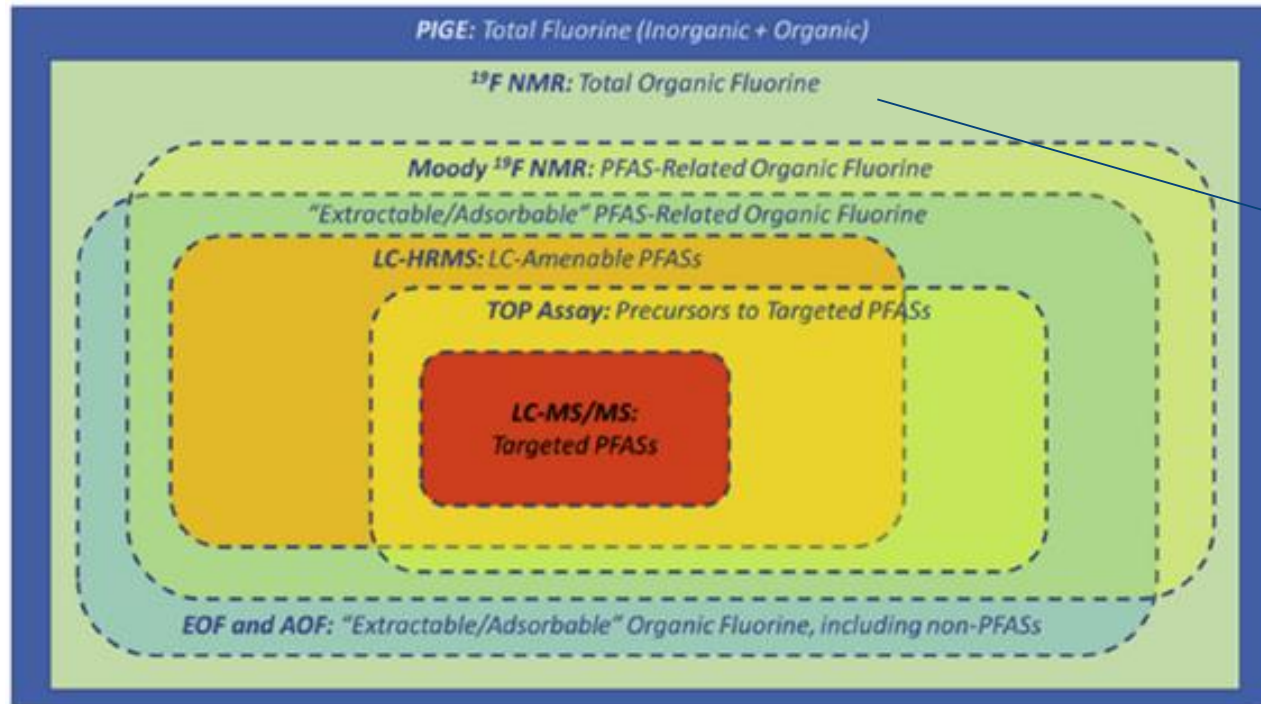
Molecules included in screening are more and more

- **Gen X** was considered one of the "new generation" PFASs because it was used as a replacement for some earlier PFASs
- **ADONA** was an alternative to PFOA used in the production of fluoropolymers.
- **Fuorotelomers** have also been discussed with concern

They are definitely among the compounds under attention for suspected hazardousness.



GRAY ZONE: PFAS selectivity and inclusivity

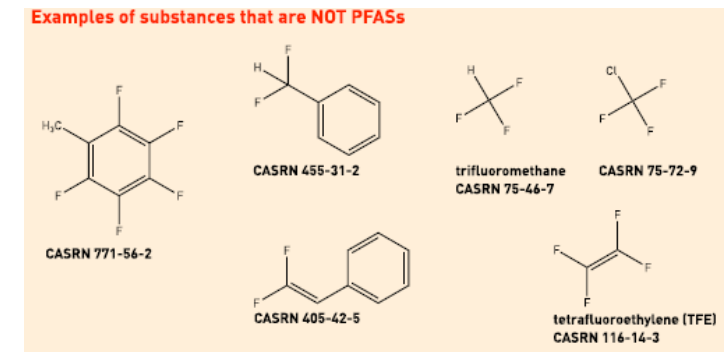


Selectivity and inclusivity associated with total organofluoride methods. Image source: McDonough, Carrie A., et al., 2019, Current Opinion in Environmental Science & Health

It is a large family of compounds; which should be the right technique to investigate them?

- **Non-specific** total determination has **limit issues** and might **include also non-PFAS**

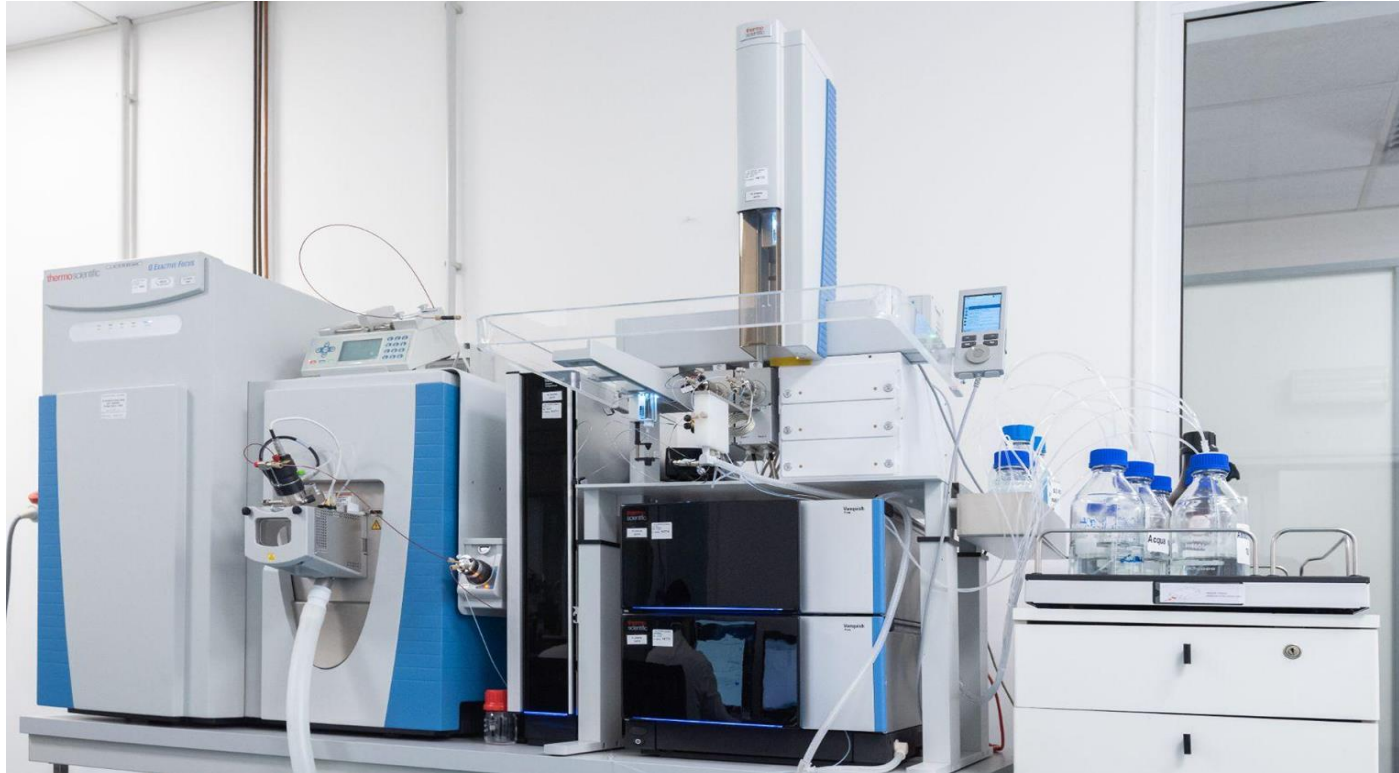
not all the organic F-C are PFAS!



- A **super specific** target **won't include all possible dangerous PFAS**.

Future harmonized legislative indications or toxicological relevance will be the drivers to decide.

Possible present and future answers?



PRESENT

Targeted analysis with HIGH RESOLUTION LC/MS ORBITRAP

- Screening of specific PFAS molecules

FUTURE

Non-targeted PFAS discovery

EPA Experience:

They are working to develop and apply high-resolution mass spectrometry techniques to conduct Non-Targeted Analysis of PFAS in the environment

Potential: HRMS permits to detect and proposed structures for ~980 new PFAS analytes (not branched isomers)

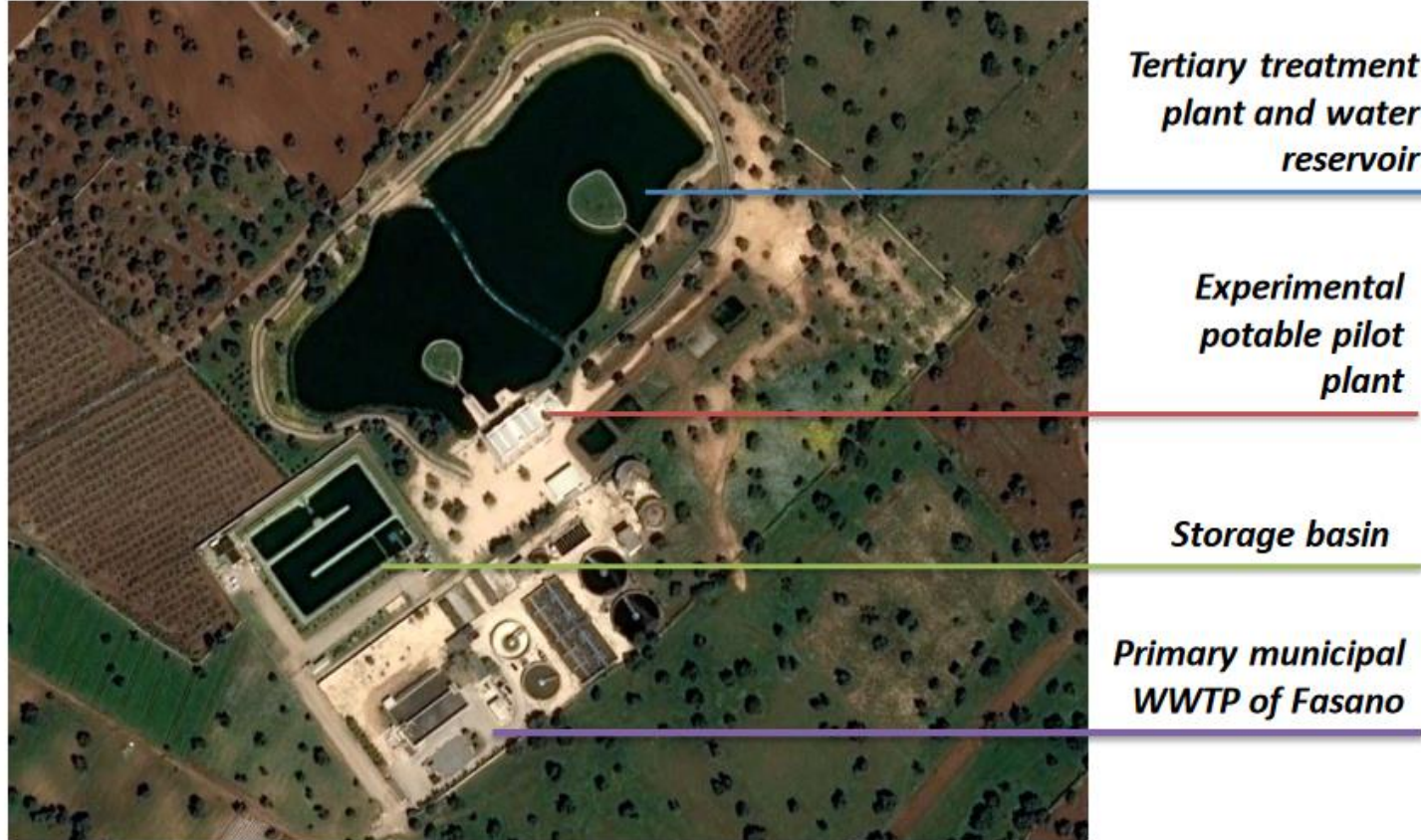
Case study

The context: reclamation plant

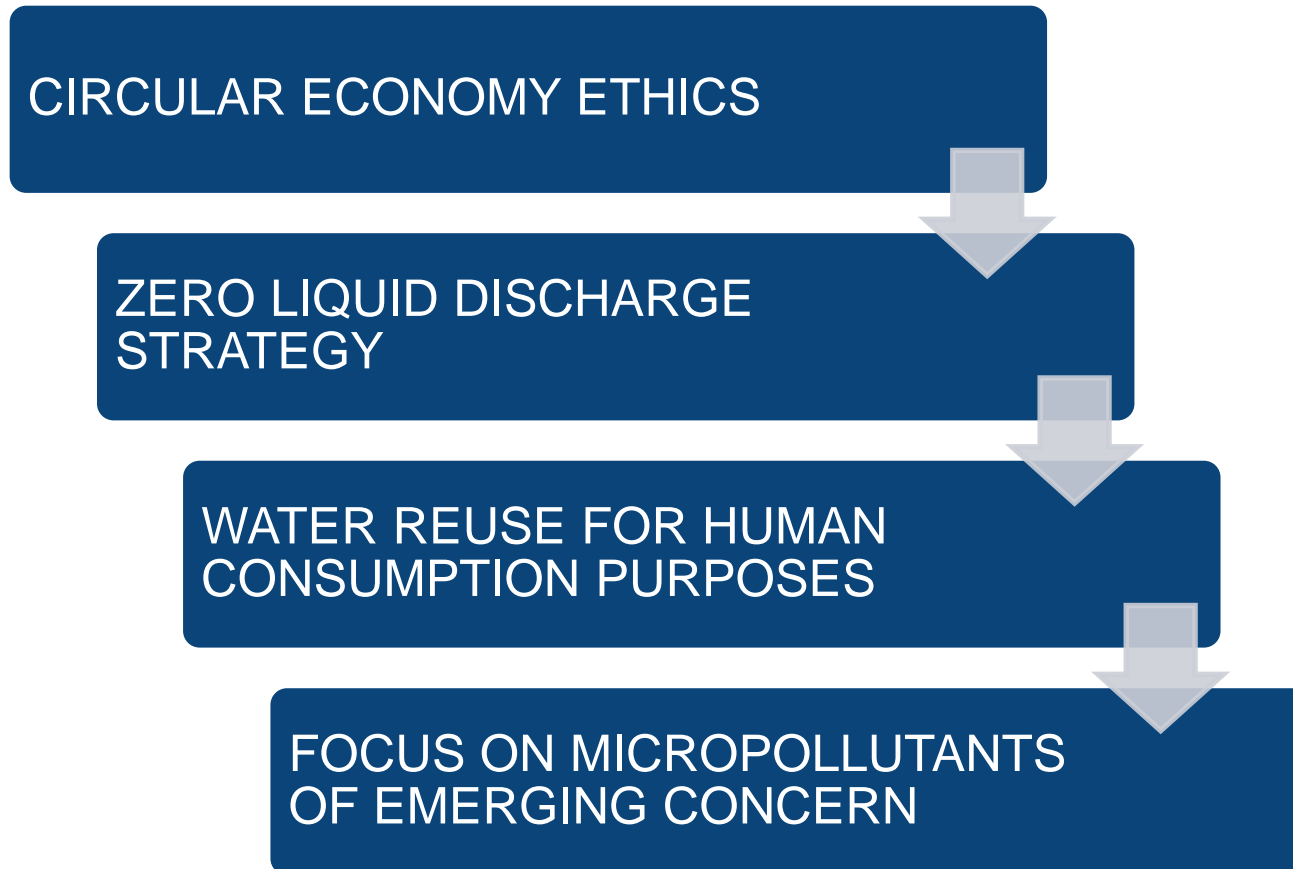
FASANO, Italy

Project by

- AquaSoil S.r.l.
- Environmental Protection Agency – Arpa Puglia
- University of Salento
- **Mérieux NutriSciences**
- University of Western Ontario



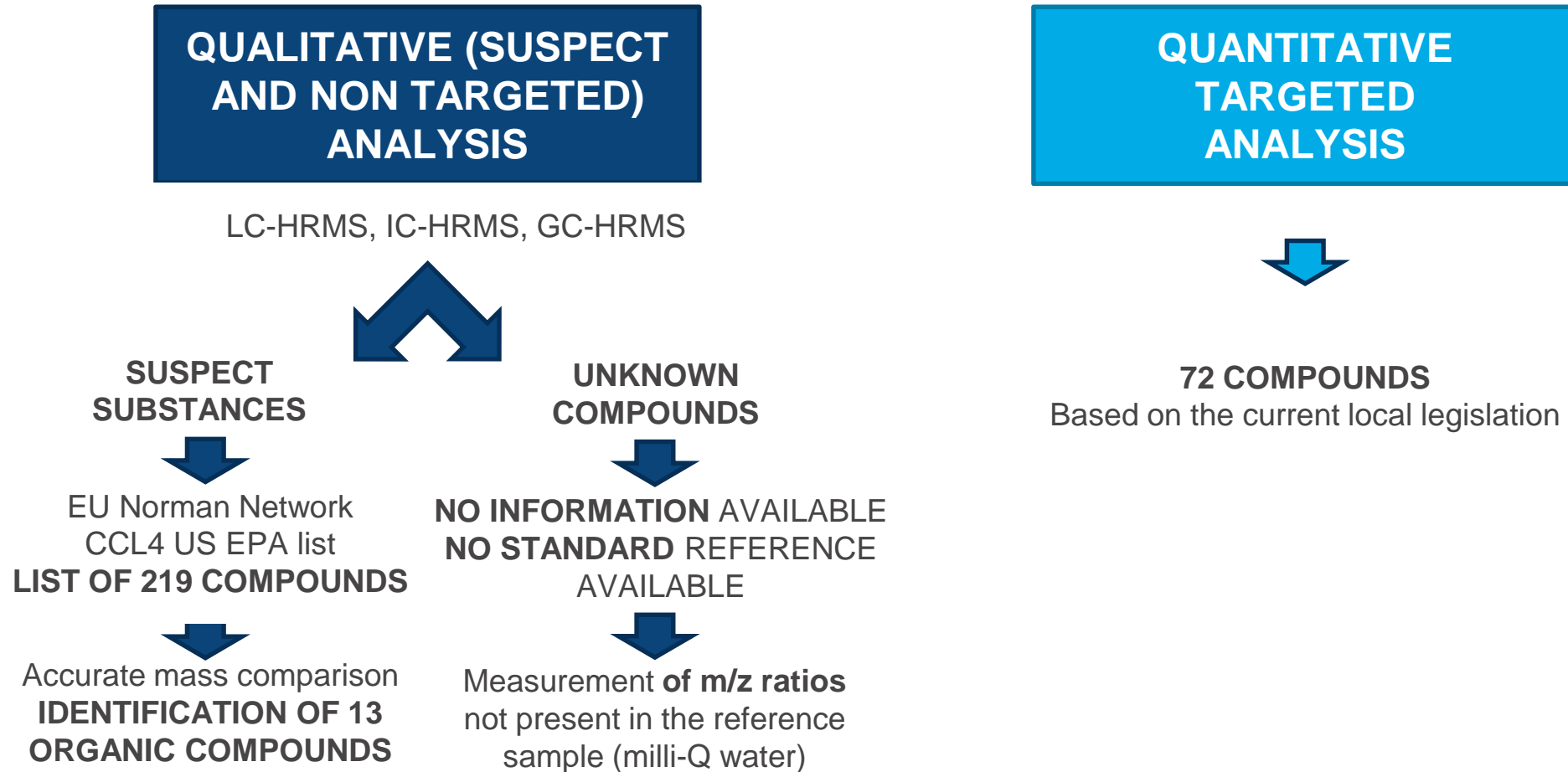
Goals of the project



GOALS

- Defining advanced treatment technologies suitable for potable purposes
- Adopting a **multilevel monitoring approach to guarantee safe water**
- Focus on **organic micropollutants of emerging concern at ultra-low concentrations**

Targeted and non-targeted



Result of targeted and «suspect analysis» – PFOA presence

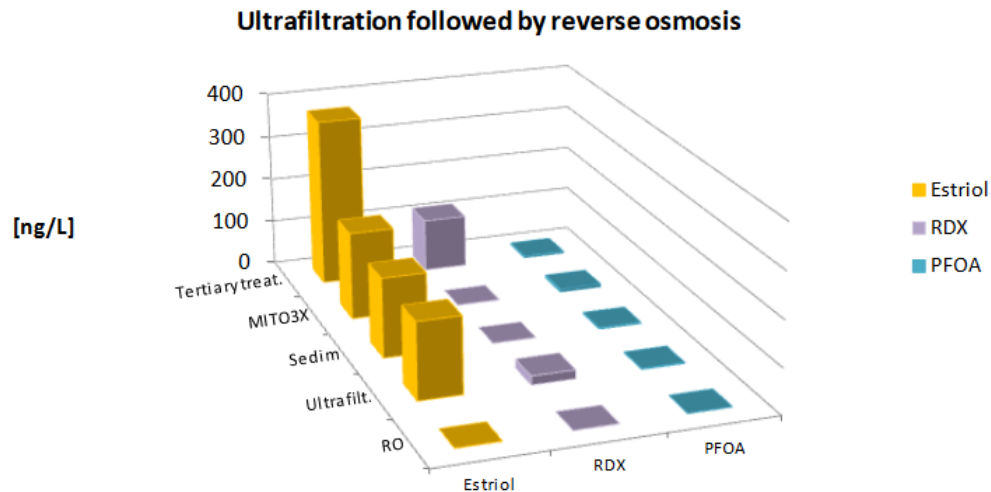
Thanks to the **TARGETED / SUSPECT ANALYSIS** it was possible to identify compounds in the inlet flow of the pilot plant:

- Butylated hydroxyanisole (BHA)
- Bis(2-ethylhexyl)phthalate (DEHP)
- Diuron
- Isoproturon
- Quinoline
- N-Methyl-2-pyrrolidone
- N-Nitrosopyrrolidine
- Norethindrone
- Terbutrin
- Estriol
- Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
- **Perfluorooctanoic Acid (PFOA)**
- Aniline

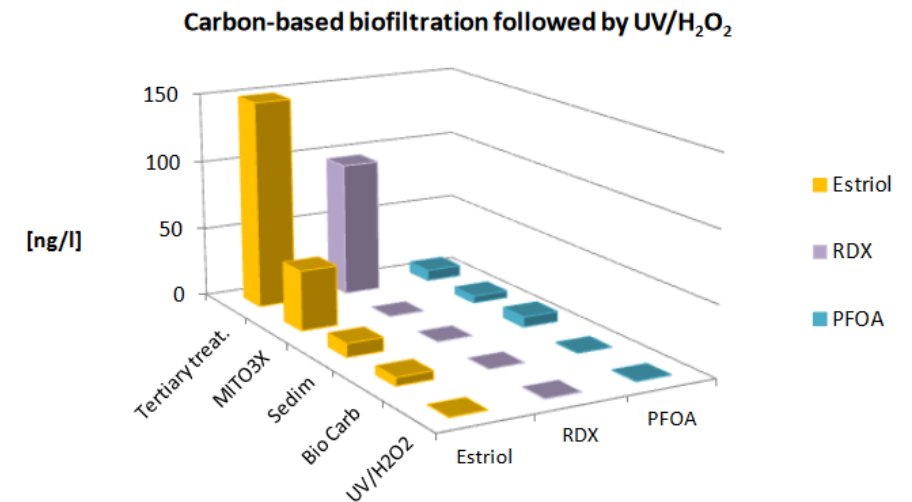
MICROPOLLUTANTS OF EMERGING CONCERN

PFOA analysis after each depuration treatment

Trend of the estimated concentrations* throughout the physical-chemical train



Trend of the estimated concentrations* throughout the biological train



It was observed that a pre-oxidative step before biofiltration increased biodegradability of organic compounds enhancing overall removal efficiency.

PFOA analysis after each depuration treatment

Averages and standard deviations of detected micropollutants (suspect screening) in each of the sampling events.

	Tertiary effluent (N = 3)	O ₃ -H ₂ O ₂ Effluent (N = 3)	AOP contactor effluent (N = 2)	Line A		Line B		Line C		
				BAC effluent (N = 2)	UV/H ₂ O ₂ effluent (N = 2)	BAL effluent (N = 2)	UV/H ₂ O ₂ effluent (N = 2)	UF effluent (N = 2)	UV/H ₂ O ₂ effluent (N = 2)	RO effluent (N = 2)
BHA	14.9 ± 13.0	12.76 ± 1.8	12.7 ± 5.1	1.3 ± 1.8	0.8 ± 1.1	4.3 ± 6.1	4.8 ± 6.7	10.8 ± 15.3	5.9 ± 8.3	1.9 ± 2.7
DEHP	130.3 ± 225.7	121.53 ± 171.9	103.09 ± 145.8	n/a	n/a	n/a	n/a	41.74 ± 59.0	45.99 ± 65.0	n/d
Diuron	50.1 ± 33.1	19.7 ± 24.6	15.8 ± 30.4	n/d	n/d	5.3 ± 3.9	1.5 ± 1.6	9.2 ± 4.8	1.0 ± 1.4	0.1 ± 0.21
Isoproturon	51.2 ± 24.9	19.6 ± 22.0	13.3 ± 18.0	n/d	n/d	1.4 ± 2.0	1.2 ± 1.7	7.8 ± 11.1	3.7 ± 5.3	0.29 ± 0.4
Quinoline	17.3 ± 9.5	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
NMP	7.9 ± 13.8	n/a	21.3 ± 30.1	7.4 ± 10.5	6.6 ± 9.3	21.3 ± 30.2	15.4 ± 21.8	16.3 ± 23.0	7.7 ± 10.9	n/d
NPYR	2.7 ± 4.7	n/a	21.1 ± 29.8	15.7 ± 22.3	11.4 ± 16.1	19.9 ± 28.1	19.2 ± 27.1	22.2 ± 31.3	18.3 ± 25.3	n/d
Norethindrone	40.3 ± 58.7	6.2 ± 5.5	7.8 ± 9.4	n/d	n/d	0.2 ± 0.2	0.2 ± 0.3	0.9 ± 1.3	2.2 ± 3.1	n/d
Terbutryn	103.8 ± 139.1	9.4 ± 8.3	6.8 ± 9.6	1.4 ± 2.0	n/d	13.7 ± 16.8	3.4 ± 4.8	20.8 ± 0.6	2.5 ± 2.7	0.3 ± 0.4
Estriol	212.2 ± 140.6	118.3 ± 106.4	92.5 ± 117.2	12.1 ± 12.1	1.4 ± 1.4	29.5 ± 7.5	21.5 ± 7.3	98.3 ± 99.0	55.8 ± 52.5	n/d
RDX	1012.3 ± 44.8	n/d	n/d	n/d	n/d	n/d	n/d	90.6 ± 13.7	n/d	n/d
PFOA	4.6 ± 3.0	5.7 ± 0.9	5.1 ± 3.0	0.4 ± 0.6	0.4 ± 0.5	4.4 ± 3.6	3.6 ± 3.2	2.1 ± 0.3	2.4 ± 0.7	n/d
Aniline	33.9 ± 58.8	51.5 ± 72.9	n/d	n/a	n/a	n/a	n/a	13.5 ± 19.0	n/d	n/d

n/d = not detected.

n/a = not available.

N = number of determinations.

Discoveries thanks to comprehensive approach



Targeted and Suspect Screening allowed to detect 13 organic micropollutants of emerging concern: it was observed that an ante and post oxidative step to biofiltration enhanced overall removal efficiency.



Non targeted analysis also allowed to classify unknown compounds on the basis of a distribution of m/z ratios associated to molecular weights: both physical-chemical and biological solutions showed better removal performance for compounds with high molecular weight.

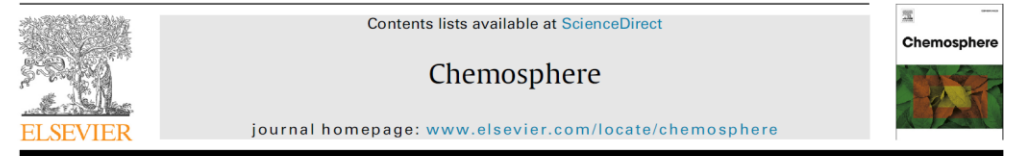
Final considerations



Publication :
www.elsevier.com/locate/chemosphere



2eme phase du projet: Exploitation des derniers résultats d'une liste de plus de 500 composés dont environ 200 composés per-fluorés



Controlling micropollutants in tertiary municipal wastewater by O_3/H_2O_2 , granular biofiltration and UV_{254}/H_2O_2 for potable reuse applications

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Conference PFAS the 13-14th of june in Paris



The poster features a dark blue header with the text 'PFAS' in large white letters, followed by 'PER- AND POLY-FLUOROALKYL SUBSTANCES' in smaller white letters. Below this, the text '2° Congrès International' and 'Gestion des Risques Environnementaux & Sanitaires' is displayed. A dark blue button with white text indicates the dates '13 & 14 juin 2023 - Paris'. The bottom section is divided into three categories: 'Partenaires', 'Entreprises', and 'Institutionnels', each with a row of logos.

PFAS
PER- AND POLY-FLUOROALKYL SUBSTANCES

2° Congrès International
Gestion des Risques Environnementaux & Sanitaires

13 & 14 juin 2023 - Paris

Partenaires

- ARET
- SFSE
- HPC INTERNATIONAL SAS
- ABF

Entreprises

- Mérieux NutriSciences
- REGENESIS
- VEOLIA
- VIACQUA
- RSK
- Purolite
- CAPTURE
- Chemours
- HARMONIC PHARMA

Institutionnels

- RIVE
- INSTITUT CANOT
- INERIS
- Ecole de santé publique Université de Montréal
- CReSP



Thank you

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