

Hugo Carronnier

*Doctor in Pharmacy,
Toxicologist specialized in
environmental toxicology*

*Project manager – risk
assessment emerging
pollutants at VALGO*



VALGO
Canada Inc.



**From Lubrizol (France) To Canada
Development of a global strategy for PFAS**

VALGO Key figures

Canada Inc.

+600

Employees around the world

6

Branches worldwide

12

Agencies in France



+650

Projects / year



+5000

Remediated sites



1008

Billed contracts



+1000

Ha recovered from our clients



+350

Proprietary Ha recovered



100

M€ revenue

Sept. 2021

New Shareholder





POSITIONING / MARKET: 360° approach

Our specificities – Our advantages – Your profit



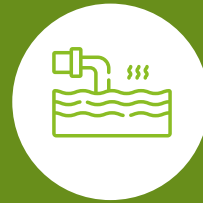
GLOBAL DIAGNOSIS of the site

- Pre global diagnosis of a brownfield
- A real value appreciation for a land property



Building REMEDIATION (Asbestos, lead...)

- National coverage
- Capability to interfere in industrial and building construction



Soil and water REMEDICATION (phreatic zone)

- Thermal desorption
- Physical-chemical treatment by Hydrosplit
- Laboratory and integrated R&D
- Applied Geophysics Department



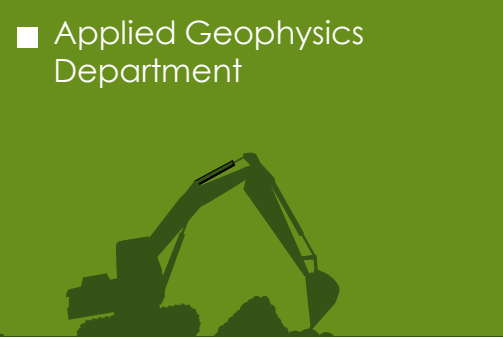
VALORIZATION of raw products

- Advice and expertise on the transformation of waste into biogas
- Polluted soil recovery
- Sea transport preferred



SITE DEVELOPMENT & VALORIZATION.

- Transformation of an obsolete production tool into a higher value-added tool (energy, logistics, etc.)





- **More than 90 years** of petrochemical pollution
- **270 hrs** of polluted land and premises
- **Seveso classification** - high
- **Partial** asbestos diagnosis



- **270 ha** recovered
- **75,000 tons** metals and **400 000 tons** concrete recycled
- **400,000 t** concrete and **55 000 t** hydrocarbon waste recycled and recovered
- **62 hrs** land remediated
- **3000 future jobs** created



From Lubrizol (France) To Canada Development of a global strategy for PFAS

The PFAS Issue

1. Context
2. The compounds
3. Exposure and toxicity

Diagnosis

1. Analytical complexity
2. Case study – Large Scale Diagnosis –
Distribution study of PFAS in the Seine River

Treatments

1. Usual treatments
2. VALGO innovative treatments





The PFAS Issue





Context : Lubrizol/Normandie Logistique Fire



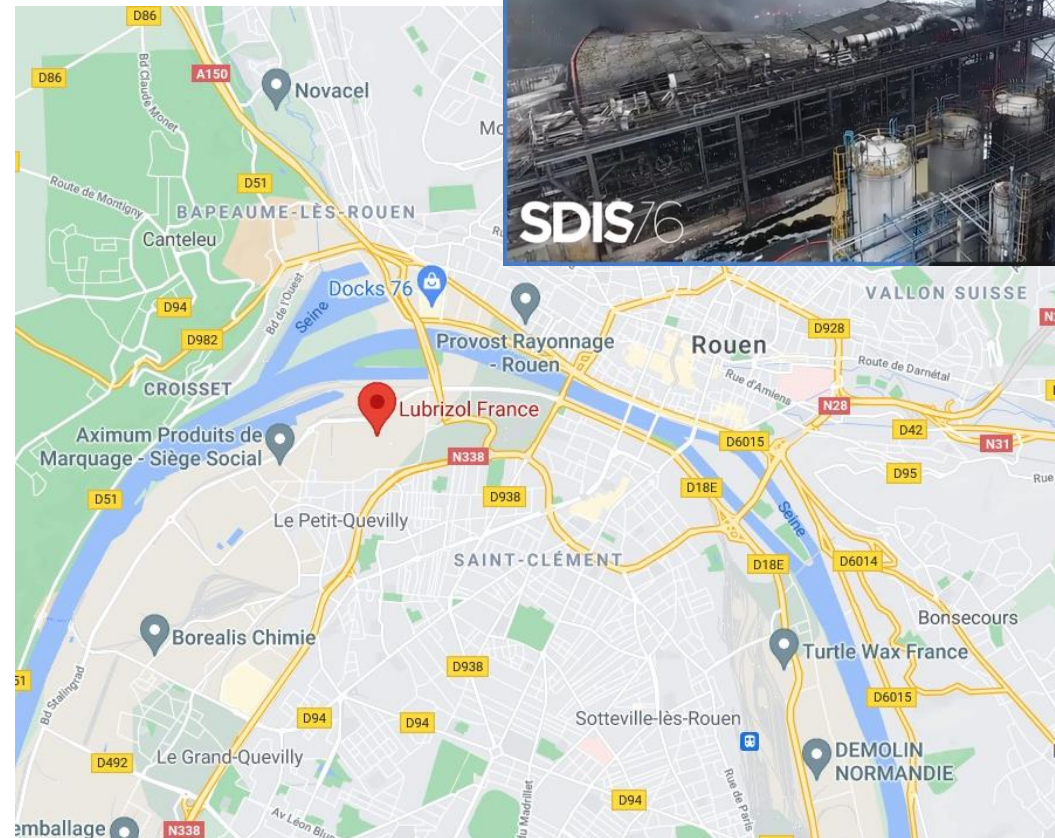
Seveso 2 site
(High Risk)



Combustion of more than **9000t** of various products



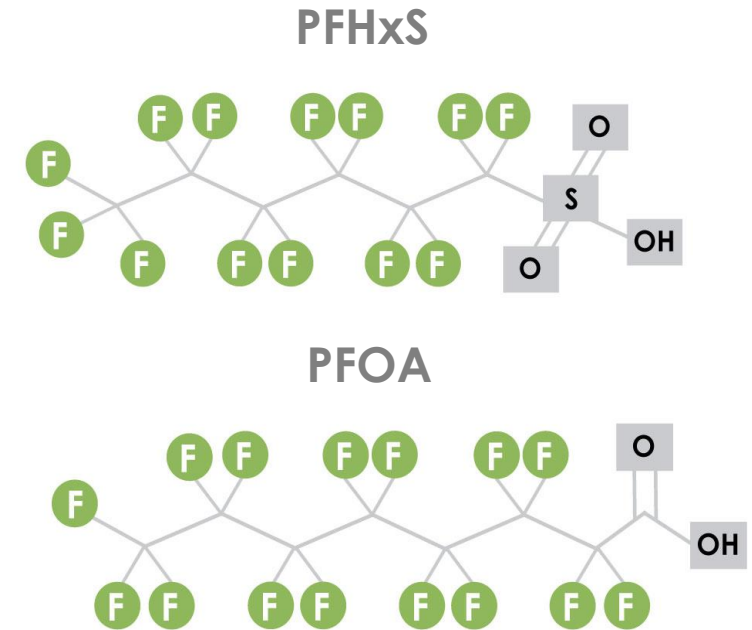
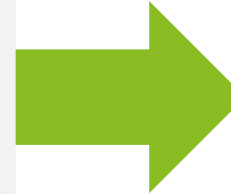
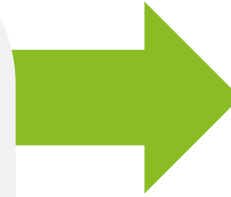
Intensive use of AFFF Foams (40 000 m³)





The compounds

- Complex family with more than 4000 Compounds
- **Defined by the C – F bond**
 - **long half life** (between 40 and 90 years)
 - Virtually non biodegradable (ECHA), even if contradictory publication indicate that long chain PFAS degrades to short chain PFA
 - Very **bioaccumulative**
- Ubiquitous in the environment



Similar chemical properties **thought not identical**



Analytical Difficulties



Treatment difficulties



The compounds

Also Ubiquitous in consumer goods



AFFF



Electronic



Solar cream



Inc



Textile
(GoreTex)



Motor oils



Food packaging

Regulatory values:

	Matrices	PFOS (ng.L ⁻¹)	PFOA (ng.L ⁻¹)
E-U (2022-2027)	All waters	$\sum 20 \text{ PFAS} = 100$	
GERMANY 2006		$\sum \text{PFOS} + \text{PFOA} = 300$	
UK 2009		1000	300
US-EPA 2016		70	70
NETHERLAND2011		530	-
SUÈDE 2014		90	90
ATSDR 2018		Tap Water	11
NETHERLAND (2011)	Groundwater	23	-
Health Canada (2018)	Tap water	200	600



Toxicity

- Multiple ways of exposure
- Multiple toxicity
 - ➔ Moderate hepatic toxicity
 - ➔ Immunological toxicity
 - ➔ Metabolic toxicity
 - ➔ Pre and postnatal development disorders
 - ➔ Endocrine disrupting effect
 - ➔ Promotes cancers

CONSEQUENCES ON HUMAN HEALTH

1NG/L

PFAS are reducing the mean concentration of vaccine antibody in children from 1ng/L



*Nanogram/liter

Increase of **x2** of the plasmatic concentration of PFAS is leading to a **decrease of 49%** of the plasmatic concentration of post vaccinal antibodies

(Grandjean 2012) (Grandjean 2013)



Etude PFAS – juin2021 © VALGO

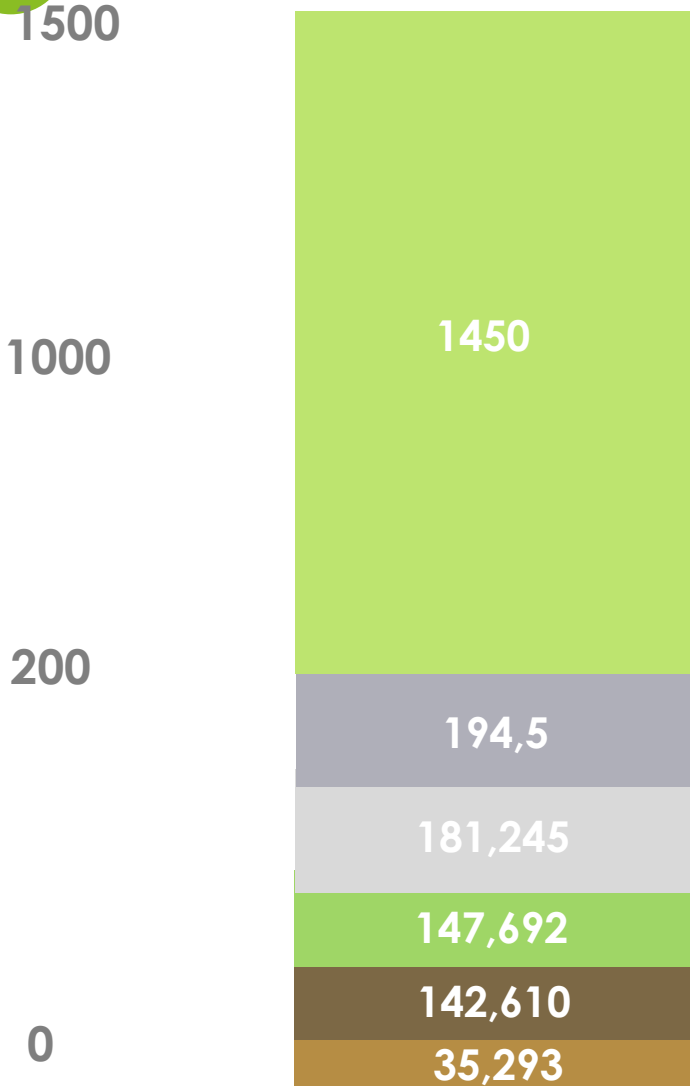
PFAS diagnosis

Analytical complexity



Analytical complexity

PFAS and TOF concentration in groundwater at G4 site (ng/L)



■ Cross contamination:

■ Analytical blindness

➔ Which analysis?

➔ Which compounds?

PFAS are easily undetected with inappropriate analysis or can be overestimated without a good methodology

■ PFOS + PFOA

■ 16 compounds

■ 20 compounds

■ 60 compounds

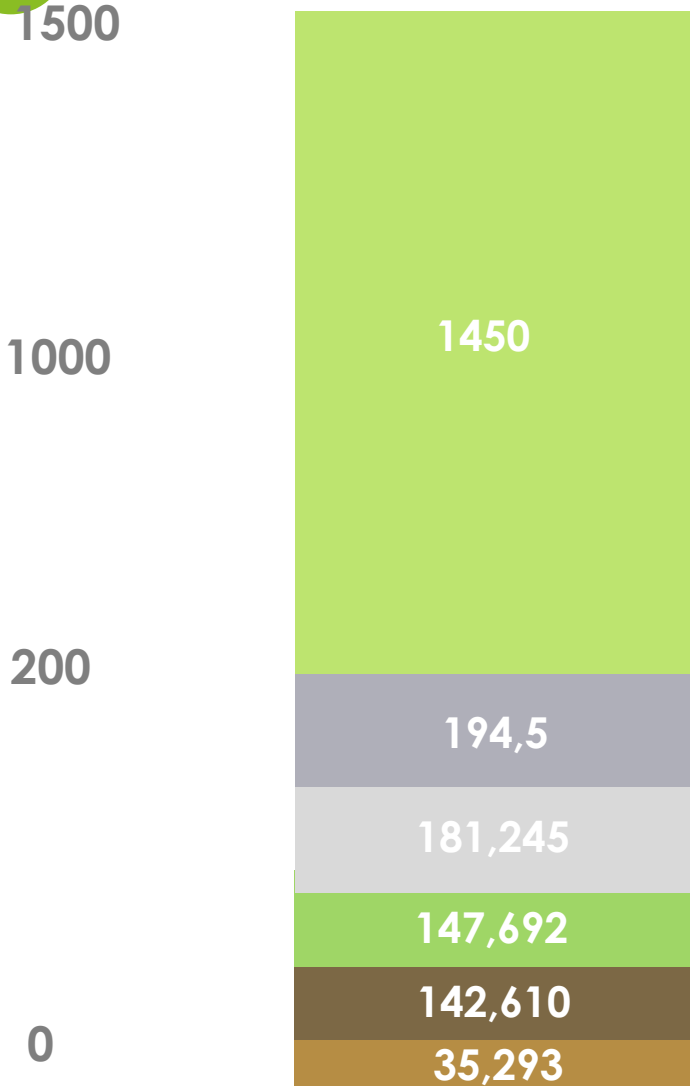
■ 200 compounds

■ TOF



Analytical complexity

PFAS and TOF concentration in groundwater at G4 site (ng/L)



PFOS + PFOA
 16 compounds
 20 compounds
 60 compounds
 200 compounds
 TOF

Which analysis?

- **Quantitative mass spectrometry**
 - + Well known, efficient, low LQ
 - Limited list of PFAS (not suitable for atypical or industrial contamination)
- **“Fingerprint” mass spectrometry**
 - + Identification of the main contaminants, of new PFAS
 - Not quantitative, limited number of identified PFAS (not suitable for a contamination study)
- **Top Assay**
 - + Identification of precursors
 - Degradation of some PFAS, only measures a limited number of short chain PFAS (not suitable for a contamination study)
- **CIC**
 - + Total Organic Fluorine
 - Very High limit of quantification (not suitable on moderately contaminated sites)



Solutions to deal with analytical complexity

■ Cross contamination:

Strict protocol with :

- ➔ PFAS Free equipment (lab coat, gloves, containers, pumps...)
- ➔ Prohibition of some textile, cosmetics, inc...
- ➔ Blanc Strategy (LOQ 0,1ng/L)

■ Analytical blindness

Working with the montreal University:

- ➔ LOQ < 0,1ng/L
- ➔ Thoughtfull use of all analytical processes (**60 compound Mass spectrometry**, CIC, Fingerprint...)

Université 
de Montréal

Targeted analysis on 200 PFAS

1/ First quantified analysis on 60 PFAS → identification of main contaminants
2/ Semi quantification of 140 other PFAS **selected regarding the first results**



Etude PFAS – juin2021 © VALGO

PFAS diagnosis

Case study – Distribution study
of PFAS in the Seine River



Case study

- **Surface water**
- Sediments
- Groundwater
- Biological samples

Largest study on PFAS on the Seine River :

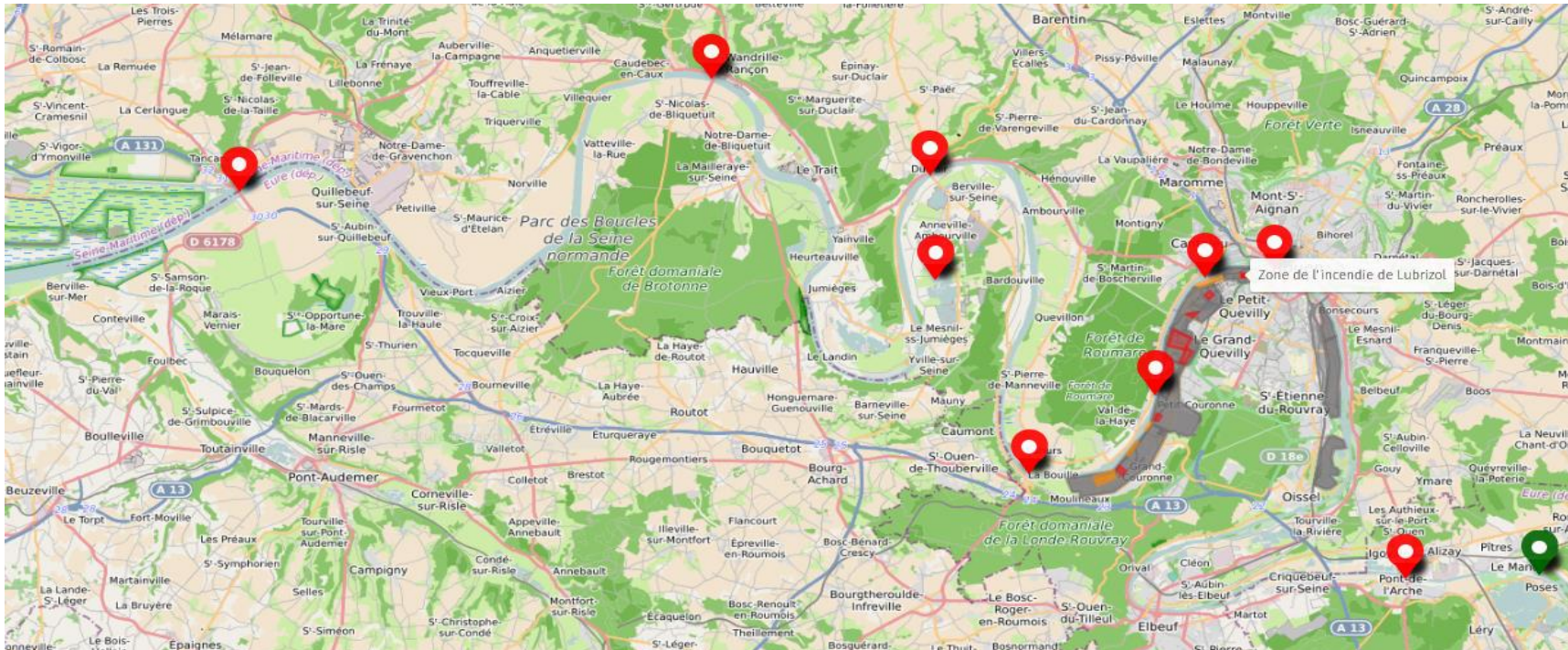
- ➔ **170 km (106 miles)** on the last segment of River
- ➔ **100 sampling spots**+ **60 secondary samples**
(*second study*)
- ➔ Analysis of all environmental matrices





Case study

- Surface water
- Sediments
- Groundwater
- Biological samples

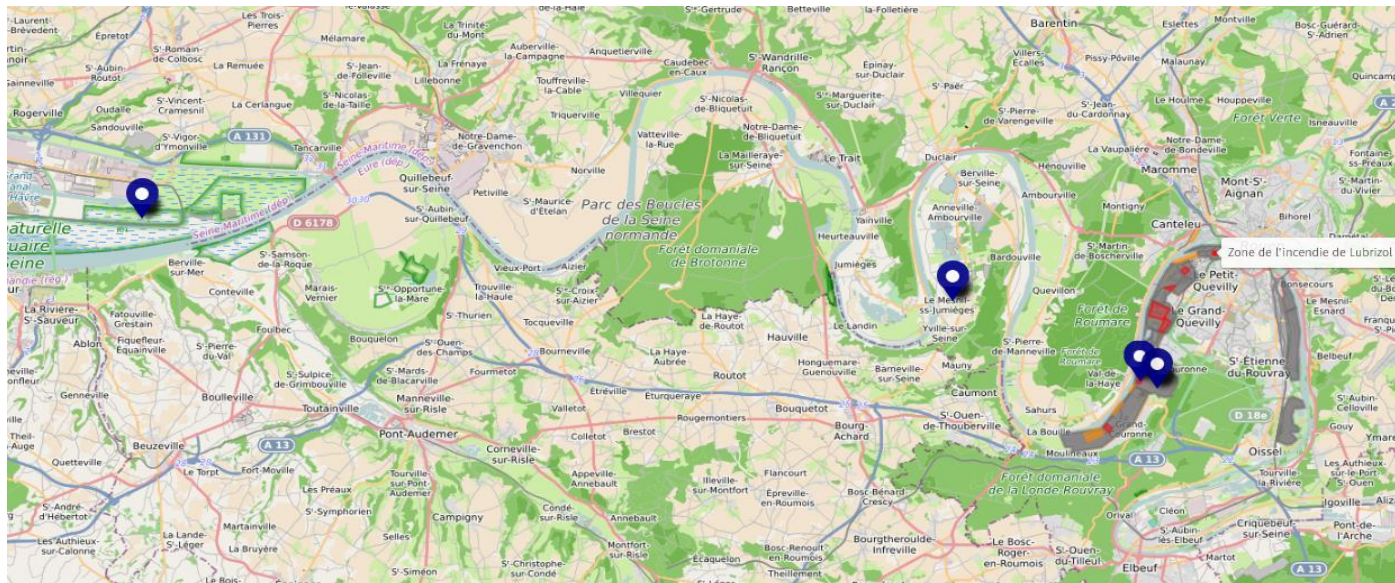


- 3 Sampling spots (on each bank and on riverbed)



Case study

- Surface water
- Sediments
- **Groundwater**
- Biological samples



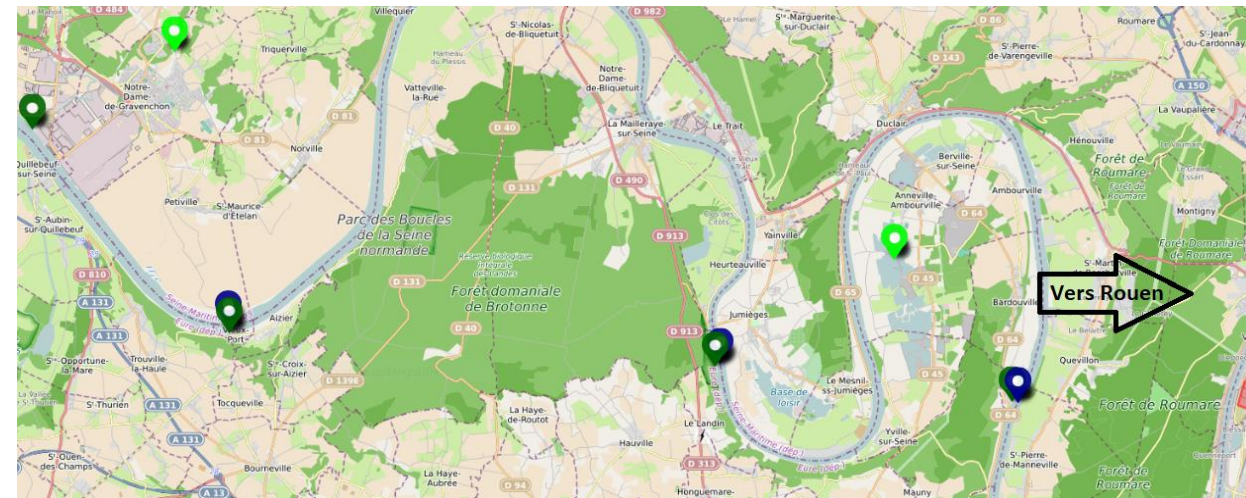
5 to 22 m deep



Case study

- Surface water
- Sediments
- Groundwater
- **Biological samples:**

- **Vegetals:** *Butomus umbellatus* sampled on the last part of the Seine river and before Paris
- **Plankton:** sampled on the last part of the Seine river and before Paris
- **Fishes:** Scientific angling fishing leading to the capture of Sander (*Sander lucioperca*) and Roach (*Rutilus rutilus*)
Control from the **OFB** Sample Library (2008-2010)





Case study: Results

- **River water**
- Sediments
- Groundwater
- Biological samples

Low but global contamination

Close to the ANSES data from 2011, inferior to the ANSES data from 2009



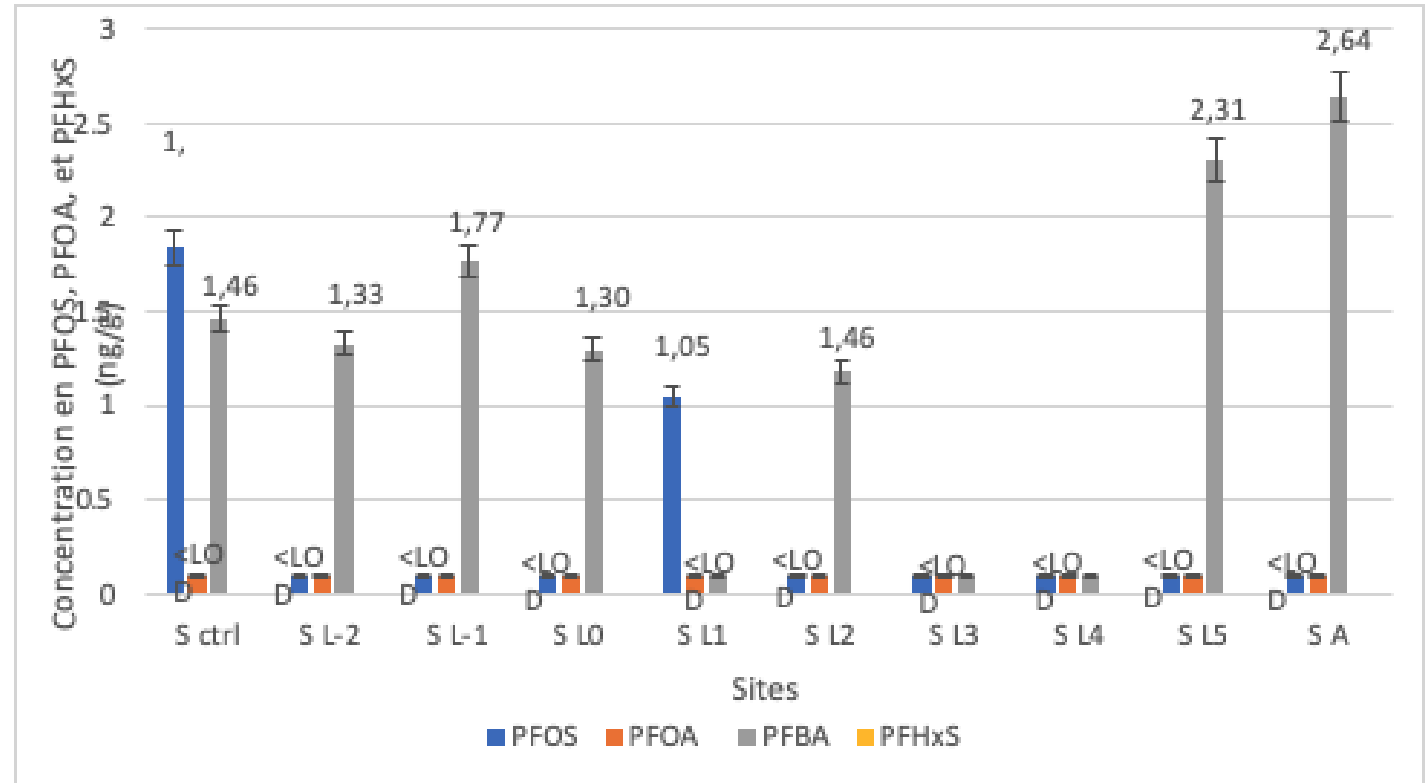


Case study: Results

- River water
- **Sediments**
- Groundwater
- Biological samples

Higher than usual values in similar areas (0,2 – 0,5 ng/g)

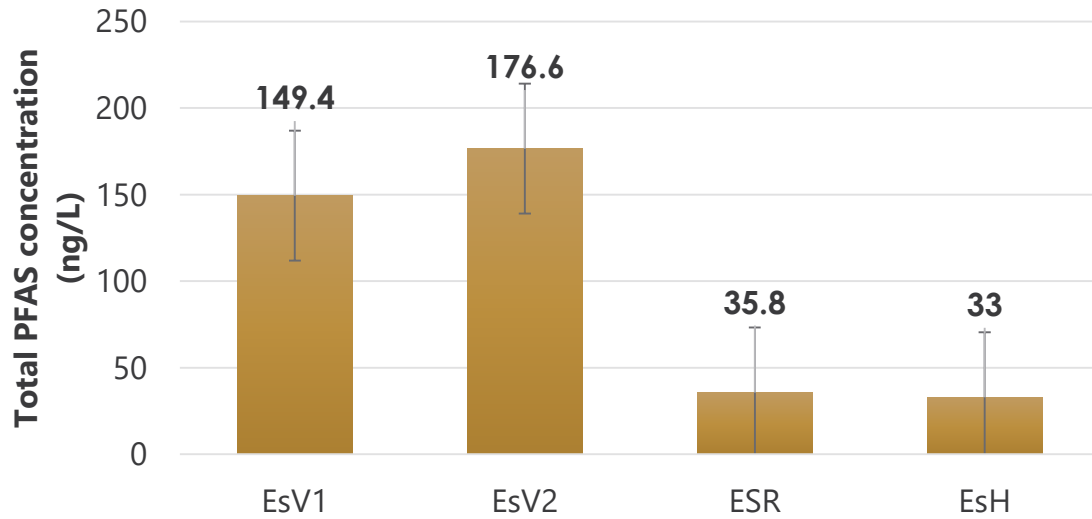
Global concentration of PFAS in sediments (ng.g^{-1}), <LOD : Under the limit of detection





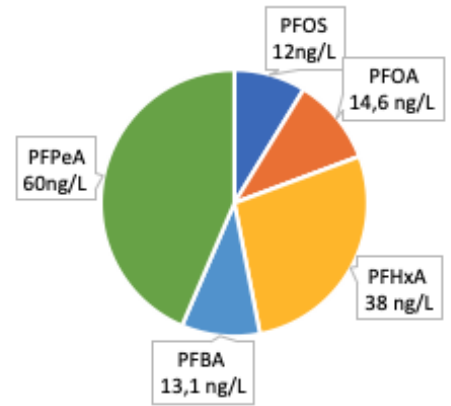
Case study: Results

- River water
- Sediments
- **Groundwater**
- Biological samples

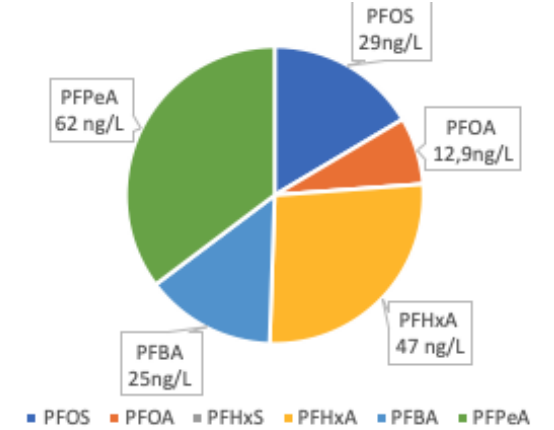


Superior to the expected results (ANSES 2011) :
between 1 and 10 ng/L

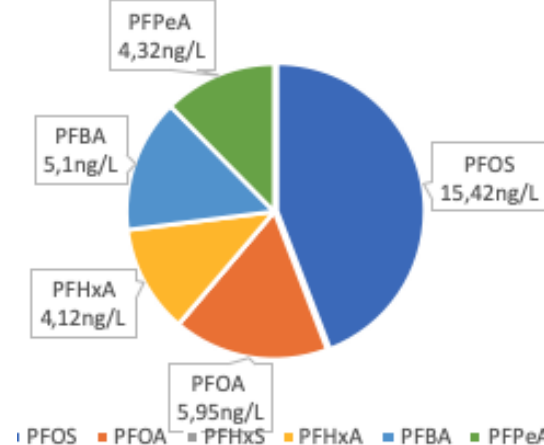
PFAS relative concentration at V1 site



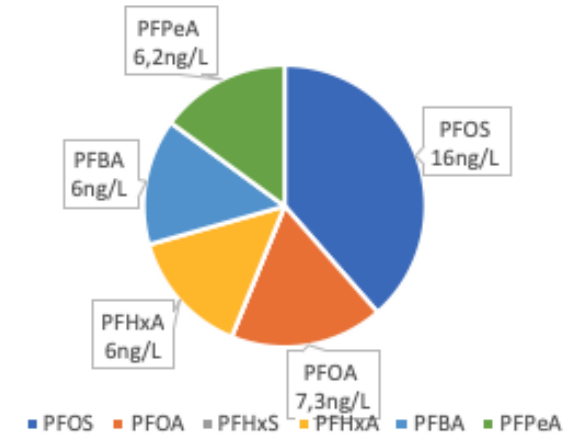
PFAS relative concentration at V2 site



PFAS relative concentration at R site



PFAS relative concentration at H site





Case study: Results

- Vegetals
- Plankton
- **Fishes**

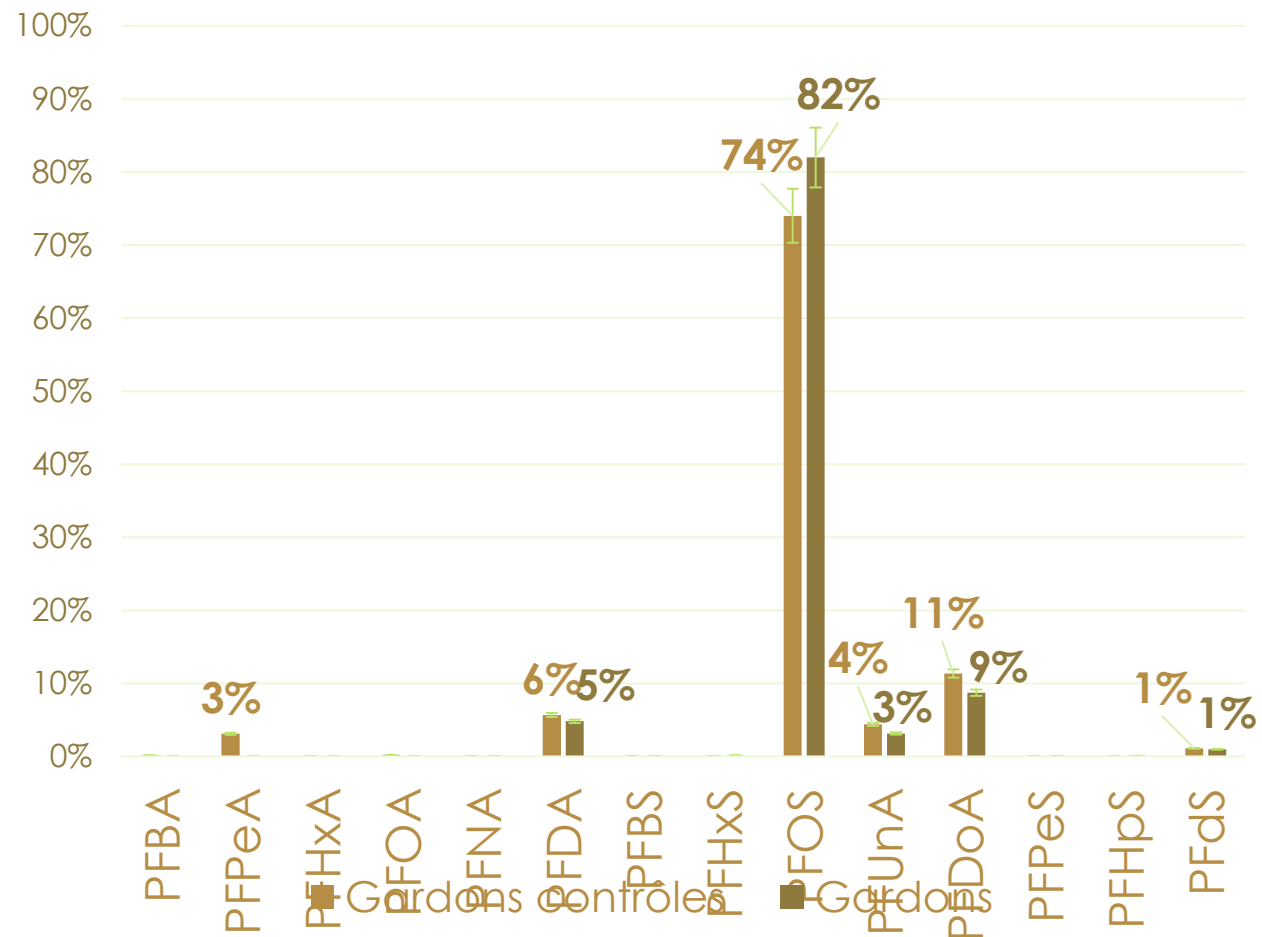
BMF S-G: 2.16

BMF S-P: 11.72 - 4.65

BMF: G-P: 5.4 - 2.16

High PFOS affinity to the blood leads to an Over-contamination by this specific PFAS

Roach





Conclusion



Ubiquitous contamination linked to the industrialization and urbanization of the Seine Valley



Higher concentration because of repeated use (Production, firefighter training...)



Lowering of the contamination of the aquatic fauna. Remain a good bio-indicator due to biomagnification



A single Use of PFAS is not leading to an heavy contamination (dilutive effect)



High risk of exposure of general public in the area



Risk study related on the consumption of PFAS contaminated water in Rouen



Treatments

Usual treatments

Treatments



Exposure directly linked to the **consumption of contaminated water** **75% of exposure (Hoffman 2011)**



Large experience on soil treatment (Petroplus refinery)

- Treatment of contaminated water
 - ➔ Usual treatment work
 - ➔ **Innovant treatment are usefull to reduce costs**
- but soil is also important, because **PFAS contained in the soil can recharge groundwater**
 - ➔ Partneship with french academics and research institute to determine the comportment of PFAS in the soil : Project IPANEMA
 - ➔ Usuals treatment (thermal desorption, washing...)

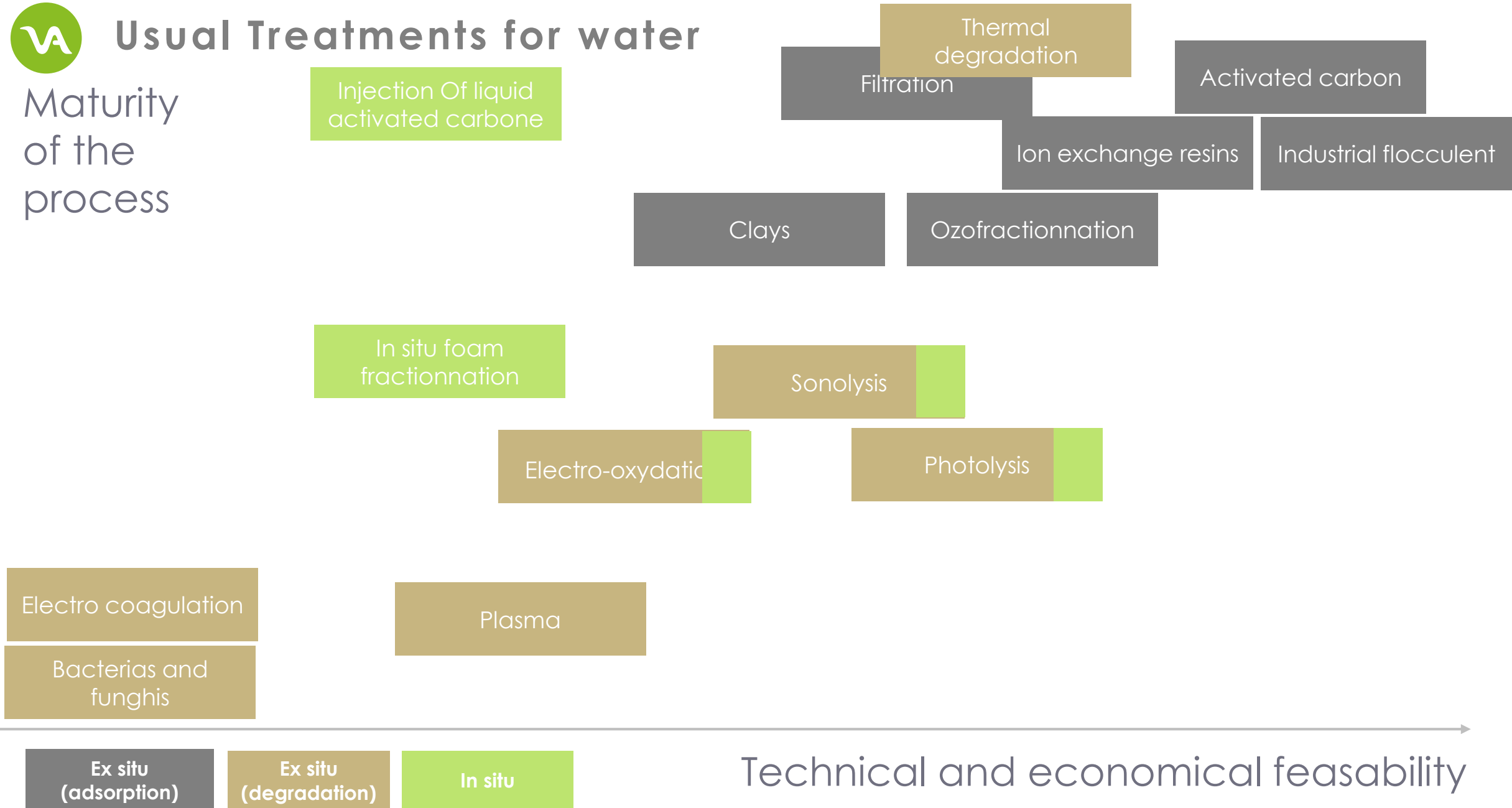


Usual Treatments for water

On the market

Maturity of the process

Experimental



Technical and economical feasibility

Ex situ (adsorption) Ex situ (degradation) In situ



Usual Treatments

Activated carbon

- + Efficient on long chain PFAS well known and easy to use
- Low efficiency for short chain PFAS (0% on GenX) Highly dependent on co-contaminants
High quantity of wastes (difficult and expensive regeneration (>700°C))

Ion exchange resins

- + Higher sorption capacity than GAC
Better efficiency on short chain PFAS than GAC
Can reach low concentrations (<70ng/L)
- Fast chemical exchange saturation
Unefficient on positively charged PFAS
A large number of interaction with other contaminants
Difficult regeneration

→ **Comprehensive use of remediation methods according to the contamination**

→ **The right process on the right contamination**

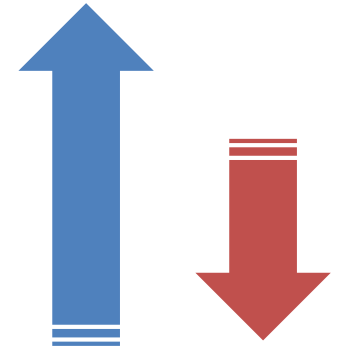
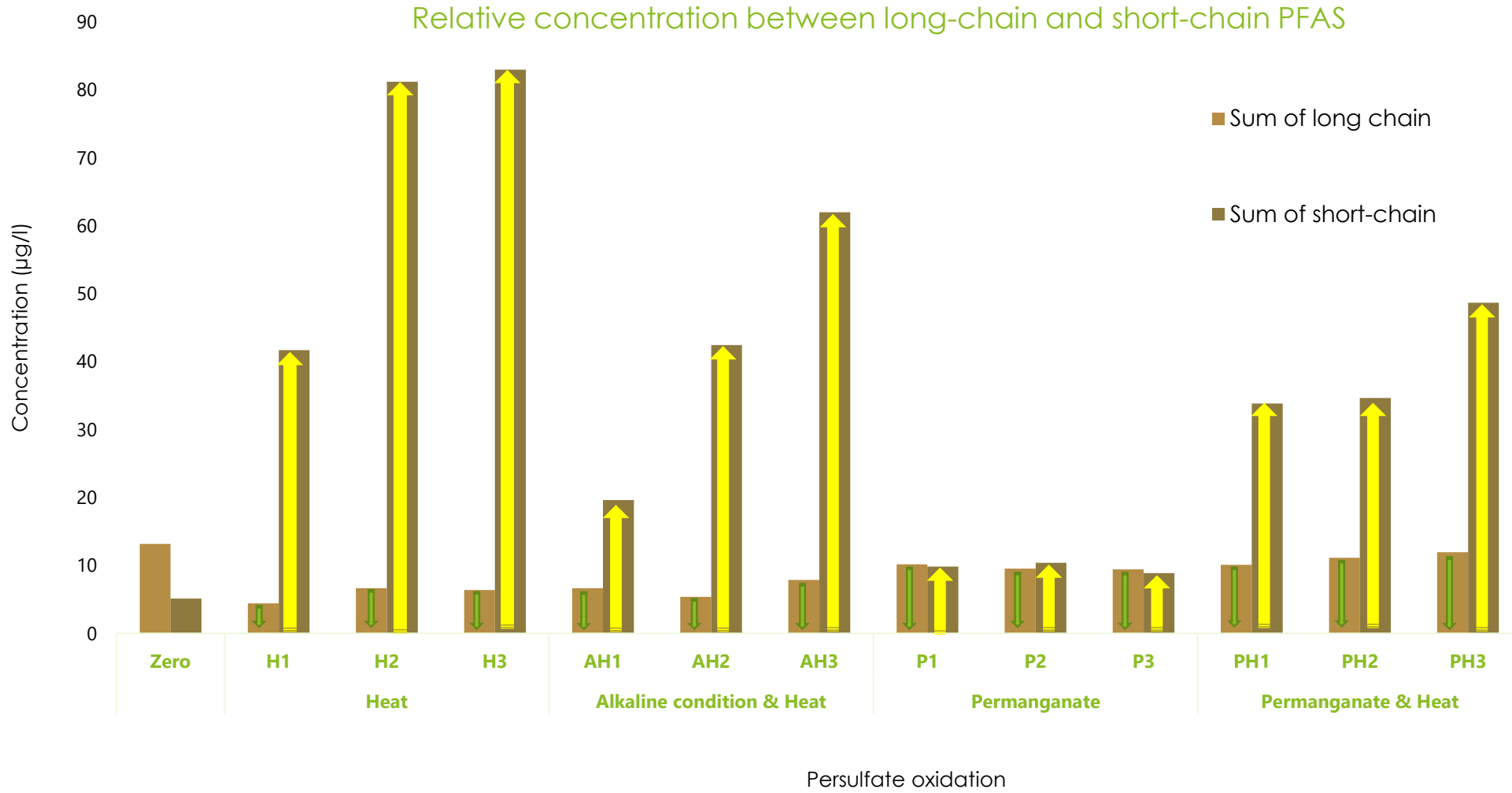


Treatments

VALGO Innovative treatments



Advanced oxidation



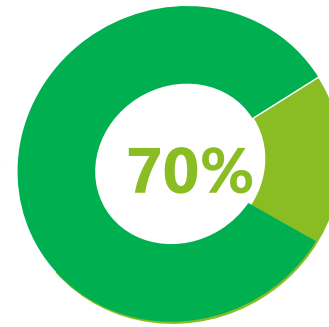
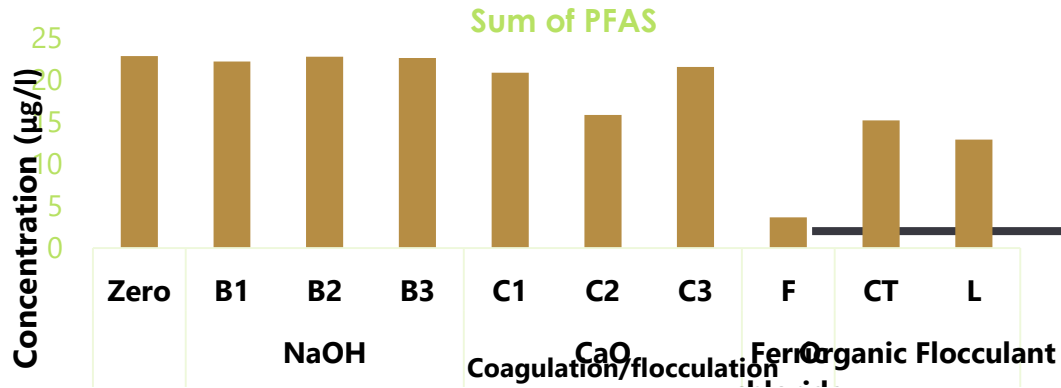
PFCAs PFASs

- Degradation of long-chain PFAS creates short-chain PFAS
- Challenge in quantification of destroyed PFAS

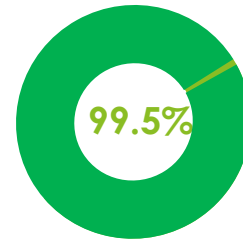


Advanced Coagulation/Flocculation

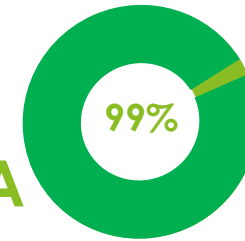
Usual coagulation / Flocculation



Most effective commercial flocculent



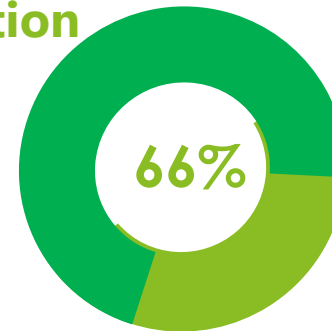
PFOA



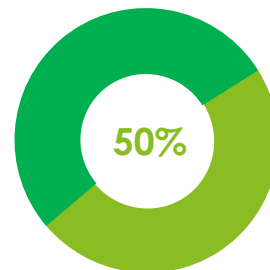
PFOS

Valgo Biological innovant coagulation / Flocculation

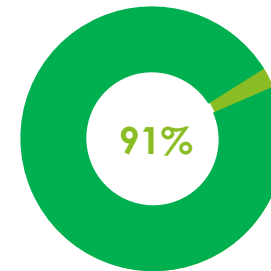
Patent in progress



Almost as efficient as the most efficient commercial flocculent **(without optimization)**



PFOA



PFOS



Treatment of contaminated site

Before treatment Diagnosis is essential

- ➔ Adaptation to the site and the contaminants
- ➔ Considerate the whole contamination

Usual strategies work

- ➔ If they are used properly, but can be expensive

Innovant processes are developped

(patent in perspective)

- ➔ Biological like process:
Organic Protein
- ➔ advanced oxydation

2022/2023: Pilote study of Valgo in Canada

Optimization usual treatments with a modular organization

- ➔ Adaptability to the site and the contamination
- ➔ 2023/2024: Full scale study of our innovative treatment processes





Potentially
contaminated site
by AFFF foams



Potentially
contaminated
Refinery

■ The right diagnosis

- ➔ Correct concentration
- ➔ Unique PFAS signature

■ The right treatment

- ➔ Adapted to the site
- ➔ Adapted to the concentration
- ➔ Adapted to PFAS

***Each site should be correctly
diagnosed and deserve an
adapted treatment***



**Thank you
for your attention**



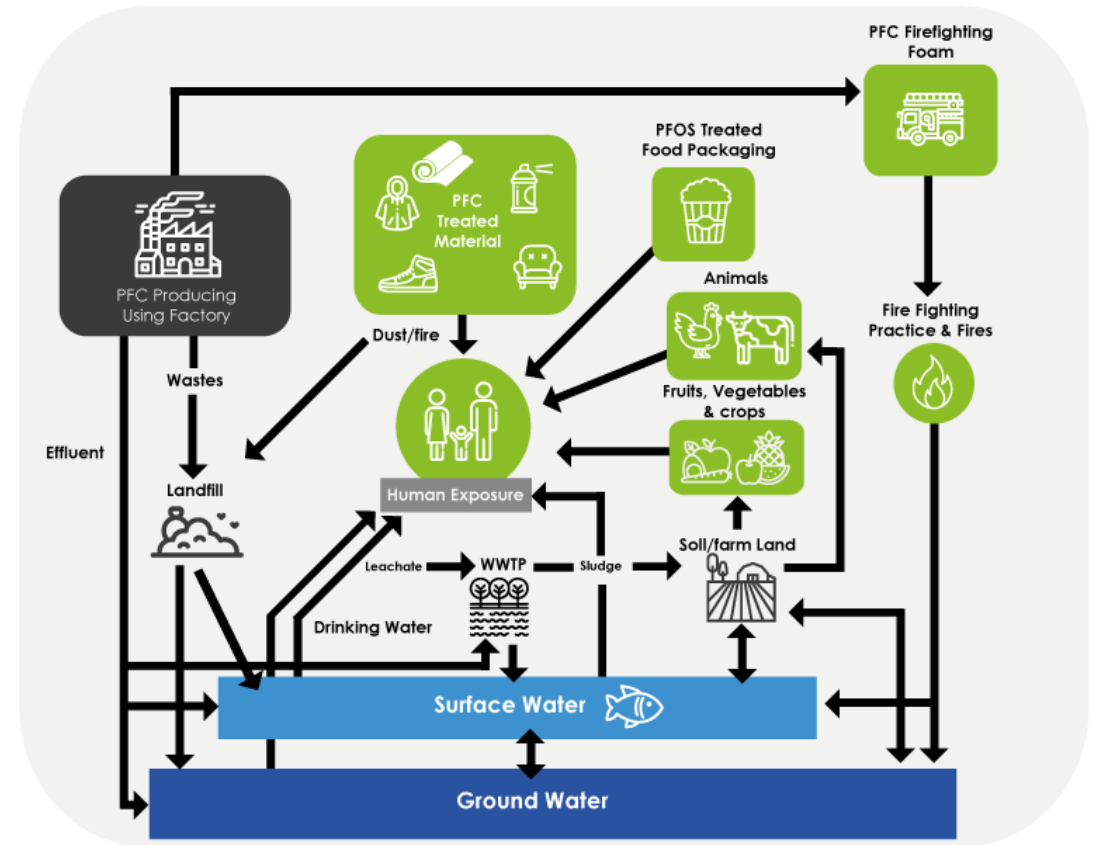
How are we exposed?

There are multiple ways of contamination in the general population:

- Drinking water (75% (Hoffman et al., 2011))
- Food
- Textile (mainly on children)

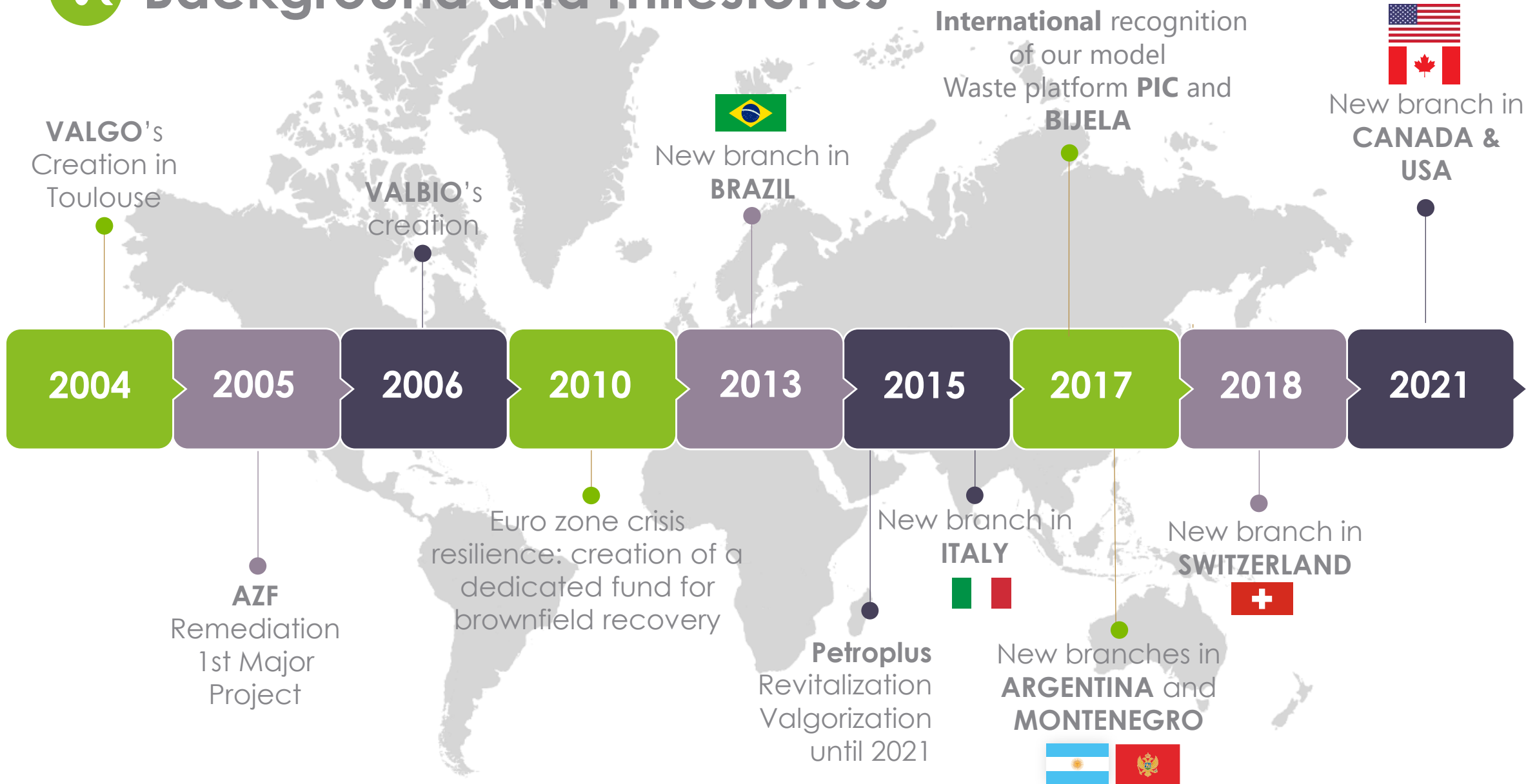
➔ In Developed countries, the plasmatic concentration of PFAS varies between **5 and 50 µg/L**

➔ Variable according to the geographical location and the professional occupation





Background and milestones





VALGO rization

