VALGO Canada Inc.

Université de Montréal

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Doctor in Pharmacy, Toxicologist
specialized in environmental toxicology

Project manager – risk assessment emerging pollutants at VALGO

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PhD, Environmental & analytical chemistry

Research Associate at Université de Montréal, Department of Chemistry

Differences and similarities in PFAS occurrence in Europe and Quebec

Key figures

+600
Employees around the world

6
Branches worldwide

100
M€ revenue

12
Agencies in France

Sept. 2021
New Shareholder
TIKEHAU CAPITAL

+650
Projects / year

+5000
Remediated sites

1008
Billed contracts

+1000
Ha recovered from our clients

+350
Proprietary Ha recovered

VALGO Canada Inc.

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 REMEDIATION (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.)

+90 years

of petrochemical pollution

270 htrs

of polluted land and premises

HIGH

Seveso classification

PARTIAL

Absestos diagnosis

270 HA

recovered

75 000 t

metals and **400 000 tons** concrete recycled

400 000 t

concrete and **55 000 t** hydrocarbon waste recycled and recovered

62 htrs

land remediated

3000

future jobs created

Université de Montréal

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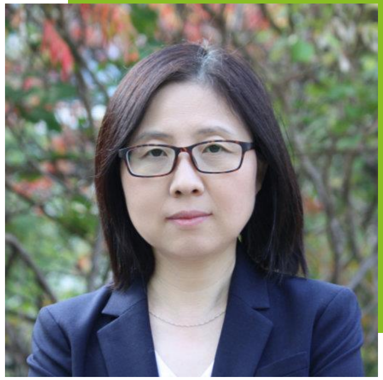

Jinxia Liu

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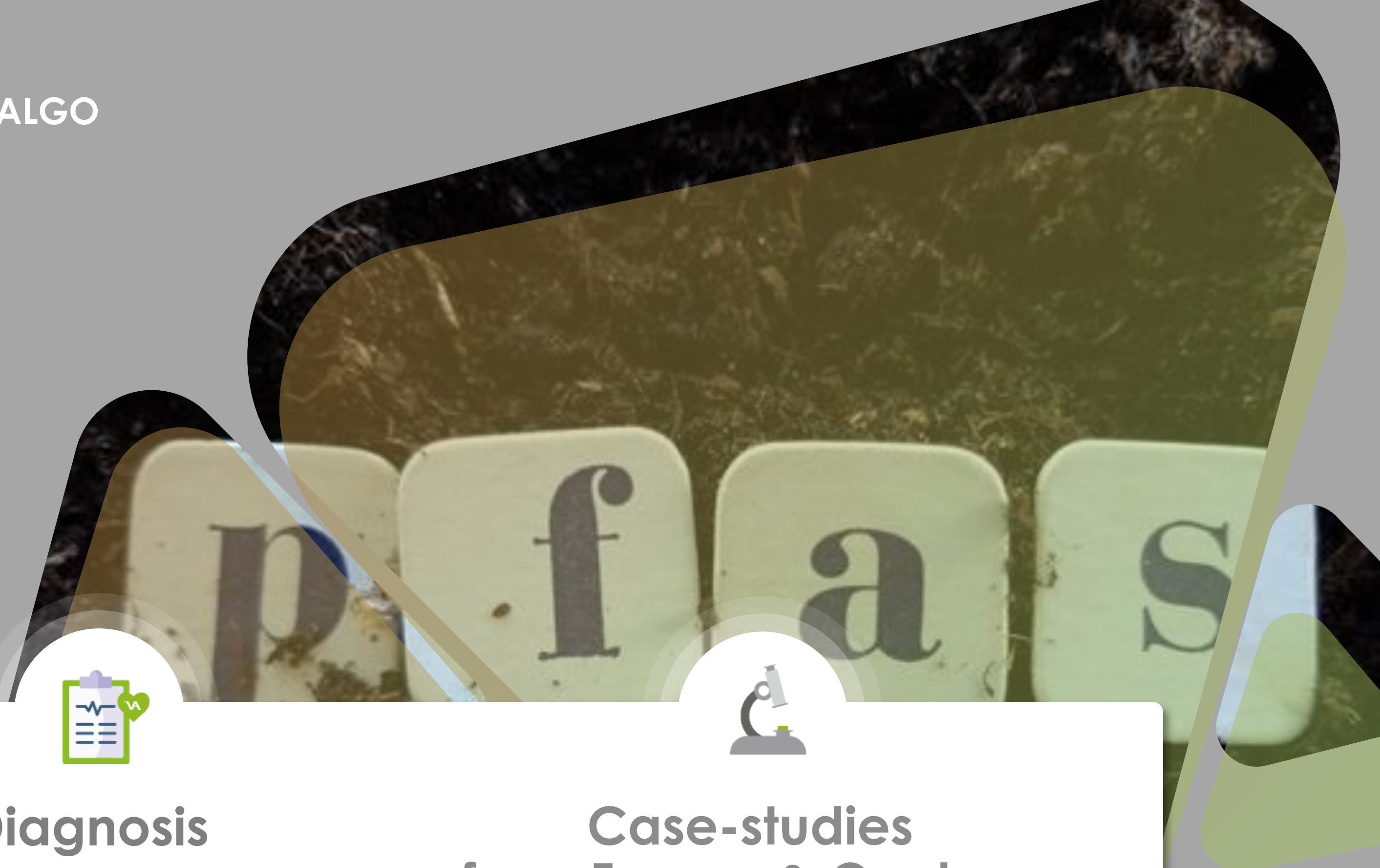
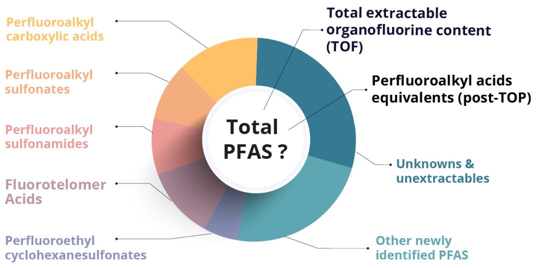
Differences and similarities in PFAS risk in Europe and Quebec



The PFAS Issue

Diagnosis



Case-studies from France & Quebec

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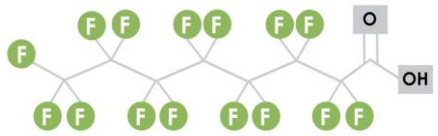
The PFAS issue

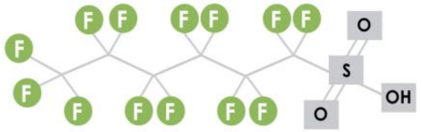
Per- and polyfluoroalkyl substances

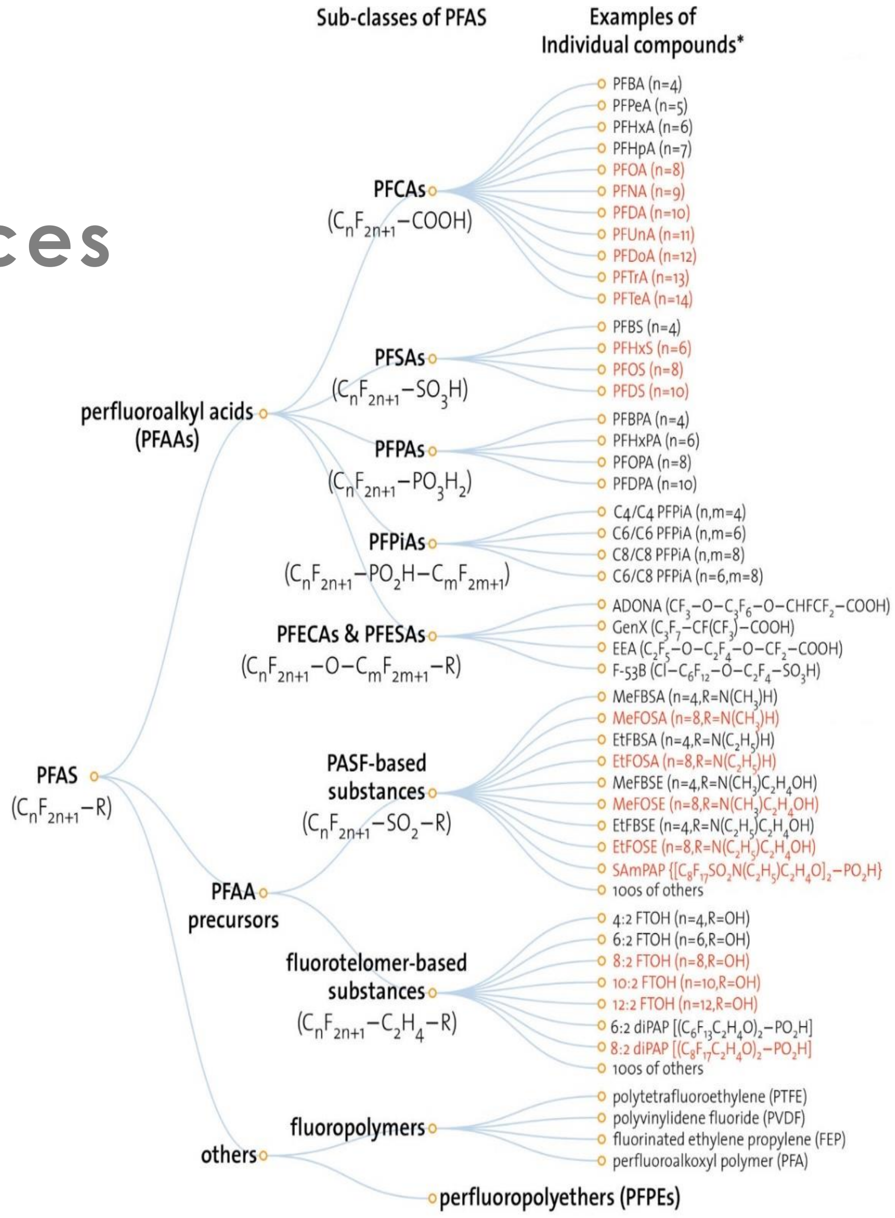
- Complex family with more than 6000 compounds
- **Properties imparted by the C–F bond**
  - ➡ **long half lives**
  - ➡ PFCAs/PFSAs virtually non biodegradable (ECHA)
  - ➡ Very **bioaccumulative** (long-chain PFAS)
- PFAS ubiquitous in the environment

PFOA



PFHxS





Wang et al. ES&T 2017

Major applications

Massively used in consumer goods, specialty formulations, and certain industrial processes

Electronics | AFFFs | Cosmetics | Ink | Textiles | Motor oils | Food packaging

Regulatory development

Guidelines for water

	Matrices	PFOS ($ng.L^{-1}$)	PFOA ($ng.L^{-1}$)
EU (2022-2027)	All waters	∑ 20 PFAS = 100 and ∑ PFAS = 500	
GERMANY 2006	Tap Water	∑ PFOS + PFOA = 300	
UK 2009	Tap Water	1000	300
US EPA 2016	Tap Water	70	70
THE NETHERLANDS 2011	Tap Water	530	-
SWEDEN 2014	Tap Water	90	90
ATSDR 2018	Tap Water	11	7
THE NETHERLANDS 2011	Groundwater	23	-
Health Canada 2018	Tap water	200	600
Minnesota	Tap water + Groundwater	35	15

ANSES 2018, ITRC 2019

- Mainly indicative values, **some regulatory limits** (USA, Denmark, Australia, New Zealand, …)

- **European Union:**
  - **REACH** (PFOS, PFOA, PFHxS), **More use restrictions to come (All PFAAs from C3 to C14)**
  - **Stockholm Convention** (PFOS and PFOA), registration submission of 2000 compounds in the "ban list" to come
  - **Water Framework Directive (WFD)** 2022-2027

- **USA and Canada:**
  - **Industrial phase-out** of PFOS by 3M (2000-2002), use of PFOA replacements (ADONA, GenX)
  - PFOS **phased out of commerce** in Canada and the USA in 2002
  - **Environmental Performance Agreement** (2009-2015, Canada) to ban PFOA and PFCAs
  - **Ban of PFOS-based AFFFs** in Canada as of May 2013

Toxicity

- Multiple pathways of exposure
- Multiple toxicity
  - Moderate hepatic toxicity
  - Immunological toxicity
  - Metabolic toxicity
  - Pre and postnatal development disorders
  - Endocrine disrupting effects
  - Carcinogenicity

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)

PFAS diagnosis

Analytical complexity

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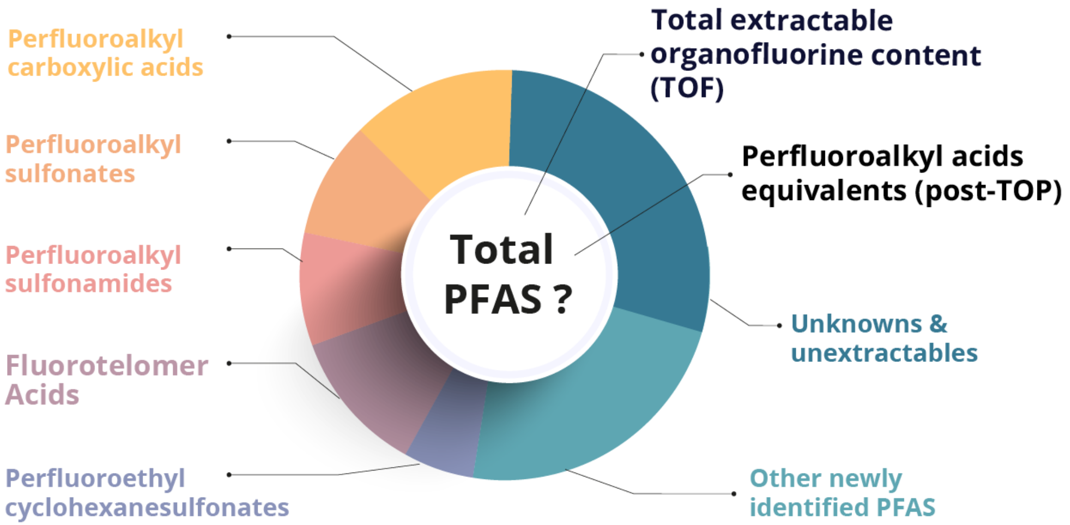
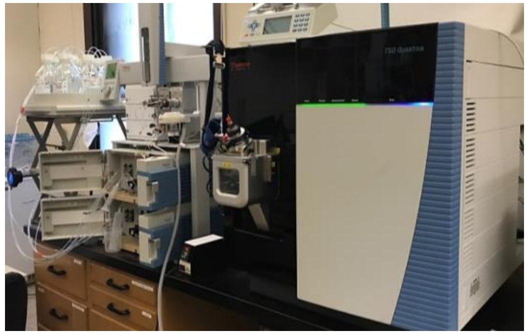
PFAS analytical methods

- 65+ anionic PFAS and 10+ zwitterionic PFAS with authentic standards
- Surrogate parameters for total PFAS: TOP assay and TF-CIC
- Nontarget analysis: HRMS data filtering using Kendrick mass defects



Dionex UHPLC
Thermo Q-Exactive Orbitrap MS

UltiMate 3000 UHPLC
Thermo Quantiva QqQ MS



Example PFAS-funded research – Prof. Sauvé's lab (UdeM)

- 2019-Present. Expanded analytical methods for zwitterionic, cationic and anionic PFAS (funded by SERDP).
- 2018-Present. Bioaccumulation and biomagnification of PFAS in a St. Lawrence River food web (CMP funding to Environment Climate Change Canada).
- 2018-2020. Nontarget screening of PFAS in biosolids for land application (with funding from French INRAE).
- 2017. PFAS in textiles (funded by the North American Commission for Environmental Cooperation, NAFTA/ALENA).
- 2014-Present. Environmental assessment of PFAS at AFFF-impacted sites, including the Lac-Mégantic (QC) accident site and federal contaminated sites (funded by NSERC).

Collection of >100 AFFFs obtained to support analytical method development

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Ultrasensitive method for PFAS analysis in tap water

- Automated pre-concentration (Autotrace 280) using weak-anion exchange SPE
- Streamlines lab work
- Good recovery of zwitterionic & anionic PFAS
- Excellent limits of detection
  LOD ESI(-) PFAS 0.001-0.08 ng/L
  LOD ESI(+) PFAS 0.003-0.05 ng/L
- Applied for target & nontarget screening

1000X pre-concentration factor achieved with automated off-line SPE (Dionex Autotrace 280)

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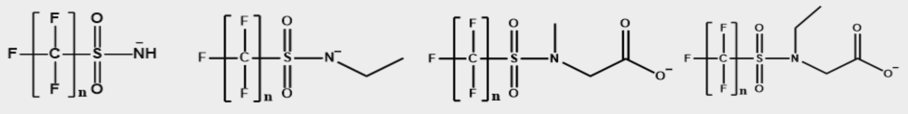
Example classes of target / suspect PFAS amenable to LC-HRMS

Historical PFAAs

(1) (2)

ESI(-) ECF-sulfonamides

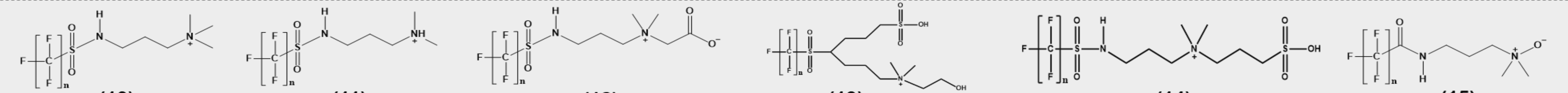


(3) (4) (5) (6)

Other ESI(-) ECF derivatives

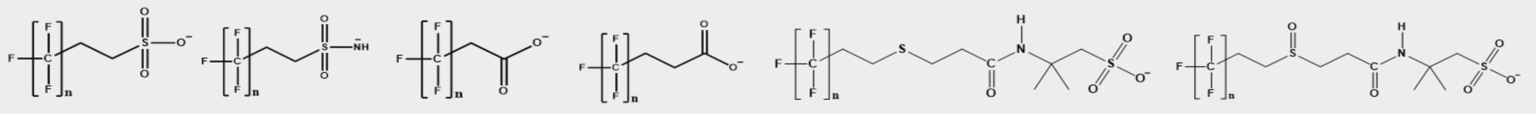
(7) (8) (9)

ESI(+) ECF precursors



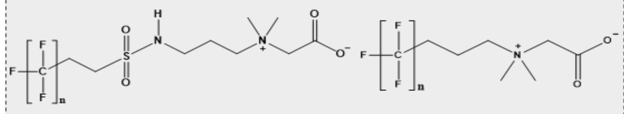
(10) (11) (12) (13) (14) (15)

ESI(-) fluorotelomers



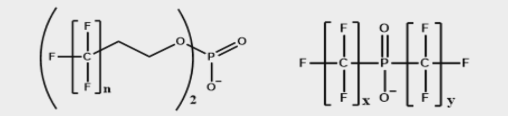
(16) (17) (18) (19) (20) (21)

ESI(+) fluorotelomers



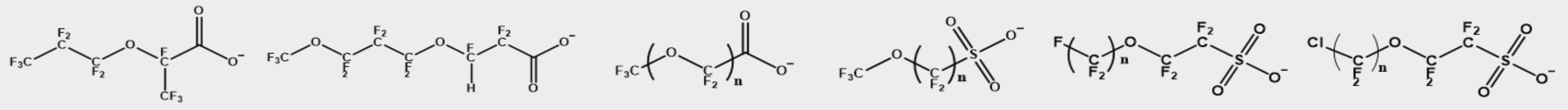
(22) (23)

P-derived PFAS



(24) (25)

Fluoroalkyl ethers

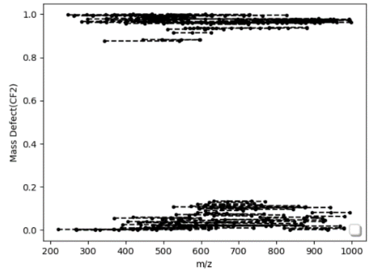


(26) (27) (28) (29) (30) (31)

Nontarget screening workflow (Q-Exactive Orbitrap)

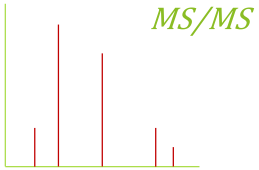
Data acquisition
LC-HRMS (Full Scan)

Blank subtraction (pairwise)
Elimination of peaks <10E4



Kendrick mass defect filtering
(Python script)

Identification of candidates
Automated library search (script)
Patent examination



Confirmation with reference chemicals, when available
Annotation of HR-MS/MS spectra

Identification confidence

Level 1: Confirmed structure by reference standard
Level 2: Probable structure a) by library spectrum match b) by diagnostic evidence
Level 3: Tentative candidate(s) structure, substituent, class
Level 4: Unequivocal molecular formula
Level 5: Exact mass of interest

Confidence levels
assigned per
Schymanski's scale

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Case Study – Typical contamination in France and in Quebec

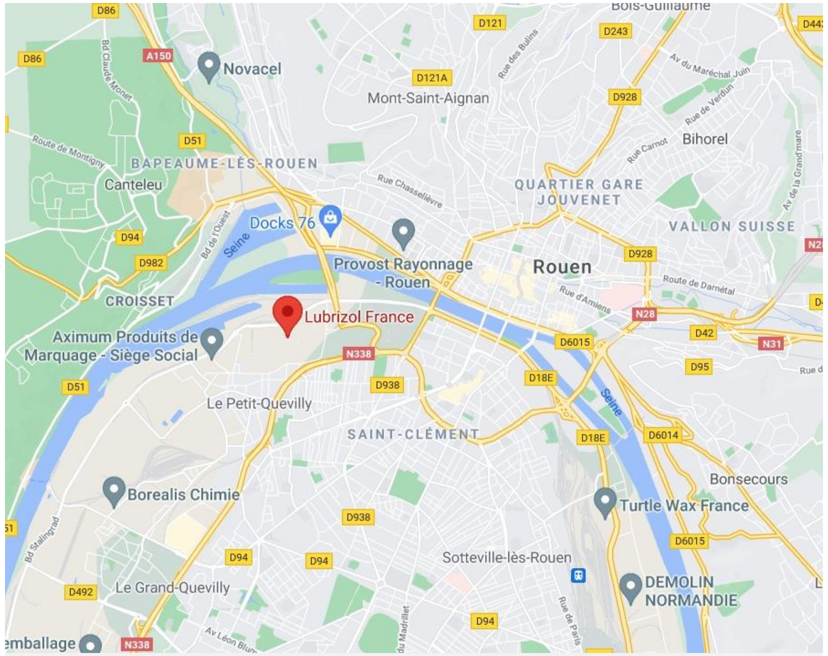
Part 1 - France

Context : Lubrizol/Normandie Logistique Fire

Seveso 2 site (High Risk)

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

Intensive use of AFFF Foams ($40\ 000\ m^3$, water diluted)



Samples:
- Groundwater
- Treated Groundwater
- Network Water
- Tap water
- Wastewater

Analysis:
- Mass spectrometry 60 compounds
- Mass spectrometry 200 compounds
- Non targeted mass spectrometry
- CIC ➡ Total Organic Fluorine

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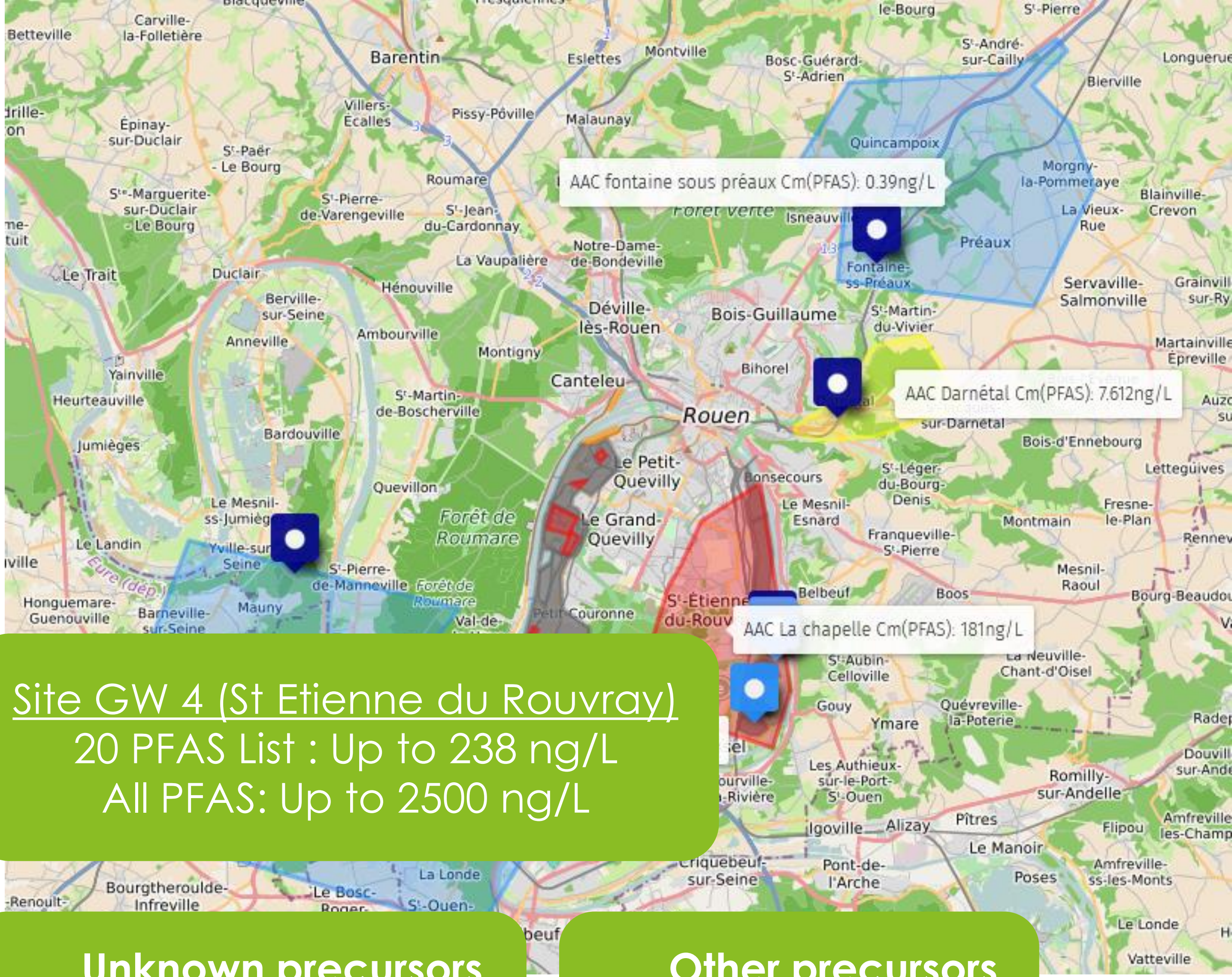
Results

Groundwater

High contamination of groundwater (compared to spring water), locally higher than the regulatory values

Indicative WFD limits:
- 20 PFAS list : **100** ng/L
- All PFAS: **500** ng/L

High-resolution mass spectrometry fingerprinting: The main contaminants in **most samples are novel anionic or zwitterionic precursors**



Site GW 4 (St Etienne du Rouvray)
20 PFAS List : Up to 238 ng/L
All PFAS: Up to 2500 ng/L

Unknown precursors
- C15H21O3N2F9
- C9H13O2N27

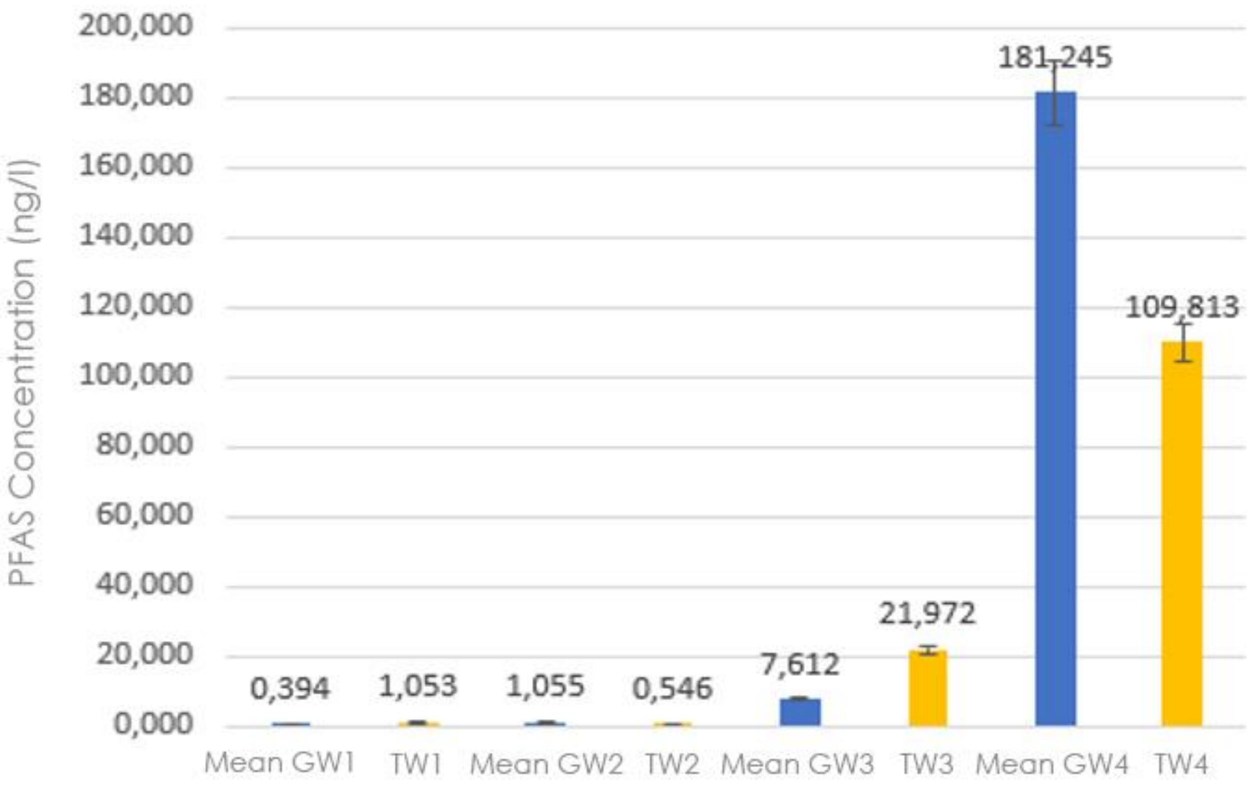
Other precursors
- 6:2 FTAB
- 6:2 FTSAS

Results

Treated Groundwater

Usual treatments are not effective (39-50%) sometime have an opposite effect (change and regeneration of consumables)

Treatments:
- TW1 : Ultrafiltration
- TW2 : GAC + GAC
- TW3: GAC + Ultrafiltration
- TW4: GAC



Results

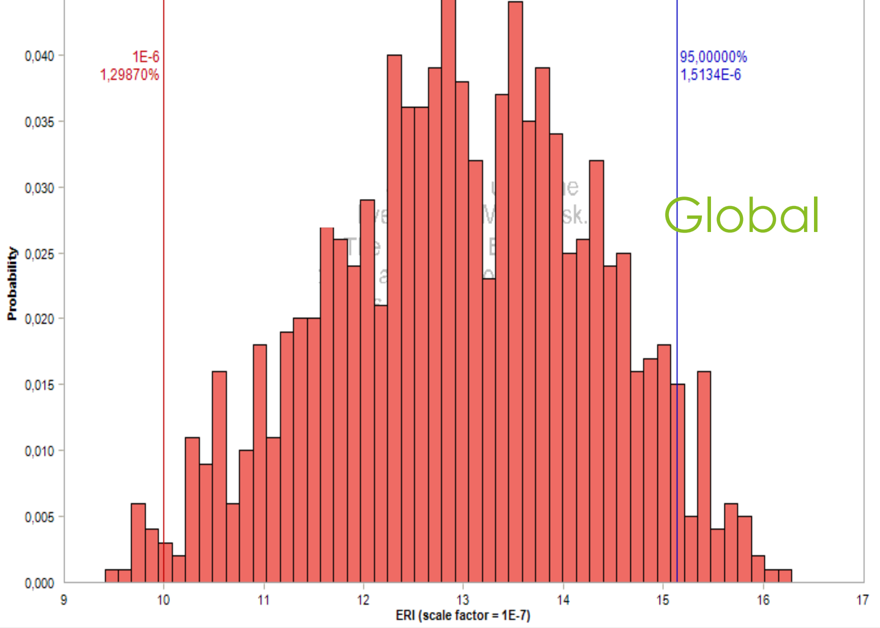
Tap water

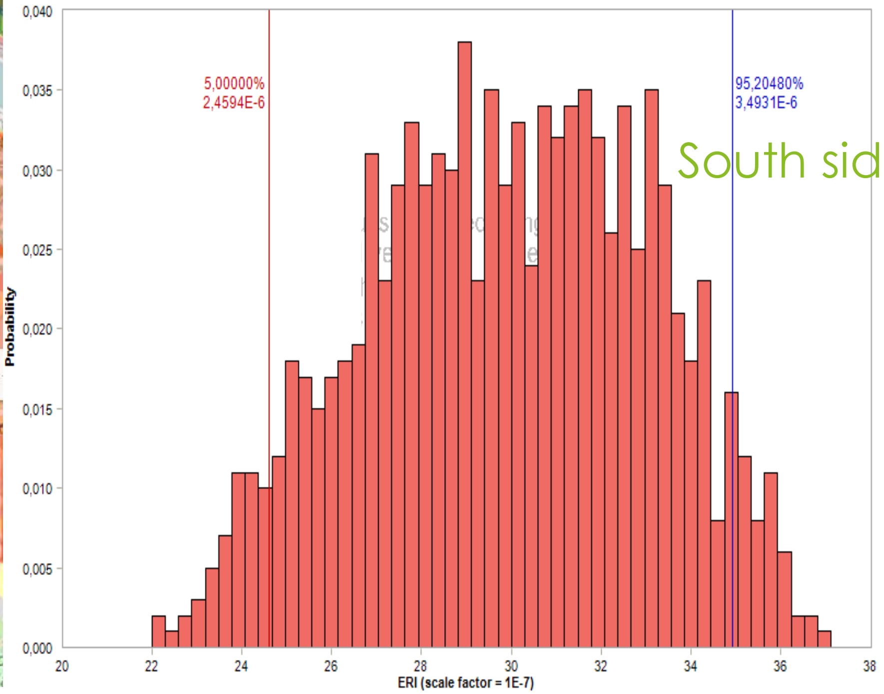
- Lower concentration to the North due to dilution effect of other water sources
- Low concentration in hospitals (Post Treatment)
- Main analytes: New precursors (e.g., the **zwitterion 6:2 FTAB**), PFCAs and short-chain PFAS (low treatment efficiency)

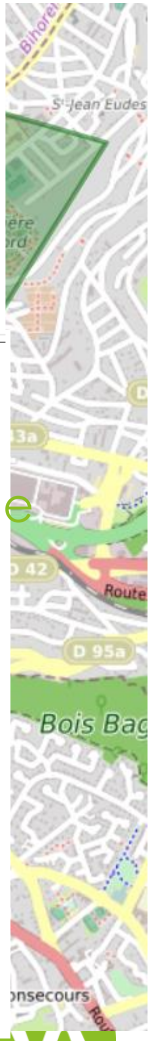
Risk Study:

➡ **Carcinogenic** risk not negligible
➡ Higher risk on the south side
➡ Higher concentrations in St. Etienne du Rouvray

➡ **Only for PFOS and PFOA (2 available Cancer slope factor)**







St Etienne du Rouvray

Results

Wastewater

- PFAS from urban wastewater but also from industrial activity ➡ Mainly precursors (e.g., **zwitterion: 6:2 FTAB**)
- Low removal rate **7%**
- High environmental contamination : **194 ng/L**

➡ **80 000 000 L/day**

➡ **>15 kg PFAS/day**

What about the sludge?

➡ *Incineration*

➡ *Land Application*

Case Study – Typical contamination in France and in Quebec

Part 2 - Quebec

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Quebec case study 1 – Surface waters (UdeM)

- 400+ surface water samples collected in Quebec province, including the St. Lawrence (1000-km gradient), major tributaries, and smaller rivers.
- Samples evaluated for 40+ target PFAS, including **novel zwitterions**.
- Select samples were also evaluated using nontarget screening.

St. Lawrence River

2018-2021 (n ~ 200)

Estuary/Gulf

2020-2021 (n ~ 80)

Tributaries

2018-2021 (n ~ 150)

Background sites

2020-2021 (n ~ 30)

★ Not routinely monitored in Quebec at this time

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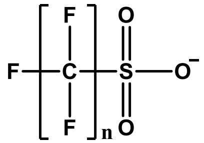
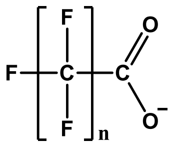
Quebec case study 1 – Surface waters (UdeM)

- 25+ classes of PFAS detected in Quebec river waters.
- Specific AFFF precursors prevalent in small-scale impacted rivers and creeks.
- Specific ECF PFAS characteristic of the St. Lawrence River.

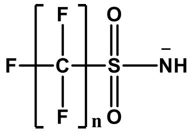
St. Lawrence River



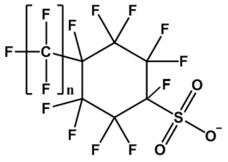
PFOS & homologs



PFOA & short-chain homologs

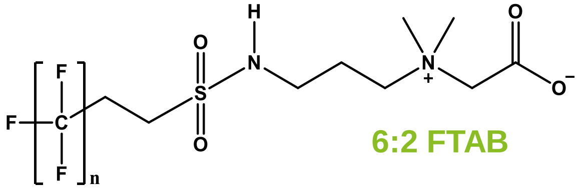
★ 

Short-chain sulfonamides

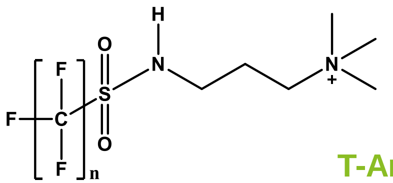
★ 

PFECHS

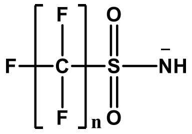
AFFF-impacted rivers

★ 

6:2 FTAB

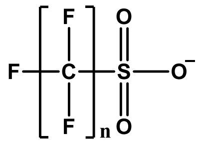
★ 

T-AmPr-FHxSA

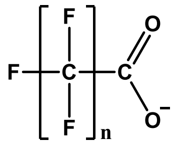
★ 

Short-chain sulfonamides

Background sites



PFOS & homologs

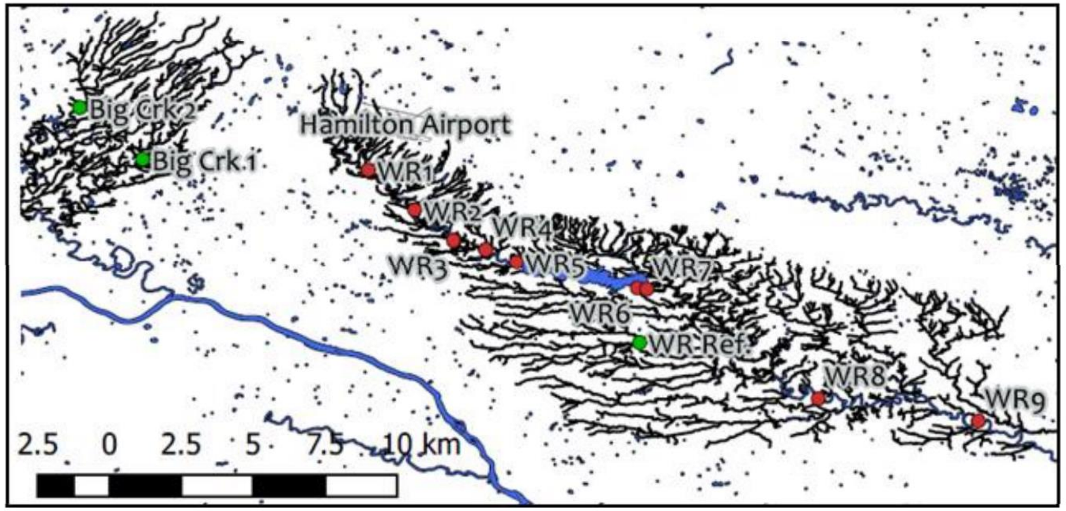


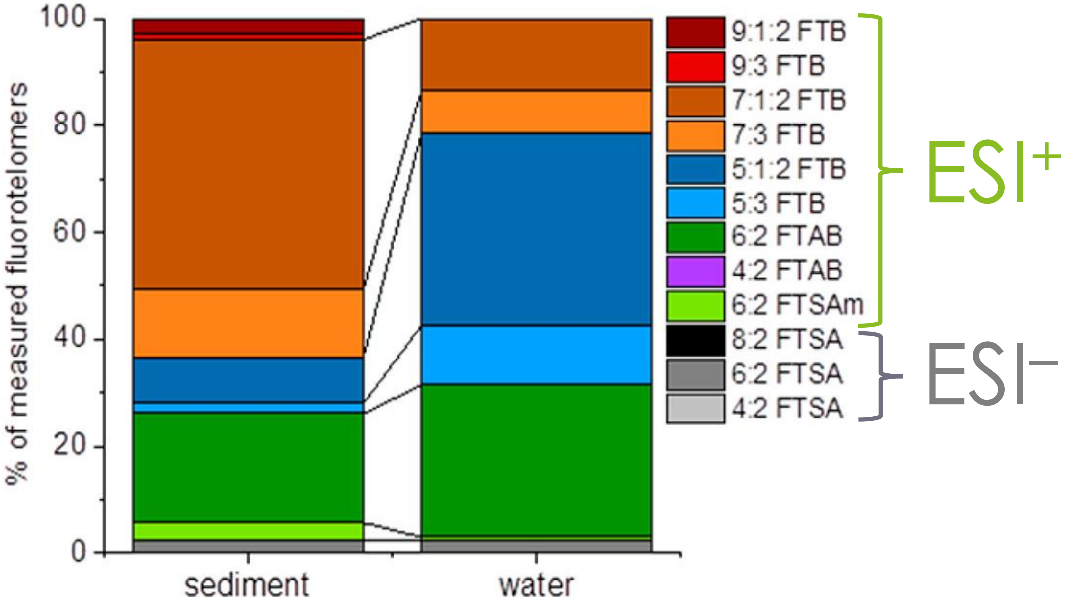
PFOA & short-chain homologs

Munoz et al. In prep.

6:2 FTAB and other betaines also reported in southern Ontario

(A study by D'Agostino & Mabury – U of Toronto)





ESI+ fluorotelomer betaines

>95% of total measured fluorotelomers

Welland River watershed

WR1 – imm. downstream Hamilton Airport

D'Agostino & Mabury *ES&T* 2017

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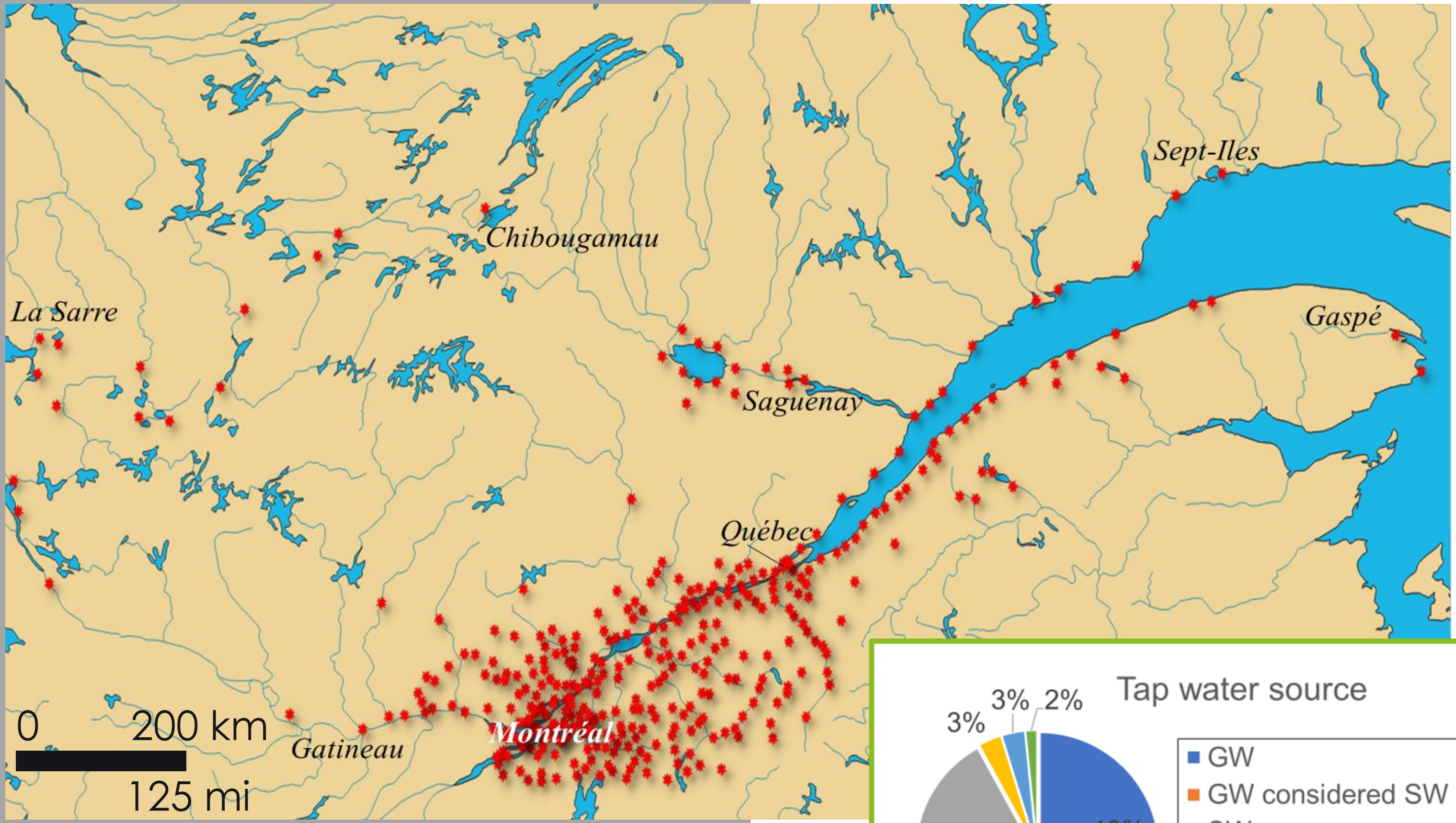
Quebec case study 2 – Tap water (UdeM)

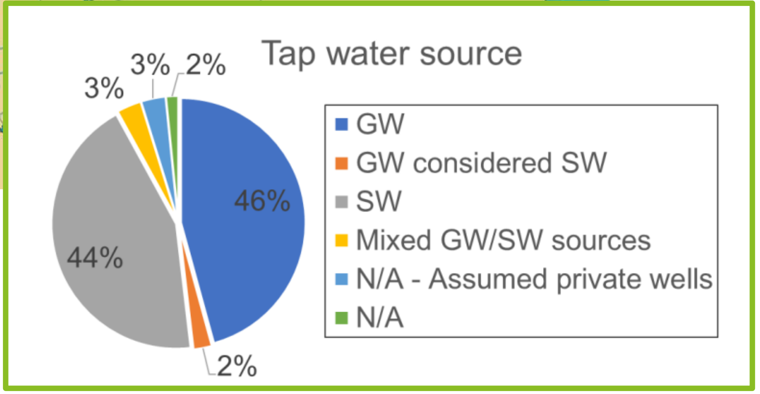
+ 460

tap water samples collected in QC over 3 years (2018-2020) for PFAS analysis.

376

distinct municipalities, most corresponding to public distribution water.





Munoz et al. In prep.

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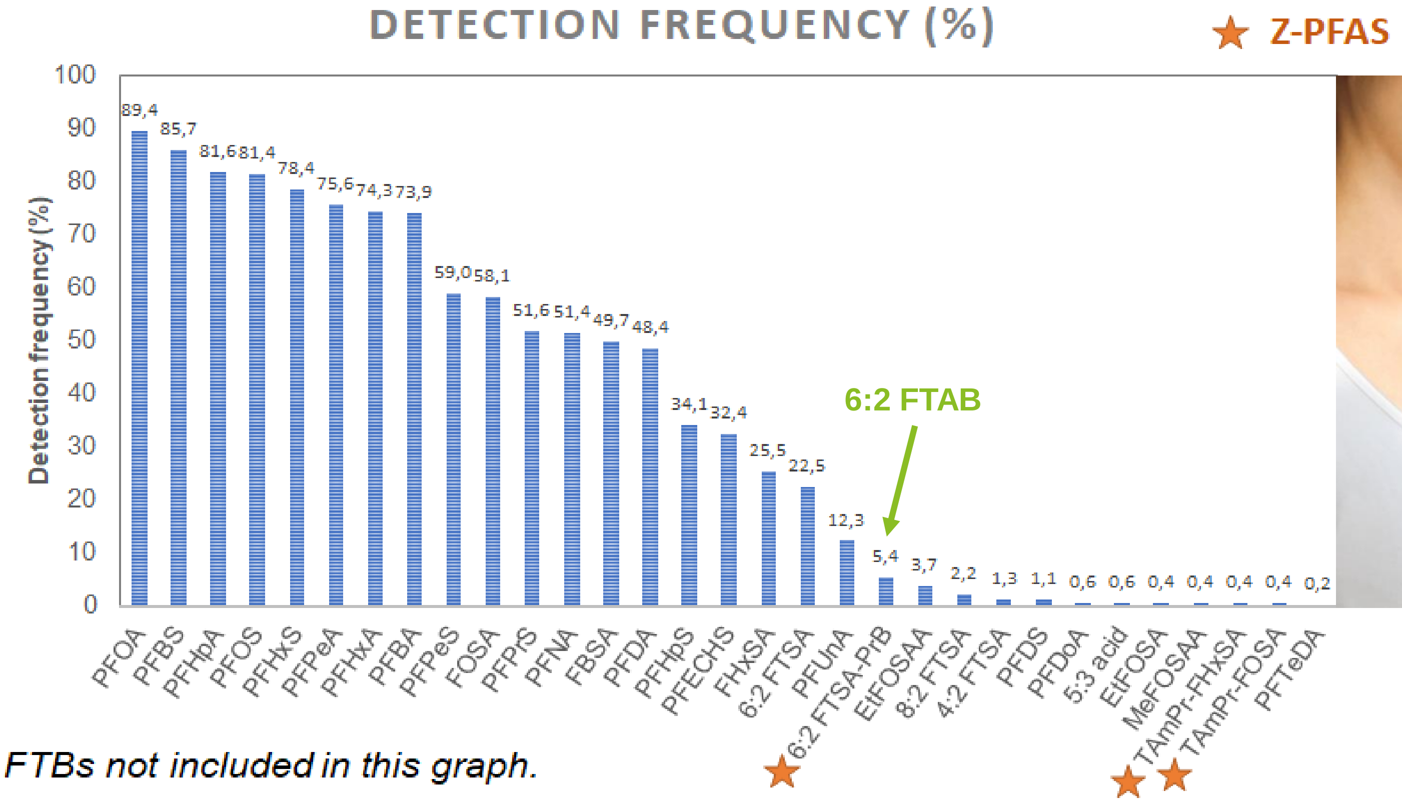
Quebec case study 2 – Tap water (UdeM)



Note: *FTBs not included in this graph.*

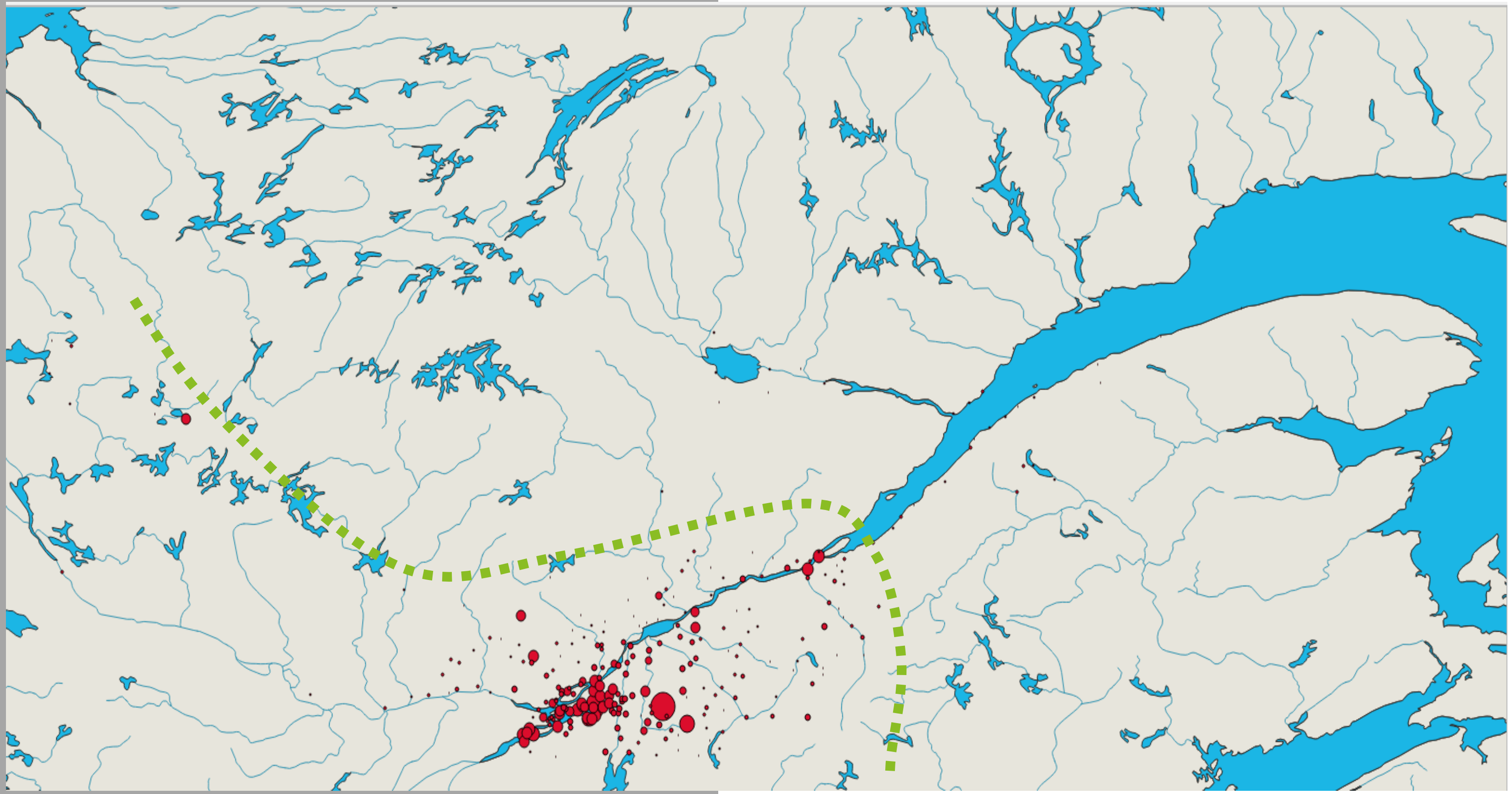
- PFOS/PFOA detected in more than 80% of >400 tap samples.
- No sample surpassed Health Canada guidelines for PFOS/PFOA.
- Zwitterionic PFAS can persist through drinking water treatment trains.

Munoz et al. In prep.

PFOS in tap water (ng/L, average per sampling site)

MAX = 13 ng/L

DW advisory levels
Health Canada
600 ng/L
USEPA 70 ng/L



Low levels East of this line

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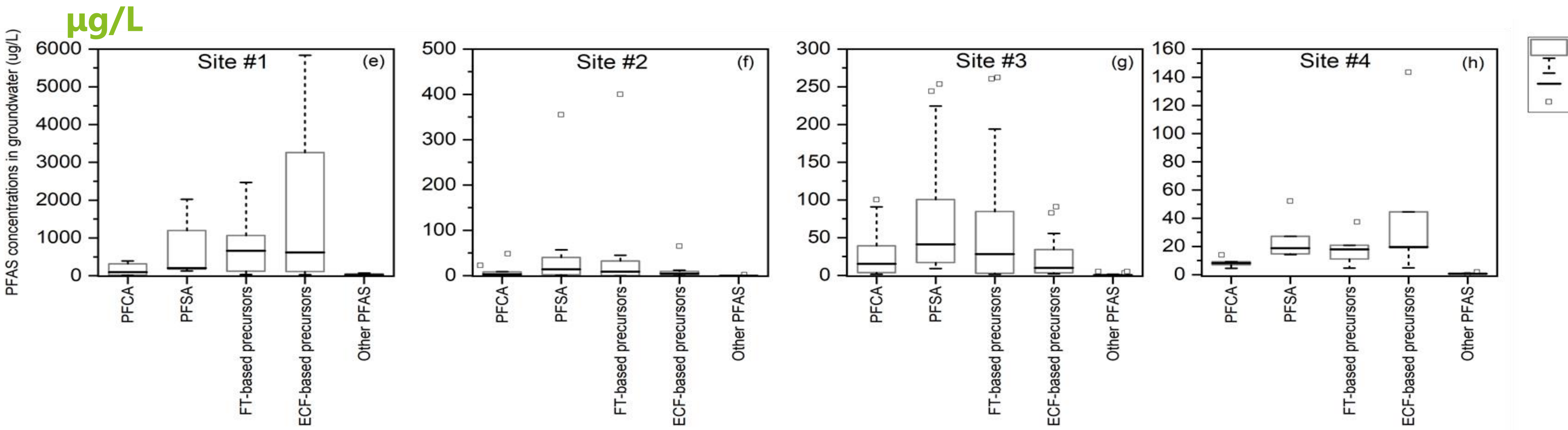
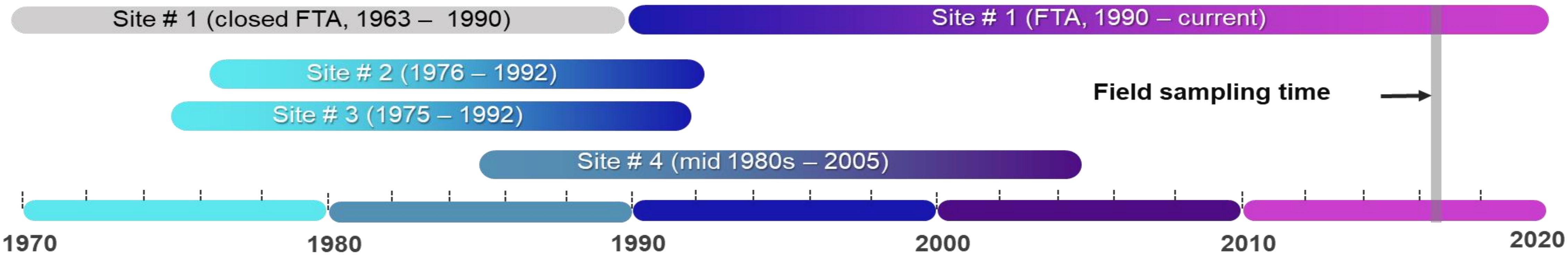
Canadian case study – Groundwater at AFFF sites (UdeM/McGill)





Min Liu et al. *ES&T* 2022

Differences and similarities

Differences and similarities

France

Main sources:

- 1/ Former or current industrial areas (chemical, paper, electronics, and Seveso sites)
  2/ Airports
  3/ Wastewater treatment plants
- Industries located around majors cities
  ➡ Potential threat to drinking water supplies (mainly groundwater as source)
- Exposure linked to the consumption of contaminated water

Quebec

Main sources:

- 1/ Airports, military bases
  2/ Petrochemical & mining industries
  3/ Wastewater treatment plants, landfills
- Drinking water of main cities produced mostly from large rivers, reducing contamination (dilution effects)
- Exposure also linked to diet (fish, marine mammals…), for instance in Northern populations

Differences and similarities

- **Fire training area sites** may be viewed as a priority due to high (though localized) contamination
  ➡ Soil contamination near the FTA source zone – remediation needed
  ➡ Extremely high concentrations in groundwater (mg/L levels)

- **Some fluorotelomer precursors have emerged in recent years, both in France and in Canada**
  - An example is the zwitterion 6:2 FTAB (a betaine-based PFAS) – found in France,[1,2] Quebec,[3,4] and Ontario[5]
  - Found in wastewater, biosolids for land application, groundwater, surface water, and treated tap water
  - Rarely (or never) analyzed by commercial and/or research laboratories

- Phased approach to **regulate historic and new PFAS** (new restrictions/guidelines being developed)

[1] Boiteux et al. *Stoten* 2017. [2] Munoz et al. *Talanta* 2016.
[3] Liu et al. *ES&T* 2022. [4] Mejia-Avendaño et al. *ES&T* 2017.
[5] D'Agostino & Mabury *ES&T* 2017.

Thank you for your attention