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Université de Montréal

Comprehensive Profiling of PFASs in Environmental Waters: Analytical Method Implementation and Preliminary Monitoring Results

Sébastien Sauvé, Gabriel Munoz, Sung Vo Duy
(Université de Montréal)

Jinxia Liu

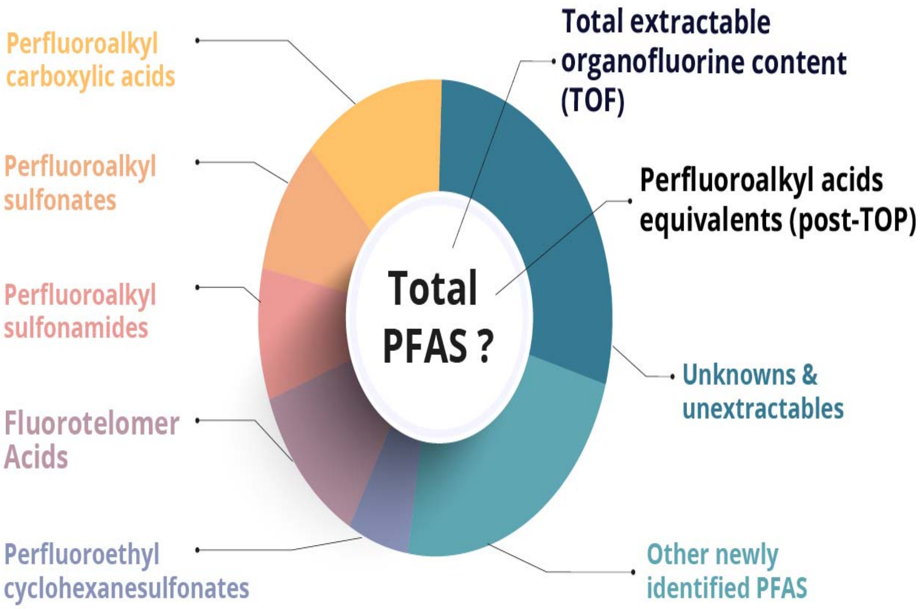
(McGill University)

Problem statement

- AFFF-impacted samples contain a high number of PFAS with unknowns, challenging for chemical analysis

- Standard analytical methods for individual PFAS need significant updates
  - Available standard methods: EPA Method 537(drinking water), ASTM 7979-17 (groundwater, surface water, wastewater, sludge), ASTM D7968-17a (soil)
  - Analytes covered include mostly the legacy PFAS (anionics or neutrals)

- Alternative methods for total PFAS determination are necessary
  - Total oxidizable precursor (TOP) assay
  - Total extractable organofluorine content (TOF)
  - Substantial development required to improve reproducibility and reliability



ER19-1157 – Project technical objectives

***Overarching goal** – develop a set of improved sample preparation procedures and instrumental methods that can encompass a large breadth of anionic, cationic, and zwitterionic PFASs typically present in AFFF-impacted environmental samples*

Specific Objectives

- ❑ Standardize analytical methods for compound-specific PFAS analyses that cover major types of PFAS, with suitable analytical validation performance
- ❑ Develop and validate procedures to determine total PFAS via TOP assay
- ❑ Develop and validate procedures to determine total PFAS in terms of TOF

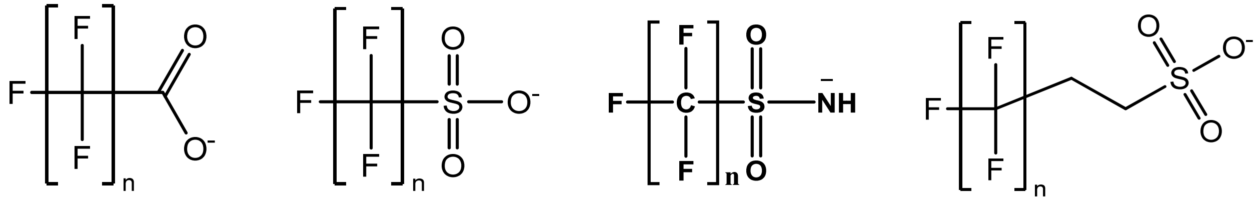
Jinxia Liu (PI)
McGill

Sébastien Sauvé (Co-PI)
Université de Montréal

Kela Weber (Co-PI)
Royal Military College of Canada

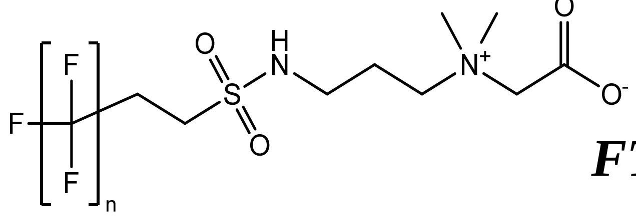
PFAS discussed in this presentation

Well-known / legacy PFAS (pre-existing methods)



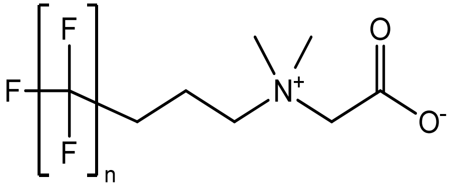
Newly-identified PFAS, new challenges

- Fluorotelomer sulfonamido betaines



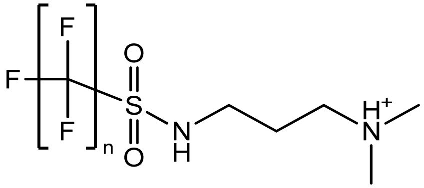
FTAB

- Fluorotelomer betaines



FTB

- Perfluoroalkyl sulfonamido amines



PFHxSAm

Research hypotheses for expanding analytical methods

Instrumental analysis

- ☐ Transferring LC-MS methods to newly identified PFAS not a major challenge
- ☐ QA/QC compliance may still be difficult without suitable internal standards

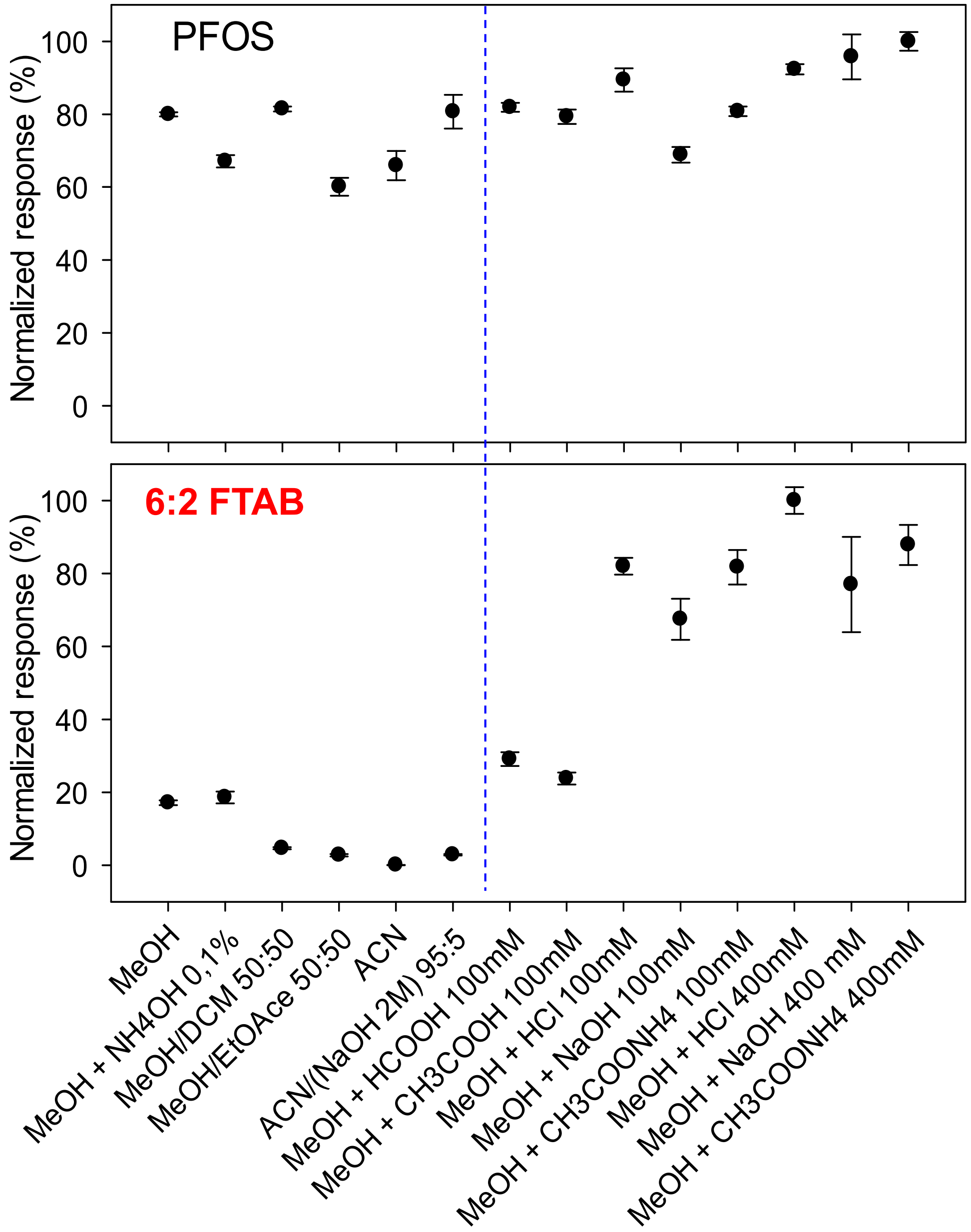
Extraction methods

- ☐ Extraction methods of old PFAS may not be transferable as-is to new ones
- ☐ Solids (e.g., soil, fish muscle) may present additional challenges

Implementing TOP assay

- ☐ Matrix interfering components could preclude an efficient conversion
- ☐ Oxidative yields of precursors should be compared with and without matrix
- ☐ Complexity of postoxidation extracts may require cleanup prior LC-MS

Extraction methods – Examples of pitfalls noted



PFAS extraction from soil was tested in AFFF-impacted soil

PFOS: limited variations with extraction conditions

6:2 FTAB: strong influence of solvent nature

Pre-existing methods would not work well for 6:2 FTAB

Extraction with MeOH (no additive) would lead to a five-fold underestimation of FTAB level

G. Munoz et al. *Analytica Chimica Acta* 2018

General methodology

1. Problem statement – knowledge gaps and research hypotheses
2. Verify suitability of LC-MS instrumental methods: fit for purpose?
3. Optimization of extraction methods, including pre-existing ones
4. Extensive method validation using certified standards and AFFF spikes
5. QA/QC compliance for routine application to long sample series

3.1

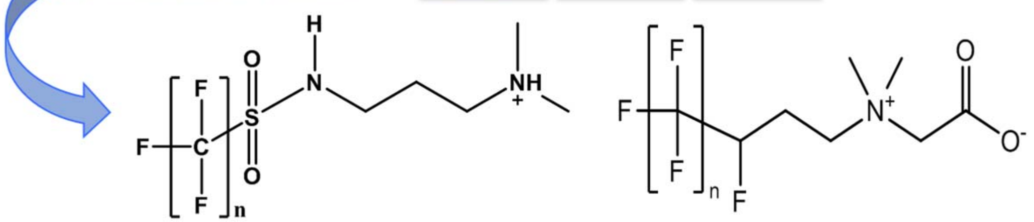
Optimization using field samples

3.2

Optimization using AFFF-amended samples

4

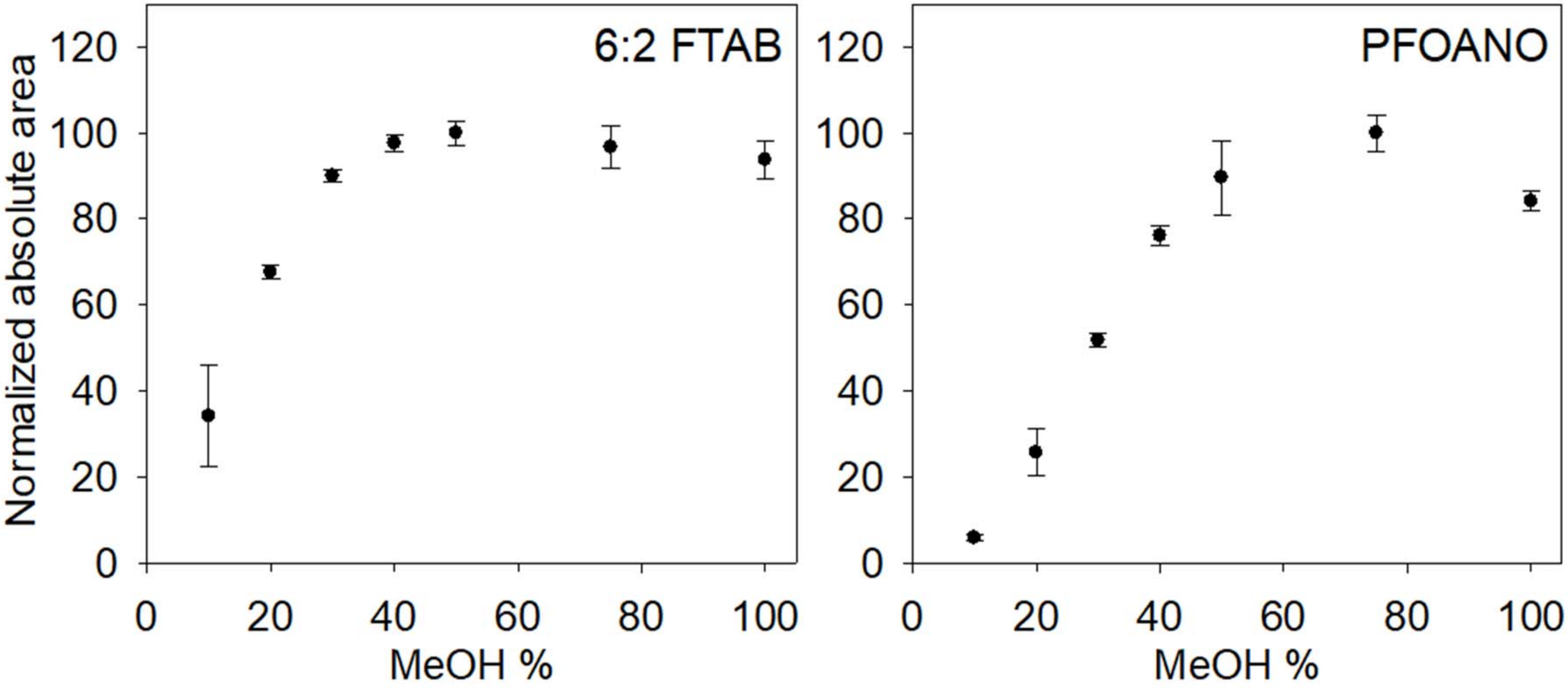
Recovery & matrix effect evaluation



Preliminary results – WP1a (water matrices)

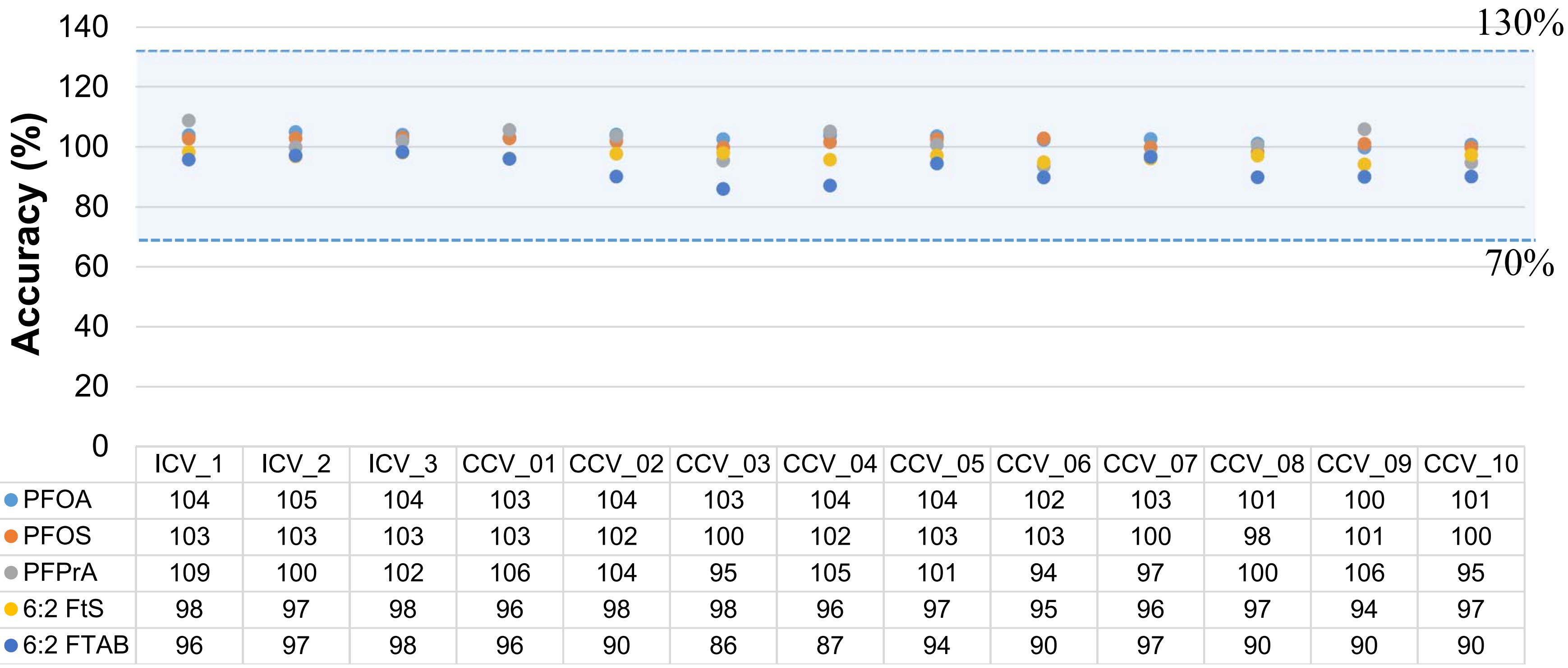
Dilute and shoot method applied to AFFF-impacted water

- ☐ Diluting with HPLC-water leads to sorption artifacts of amphoteric PFAS
- ☐ This can cause time-dependent variations during the LC-MS sequence
- ☐ Organic solvent content of >70% recommended for QA/QC compliance



D. Martin et al. *Talanta* 2019

Quality Control charts – ICV and CCV along LC-MS sequence



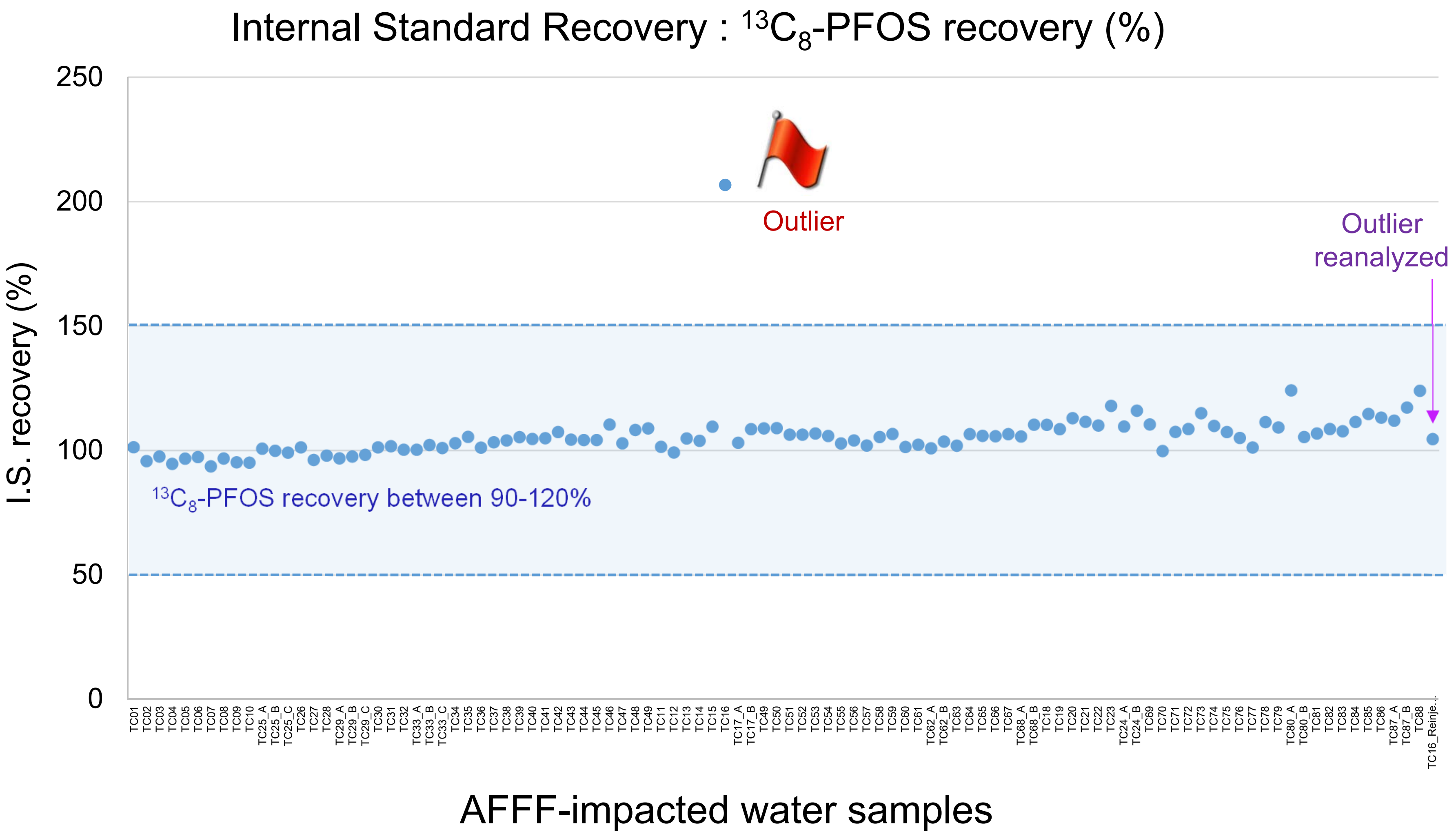
	ICV_1	ICV_2	ICV_3	CCV_01	CCV_02	CCV_03	CCV_04	CCV_05	CCV_06	CCV_07	CCV_08	CCV_09	CCV_10
● PFOA	104	105	104	103	104	103	104	104	102	103	101	100	101
● PFOS	103	103	103	103	102	100	102	103	103	100	98	101	100
● PFPrA	109	100	102	106	104	95	105	101	94	97	100	106	95
● 6:2 FtS	98	97	98	96	98	98	96	97	95	96	97	94	97
● 6:2 FTAB	96	97	98	96	90	86	87	94	90	97	90	90	90

Initial Calibration Verification

Continued Calibration Verification
(run after every 10 field samples)

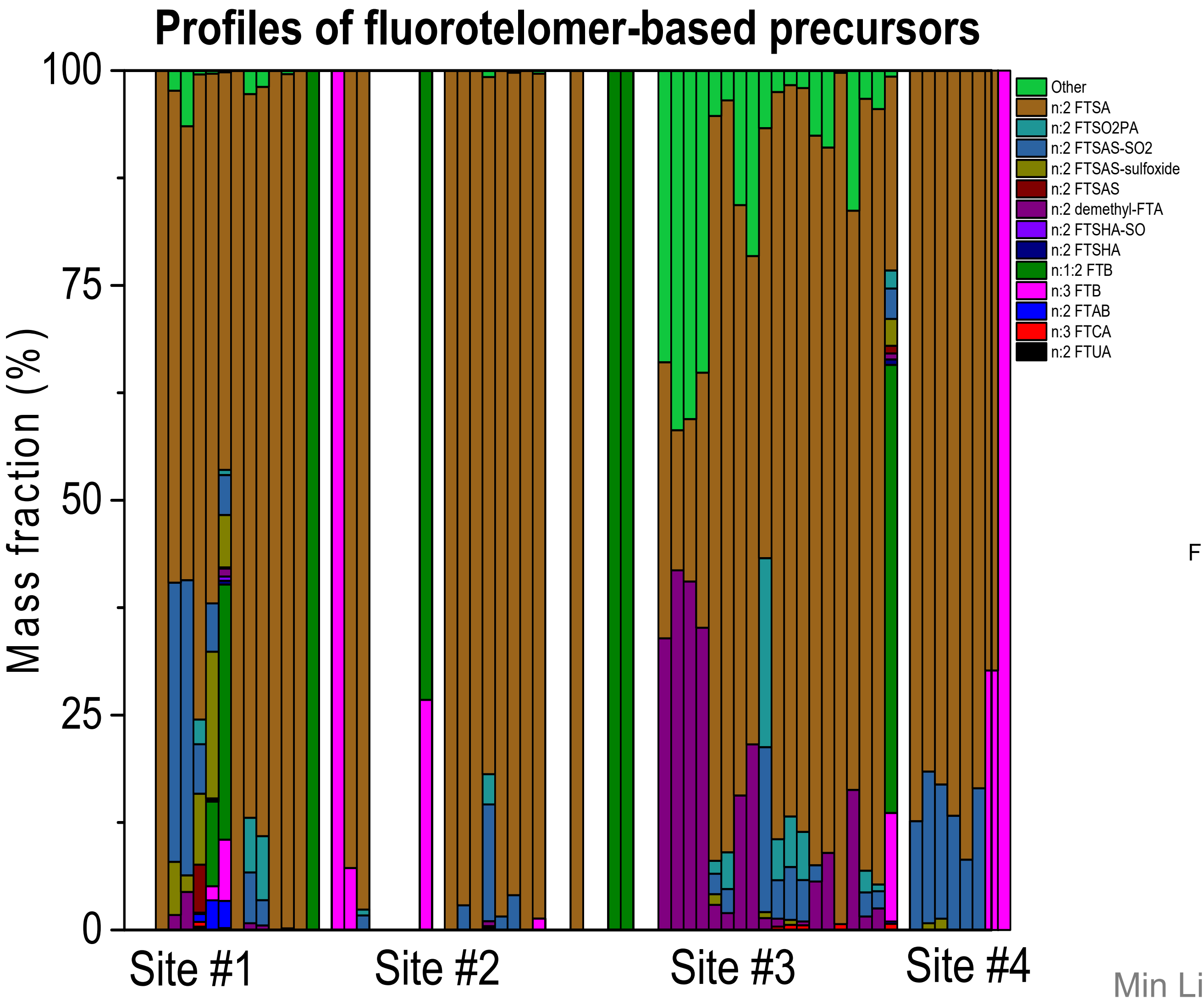
Preliminary results – WP1a (water matrices)

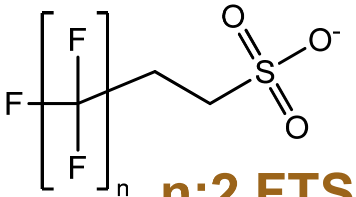
Internal standard recoveries also controlled for all samples



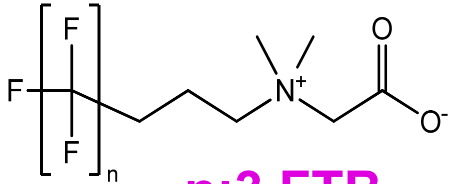
Preliminary results – WP1a (water matrices)

Example of method application to AFFF-impacted groundwater

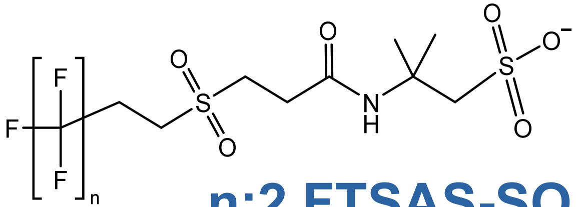




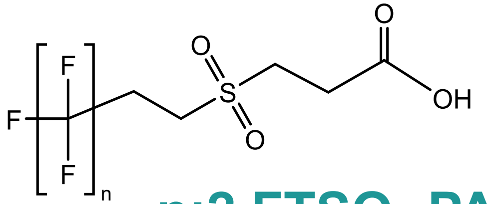
n:2 FTSA



n:3 FTB



n:2 FTSAS-SO_2



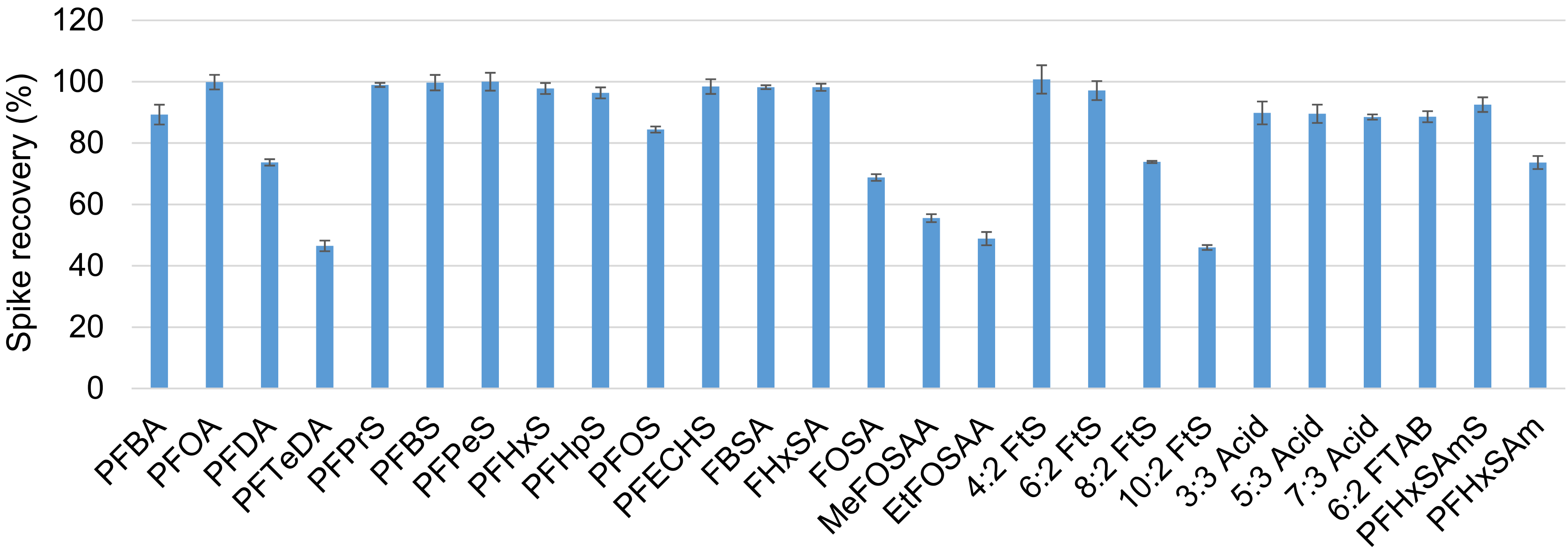
n:2 $FTSO_2$ PA

Min Liu et al., *manuscript in preparation*

Preliminary results – WP1a (water matrices)

SPE pre-concentration method applied to background water

- ☐ Preliminary test conducted on spiked tap water (500 mL)
- ☐ Automated SPE (Autotrace) leads to improved precision performance
- ☐ Suitable whole-method recoveries, including for 6:2 FTAB
- ☐ Method LOQs in the range 0.01–0.15 ng/L

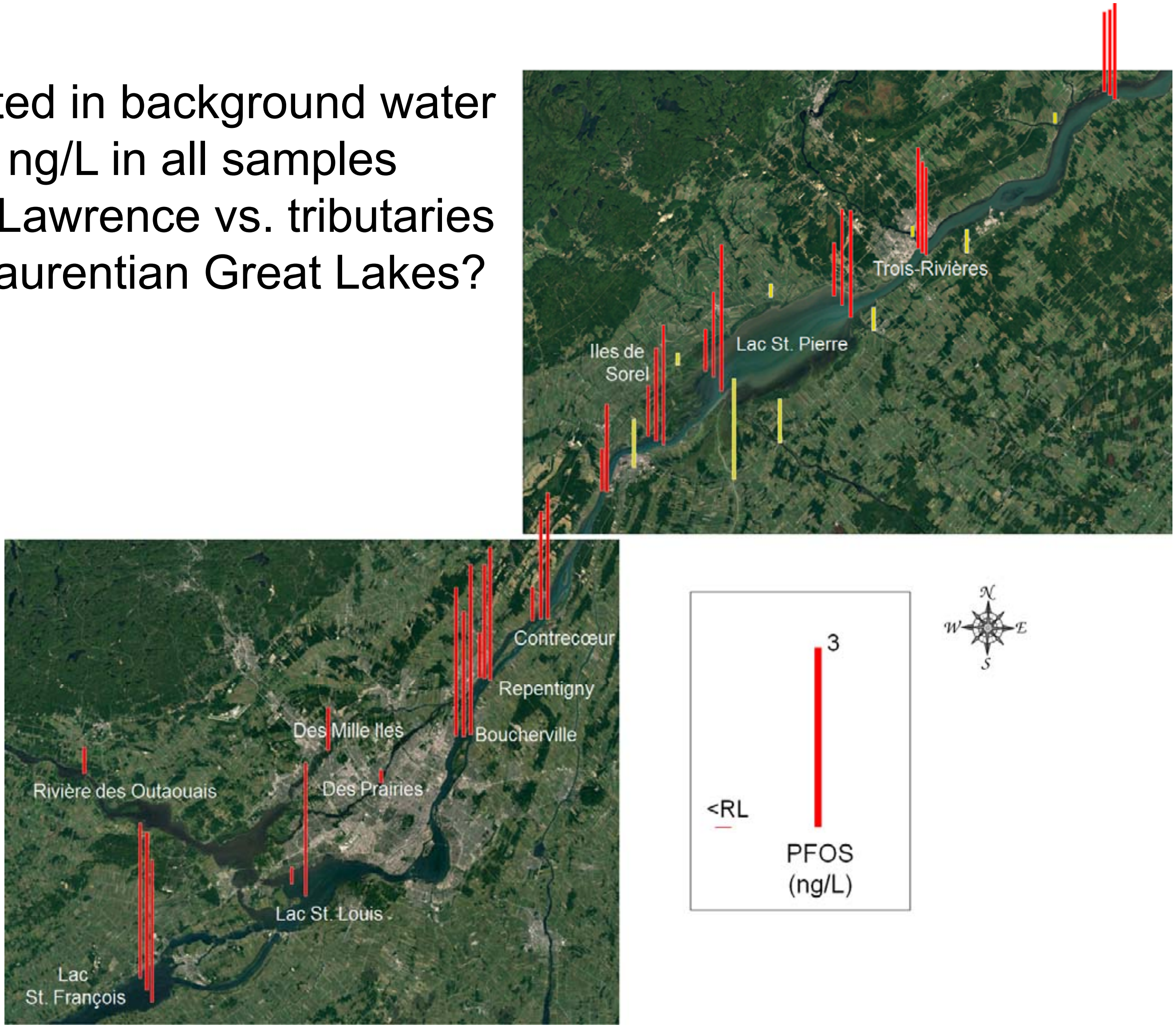


Manuscript in preparation

Preliminary results – WP1a (water matrices)

Example of SPE method application to background surface water

- PFOS widely detected in background water
- PFOS remained <5 ng/L in all samples
- PFOS higher in St. Lawrence vs. tributaries
- Major inputs from Laurentian Great Lakes?



Vaudreuil et al., manuscript in preparation

Preliminary results – WP2 (TOP Assay)

Aims of the TOP Assay

❑ Estimate total levels of PFAAs and their precursors

❑ Indirectly quantify precursors to PFAAs without authentic standards

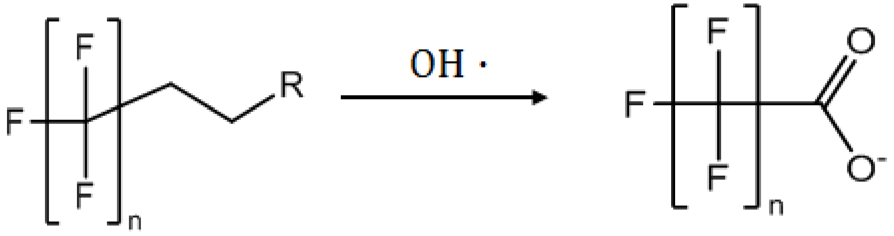
❑ Allow a better diagnosis for AFFF-contaminated sites

TOP analysis

❑ Aqueous sample oxidized in the presence of persulfate ($K_2S_2O_8$)

❑ Reaction requires thermic activation and elevated pH

❑ PFAA precursors are converted to perfluorocarboxylates

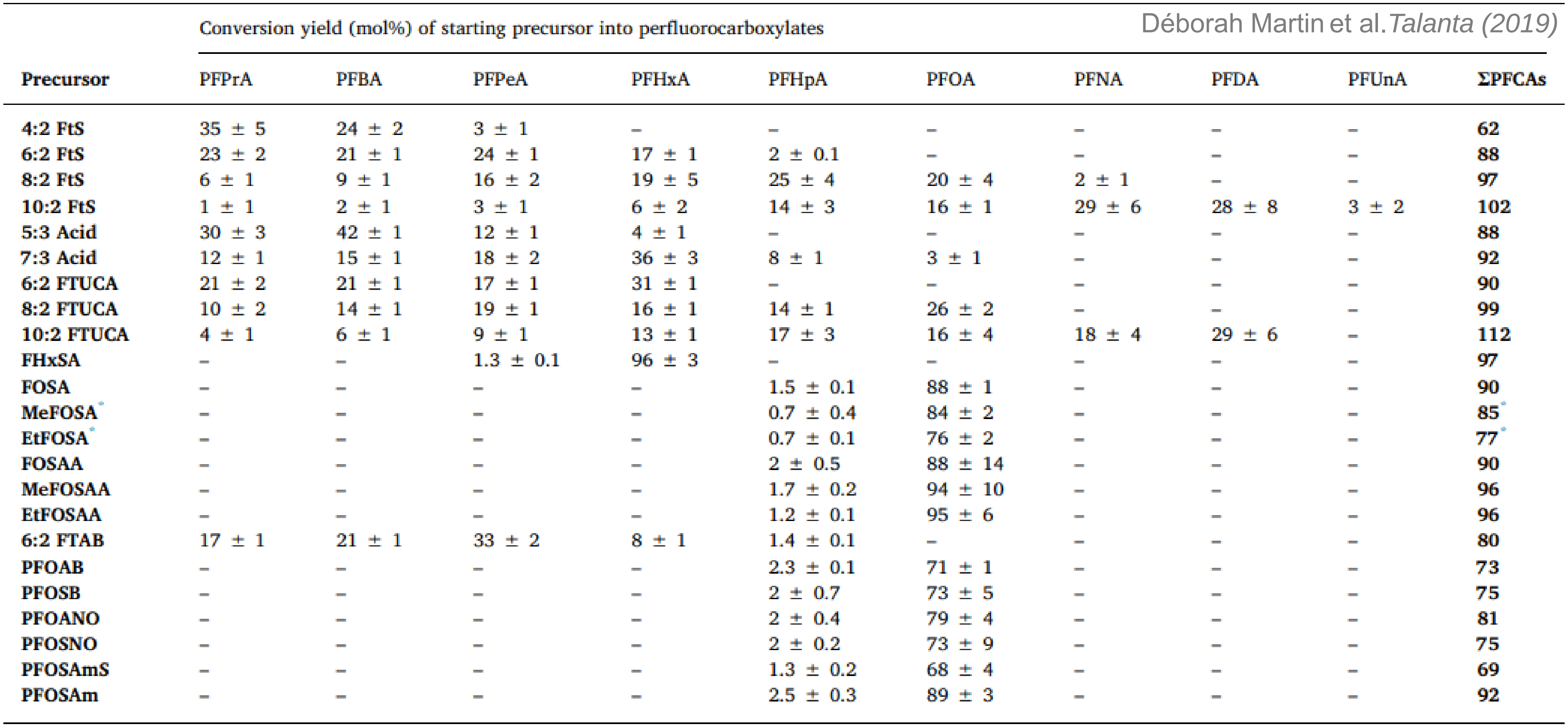


Preliminary results – WP2 (TOP Assay)

Problem statement

- The TOP Assay has been validated for just a few precursors
- No standardized method currently exists for TOP, resulting in limited reliability of generated data
- Previous studies verified conversion yields in ultrapure water, and the effect of matrix on conversion efficiency has rarely been assessed
- Matrix components could compete with PFAS for the oxidant, leading to an incomplete conversion unless pre-emptive cleanup is performed

Preliminary results – WP2 (TOP Assay)



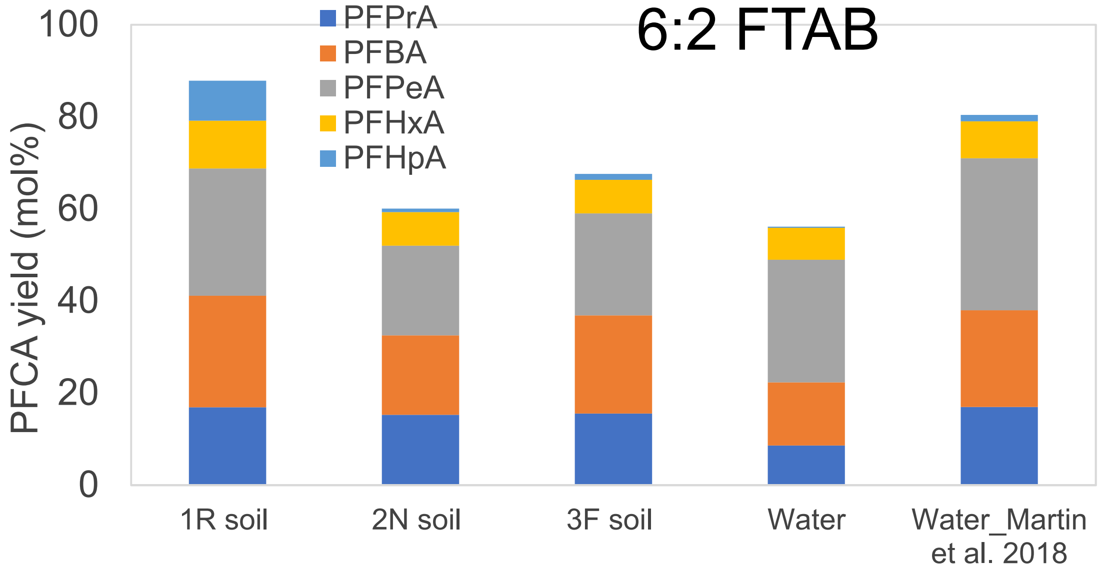
Déborah Martin et al. *Talanta (2019)*

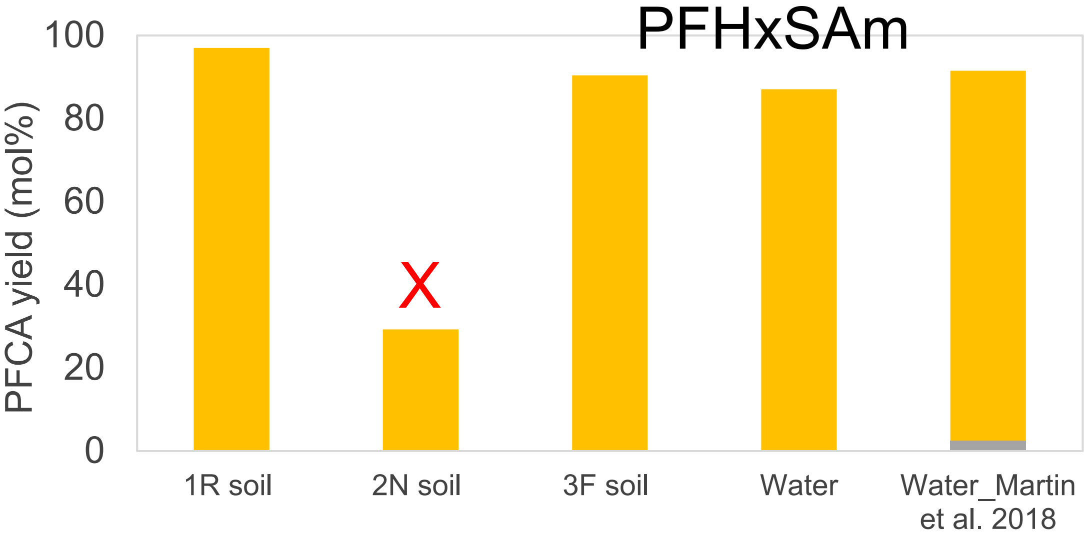
Precursor	Conversion yield (mol%) of starting precursor into perfluorocarboxylates									
	PFPrA	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	ΣPFCAs
4:2 FtS	35 ± 5	24 ± 2	3 ± 1	–	–	–	–	–	–	**62**
6:2 FtS	23 ± 2	21 ± 1	24 ± 1	17 ± 1	2 ± 0.1	–	–	–	–	**88**
8:2 FtS	6 ± 1	9 ± 1	16 ± 2	19 ± 5	25 ± 4	20 ± 4	2 ± 1	–	–	**97**
10:2 FtS	1 ± 1	2 ± 1	3 ± 1	6 ± 2	14 ± 3	16 ± 1	29 ± 6	28 ± 8	3 ± 2	**102**
5:3 Acid	30 ± 3	42 ± 1	12 ± 1	4 ± 1	–	–	–	–	–	**88**
7:3 Acid	12 ± 1	15 ± 1	18 ± 2	36 ± 3	8 ± 1	3 ± 1	–	–	–	**92**
6:2 FTUCA	21 ± 2	21 ± 1	17 ± 1	31 ± 1	–	–	–	–	–	**90**
8:2 FTUCA	10 ± 2	14 ± 1	19 ± 1	16 ± 1	14 ± 1	26 ± 2	–	–	–	**99**
10:2 FTUCA	4 ± 1	6 ± 1	9 ± 1	13 ± 1	17 ± 3	16 ± 4	18 ± 4	29 ± 6	–	**112**
FHxSA	–	–	1.3 ± 0.1	96 ± 3	–	–	–	–	–	**97**
FOSA	–	–	–	–	1.5 ± 0.1	88 ± 1	–	–	–	**90**
MeFOSA[*]	–	–	–	–	0.7 ± 0.4	84 ± 2	–	–	–	**85**[*]
EtFOSA[*]	–	–	–	–	0.7 ± 0.1	76 ± 2	–	–	–	**77**[*]
FOSAA	–	–	–	–	2 ± 0.5	88 ± 14	–	–	–	**90**
MeFOSAA	–	–	–	–	1.7 ± 0.2	94 ± 10	–	–	–	**96**
EtFOSAA	–	–	–	–	1.2 ± 0.1	95 ± 6	–	–	–	**96**
6:2 FTAB	17 ± 1	21 ± 1	33 ± 2	8 ± 1	1.4 ± 0.1	–	–	–	–	**80**
PFOAB	–	–	–	–	2.3 ± 0.1	71 ± 1	–	–	–	**73**
PFOSB	–	–	–	–	2 ± 0.7	73 ± 5	–	–	–	**75**
PFOANO	–	–	–	–	2 ± 0.4	79 ± 4	–	–	–	**81**
PFOSNO	–	–	–	–	2 ± 0.2	73 ± 9	–	–	–	**75**
PFOSAmS	–	–	–	–	1.3 ± 0.2	68 ± 4	–	–	–	**69**
PFOSAm	–	–	–	–	2.5 ± 0.3	89 ± 3	–	–	–	**92**

- ❑ We aim to document conversion yields of a wide range of precursors
- ❑ 6:2 FTAB near-quantitatively converted (80 mol%) into PFCAs
- ❑ Conversion yields are being verified in groundwater and soil matrix

Preliminary results – WP2 (TOP Assay)

TOP testing of various precursors for different soils





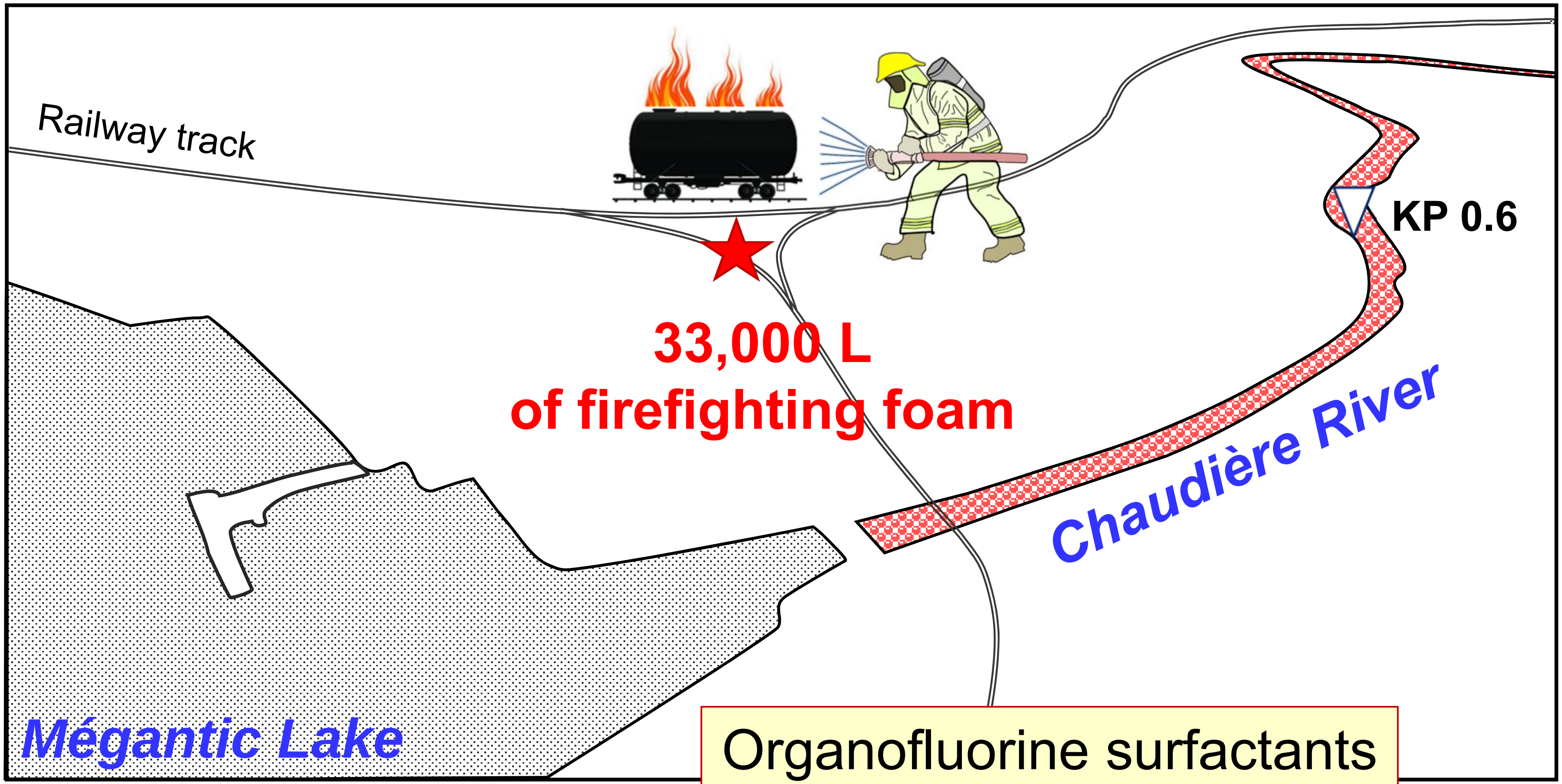
		Class	OM %
#1R	Chaudière watershed	Sandy loam	3.1
#2N	Nuns' Island	Loam	12.6
#3F	Elgar Park	Loam	4.0

Min Liu, *manuscript in preparation*

ENVIRONMENTAL ASSESSMENT

Monitoring study at the Lac-Megantic railway accident site

Monitoring study at the Lac-Megantic railway accident site

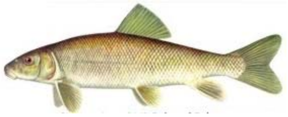


**33,000 L
of firefighting foam**

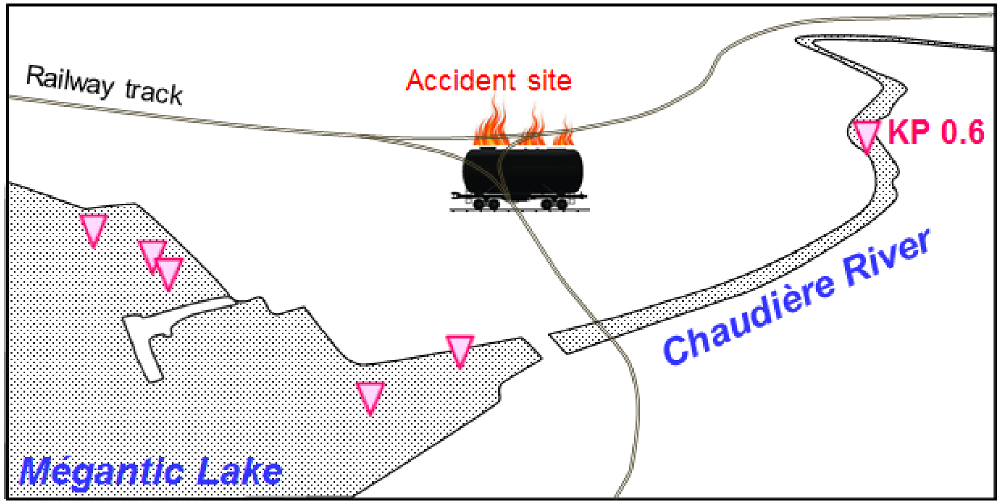
Organofluorine surfactants
(PFASs)

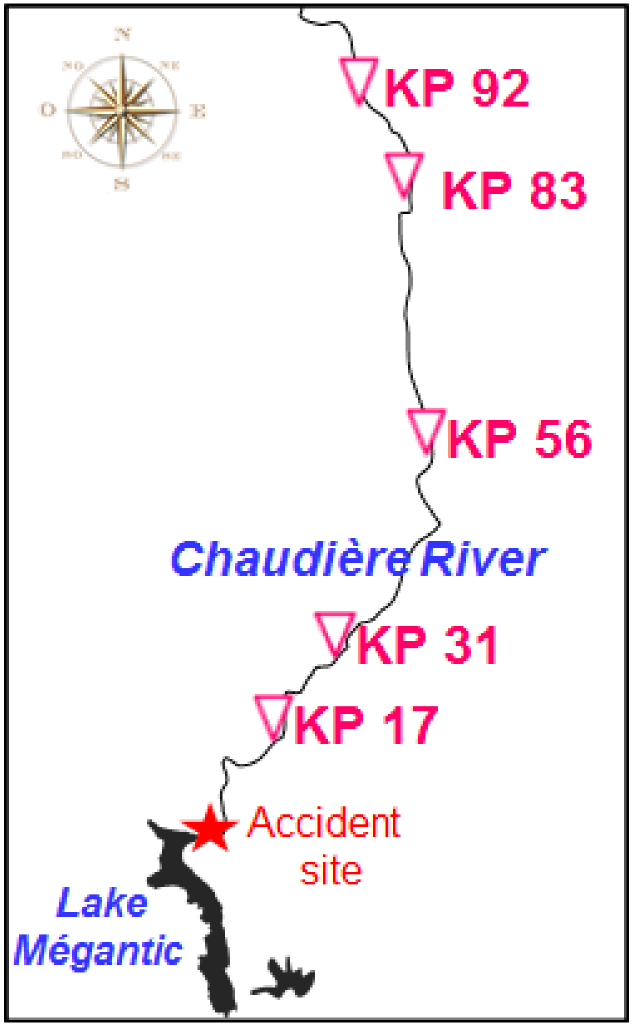
Collection of fish and sediments

Multiple campaigns in 2013 & 2014



Close to the accident site





Gradient along the Chaudière

ENVIRONMENTAL ASSESSMENT

Environmental Science & Technology Article

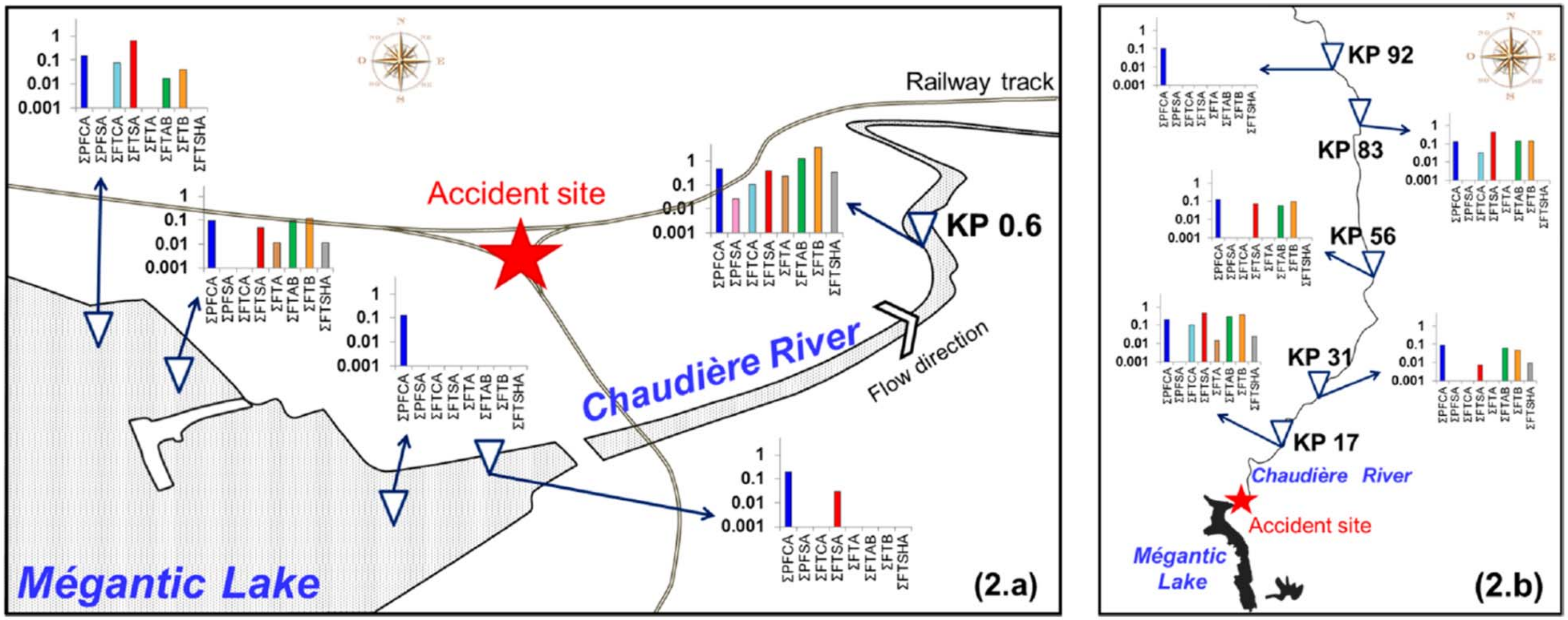


Figure 2. Spatial distribution of perfluooralkyl acids and fluorotelomer-based PFASs in 2014 sediment samples close to the accident site (2.a) and along the Chaudière River (2.b). For each sampling site, the total concentration (ng g^{-1} dw) of a given PFAS family was color-coded as follows: Dark Blue = $\sum$PFCA (perfluoroalkyl carboxylates), Pink = $\sum$PFSA (perfluoroalkyl sulfonates), Light Blue = $\sum$FTCA (fluorotelomer carboxylates), Red = $\sum$FTSA (fluorotelomer sulfonates), Brown = $\sum$FTA (fluorotelomer sulfonamide amines), Green = $\sum$FTAB (fluorotelomer sulfonamide betaines), Orange = $\sum$FTB (fluorotelomer betaines), Gray = $\sum$FTSHA (fluorotelomer thiohydroxyammonium (FTSHA) and FTSHA-sulfoxides).

Lessons learned and challenges to address

- Zwitterionic/cationic PFAS more liable to uncompensated matrix effects, due to the lack of suitable internal standards
- Extracts of high aqueous content are not suitable for some zwitterionic and cationic PFAS due to time-dependent artifacts; this would exclude on-line SPE approaches for water samples
- Cationic and zwitterionic PFAS require specific soil extractions
- TOP assay of soil extracts also appears quite challenging
- Matrix dilution prior TOP and pre-emptive SPE clean-up are options to be further investigated

Acknowledgments

sebastien.sauve@umontreal.ca

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Dr. Kela Weber
Dr. Sung Vo Duy
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