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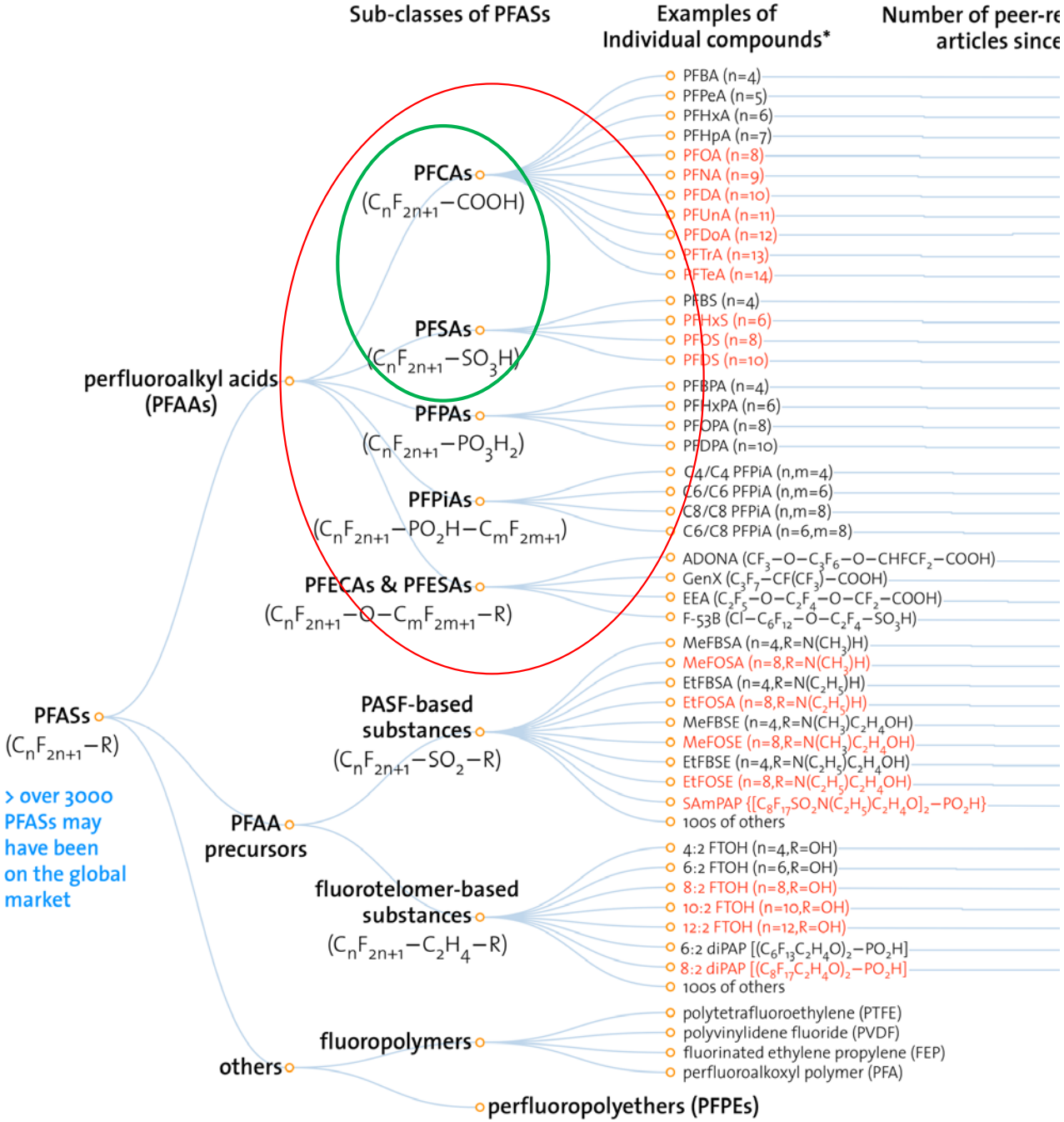
Determination of precursors of perfluoroalkyl acids in surface and wastewaters: application to some case studies

PFAS: POLY- and PER-FLUORO ALKYL SUBSTANCES



The role PFAS precursors in human exposure

- The PFAA precursors are those fluorinated chemicals that can be potentially transformed abiotically or biotically into PFCA or PFSA terminal products.

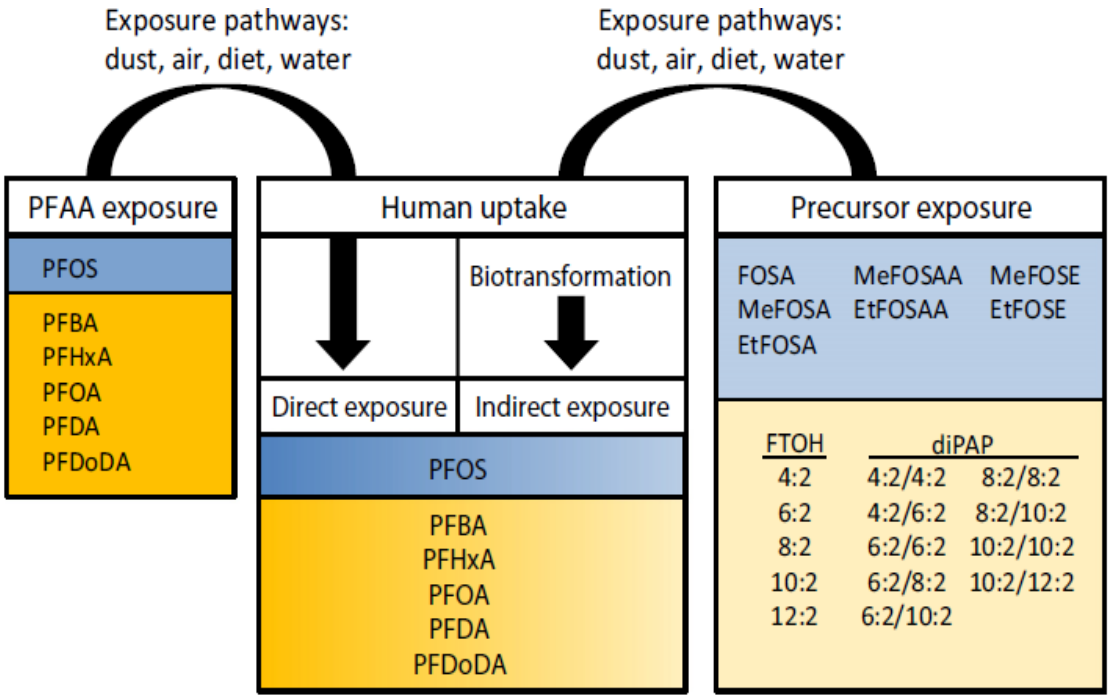


Fig. 1. Schematic of direct and indirect (precursor) exposure pathways for PFOS and PFCAs.

[Gebbink *et al.*, 2015]

PFAA precursors:

investigation methods

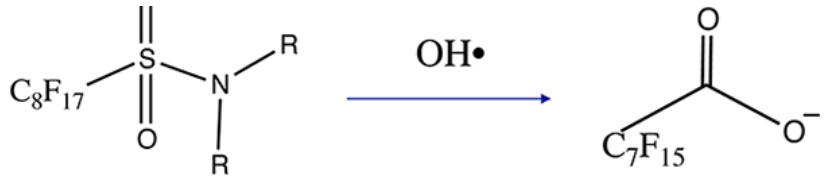
- **Total Oxidizable Precursor Assay (TOPA)**
  - Indirect technique that converts, by oxidation, precursors to measurable perfluorinated carboxylate products (PFCAs)
  - Total concentration of PFAA precursors was inferred by comparing PFCAs measured before and after oxidation
- **Retrospective screening by High Resolution MS**
  - PFAS HRMS database ≅ 350

Oxidative Conversion of PFAAs precursors

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{-\cdot}$$

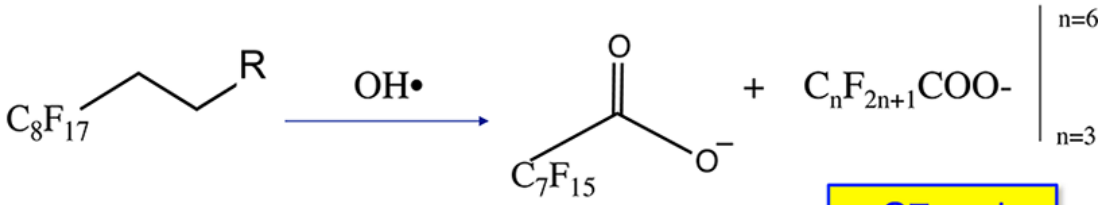
$$SO_4^{-} + OH^{-} \rightarrow SO_4^{2-} + \cdot OH$$

potassium persulfate/NaOH/85°C/6h
(Houtz and Sedlak, 2012)



C8 ECF Precursor

PFOA



C8 Fluorotelomer Precursor

PFOA

C7 and shorter PFCAs

- Houtz, and Sedlak, Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff*, Environ. Sci. Technol*. (2012)
- Dauchy *et al.*, Mass flows and fate of per- and polyfluoroalkyl substances (PFASs) in the wastewater treatment plant of a fluorochemical manufacturing facility. *Sci. Total. Environ*. (2017)

Molar Yields (%) of PFAAs from precursors oxydised by persulfate

Precursor	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	∑ PFAA
N-EtFOSAA					92 ± 4			92[Houtz]
N-MeFOSAA					110 ± 8			110[H]
FOSA					**97 ± 3**			97[H]
					82 ± 4			82[Our study]
4:2 FTS	23 ± 2	6 ±3						29[Boiteux]
6:2 FTS	22 ± 5	27 ± 2	22 ± 2	2 ± 1				73[H]
	20 ± 3	22 ± 3	21 ± 2	3 ± 0				66[B]
8:2 FTS	11 ± 4	12 ± 4	19 ± 3	27± 3	21 ± 2			90[H]
	7 ± 1	8 ± 1	17 ± 2	27 ± 3	25 ±2	2 ± 1		86[B]
6:2 FTOH		53 ± 7	7 ± 1					60[Our]
	16 ± 1	18 ± 1	4 ± 1					38[B]
8:2 FTOH		7 ± 2	37 ± 5	58 ± 5	11 ± 0			113[Our]
	5 ± 1	7 ± 1	14 ± 1	30 ± 2	11 ± 1			67[B]
10:2 FTOH			3 ± 1	6 ± 1	15 ± 2	18 ± 3	7 ± 1	49[B]

Aims and limitations of oxidation method

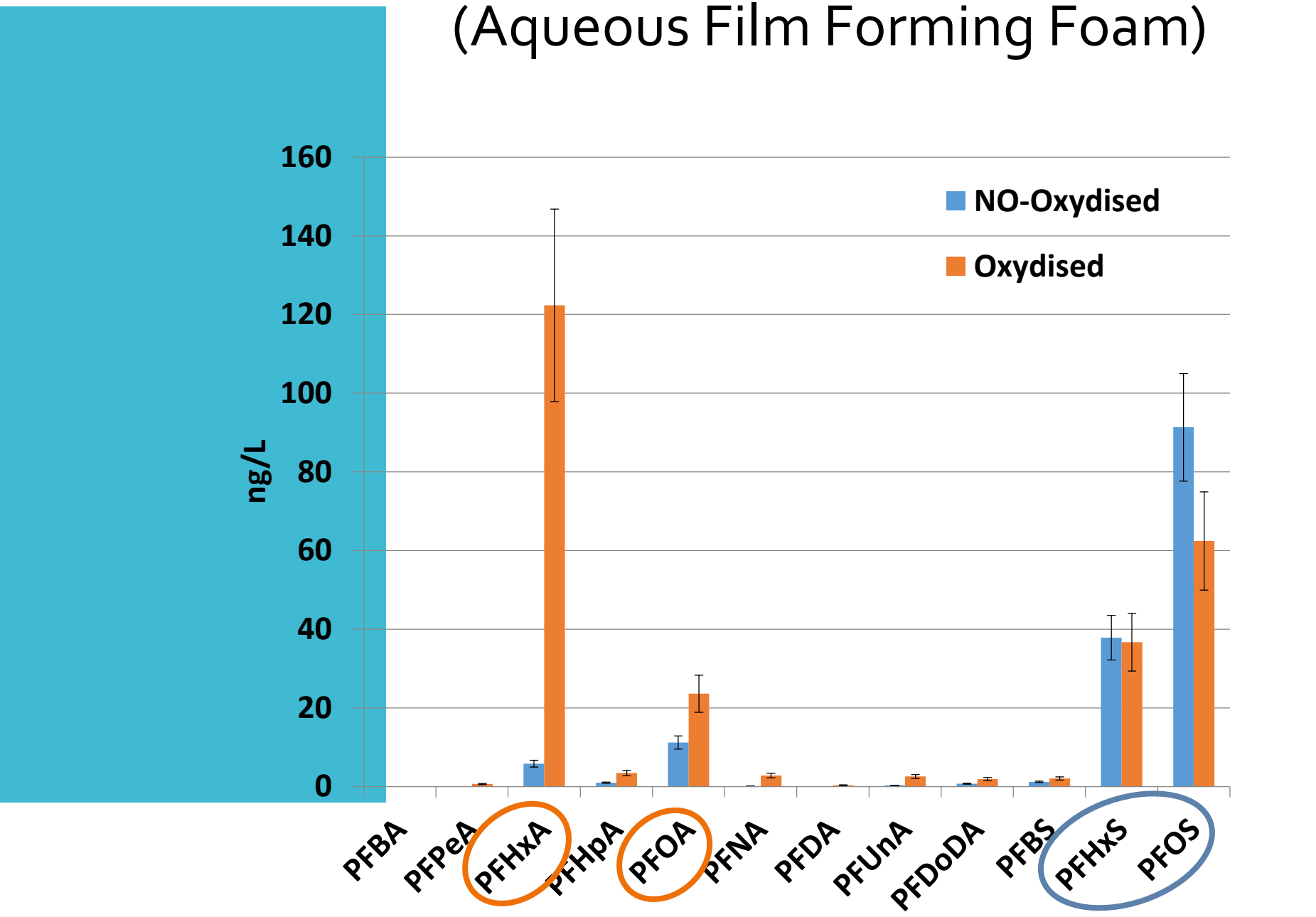
This method has been tested to:

- Trigger the retrospective analysis by HRMS to confirm precursors
- Estimate the total discharged load of PFAA (including precursors)
- Assess risks for biomagnification in aquatic ecosystems
- Estimate PFAA formation in AOP treatments

Method's drawbacks:

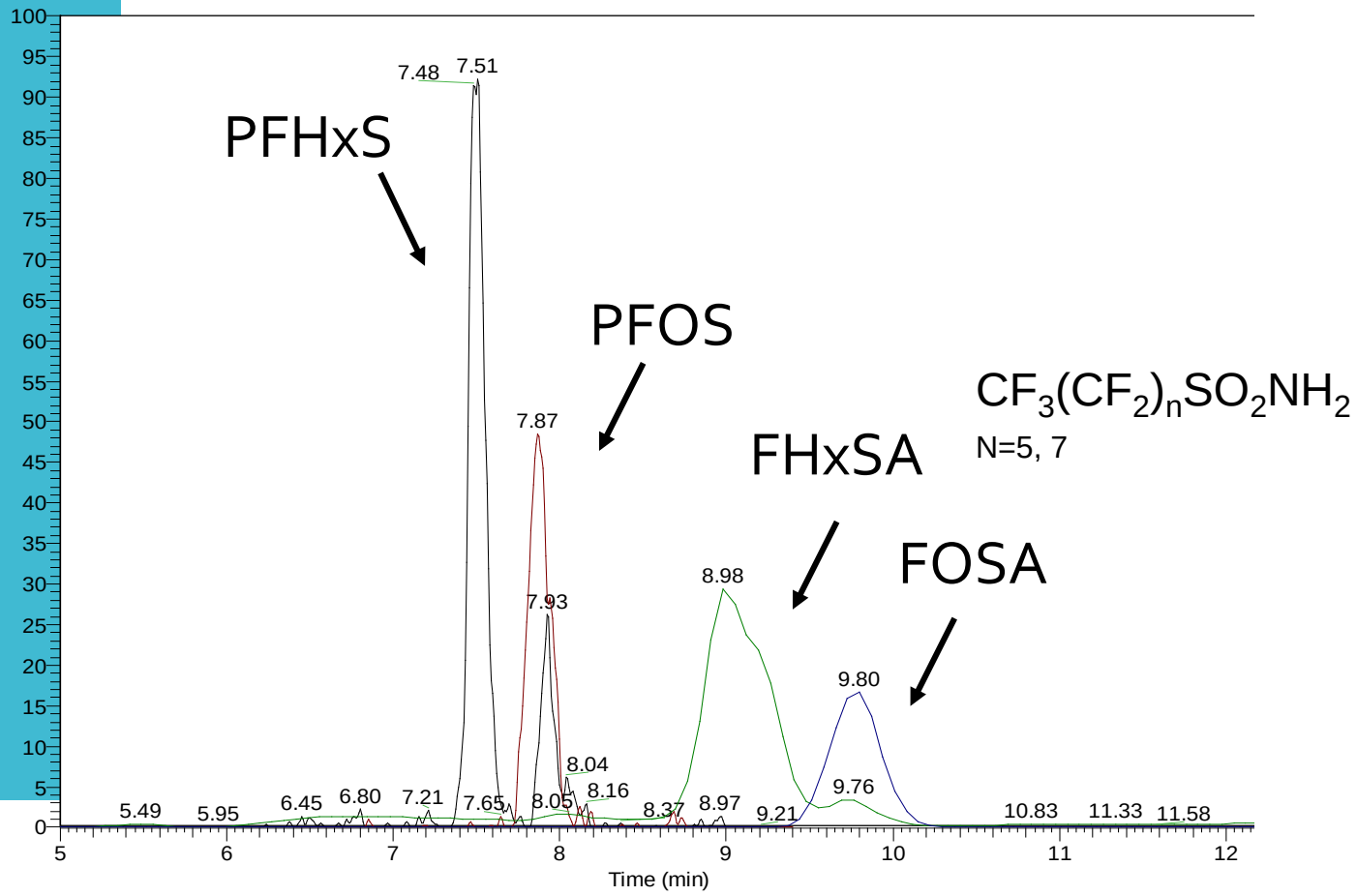
- High uncertainty, especially at low concentrations, because results are obtained as a difference between two analytical runs
- Need to tailor the oxidant concentration to the sample characteristics (e.g. wastewater, leachate)
- Persulphate oxidation does not mimic the biological transformations (e.g. FOSA)
- Some loss in PFOS by oxidation has been highlighted

Tap water impacted by Fluorinated-AFFF (Aqueous Film Forming Foam)

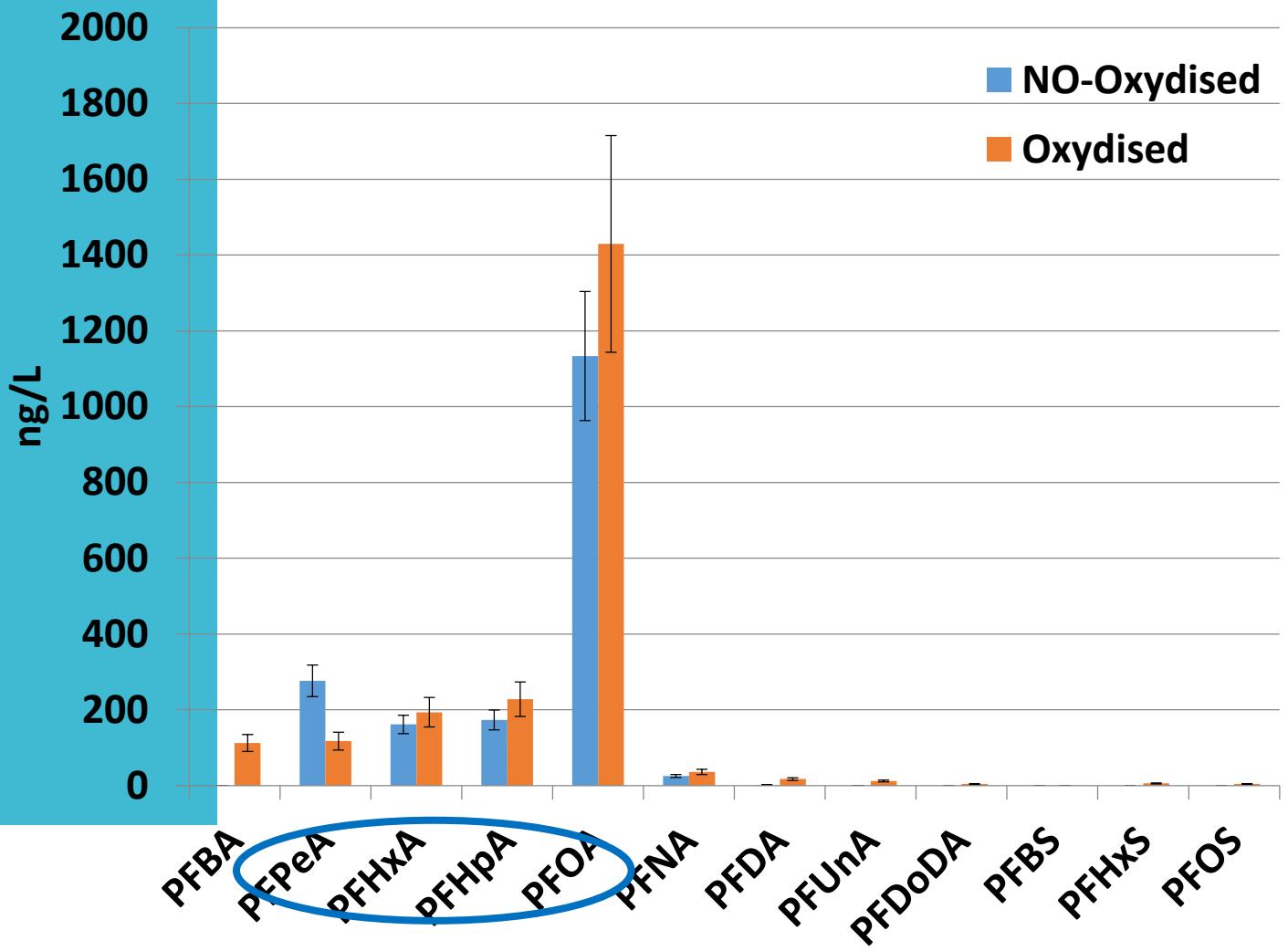


Tap water impacted by Fluorinated-AFFF

Perfluorosulfonamides are used as AFFF-components and are also considered intermediate degradation products of AFFF-components



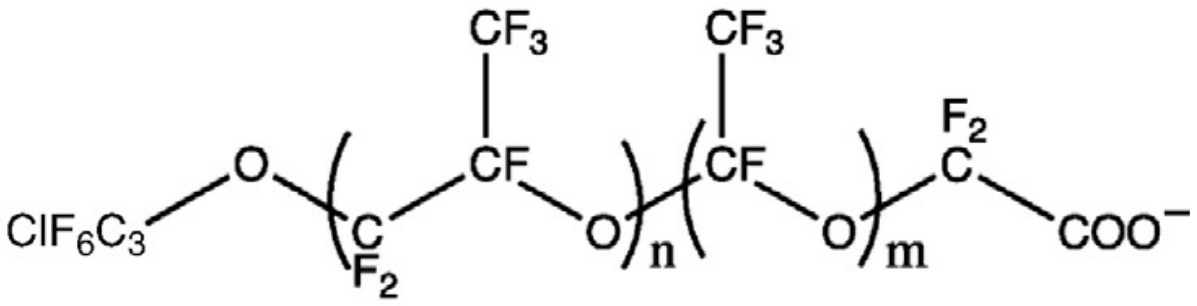
River water downstream of a fluoropolymer (PTFE) factory discharge



River water downstream of a fluoropolymer (PTFE) factory discharge

The search for PFOA substitutes

Solvay's product (CAS No. 329238-24-6)



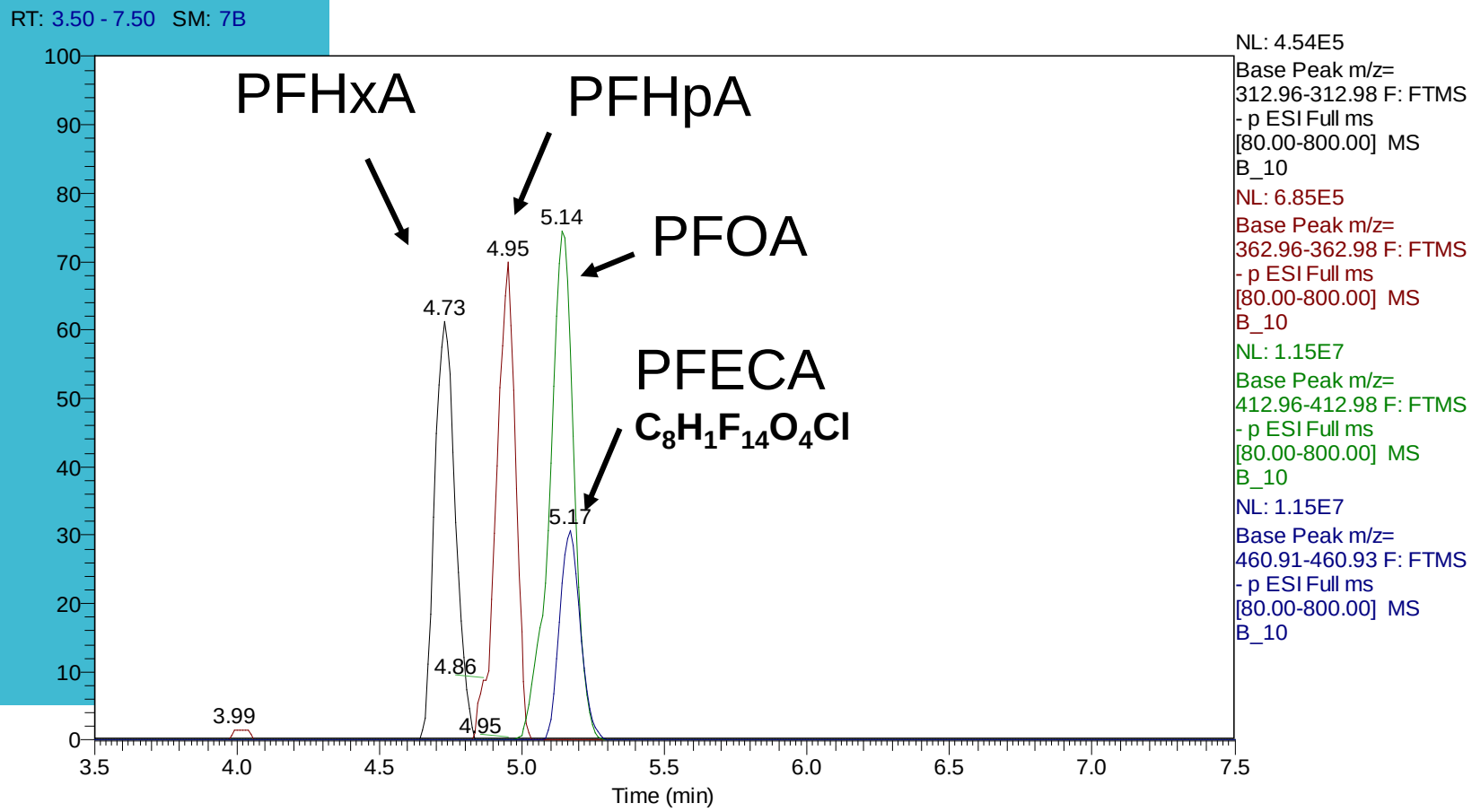
Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors

Zhanyun Wang [a], Ian T. Cousins [b], Martin Scheringer [a,*], Konrad Hungerbühler [a]

[a] Institute for Chemical and Bioengineering, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland
[b] Department of Applied Environmental Science (ITM), Stockholm University, SE-10691 Stockholm, Sweden

River water downstream of a fluoropolymer (PTFE) factory discharge

The detection of a possible chlorinated PerfluoroEtherCarboxylic acid (PFECA) in the river water



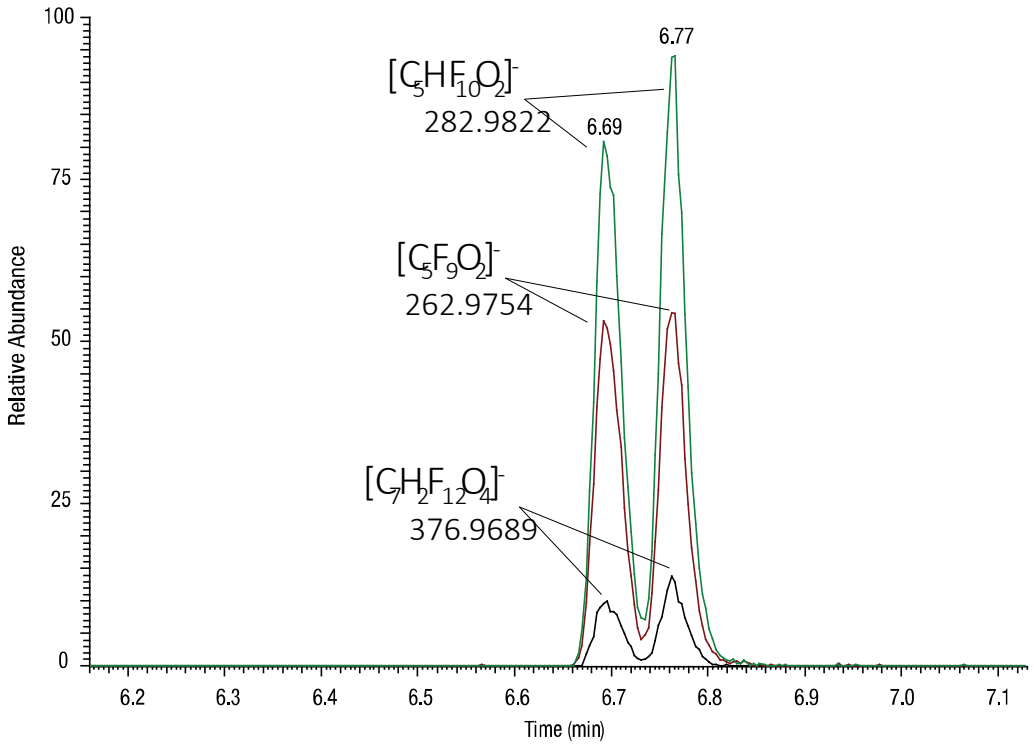
LANDFILL LEACHATE

PerFluoroEther Carboxylic Acids (PFECA)

Total PFAA	33 µg/L
PFPeA	26 µg/L
PFOA	4 µg/L

Compound Name	Formula	m/z (Delta (ppm))
ADONAisomers	$C_7H_2F_{12}O_4$	0.5722
in-source ADONAisomers fragment 1	$C_5HF_{10}O_2$	0.1388
in-source ADONAisomers fragment 2	$C_5F_9O_2$	2.4878

ADONA isomers



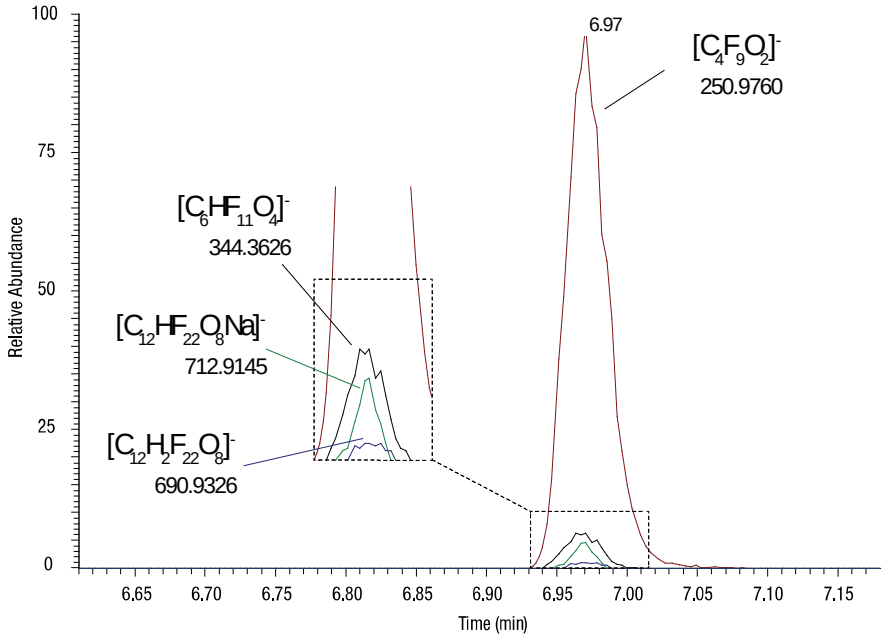
LANDFILL LEACHATE

PerFluoroEther Carboxylic Acids (PFECA)

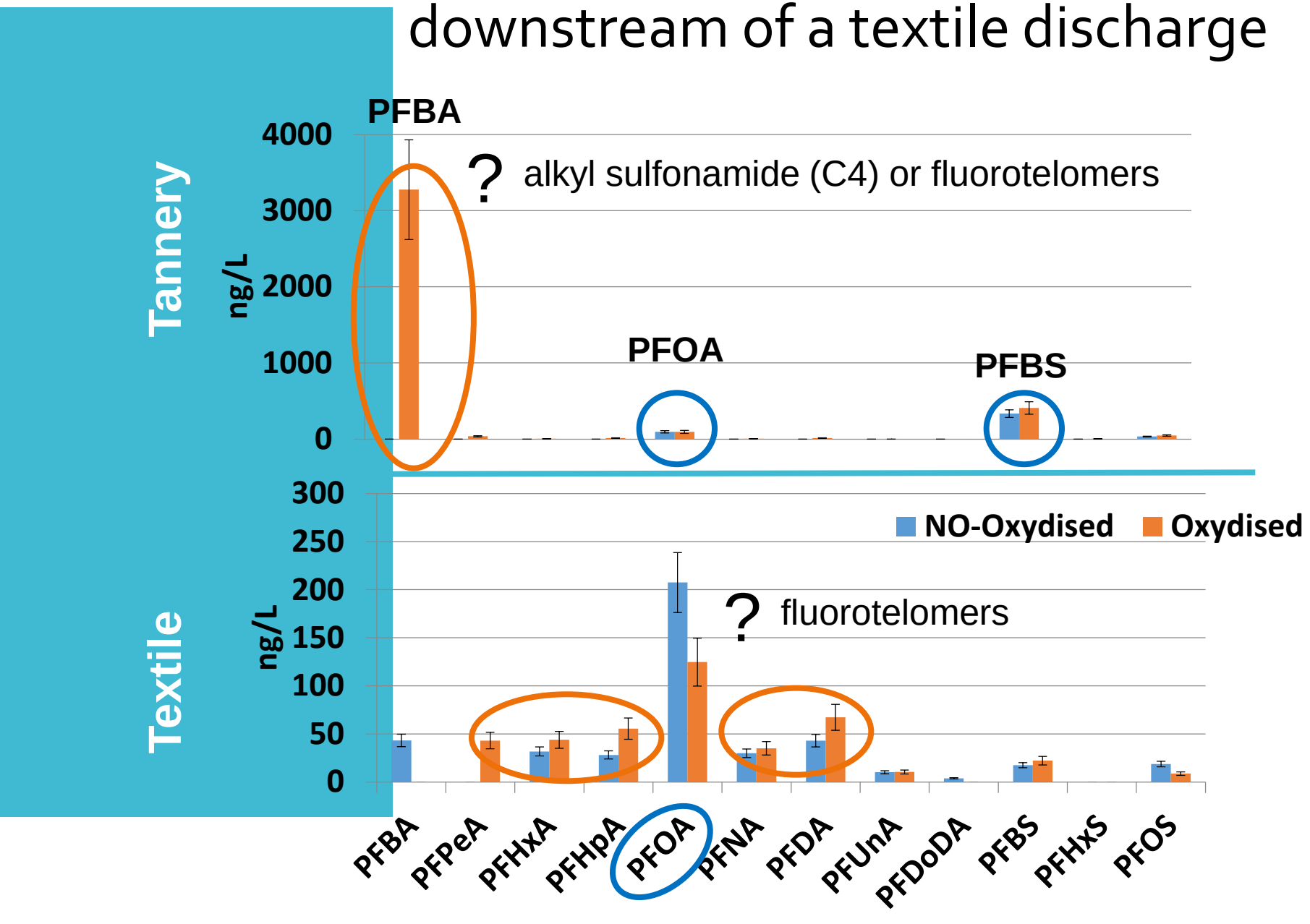
Total PFAA	33 µg/L
PFPeA	26 µg/L
PFOA	4 µg/L

Compound Name	Formula	m/z (Delta (ppm))
EEA	C6HF11O4	-0.4235
EEA [2M-H]- Adduct	C12H2F22O8	0.9661
EEA [2M-2H+Na]- Adduct	C12HF22O8Na	1.1702
in-source EEA fragment	C4F9O2	-0.5953

EEA perfluoro((2-ethyloxy-ethoxy)acetic acid



Tannery waste and river water downstream of a textile discharge



Tannery wastewater analysed by HRMS retrospective screening

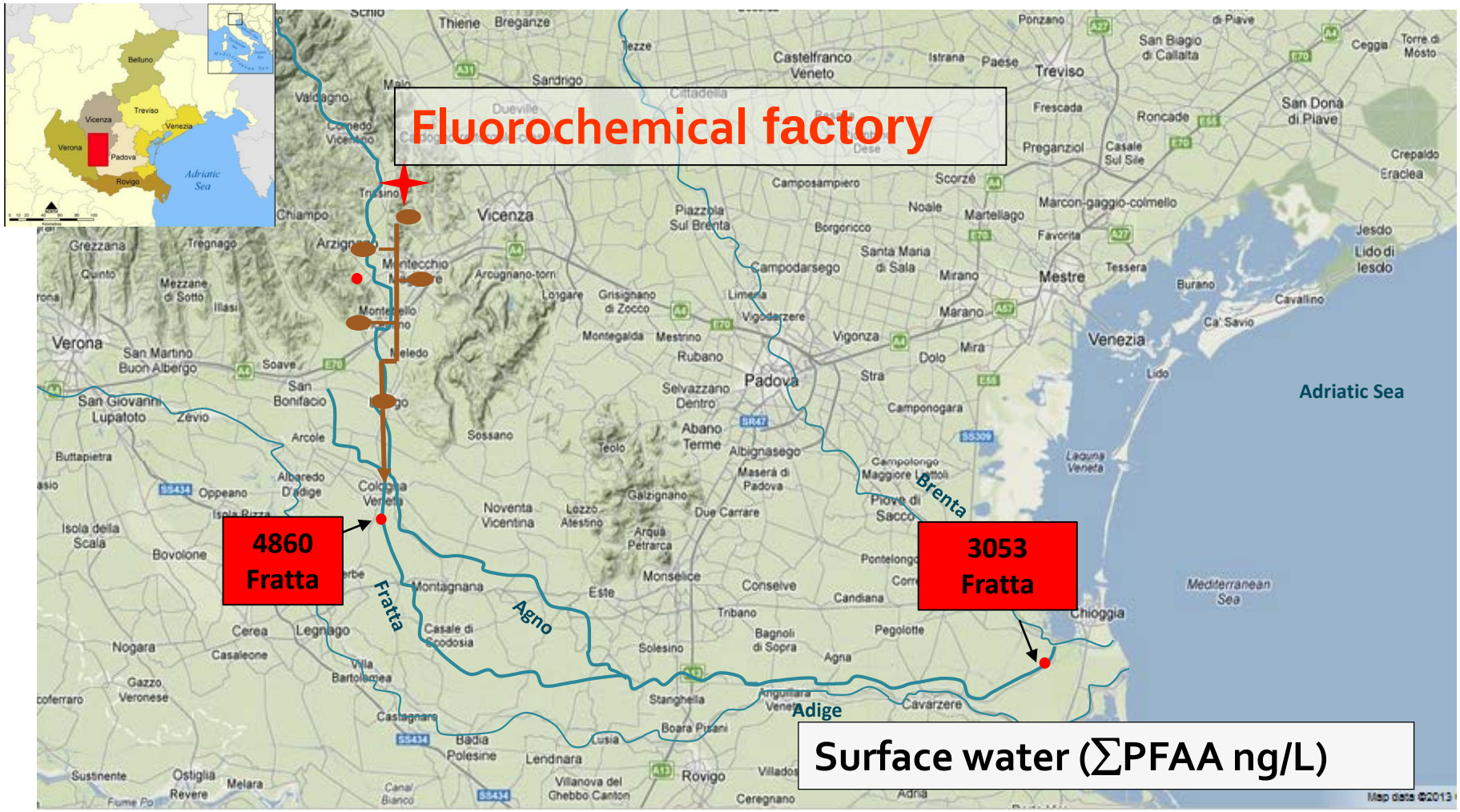
Compound Name	Formula	m/z Δ (ppm)
Perfluorobutanesulfinate	$C_4HF_9O_2S$	0.6811
4:2FTS	$C_6H_5F_9SO_3$	0.8834
6:2FTS	$C_8H_5F_{13}SO_3$	1.2046
FBSA	$C_4H_2F_9NO_2S$	1.1413
MeFBSAA	$C_7H_6F_9NO_4S$	1.2996
EtFBSAA	$C_8H_8F_9NSO_4$	0.9486

Total PFAA	341 µg/L
PFBA	259 µg/L
PFHxA	40 µg/L
PFBS	36 µg/L

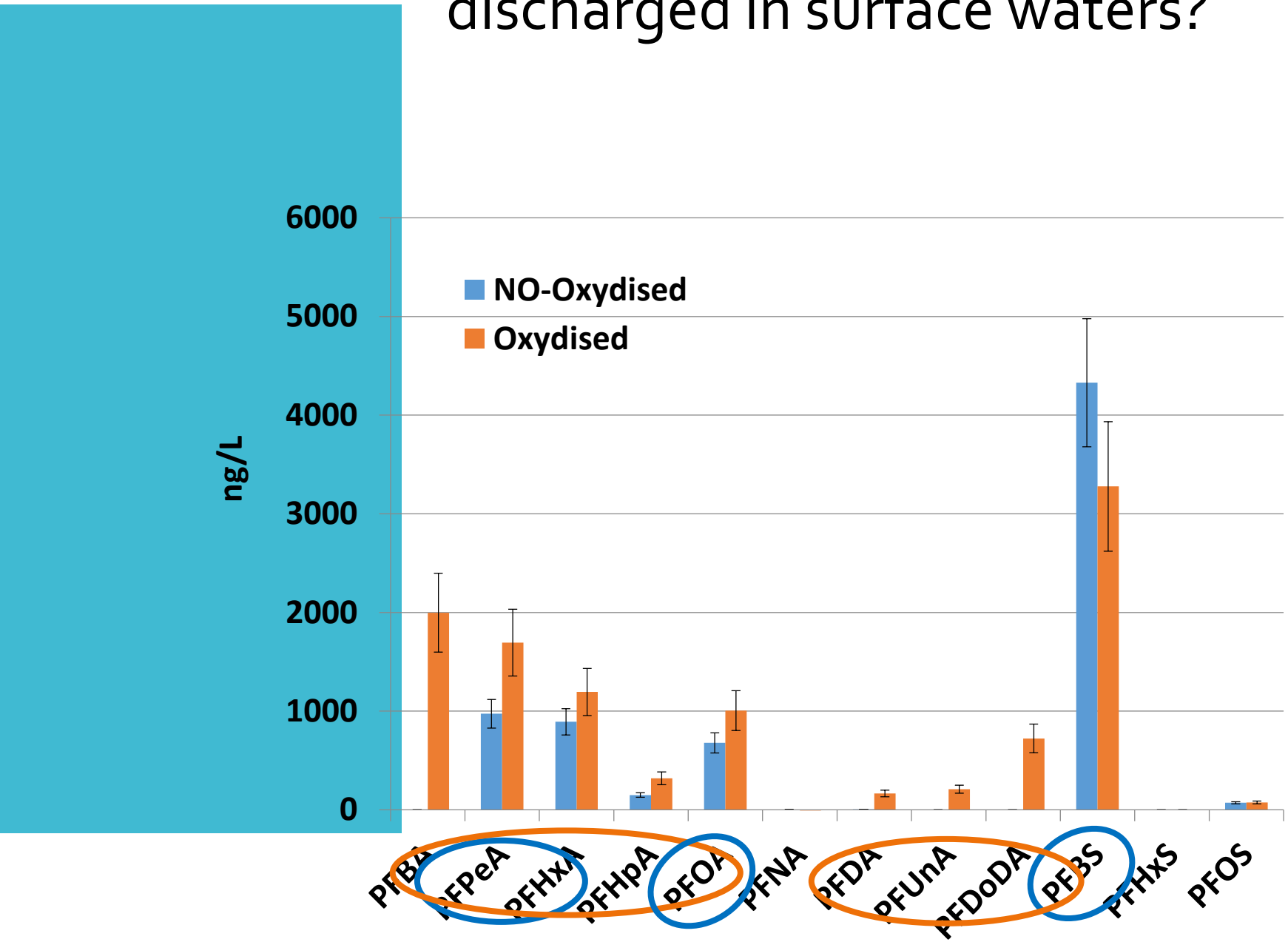
PFBS-based polymers or polymeric short-chain fluorotelomer-based polymers
6:2 FTS ≅ 50 µg/L

THE "MITENI CASE STUDY" IN VENETO, ITALY

- Fluorochemical Factory discharges in a network of WWTPs which discharge in surface waters (Fratta Gorzone channel)
- Fratta Gorzone channel comes into the sea close to Venice Lagoon

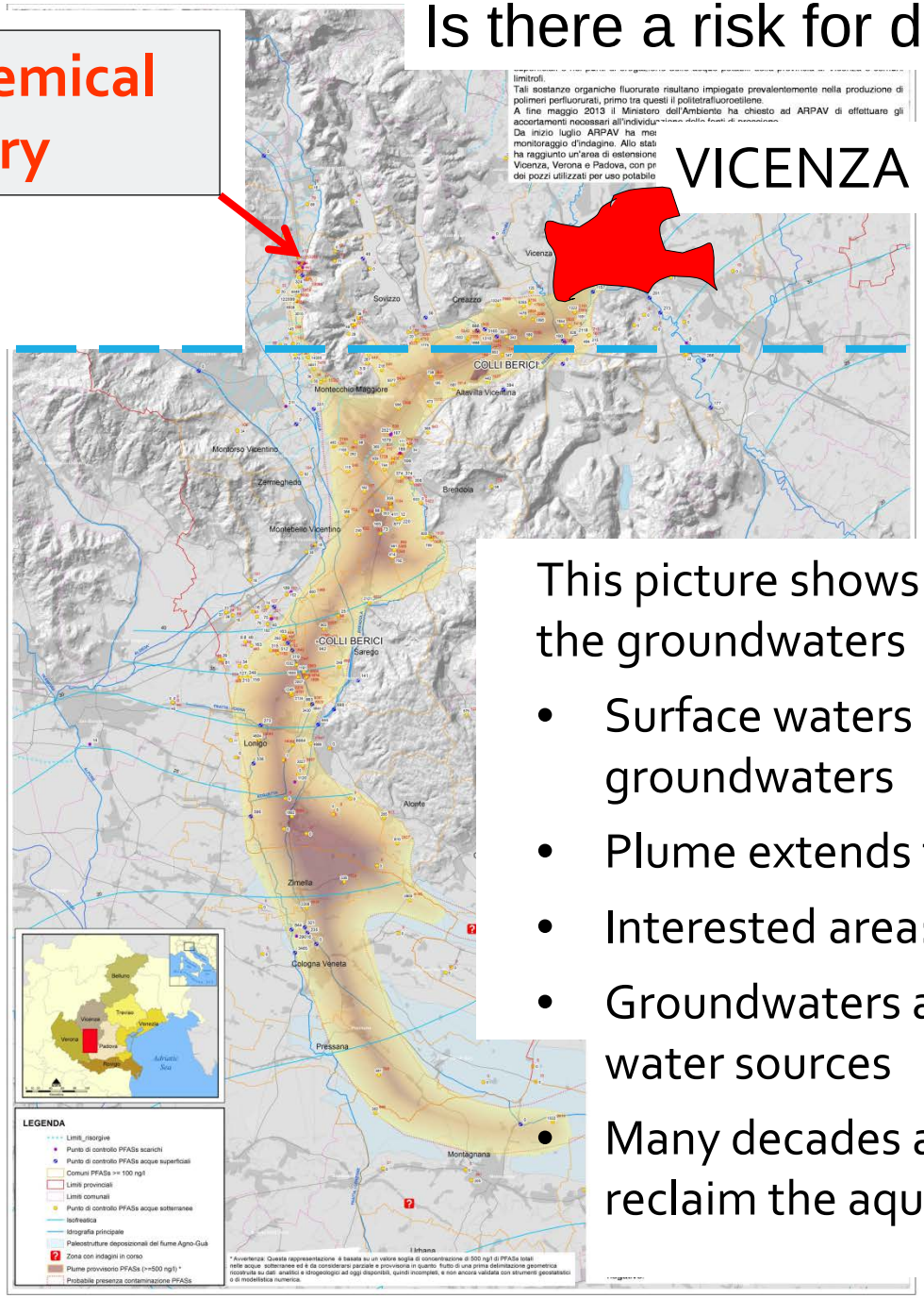


Fluorochemical factory: are precursors discharged in surface waters?



Is there a risk for drinking waters?

Fluorochemical factory

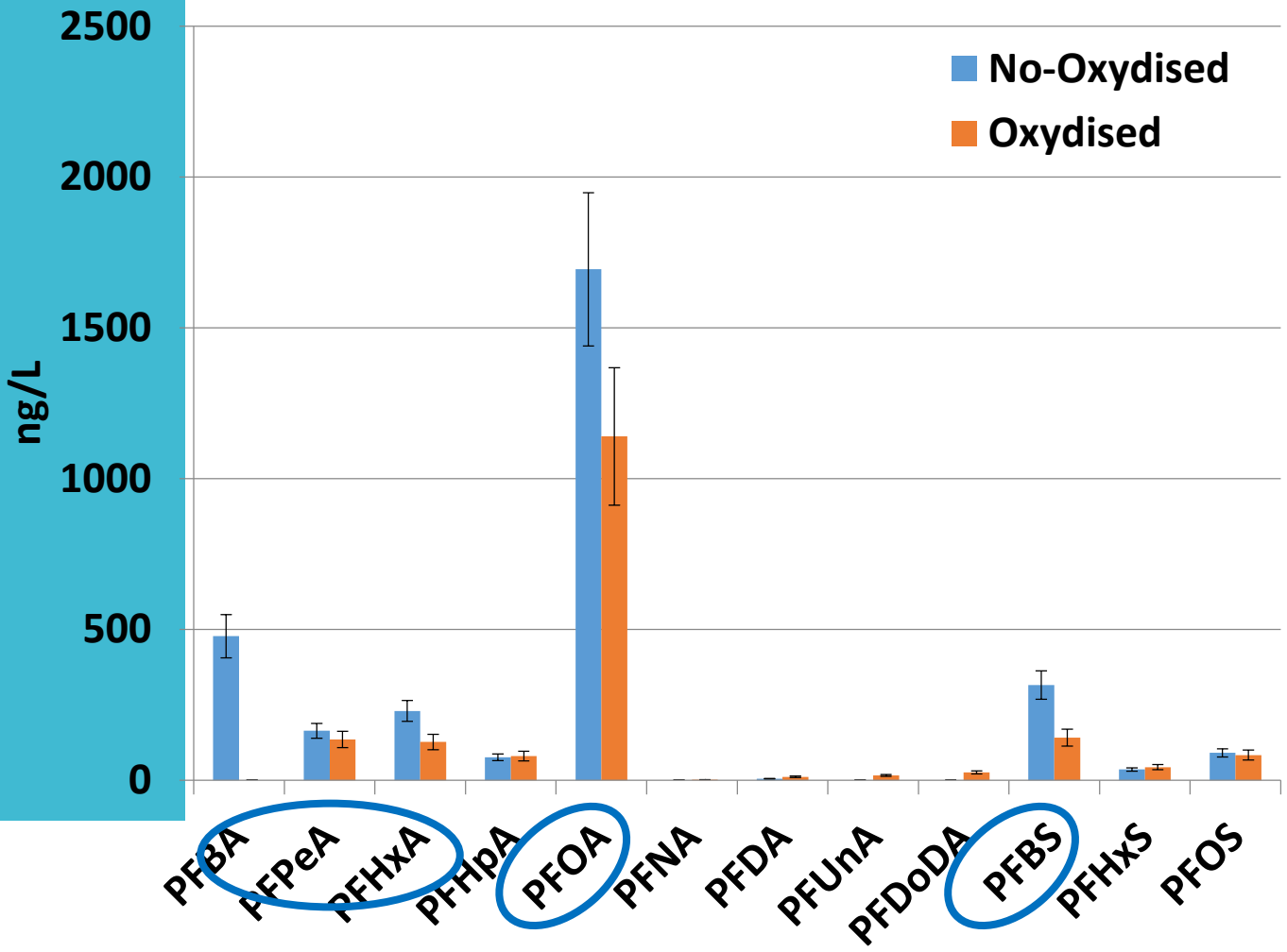


Factory is sited in an area of high permeability close to the spring line

This picture shows the plume of PFOA in the groundwaters

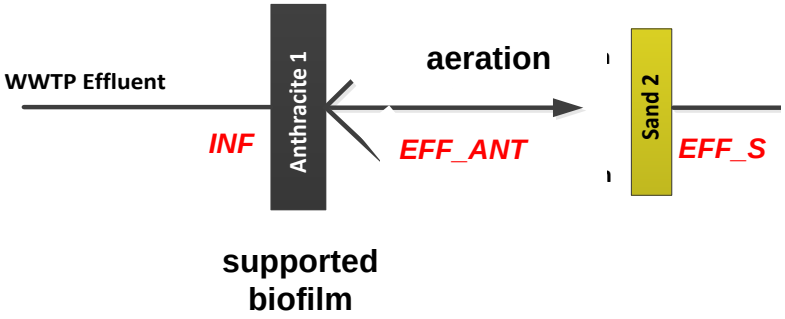
- Surface waters exchange with groundwaters
- Plume extends for about 50 km
- Interested area: 150 km^2
- Groundwaters are used as drinking water sources
- Many decades are needed to naturally reclaim the aquifer

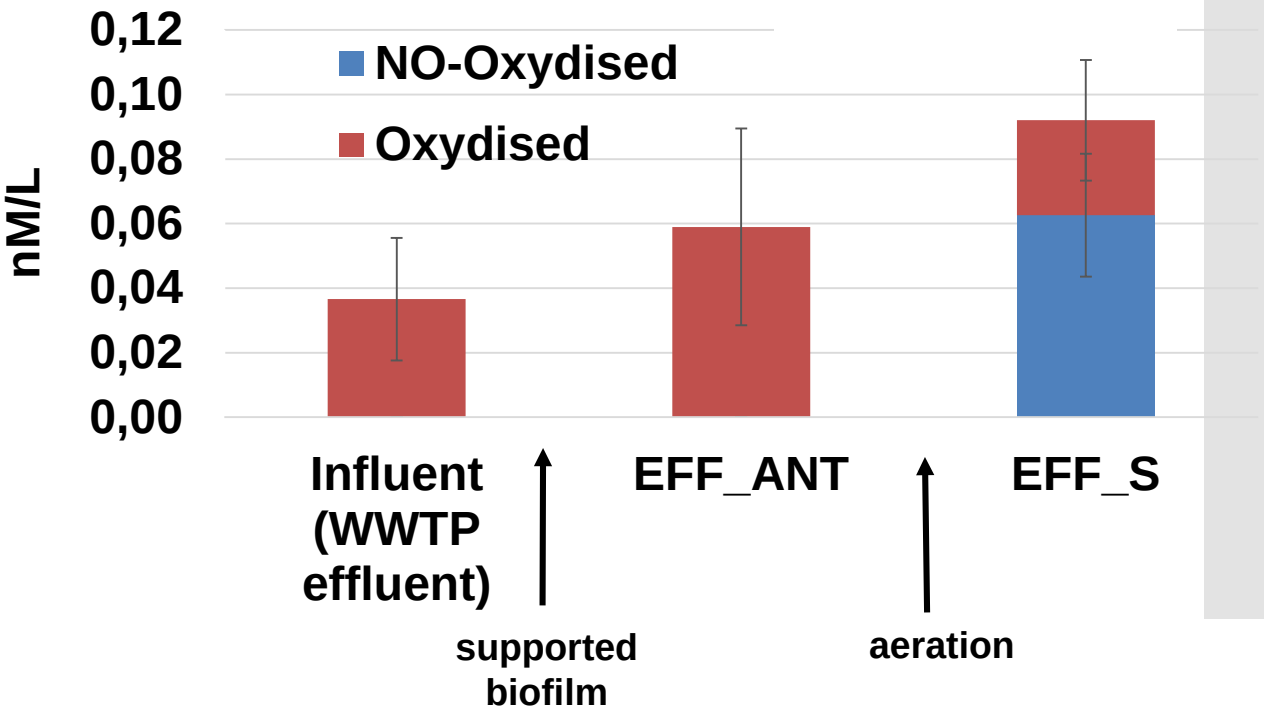
Fluorochemical factory: is there an added risk from precursors in drinking water?



FRAME Water-JPI Project

Advanced Oxidation Processes for Indirect Potable Reuse





CONCLUSIONS

- The persulphate oxidation method is a simple way to screen PFAA precursors in different water samples
- In some cases it was possible to infer the identity and concentration of the specific precursors
- Combination with HRMS retrospective screening helps to confirm or reject the hypotheses
- Results can be used for indirect estimation of the risk but some work can be done to improve the method reproducibility and uncertainty (e.g. ultra-short PFAA, different kinds of samples)

Thank you for your attention

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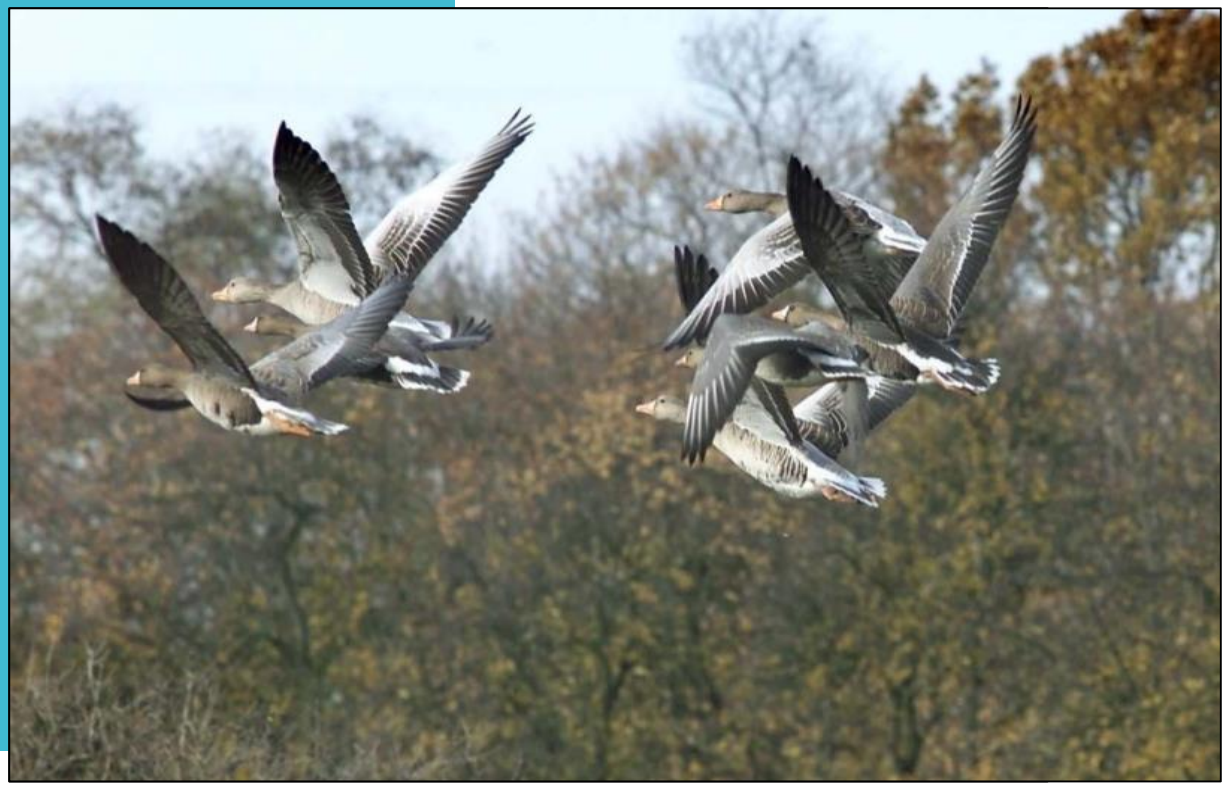
We thank dr. Peruzzo (Eurolab) for his availability to perform HRMS screening analyses



water

Invitation to submit

Emerging Organic Contaminants in Water Ecosystems

Guest Editors

Dr. Stefano Polesello, Dr. Luisa Patrolecco , Dr. Nicoletta Ademollo, Dr. Sara Valsecchi

Deadline

15 March 2019

Special Issue