Combination of Total organofluorine analysis (TOF) and total oxidizable precursor (TOP) assay for unidentified PFAS

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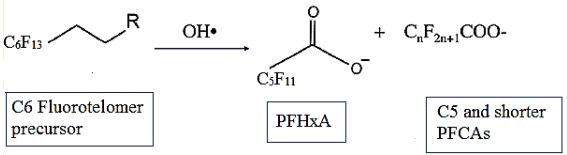
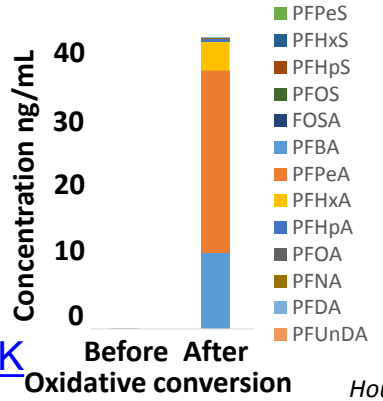
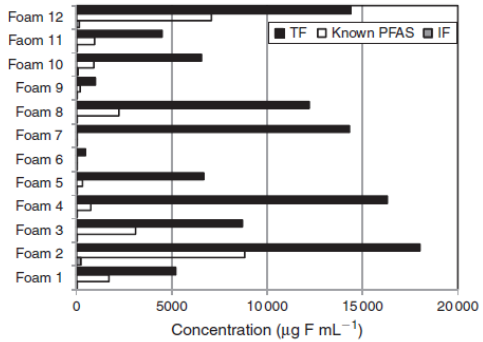
Photo: Foaming system malfunctions at Pearson airport hangar in 2015 Toronto.ctvnews.ca





LC-MS/MS

Combustion ion chromatography (CIC)



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Houtz and Sedlak 2012. Environ. Sci. & Technol., 46. 9342. Weiner et al. 2013 Environ Chem 10, 486

TOF and TOP assay

Materials and Methods:

Two firefighting foam concentrates available on the Swedish market in 2014:

Reaction and cleanup

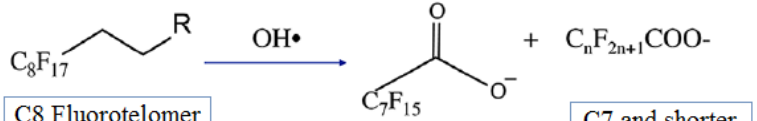
- TOP assay[1]

60mM $K_2S_2O_8$; 150 mM NaOH in 130 mL bottle; 85°C 6hr

- Modified SPE[2]

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

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



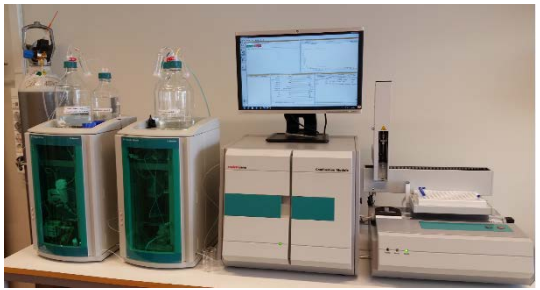
C8 Fluorotelomer precursor

PFOA

C7 and shorter PFCAs

Instrumental Analyses

- LC-MS/MS
- CIC



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[1]*Houtz and Sedlak 2012. Environmental science & technology, 46. 9342.*

[2]*ISO, 2009. ISO25101. Water quality — Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) — Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry.*

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Results and Discussion:

		ng-F/mL after 13,000x dilution	
		Without oxidative reaction	With oxidative reaction
Foam A	Neutral/ cationic	186	<50
	Anionic	<50	72
Foam B	Neutral/ cationic	916	<50
	Anionic	<50	279

- Without oxidative reaction: only neutral or cationic compounds were detected
- LC-MS/MS → all PFASs unknown
- With oxidative conversion: only anionic compounds were detected
- Imbalance of fluorine

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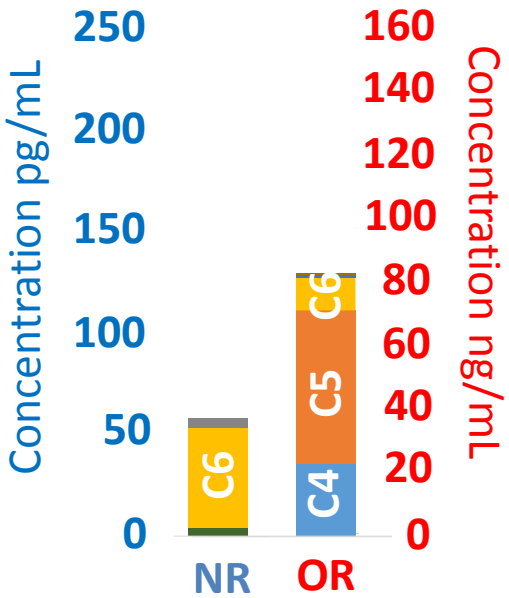
TOP assay

Results and Discussion:

Reported levels after 13,000x dilution
NR/OR: Without/With oxidative reaction

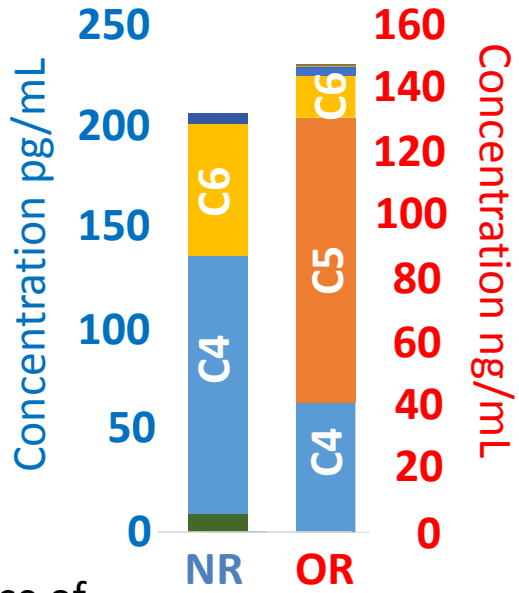
Foam A



- NR: PFHxA
- OR: Eight different PFCAs found (C4 – C11)

- NR: 6:2 FTSA, 4:2 FTSA and 8:2 FTSA
- OR: Thirteen different PFCAs found (C4 – C16)

Foam B



- 8:2FTSA
- 6:2FTSA
- 4:2FTSA
- PFOcDA
- PFHxDA
- PFTDA
- PFDoDS
- PFTrDA
- PFDoDA
- PFDS
- PFNS
- PFUnDA
- PFDA
- PFNA
- PFOA
- PFHpA
- PFHxA
- PFPeA
- PFBA

- C9 – C16 PFCAs indicates presence of other long-chain precursor compounds

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Summary and Conclusions:

- PFCA precursors were present in both foams and contributed to the unknown fraction of the TOF concentrations
- The identified unknown precursor compounds were converted from neutral/cationic to anionic after oxidation
- The base of both foam samples might be consisted of 6:2 fluorotelomer compounds
- After TOP assay, PFAS levels detected in Foam A made up for 37 – 45 % and 21 – 44 % in Foam B of the TOF concentrations
- Ultrashort chain PFASs (C2 and C3) are expected to be formed but not measured
- The mass balance after TOP shows that there still is unidentified PFASs present in the foam samples

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Comparison of TOF and TOP assay

Acknowledgements:

formas
Forskningsrådet Formas
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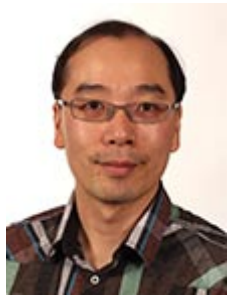

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