

# Total Oxidizable Precursor (TOP) assay

- a tool to characterize PFAS in commercial textile finishing agents and AFFF surfactants potentially containing side-chain fluoropolymers?

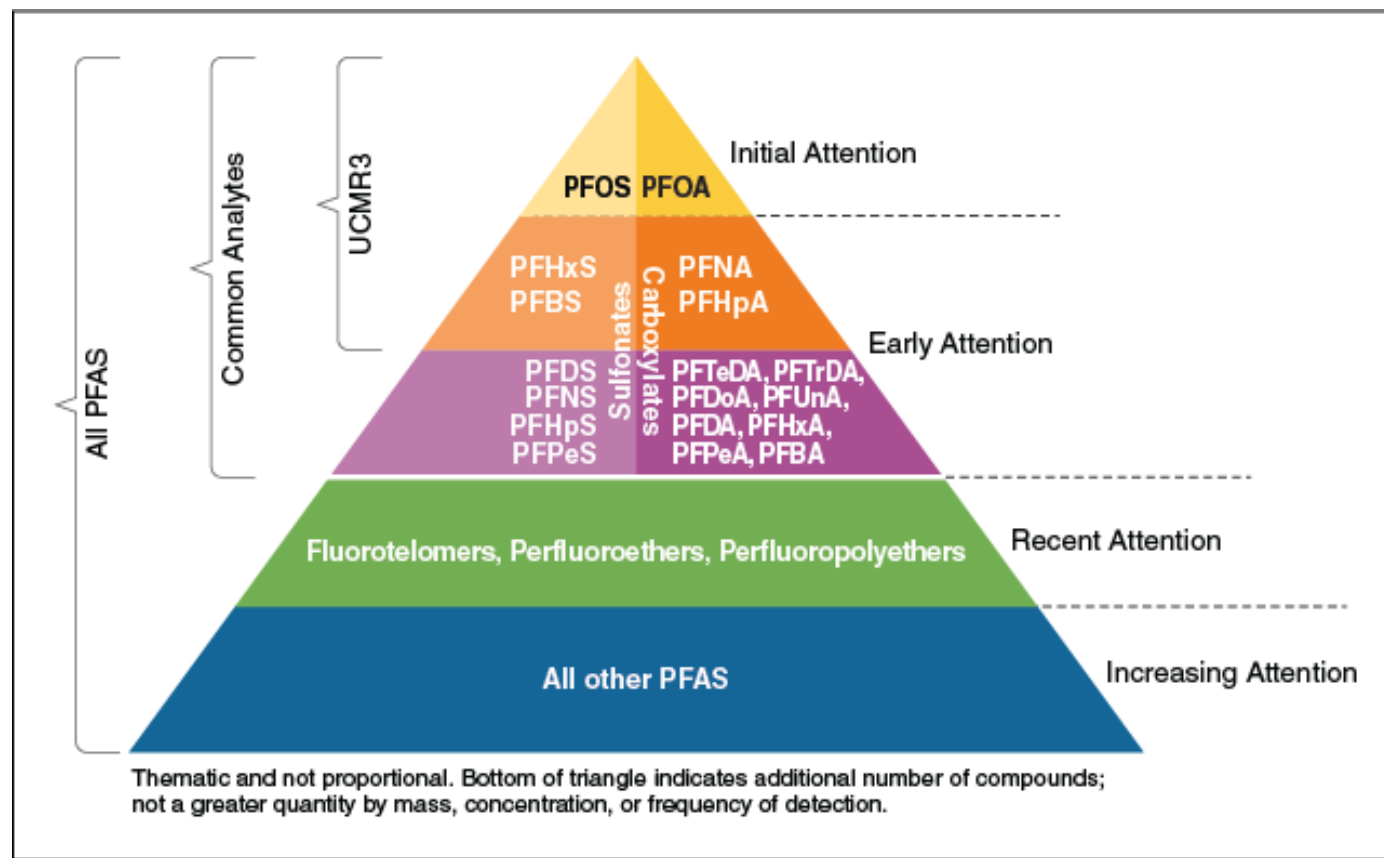
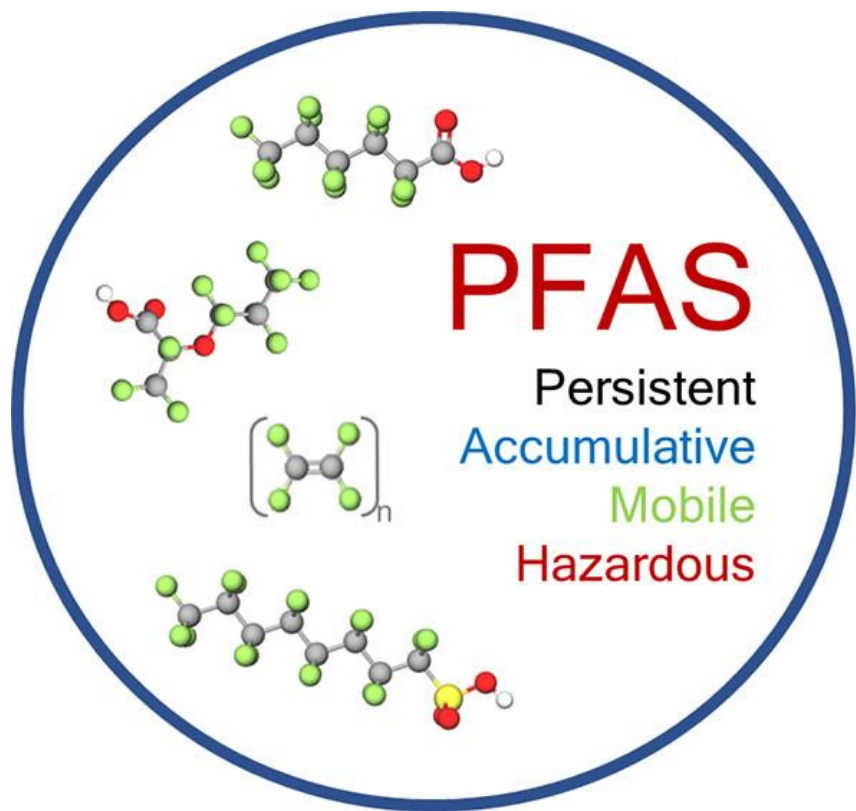


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# Background

## ■ PFAS: a big family of >10,000 “Forever Chemicals”



# Background

## ■ Industrial formulations are key sources of PFAS

- Lots of data about PFAS contamination in ambient environment exist, much less about the emissions from industrial sources.




- Some data revealed about PFAS in industrial formulations in other countries (e.g. US, EU), very few about Chinese products.

# Background

## ■ China as an example

No data → no target → no action.

- **Class B foam surfactant (FS)**
  - ✓ Designed for Class B fires - flammable liquids
- **Textile finishing agent (TFA)**
  - ✓ Water, oil and stain repellent
- **Chrome mist suppressant (CMS)**
  - ✓ Used in hard/functional and decorative chrome plating
- **Polymerization aids**
  - ✓ For the production of PTFE, PVDF, FEP, FKM, etc.



Side-chain fluoropolymer might be contained.

# Strategy for PFAS analysis

PFAS

## Commonly measured PFAS

- *GB 31604.35-2016* (2 PFAS)
- *EPA Method 537.1* (18 PFAS)
- *EPA Method 533* (25 PFAS)

## Precursors

- *TOP assay*

→ **TOP+ assay**

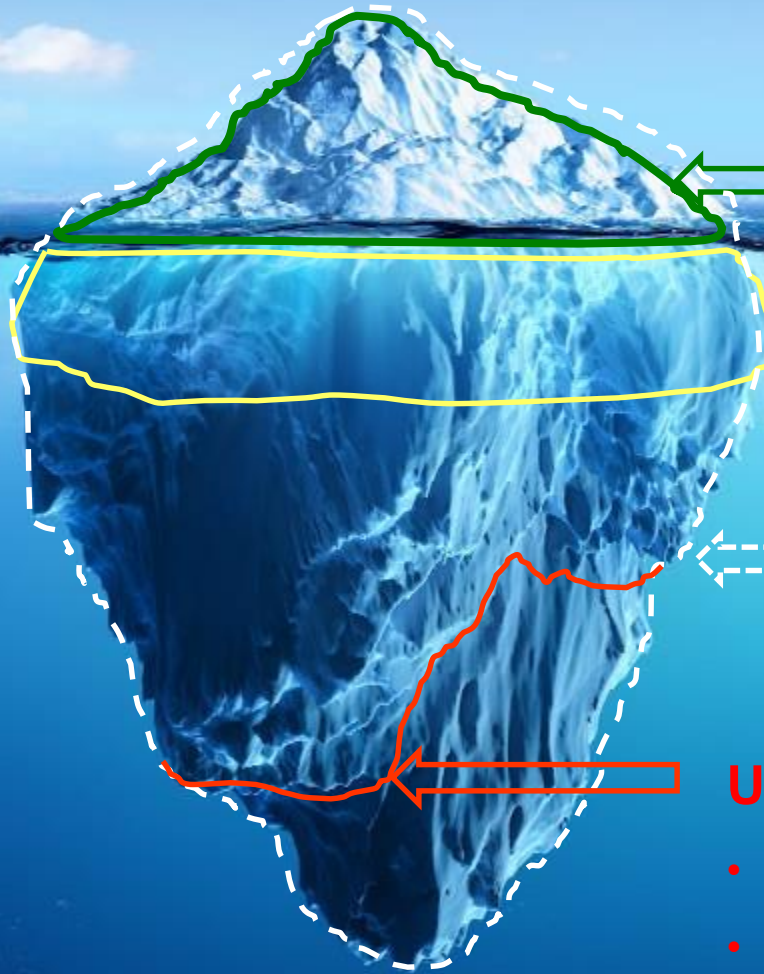
## Total organic fluorine (TOF)

- *CIC*
- *<sup>19</sup>F NMR*

→ **TROF assay**

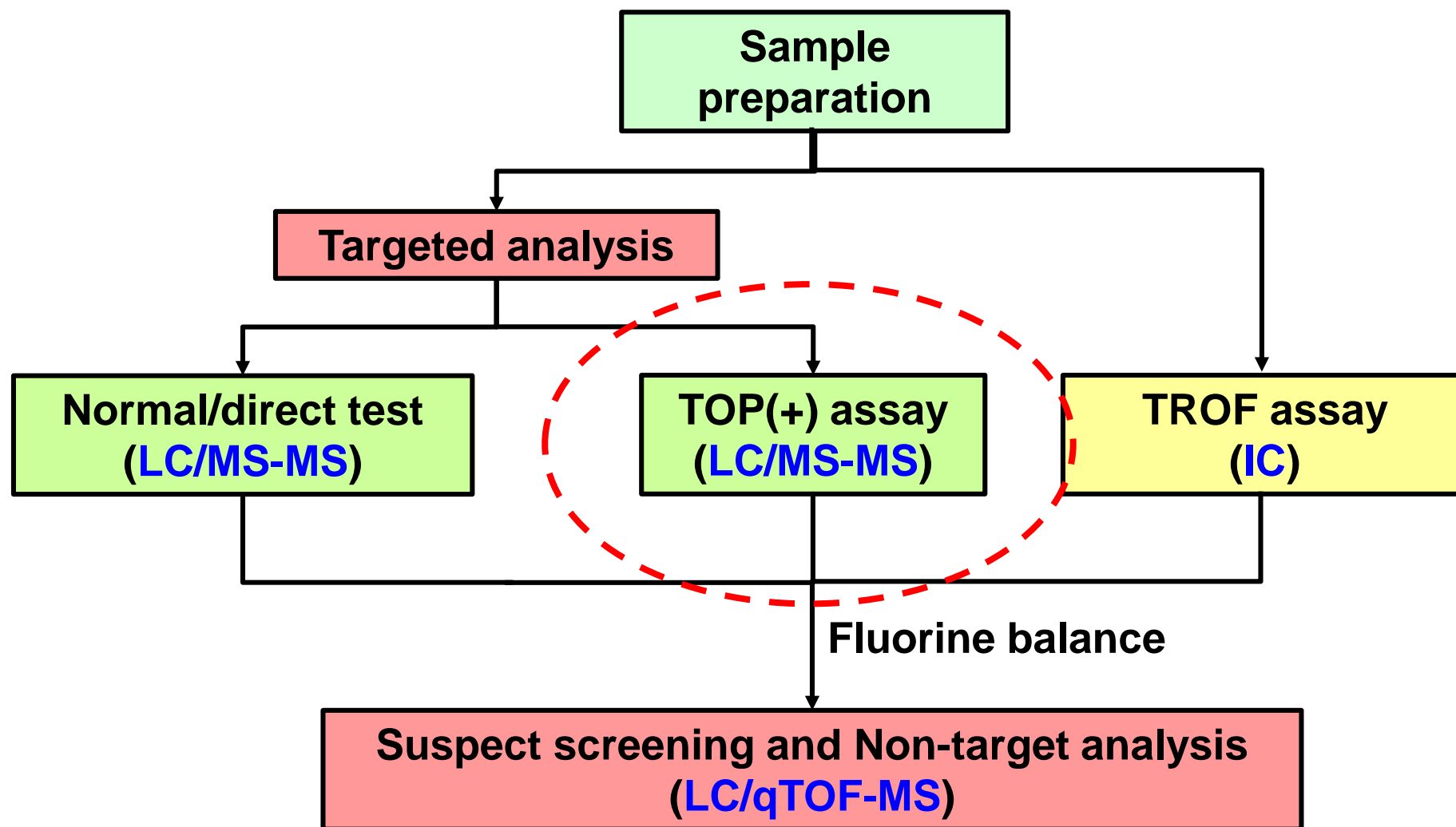
## Unknown PFASs

- *Suspect screening*
- *Non-target analysis*



# Strategy for PFAS analysis

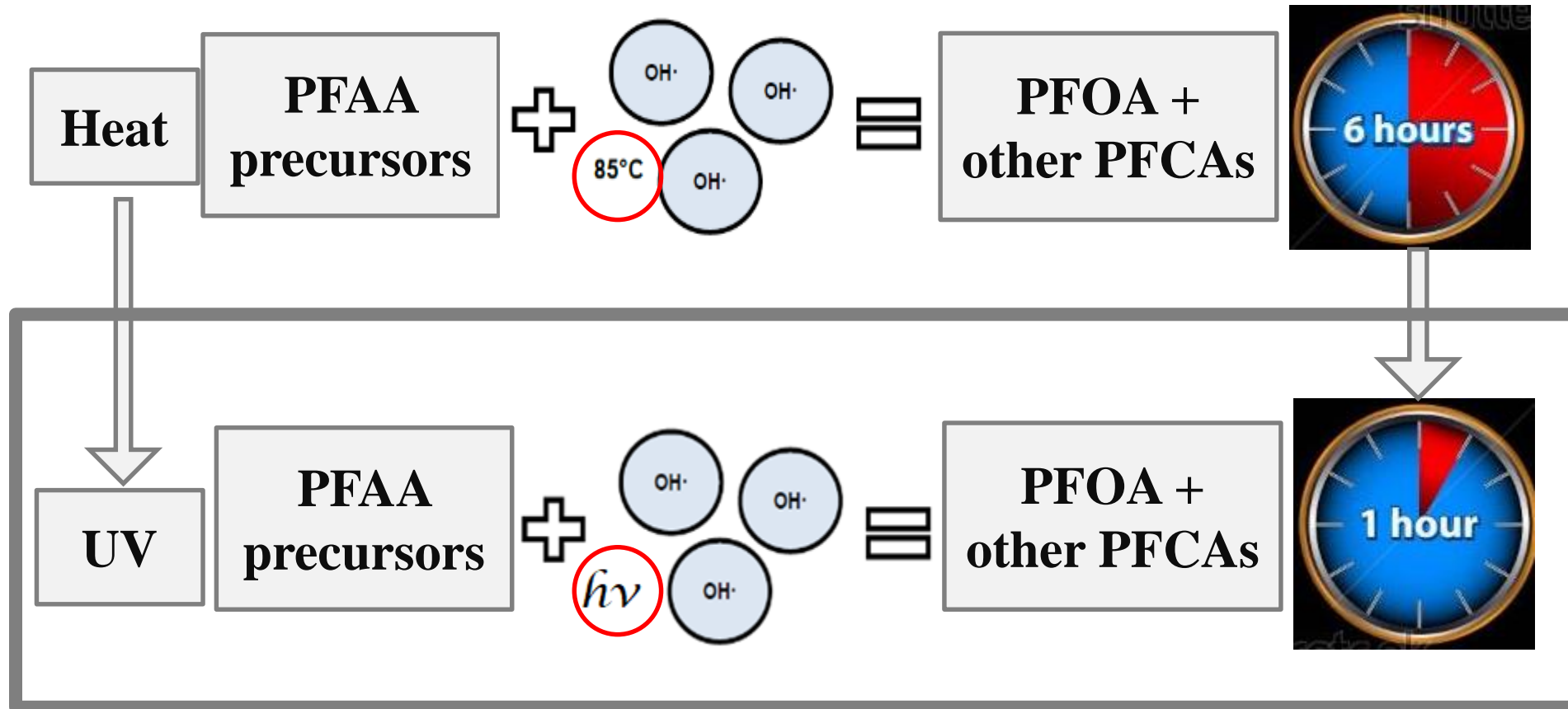
## ■ The comprehensive test protocol of PFAS



# Development of test methods

## 1. TOP+ assay: a modified TOP assay

- $UV_{254}$ -activated persulfate (60 mM  $K_2S_2O_8$ , pH=12) oxidation



# Development of test methods

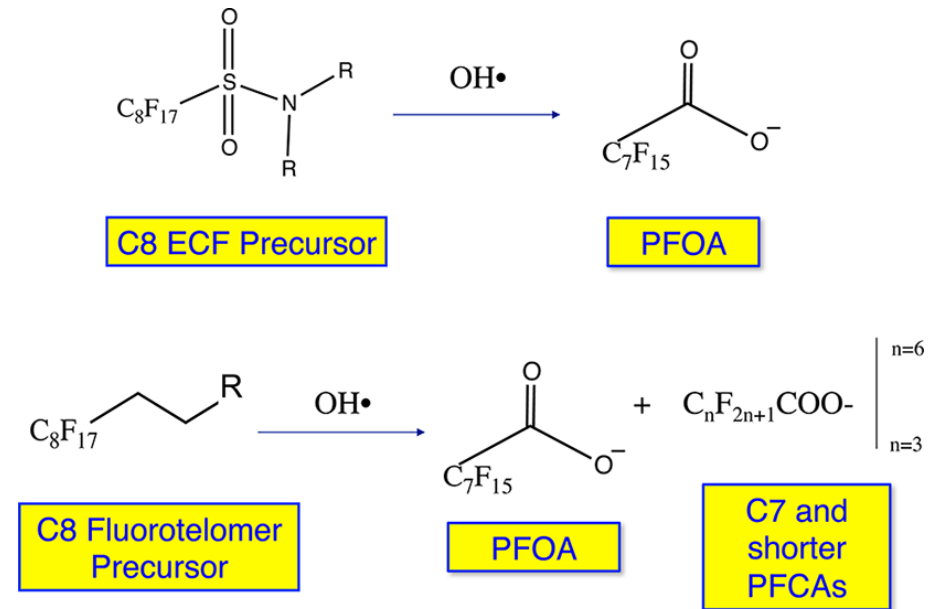
## 1. TOP+ assay: a modified TOP assay

- The mechanism of TOP assay

- ✓ Houtz and Sedlak proposed TOP assay

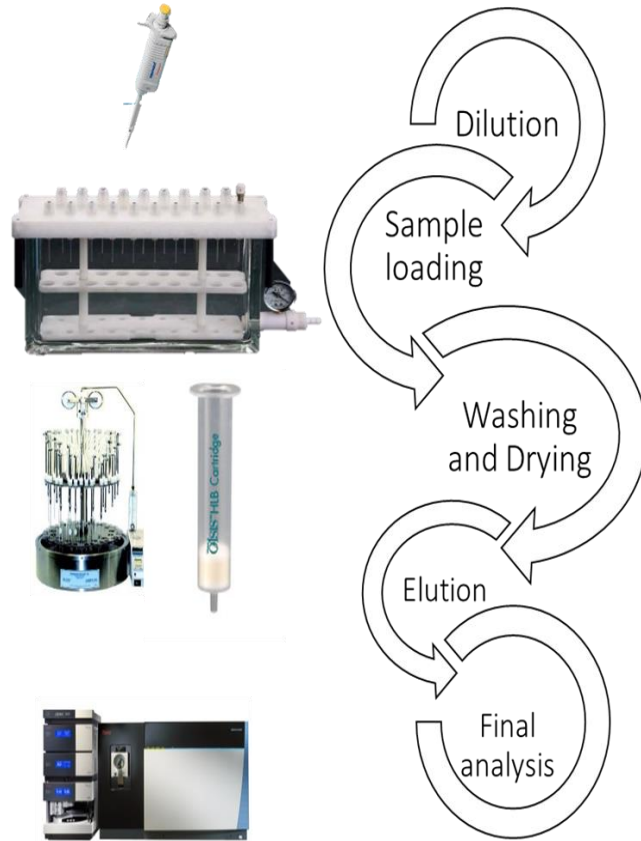


- ✓ Persulfate, heat, basic pH condition in ~6h → hydroxyl radicals lead to PFCAs precursors conversion
- ✓ Analyze PFCAs concentration for precursors concentration

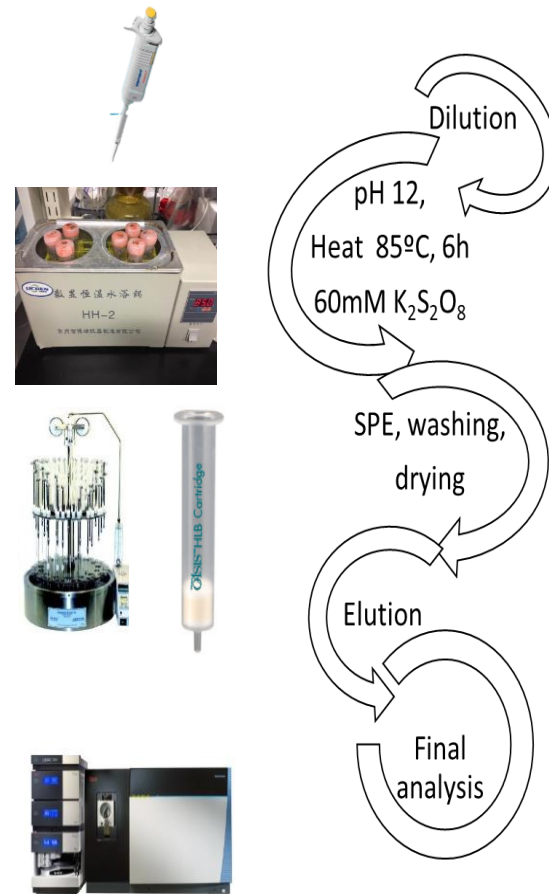




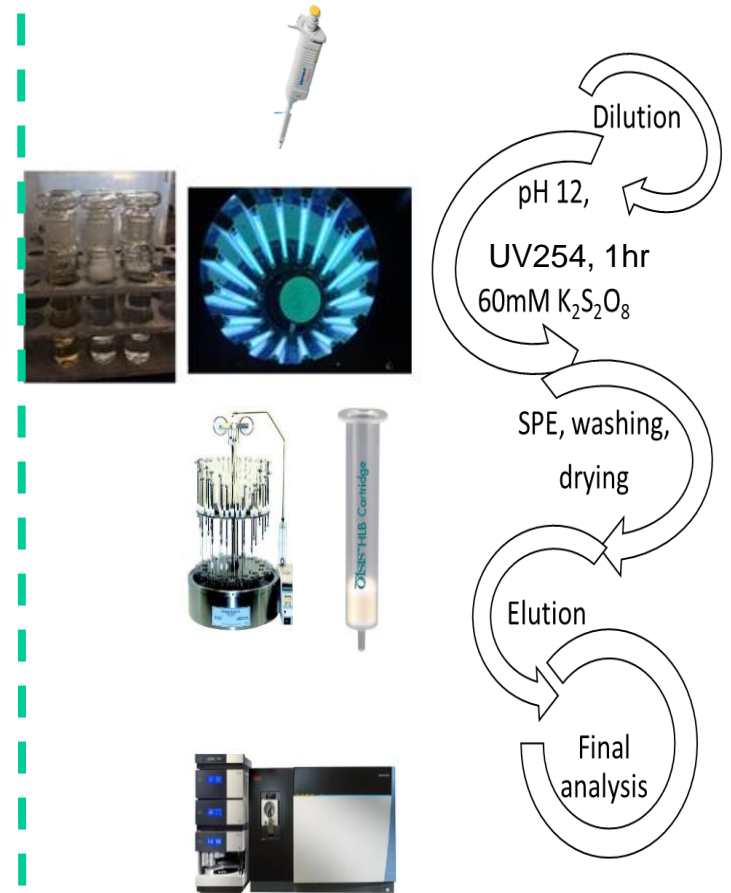
# Development of test methods



**EPA Method 537.1**



**TOP assay**



**TOP+ assay**

# Development of test methods

- Recovery comparison for typical precursors

Selected precursor	6:2 FTS	8:2 FTS	FOSA
PFBA	39.90%	31.7% ± 1.9%	12.6% ± 0.5%
PFPeA	40.2% ± 5.4%	40.5% ± 0.5%	11.0% ± 2.8%
<b>PFHxA</b>	15.70%	3.6% ± 0.6%	0.90%
<b>PFHpA</b>	5.1% ± 0.3%	6.0% ± 1.3%	2.80%
<b>PFOA</b>		21.5% ± 2.3%	76.5% ± 2.9 %
<b>PFNA</b>	-	1.75%	-
TOP assay	80 ± 5%	89 ± 2%	97 ± 3%
TOP+ assay	100.9% ± 5.3%	105.1% ± 6.4%	103.7% ± 6.2%

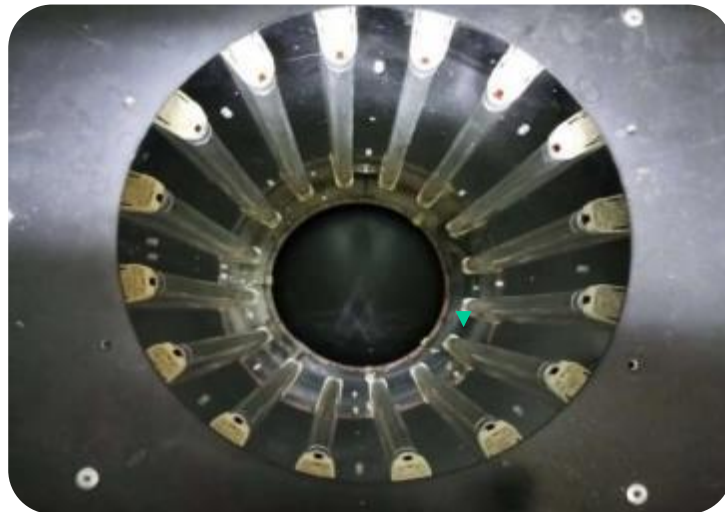
\*Corresponding  $\Delta$ PFCAs/[precursor]<sub>0</sub>

# Development of test methods

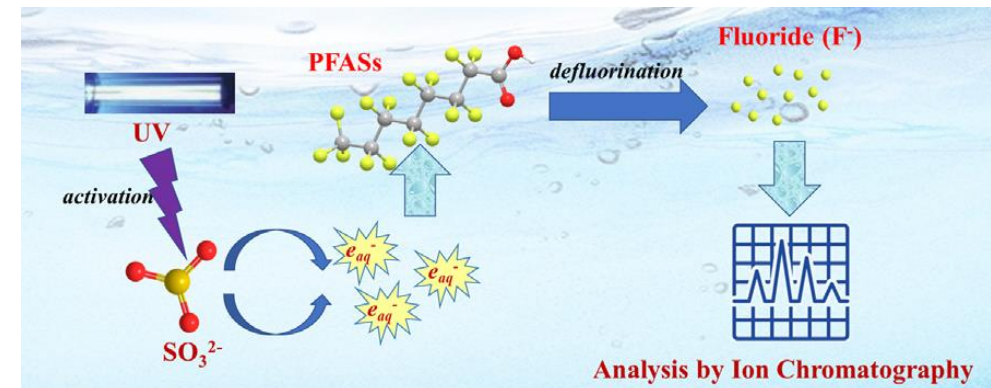
## 2. TROF assay: an alternative to CIC

Patent: ZL2018106384817

- **TROF** = **t**otal **r**educible **o**rganic **f**luorine
- **[MECHANISM]** Convert organic fluorine to inorganic fluoride using **hydrated electron ( $e_{aq}^-$ )** generated by **UV/sulfite**, an advanced reduction process (ARP)



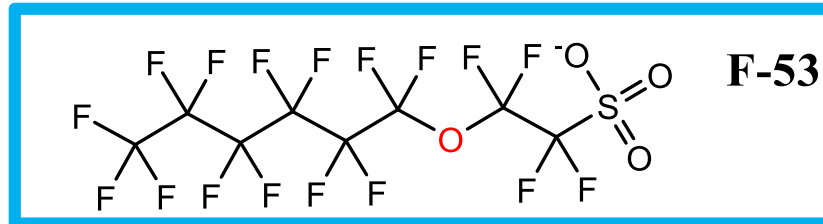
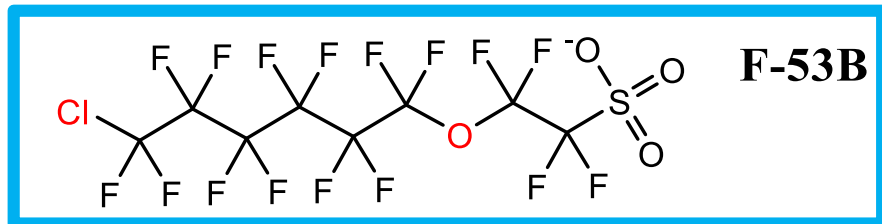
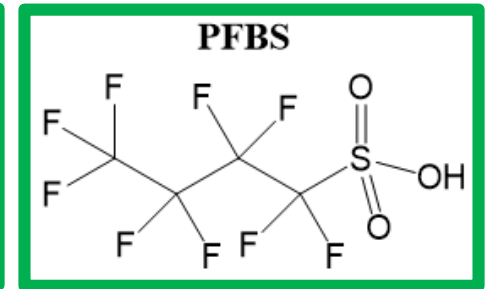
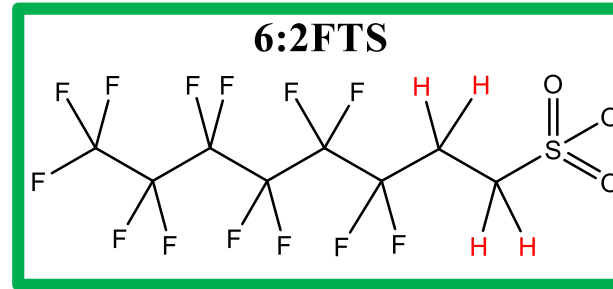
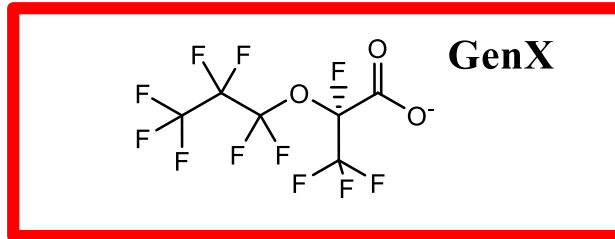
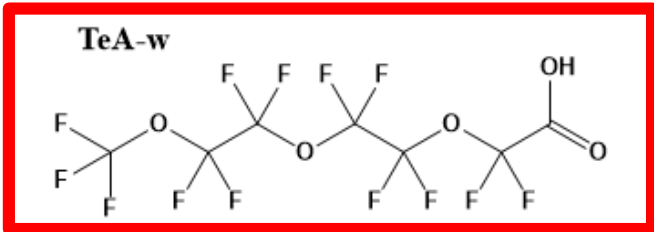
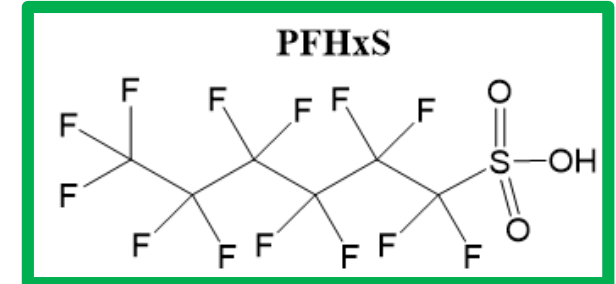
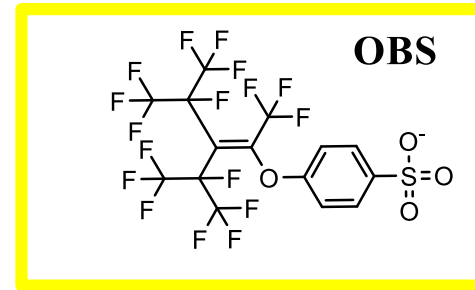
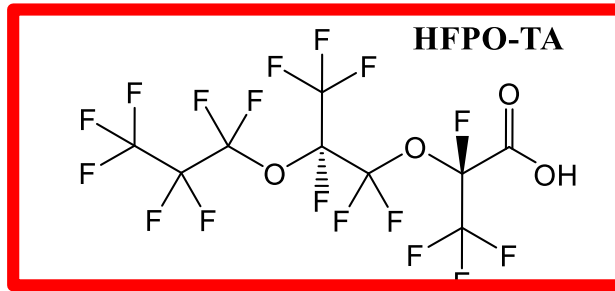
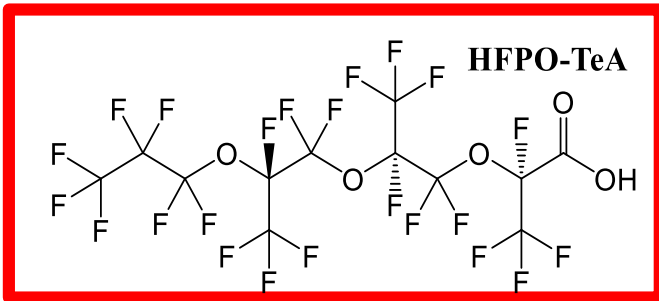
RPR200, Southern New England Ultraviolet (Rayonet) Co.



- **UV Lamp:** 253.7 nm, 16\*8.0 mW/cm<sup>2</sup>
- **[Na<sub>2</sub>SO<sub>3</sub>]** = 20 mM
- **[NaOH]** = 150 mM
- **t** = 6 h

# Development of test methods

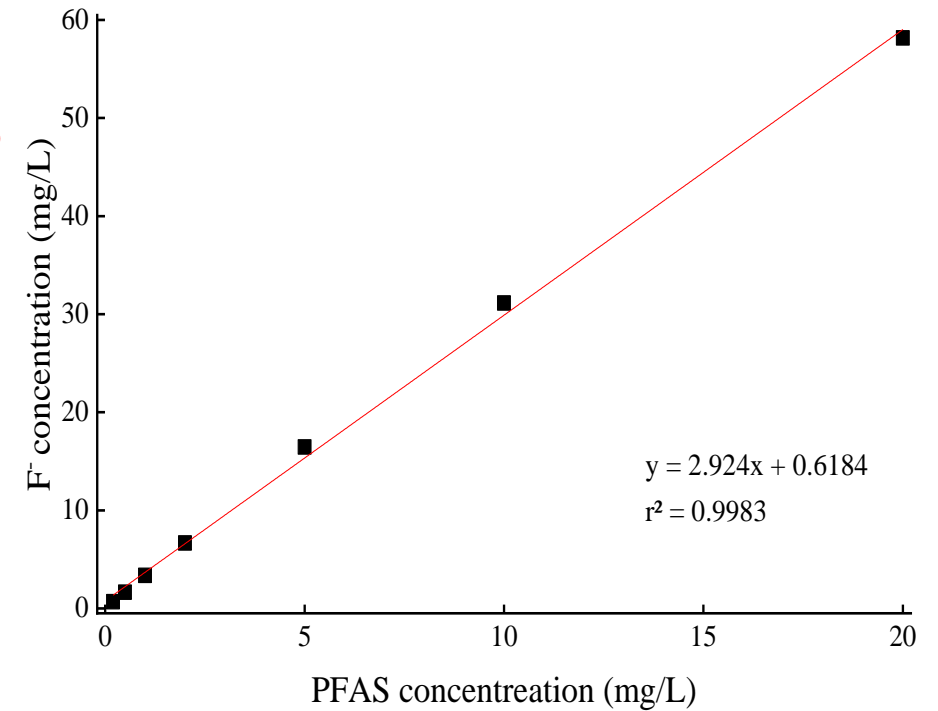
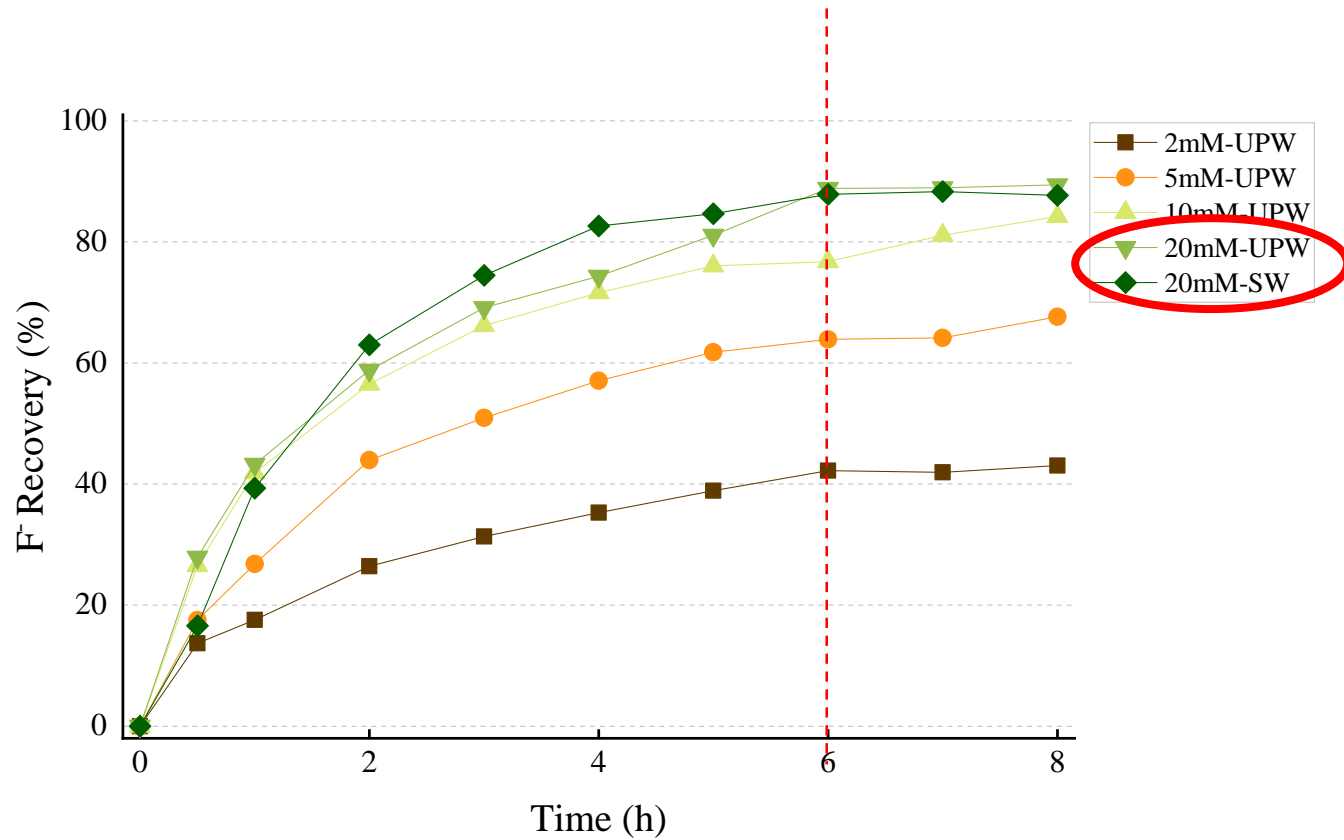
- TROF assay comes from our previous studies — successful degradation and defluorination of various PFAS by  $e_{aq}^-$  in alkaline UV/sulfite system



Bao et al., *ES&T* 2018  
Bao et al., *Water Res* 2019  
Bao et al., *Chem Eng J* 2020  
Bao et al., *J Hazard Mater* 2021

# Development of test methods

- Recovery and calibration curve



# AFFF surfactants

## ■ Fluorinated foams are dominant in China



**Class B foams**

**Fluorinated foams**

**AFFF** *aqueous film-forming foam*

**AR-AFFF** *alcohol-resistant aqueous film-forming foam*

**FP** *fluoroprotein foam*

**AR-FP** *alcohol-resistant fluoroprotein foam*

**FFFP** *film-forming fluoroprotein foam*

**AR-FFFP** *alcohol-resistant film-forming fluoroprotein foam*

**Fluorine-free foams (F3)**

# AFFF surfactants

## ■ Existing limits for PFAS in Class B foams

\* Unit: mg/L and mg/kg

Regulation	PFHxS	PFOS	PFOA	PFOA precursors (≥C7)
ECHA	-	10	0.025	0.26
Queensland	10 (PFHxS + PFOS)		50 (as fluorine) (TOP Assay C7-C14)	

### Source:

[https://businessdocbox.com/Green\\_Solutions/74918344-Annex-xvrestriction-report.html](https://businessdocbox.com/Green_Solutions/74918344-Annex-xvrestriction-report.html)

[https://echa.europa.eu/documents/10162/13641/rest\\_pfoa\\_compiled\\_opinions\\_en.pdf](https://echa.europa.eu/documents/10162/13641/rest_pfoa_compiled_opinions_en.pdf)

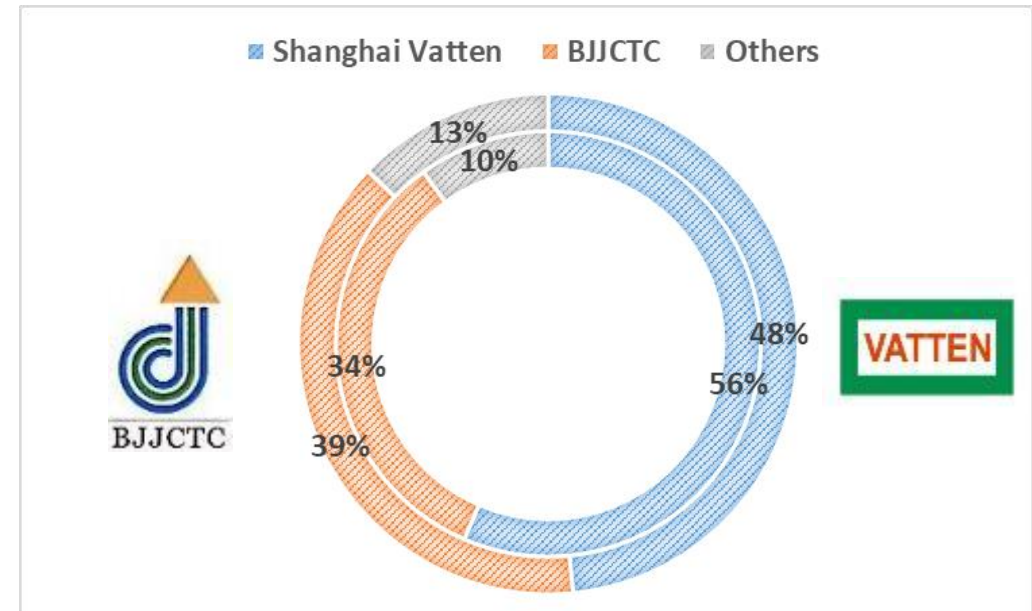
[https://www.qld.gov.au/data/assets/pdf\\_file/0025/68470/firefighting-foam-policy.pdf](https://www.qld.gov.au/data/assets/pdf_file/0025/68470/firefighting-foam-policy.pdf)

# AFFF surfactants

## ■ China is the top producer of fluorinated foams

- ~40% for **domestic** market, using **PFOS-based** surfactants **produced in China**
- ~60% for **international** market, using **telomer-based** surfactants **imported**

Year	2014	2015
Production of fluorinated foam concentrates (t)	27126.3	39341.2
Production of PFOS-based foam concentrates (t)	11592.1	15869.9
Consumption of PFOS (t)	54	74.7
Average content of PFOS (%)	0.47	0.47



**Source:** [Zhuang 2017](#)



# AFFF surfactants

## ■ Sample collection

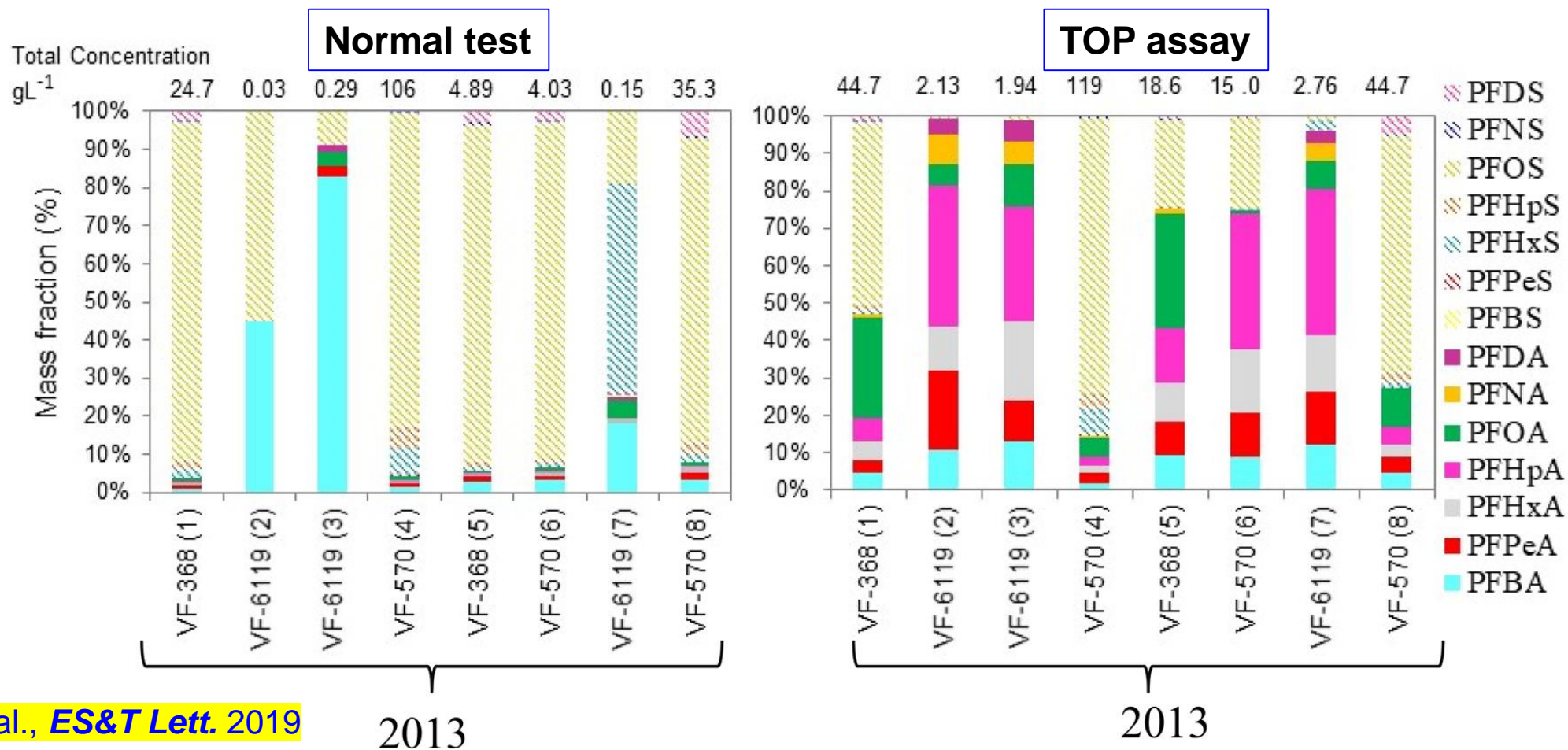
- AFFF surfactants samples collected from **Shanghai Vatten**
- The leader in Chinese market, active in R&D of non-PFOS alternatives

Purpose	Vatten FS	Chemical description
Domestic market	VF-368	C8, PFOS-based
	VF-570	
International market	VF-6119	Fluorinated copolymer
	VF-6116	
	VF-9126	C6, telomer-based
	VF-9128	
	VF-9129	

# AFFF surfactants

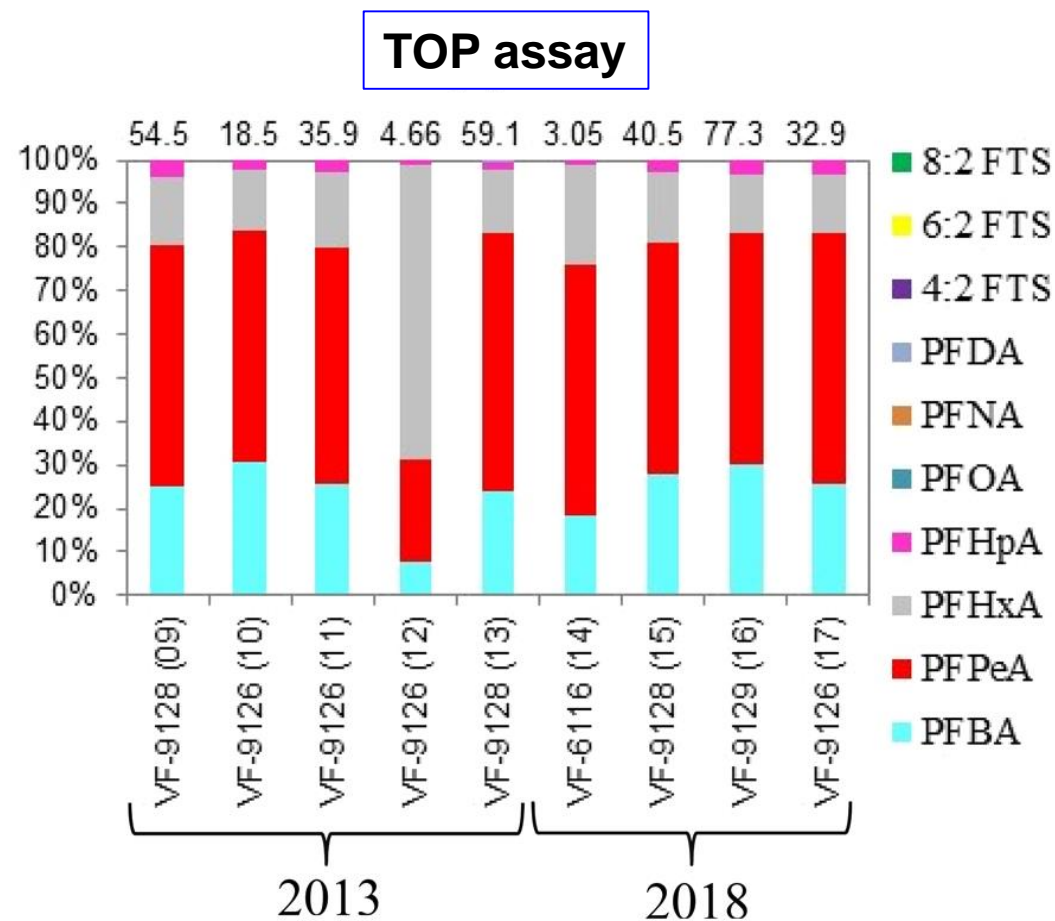
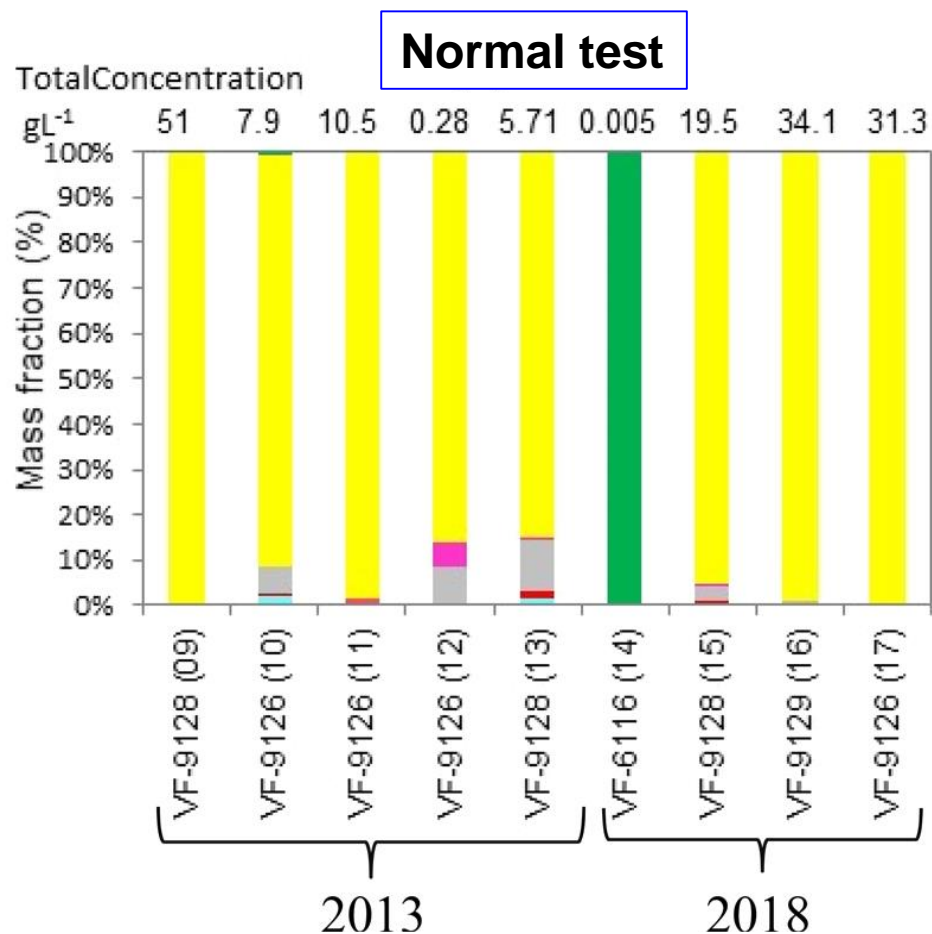
## ■ Comparison: Normal test vs. TOP assay

### • PFOS-based FS products



# AFFF surfactants

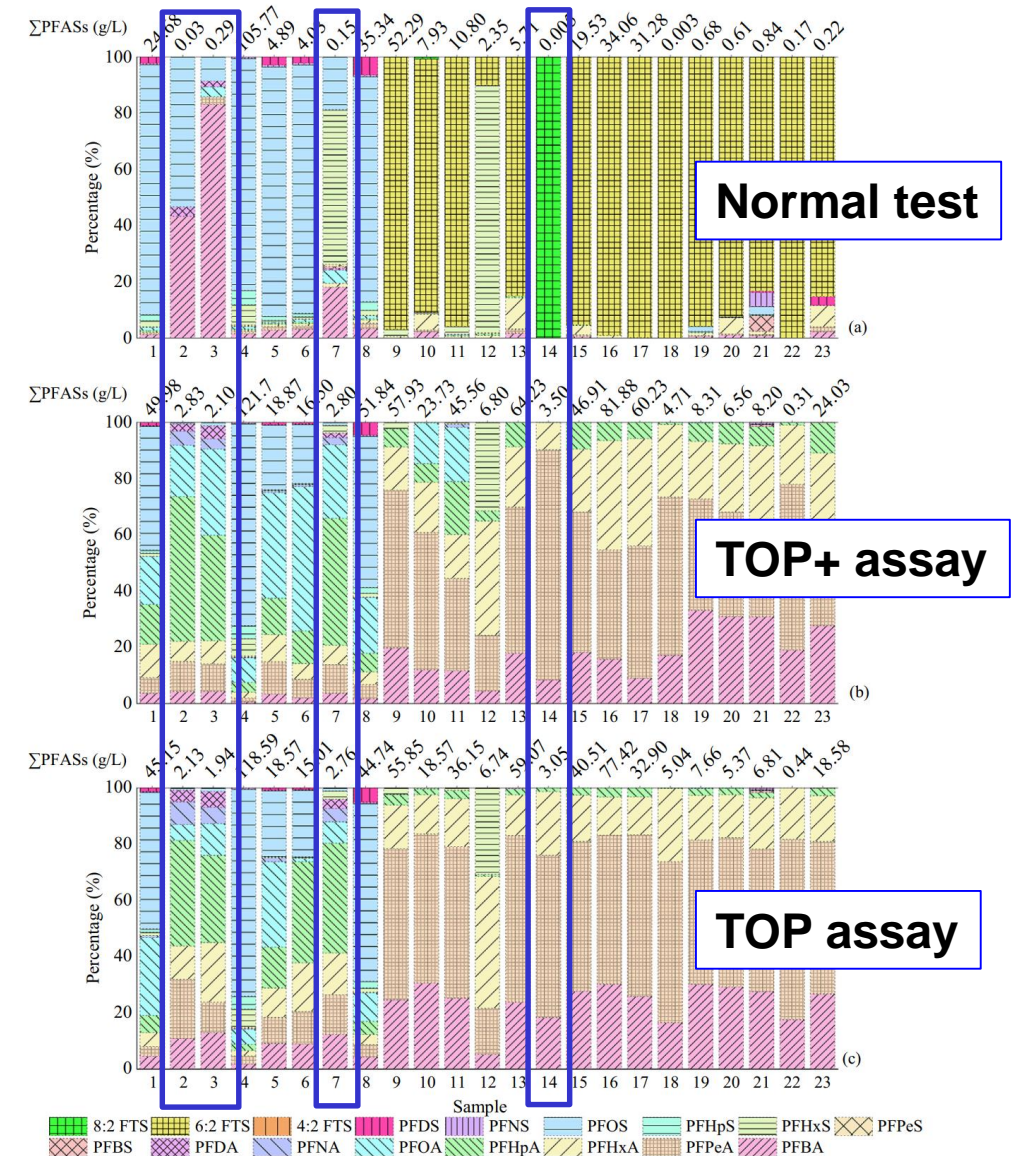
- Telomer-based FS products**



# AFFF surfactants

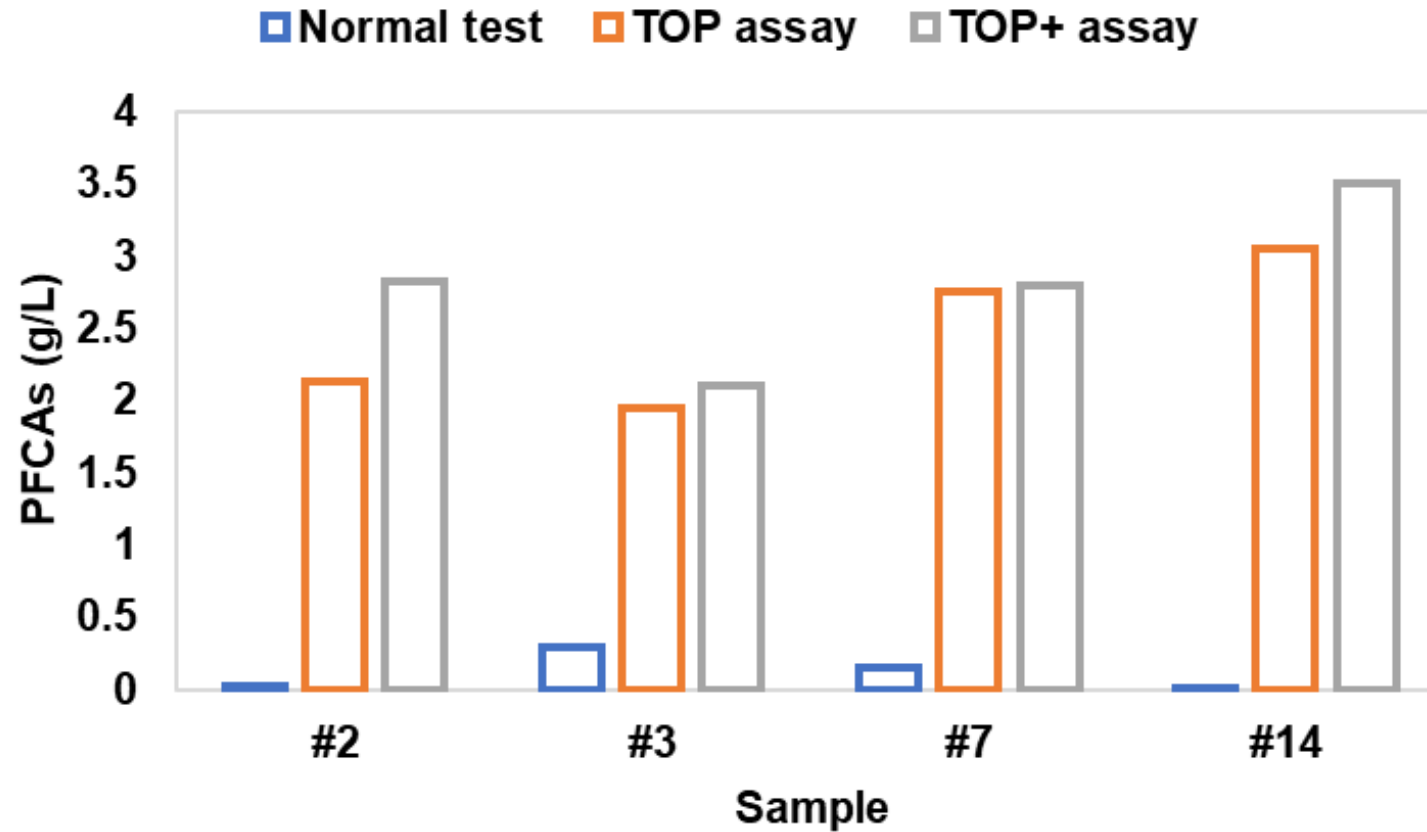
## Comparison: also TOP+ assay

Number	Sample name	Production date	Main components
1	VF-368-1	2013	C8
2	VF-6119-2	2013	C8, copolymer
3	VF-6119-3	2013	C8, copolymer
4	VF-570-4	2013	C8
5	VF-368-5	2013	C8
6	VF-570-6	2013	C8
7	VF-6119-7	2013	C8, copolymer
8	VF-570-8	2013	C8
9	VF-9128-9	2013	C6
10	VF-9126-10	2013	C6
11	VF-9126-11	2013	C6
12	VF-9126-12	2013	C6
13	VF-9128-13	2014	C6
14	VF-6116-14	2018	C6, copolymer
15	VF-9128-15	2018	C6
16	VF-9129-16	2018	C6
17	VF-9126-17	2018	C6
18	VF-6116-18	2019	C6
19	VF-9126-19	2019	C6
20	VF-9128-20	2019	C6
21	VF-9129-21	2019	C6
22	VF-FB6-22	2019	C6
23	VF-LSB-23	2019	C6



# AFFF surfactants

## ■ Comparison: also TOP+ assay



# Textile finishing agents

## ■ Sample collection

- Textile finishing agents (TFAs) directly purchased from Chinese market

No.	Sample name	Components	Vendors	Sampling year
Telomerization technology based TFAs				
FA 1	PHOBOL CP-SLA	C6	Shanghai Lutong	2017
FA 2	LT-EC601	C6		
FA 3	LT-710	NA		
FA 4	AGE-7800	C6		
FA 5	LT-A05	C6		
FA 6	FSJ	C6		
FA 7	LG-630	NA		
Electrochemical fluorination based TFAs				
FA 8	S34	C6	Hubei Hengxin;	2013
FA 9	S35	C4		
FA 10	S42	C6	Wuhan Fengfan surface engineering co., Ltd	
FA 11	S43	C6		
FA 12	S44	C4		

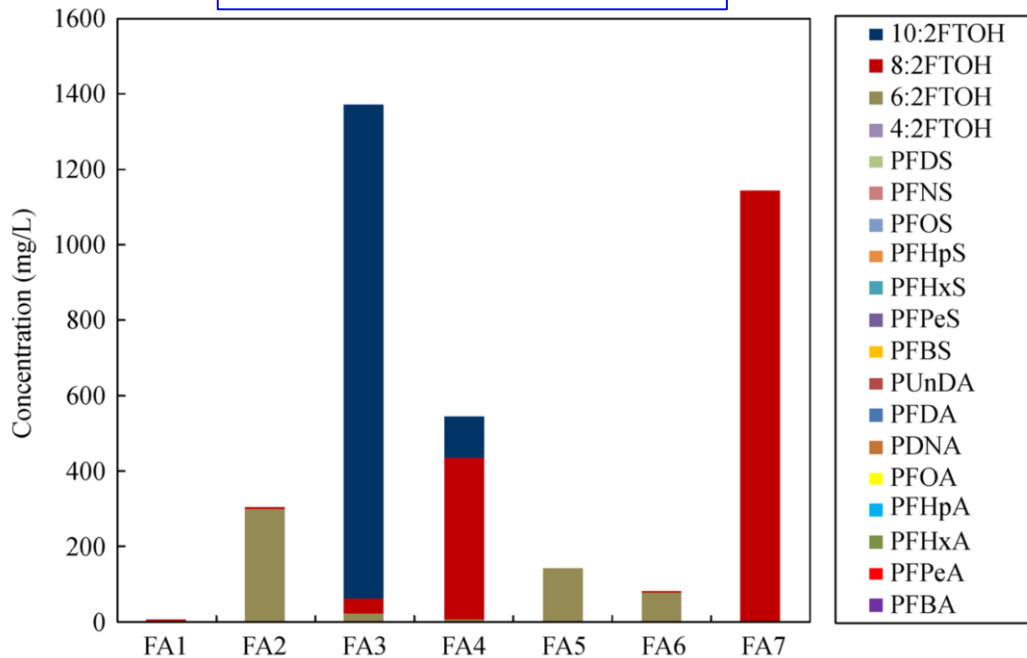
\*C4 and C6 belong to short-chain technology; NA (not available)

# Textile finishing agents

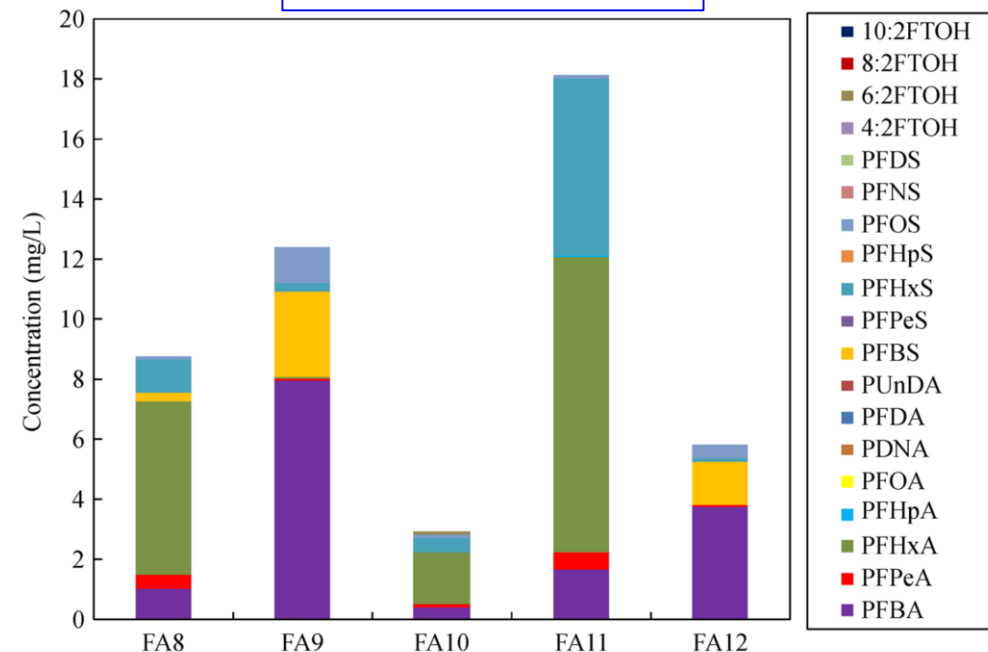
## ■ Comparison: Normal test vs. TOP assay

- Nearly zero PFCAs found in Normal test using LC/MS-MS
- Together with GC/MS for FTOHs:

Telomer based TFAs

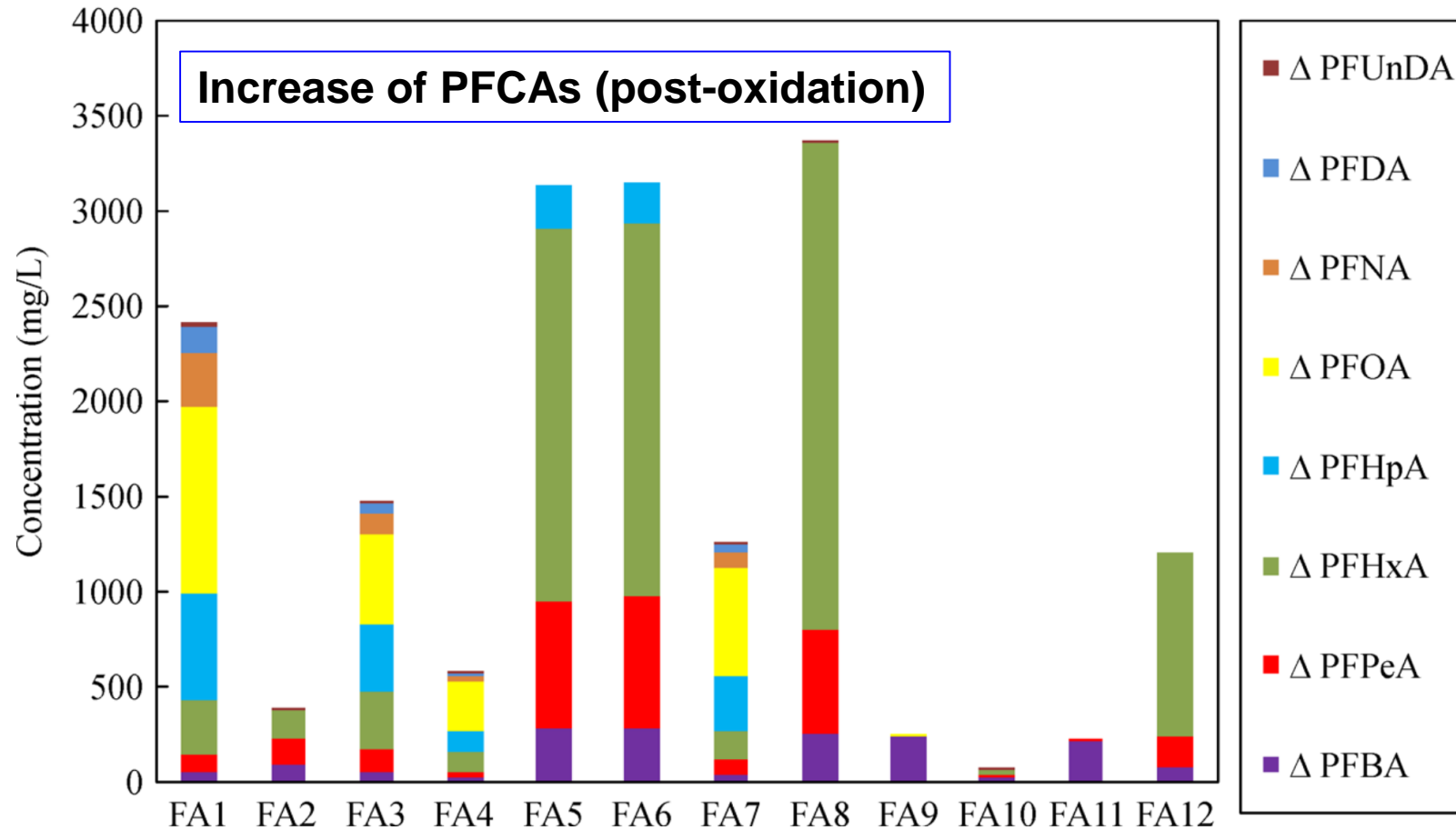


ECF based TFAs



# Textile finishing agents

- **TOP assay**

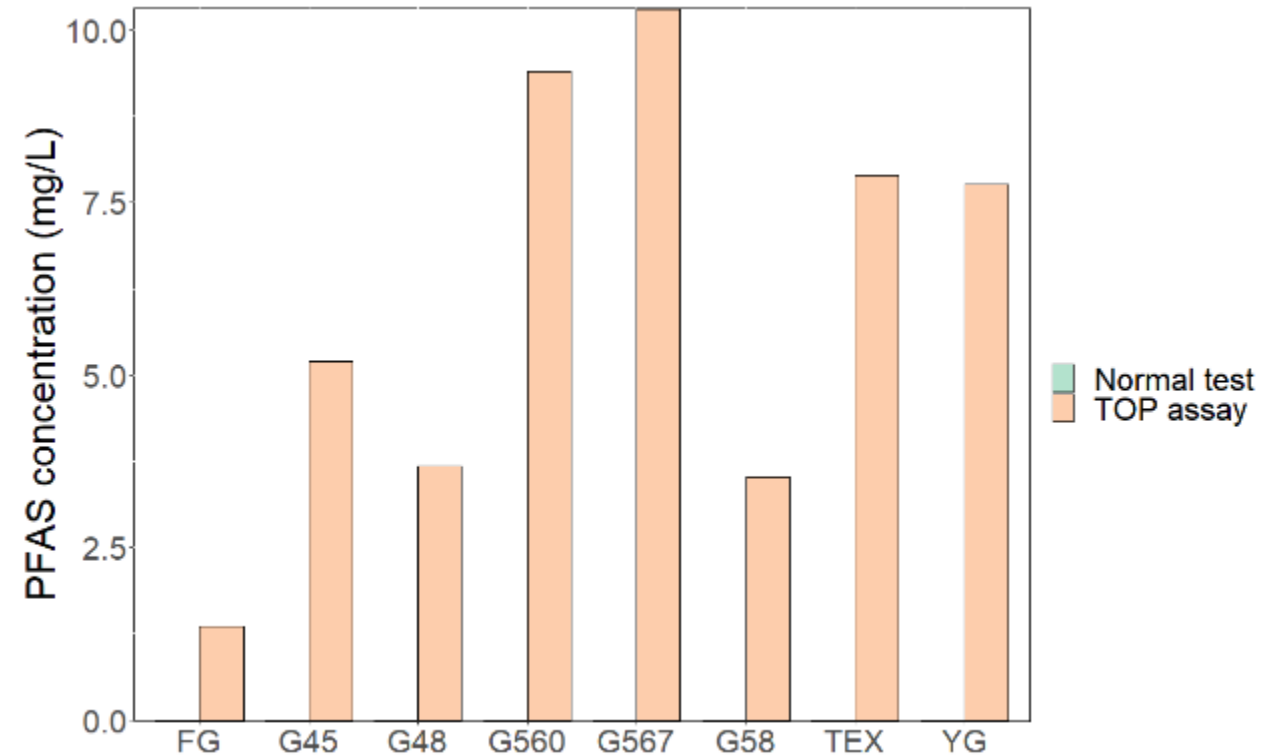




# Textile finishing agents

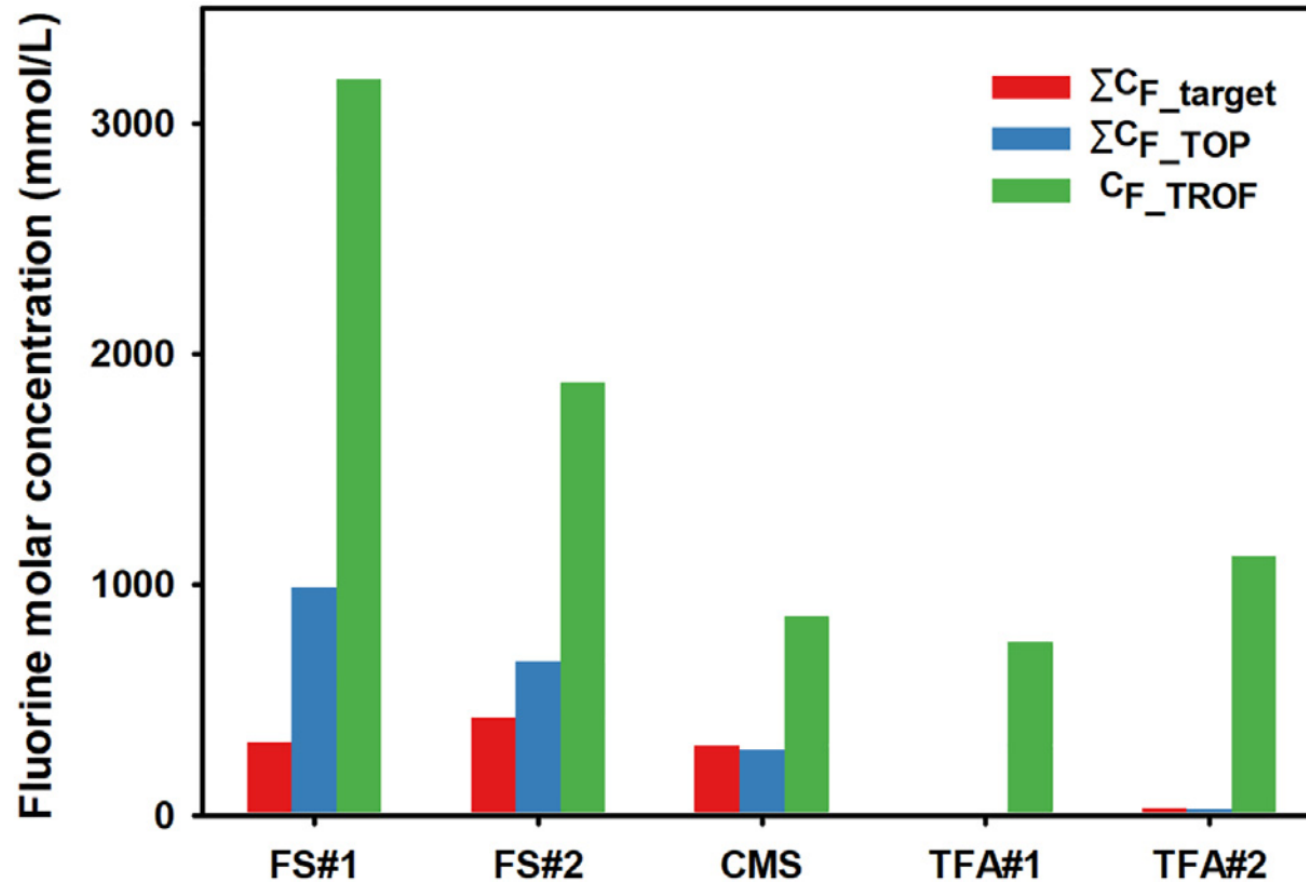
- Application for a new set of TFA samples (2021)

Sample #	Company	Country	Name
FG	Zhanhe	China	NEXGARD FG-821
G45	Daikin	Japan	TG-4575
G48	Daikin	Japan	TG-4875C
G560	Daikin	Japan	TG-5601
G567	Daikin	Japan	TG-5671
G58	Daikin	Japan	TG-5871
TEX	Deke	China	TECHNOLOGY 706
YG	Yugan	China	YG-450



# Textile finishing agents

- Big gap exists in terms of F mass balance



Sample #	Type of sample	Supplier
FS#1	AFFF surfactant 1	Vatten
FS#2	AFFF surfactant 2	Vatten
CMS	Chrome mist suppressant	ATOTECH
TFA#1	Textile finishing agent 1	Sunichem
TFA#2	Textile finishing agent 2	Sunichem

# Textile finishing agents

## \* Consistency with a recent ES&T paper



pubs.acs.org/est



Article

### Per- and Polyfluoroalkyl Substances in North American School Uniforms

Chunjie Xia, Miriam L. Diamond, Graham F. Peaslee, Hui Peng, Arlene Blum, Zhanyun Wang, Anna Shalin, Heather D. Whitehead, Megan Green, Heather Schwartz-Narbonne, Diwen Yang, and Marta Venier\*

Cite This: <https://doi.org/10.1021/acs.est.2c02111>

Read Online

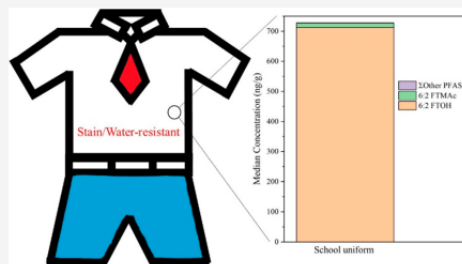
ACCESS |

Metrics & More

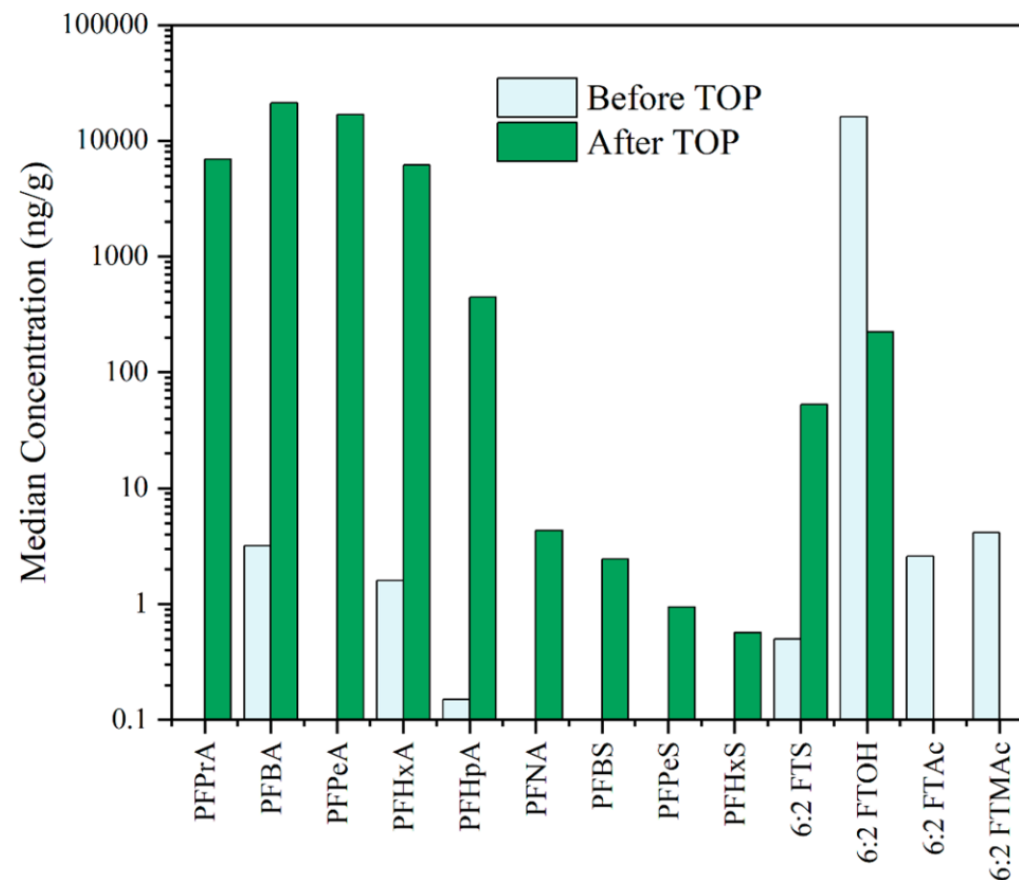
Article Recommendations

Supporting Information

**ABSTRACT:** We analyzed 72 children's textile products marketed as stain-resistant from US and Canadian stores, particularly school uniforms, to assess if clothing represents a significant route of exposure to per- and polyfluoroalkyl substances (PFAS). Products were first screened for total fluorine (total F) using particle-induced  $\gamma$ -ray emission (PIGE) spectroscopy ( $n = 72$ ), followed by targeted analysis of 49 neutral and ionic PFAS ( $n = 57$ ). PFAS were detected in all products from both markets, with the most abundant compound being 6:2 fluorotelomer alcohol (6:2 FTOH). Total targeted PFAS concentrations for all products collected from both countries ranged from 0.250 to 153 000 ng/g with a median of 117 ng/g (0.0281–38 100  $\mu\text{g}/\text{m}^2$ , median: 24.0  $\mu\text{g}/\text{m}^2$ ). Total targeted PFAS levels in school uniforms were significantly higher than in other items such as bibs, hats, stroller covers, and swimsuits, but comparable to outdoor wear. Higher total targeted PFAS concentrations were found in school uniforms made of 100% cotton than synthetic blends. Perfluoroalkyl acids (PFAAs) precursors were abundant in school uniforms based on the results of hydrolysis and total oxidizable precursor assay. The estimated median potential children's exposure to PFAS via dermal exposure through school uniforms was 1.03 ng/kg bw/day. Substance flow analysis estimated that ~3 tonnes/year (ranging from 0.05 to 33 tonnes/year) of PFAS are used in US children's uniforms, mostly of polymeric PFAS but with ~0.1 tonne/year of mobile, nonpolymeric PFAS.



**KEYWORDS:** school uniforms, children's products, PFAS, fluorotelomer alcohols (FTOHs), fluorotelomer methacrylates (FTMAcs), PFAS dermal exposure, PFAS substance flow analysis, PFAS hydrolysis, total oxidizable precursor (TOP) assay



Source: Xia et al., *Environ. Sci. Technol.*, 2022

# Summary

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## ■ Conclusions

- Normal test using LC/MS-MS is not effective for industrial formulations containing (side chain) fluoropolymers. Significant increase of PFCAs can be found when using TOP(+) assay for such samples.

- ✓ AFFF surfactants

- ✓ Textile finishing agents (TFAs)

- The results from TOP+ assay are quite comparable with TOP assay.
- **Suspect screening and non-target analysis are necessary for a mass balance of fluorine (F).**

\* Ref.: Liu et al., *Environ. Int.* 2022 (<https://doi.org/10.1016/j.envint.2022.107398>)

- Further investigation is needed with the cooperation of the producers.



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**Thank you!**