PFAS analysis in Class B fire-fighting foams: Methods and Practice
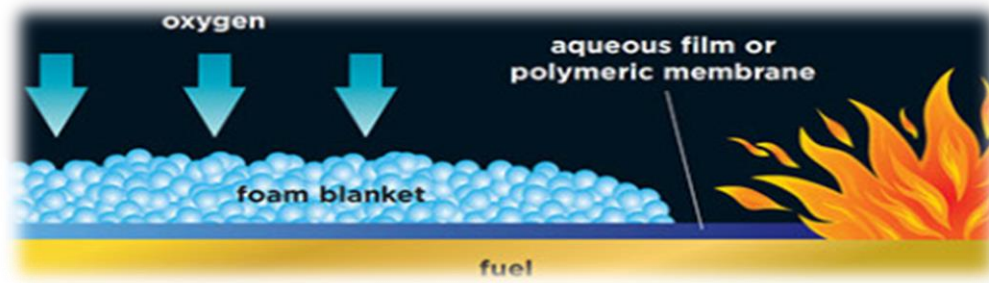
Jun HUANG, Ph.D

Professor of Environmental Chemistry
School of Environment, Tsinghua University
BCRC/SCRC China
Tel.: +86-10-62792598
E-mail: huangjun@tsinghua.edu.cn

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Background

■ **Class B foams:** designed for Class B fires - flammable liquids

Class B foams

Fluorinated foams

Fluorine-free foams (**F3**)

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*

Background

■ **PFAS release from fire-fighting foam**

WWTP → Ambient Water → DWP → Tap water
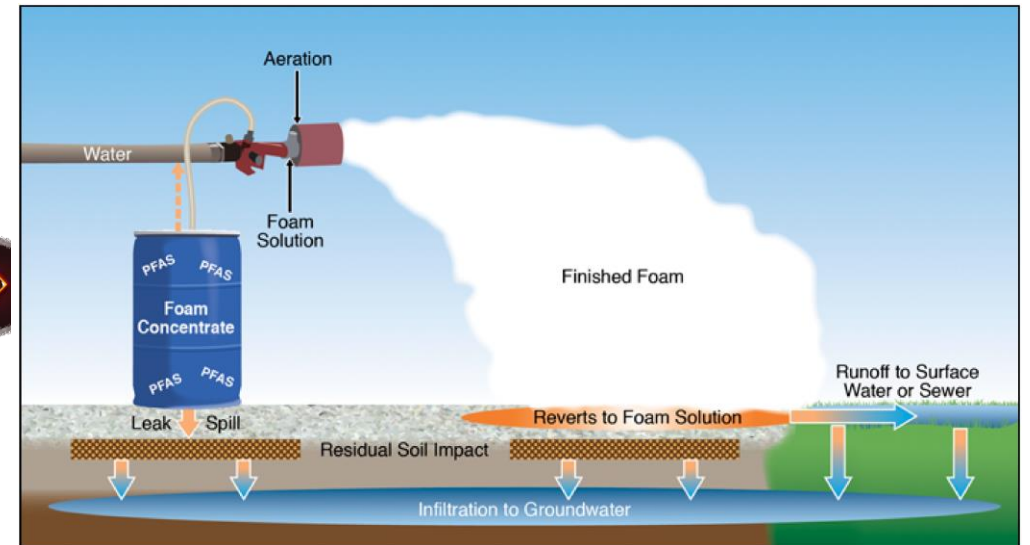
Background

■ **PFAS in foams - a changing story since 1963**

2023 — Publication of **fluorine-free foam** MilSpec by U.S. Navy[22]

2022 — Congress passed Protecting Firefighters from Adverse Substances Act (PFAS Act)

2021 — **PFAS Strategic Roadmap:** EPA's Commitments to Action 2021-24

2020 — Launch of GreenScreen certification of PFAS-free AFFF

2019 —
- Congress directed DoD to phase out PFAS in AFFF by 2024
- Congress required PFAS blood tests for military firefighters

2018 — **EPA released the 'PFAS Action Plan'**

2015 —
- European Union restricted PFOA in AFFF and turnout gear
- U.S. DoD replaced PFOS with PFBS in AFFF[18]

2009 — **EPA released the 'Long-Chain Perfluorinated Chemicals Action Plan'**

2002 — Warning to aviation industry about risks of PFOS in AFFF[8]

1983 — PFAS potential harms identified by 3M[17]

1976 — PFAS added in turnout gear[2] (firefighters' personal protective equipement)

1963 — U.S. Navy patented the first PFAS-containing AFFF[1]

https://doi.org/10.1021/acssuschemeng.3c01124
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Main foam fluorosurfactants:

- PFOSF based formulations using ECF technology
- C8-telomer based formulations using fluorotelomerization technology
- C6-telomer based formulations using fluorotelomerization technology
- Others (e.g. OBS)

Background

PFAS in foams - regulatory limits

- **EU:** POPs regulation; 1000 ppb for PFAS proposed

- **DOE/USA:** 1 ppb for PFAS in MIL-PRF-32725

- **Queensland (Australia):** See details below

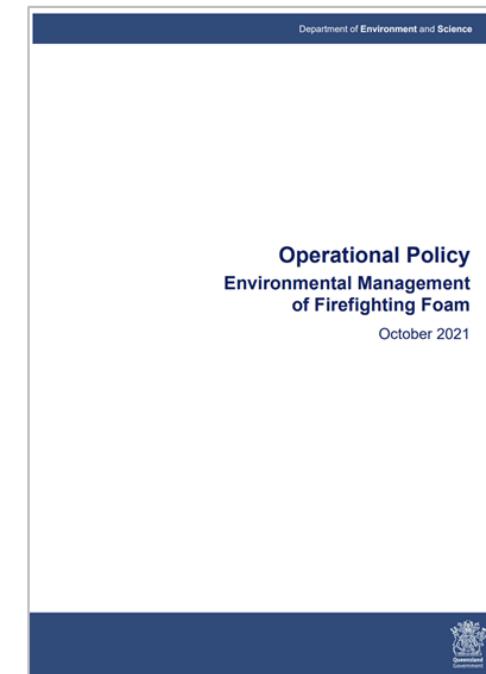**Table 4.1A – PFAS limits in non-persistent (fluorine-free) foam concentrates**

PFAS or fluorine content	Limit (mg/kg)
Perfluoroalkyl sulfonates and precursors ≥C4 to C12, the sum of the compounds. (PFBS+PFPeS+PFHxS+PFHpS+PFOS+PFNS+PFDS+PFDoS+precursors)	10 (sum)
Perfluoroalkyl carboxylates ≥C4 and higher homologues as the sum of the TOP-A analyses results for C4 to C14 compounds (TOP-A C4-C14).	50 (as fluorine)

Table 4.1B – Non-persistent foam (fluorine-free) concentrates and cross-contamination, simplified certification

Fluorine content	Limit (mg/kg)
Total organic fluorine (by combustion ion chromatography, TOF-CIC).	6.4 (as fluorine)

Table 4.2A – PFAS (long-chain) limits in persistent short-chain (C6-pure) foam concentrates

Compounds	Limit (mg/kg)
Perfluoroalkyl sulfonates and precursors ≥C4 to C12, the sum of the compounds. (PFBS+PFPeS+PFHxS+PFHpS+PFOS+PFNS+PFDS+PFDoS+precursors)	10 (sum)
Perfluoroalkyl carboxylates ≥C7 and higher homologues as the sum of the TOP-A analyses results for C7 to C14 compounds (TOP-A C7-C14).	50 (as fluorine)

Department of Environment and Science

**Operational Policy
Environmental Management
of Firefighting Foam**

October 2021

Queensland Government

Methods for PFAS analysis

■ **Tools for PFAS analysis in foam samples**

- **Targeted PFAS**: direct analysis using LC/MS-MS and GC/MS

- **Total oxidizable precursors (TOP)**: heat activated persulfate oxidation + LC/MS-MS

- **Total organic fluorine (TOF)**: combustion ion chromatography (CIC)

- **Unknown PFAS**: untargeted analysis using LC/HRMS (e.g. TOF, Orbitrap)
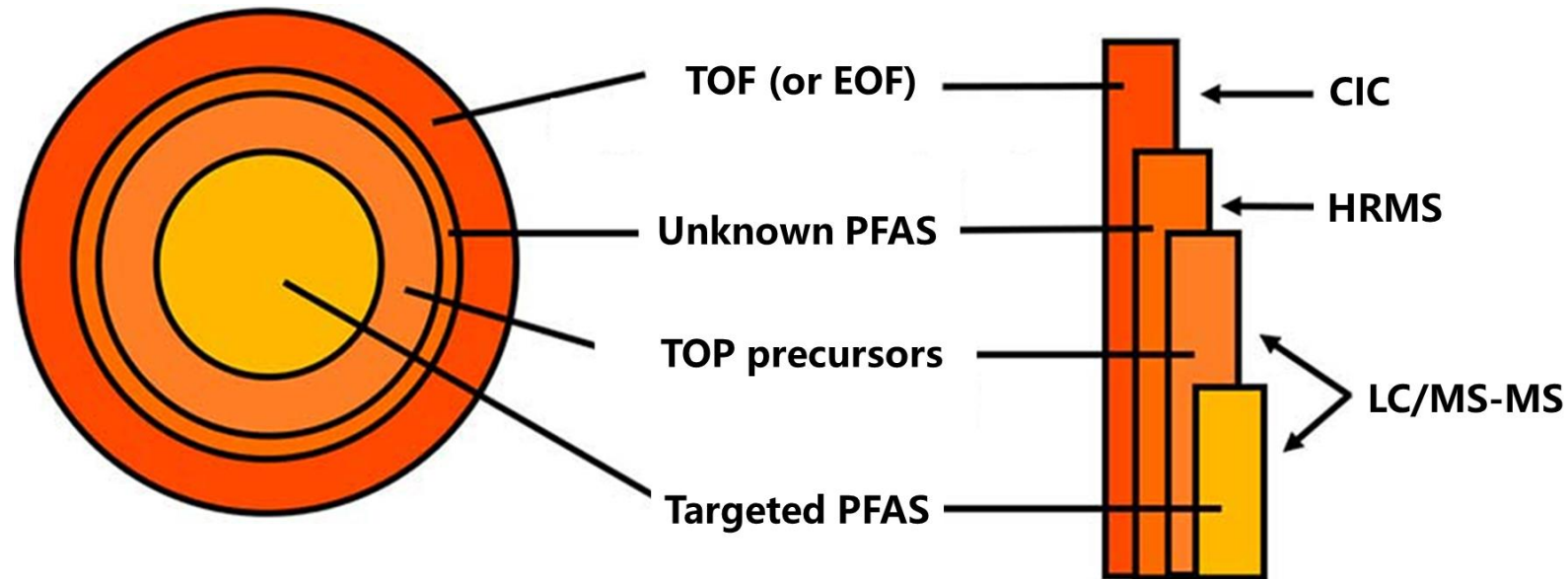
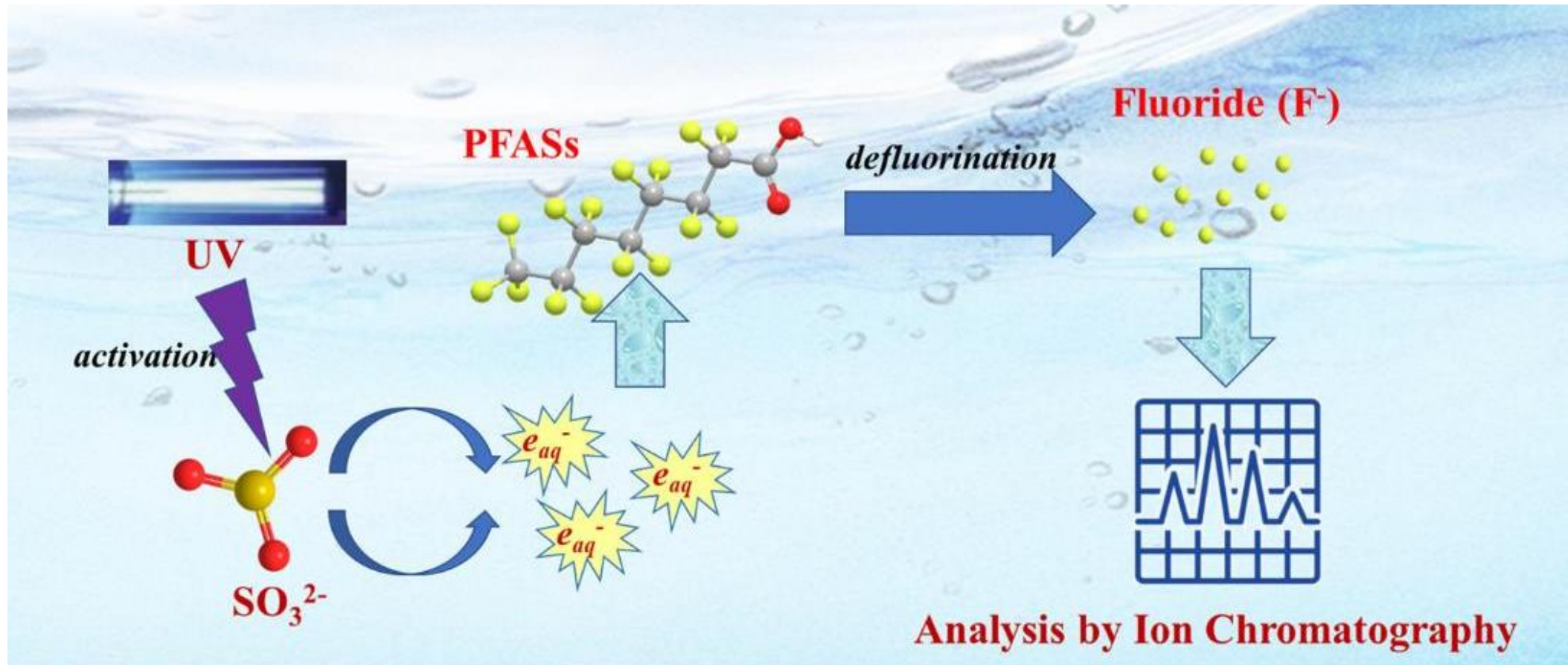# Methods for PFAS analysis

■ **Two new tools we developed**

- **UV-based total oxidizable precursors (TOP+)**: UV_{254}-activated persulfate oxidation + LC/MS-MS
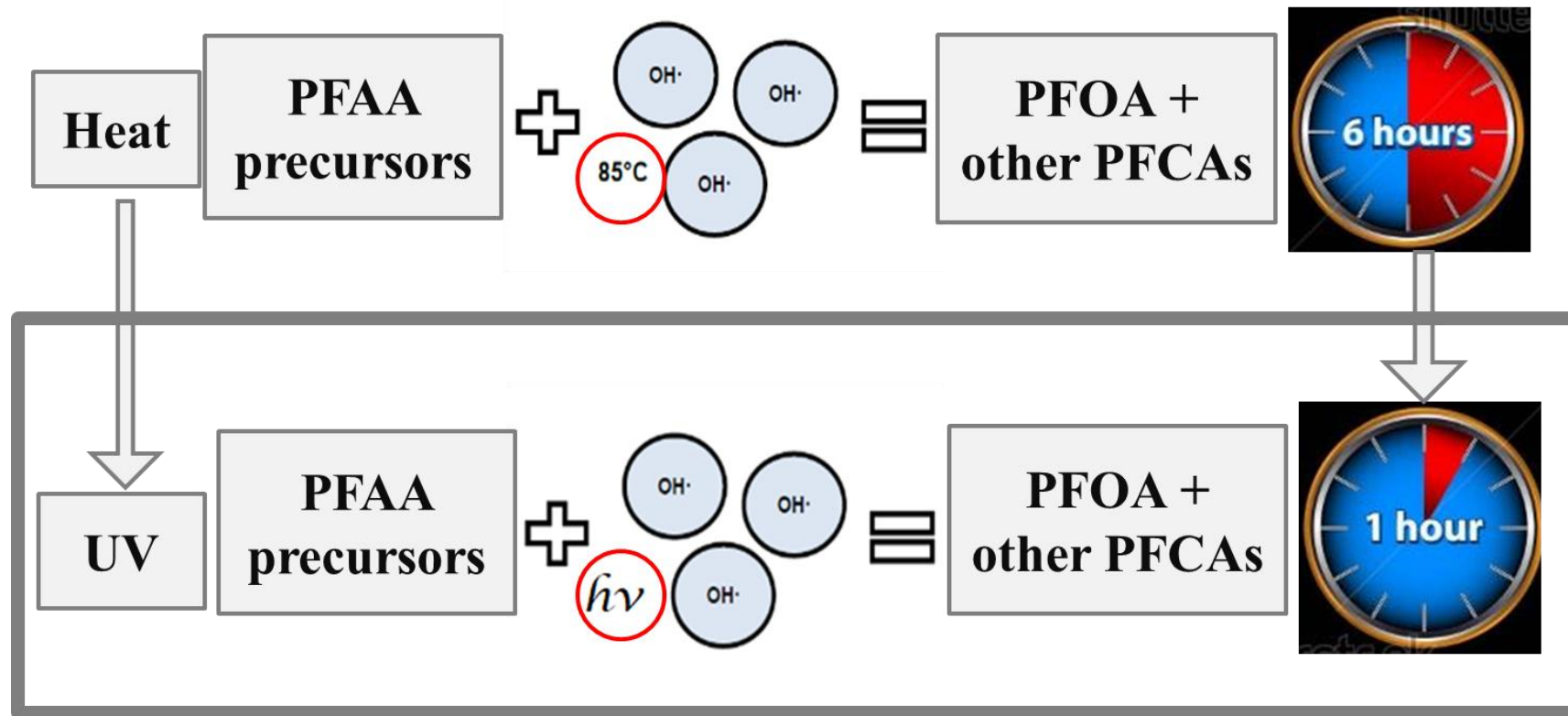
Methods for PFAS analysis

- **Total reducible organic fluorine (TROF)**: hydrated electron reduction + IC
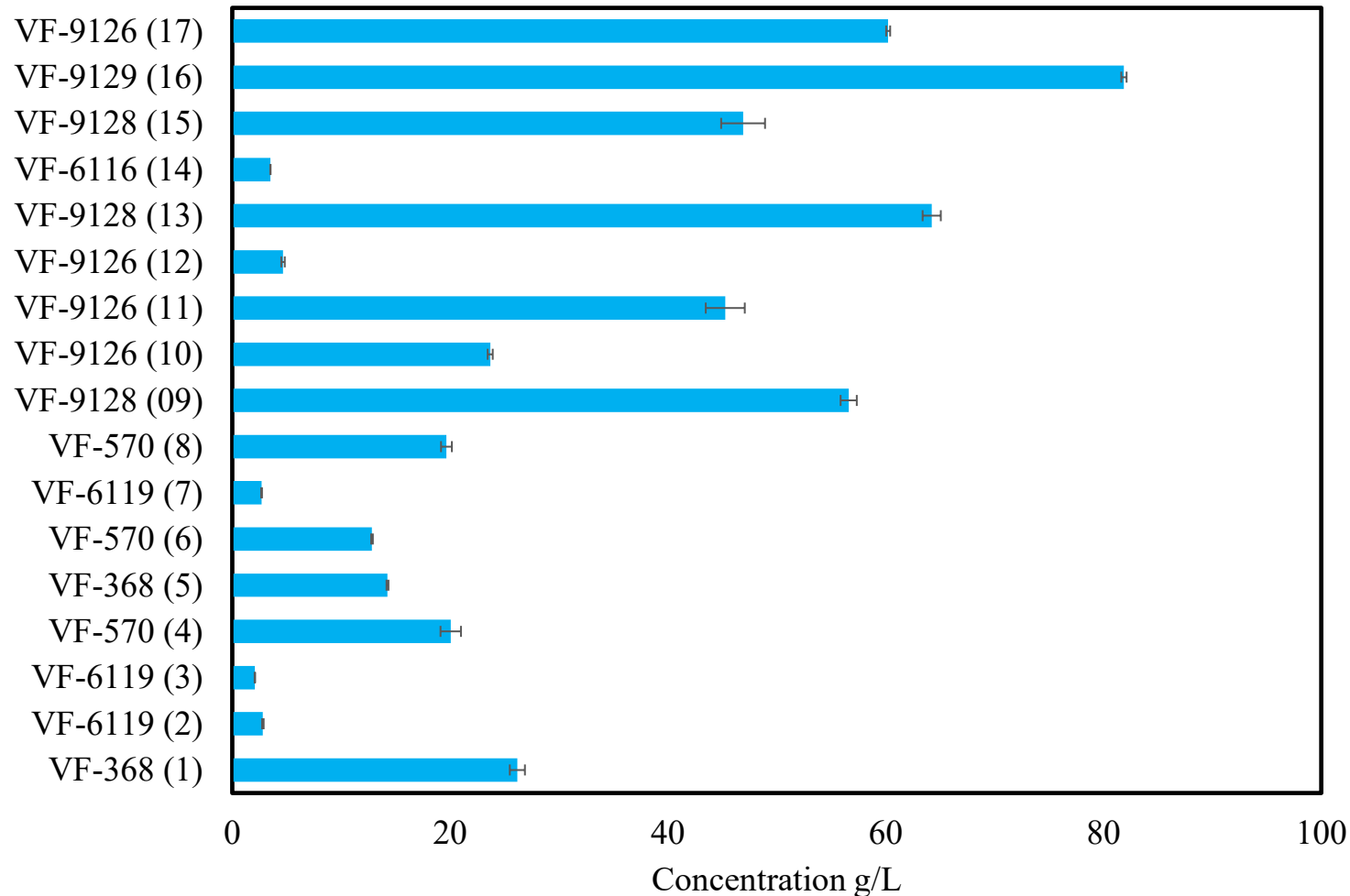
Practice in China

■ **Foam surfactants**

- PFOS-based products
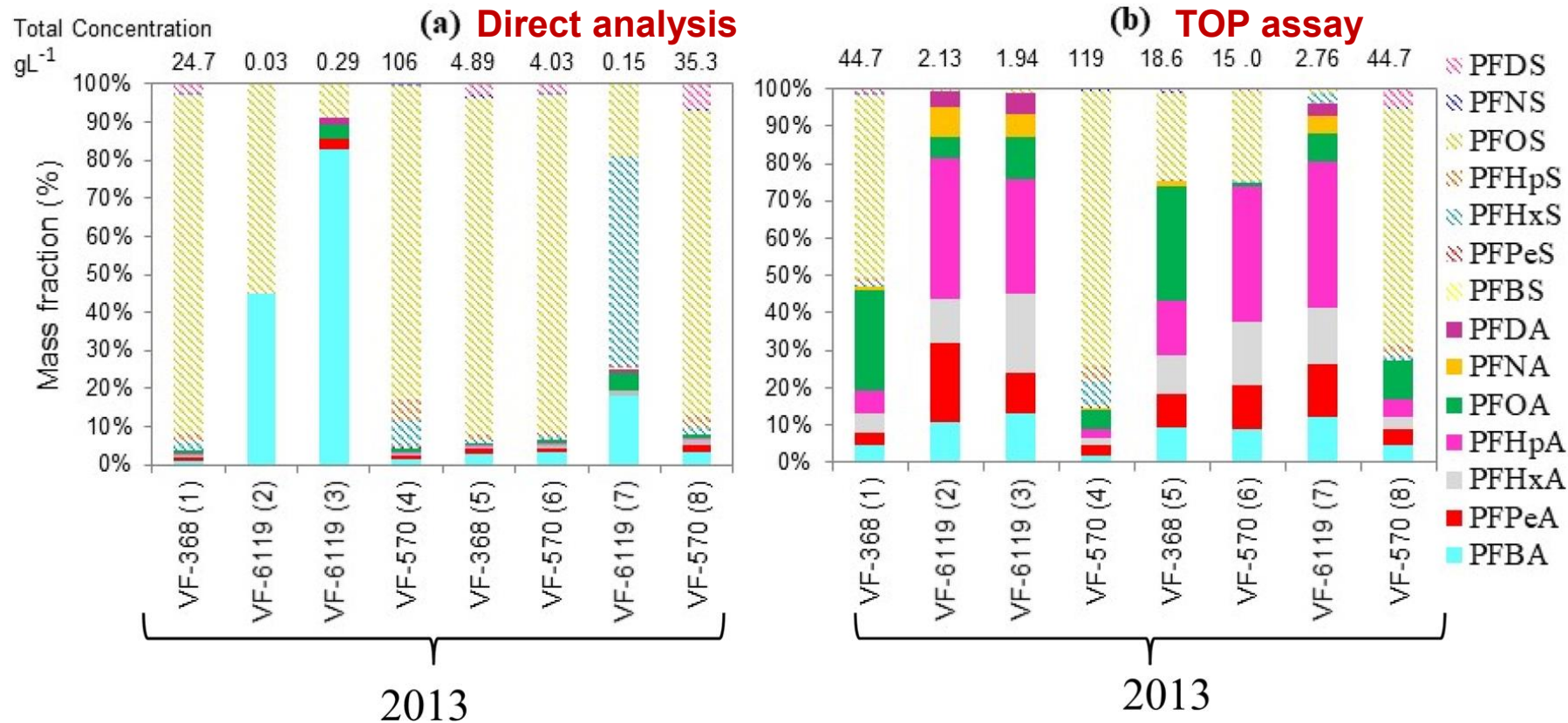
Mumtaz et al., Per- and Polyfluoroalkyl Substances in Representative Fluorocarbon Surfactants Used in Chinese Film-Forming Foams: Levels, Profile Shift, and Environmental Implications. *Environmental Science & Technology Letters*. 2019, 6(5): 259-264 (DOI: 10.1021/acs.estlett.9b00154)
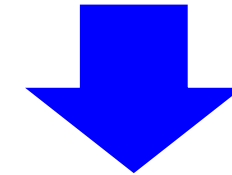
Practice in China

- Telomer-based products

Practice in China

■ **PFCAs increase under TOP(+) assay**

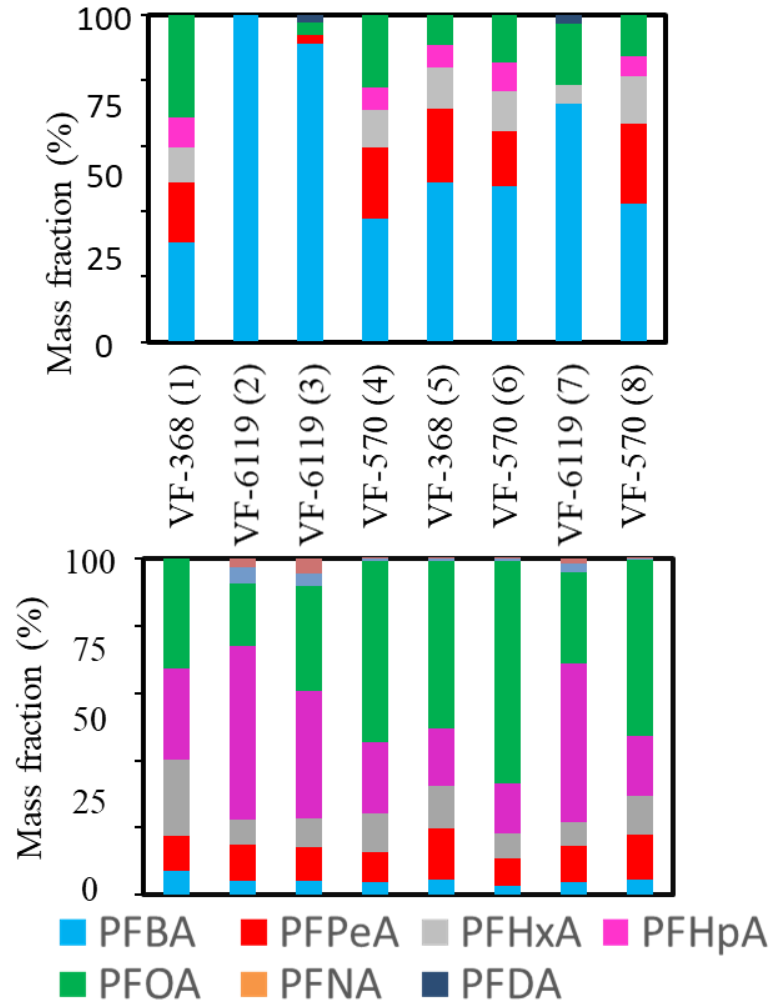**Direct analysis**
ND-4.29 g/L

TOP assay
1.92-77.32 g/L

TOP+ assay
2.07-81.8 g/L
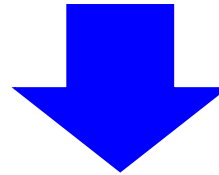
Practice in China

■ **PFCAs increase under TOP+ assay**
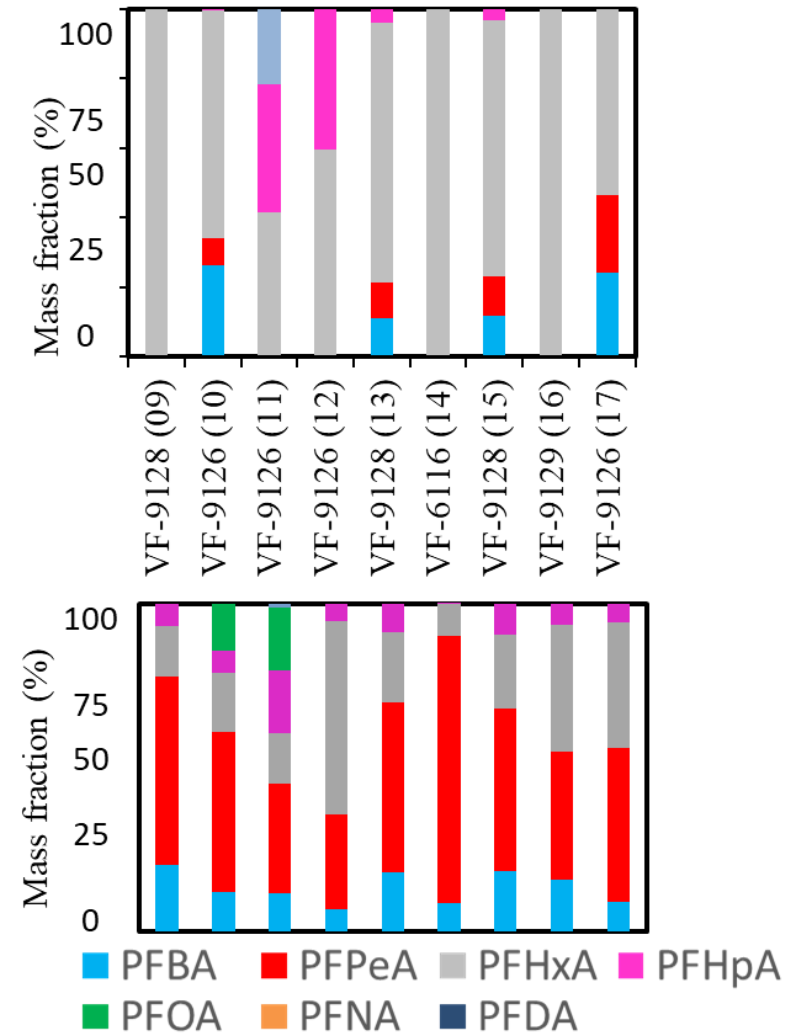

Direct analysis

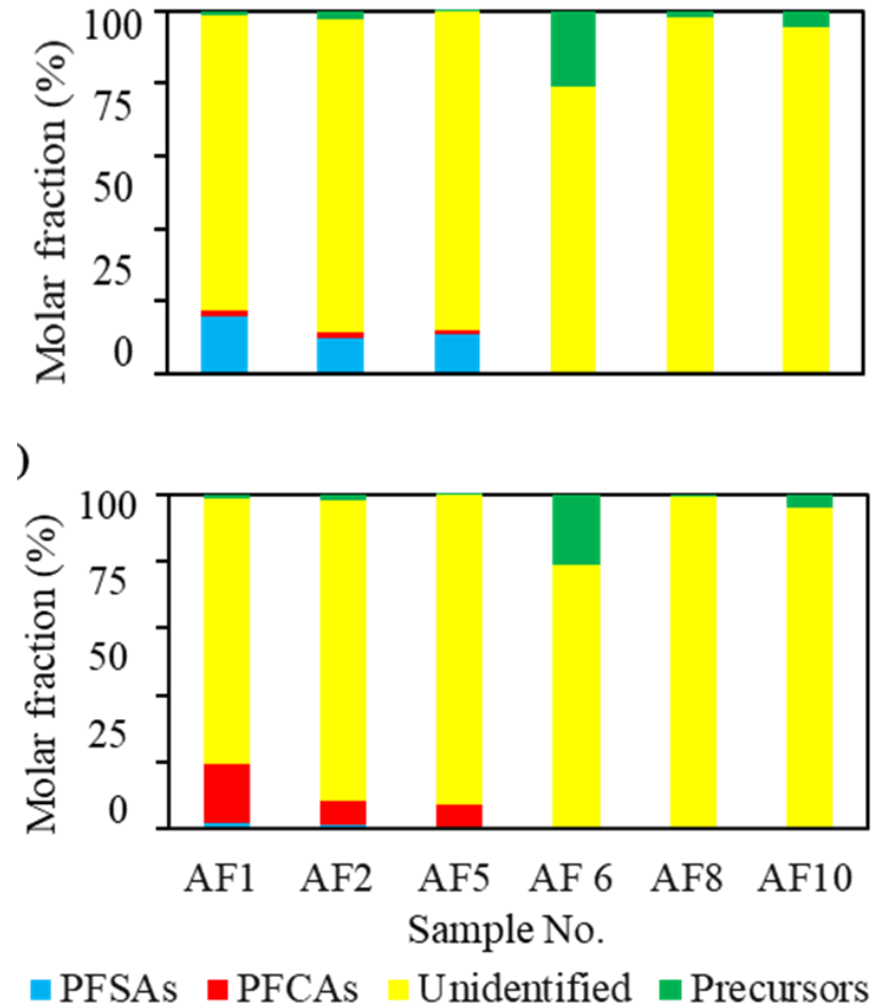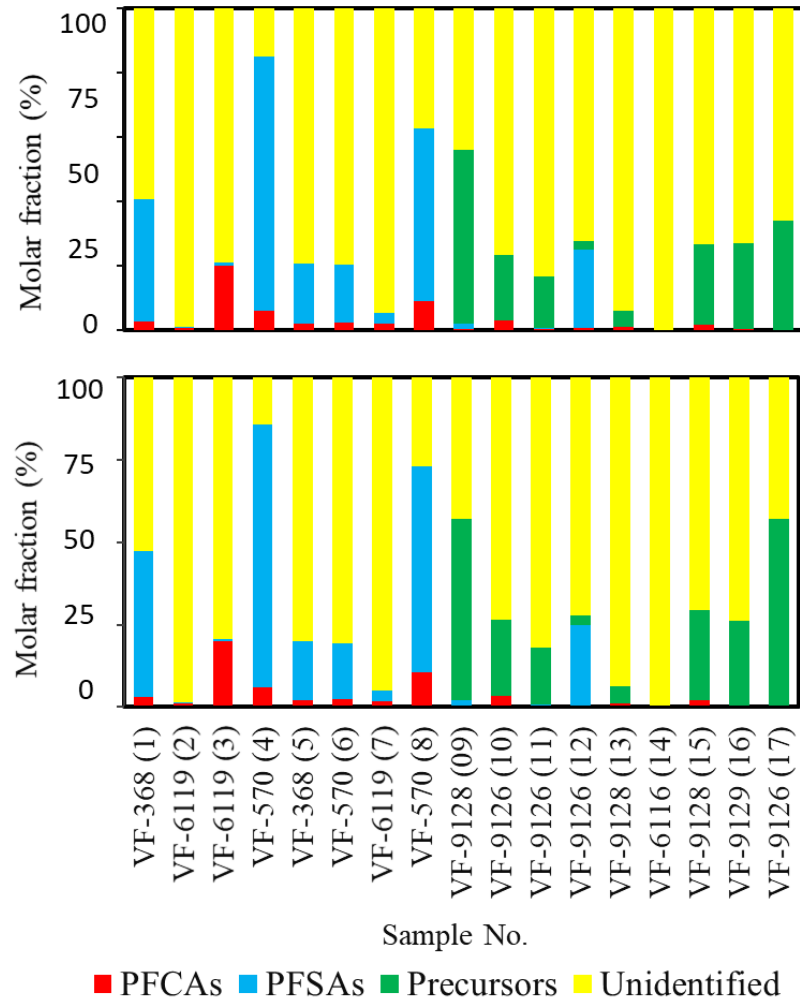0.01-2.81 g L^{-1} 0.005-0.28 g L^{-1}

TOP+ assay

2.08-26.2 g L^{-1} 3.5 - 60.2 g L^{-1}
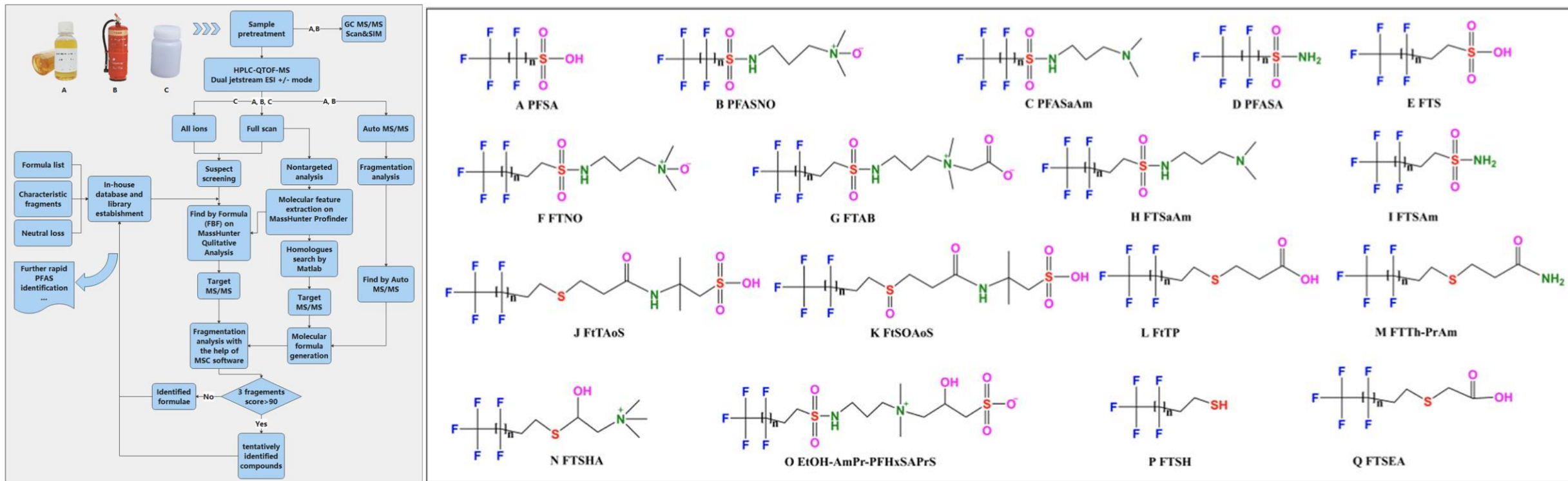
Practice in China

■ **TOP assay vs. TOP+ assay**

Practice in China

■ HRMS analysis

- A workflow of suspect screening and nontargeted analysis of PFAS was established
- Various of PFAS structures were found in the samples.

Practice in China

■ **PCA analysis for detailed PFAS profiles of foam surfactants**

ECF-based SF

Telomer-based SF

Practice in China

■ **Compliance with the reference regulations**

compound	range in Chinese AFFF (mg L^{-1})		ECHA limit (mg L^{-1})	Queensland limit (mg L^{-1})
	domestic	2018 alternative		
PFOS	69−703	ND	10	PFOS + PFHxS, 10
PFHxS	0.42−9.54	ND	−	
PFOA	0.416−17.0	ND	0.025	PFOA + PFOA precursors, 50 (as fluorine)
PFOA precursors (≥C$_7$)^a	9.44−395	ND−0.144	1	

^{a}The ECHA index is related to all compounds with a seven-carbon perfluorinated chain attached to a carbon and all compounds with an eight-carbon perfluorinated chain. The Queensland Government index concerns all PFCA with a perfluorinated chain of at least seven carbons.
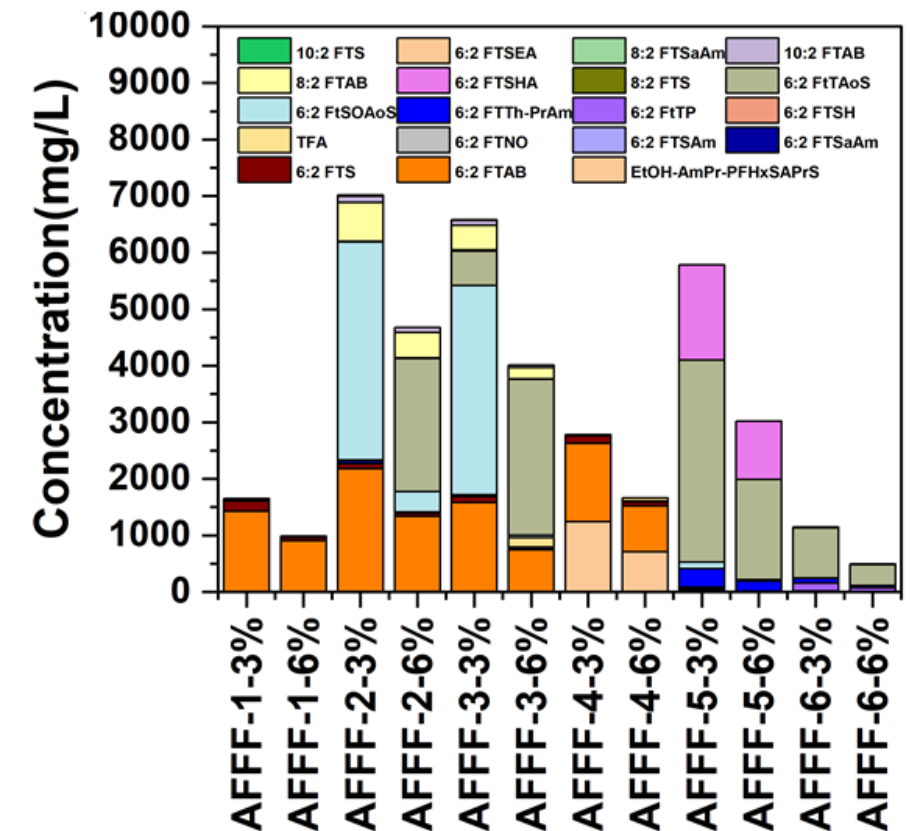
Summary

■ Conclusion

1. Regulatory limits for PFAS in foams already exist in EU, USA and Australia, which require comprehensive test methods such as targeted PFAS analysis, TOP assay, TOF by CIC.

2. Test methods and instruments are well developed for the purpose:
   - **CIC**: TOF (or EOF)
   - **LC/MS-MS**: targeted PFAS
   - **GC/MS**: neutral PFAS (e.g. FTOHs)

3. Advanced suspect and nontargeted analysis using HRMS can provide additional information about unknown PFAS, which can be useful to realize the fluorine mass balance of test results.

4. The practice in China demonstrate the substitution of PFOS based foams to C6-telomer based foams, which can be attributed to China's responsible implementation of the Stockholm Convention.

Thanks for your attention!