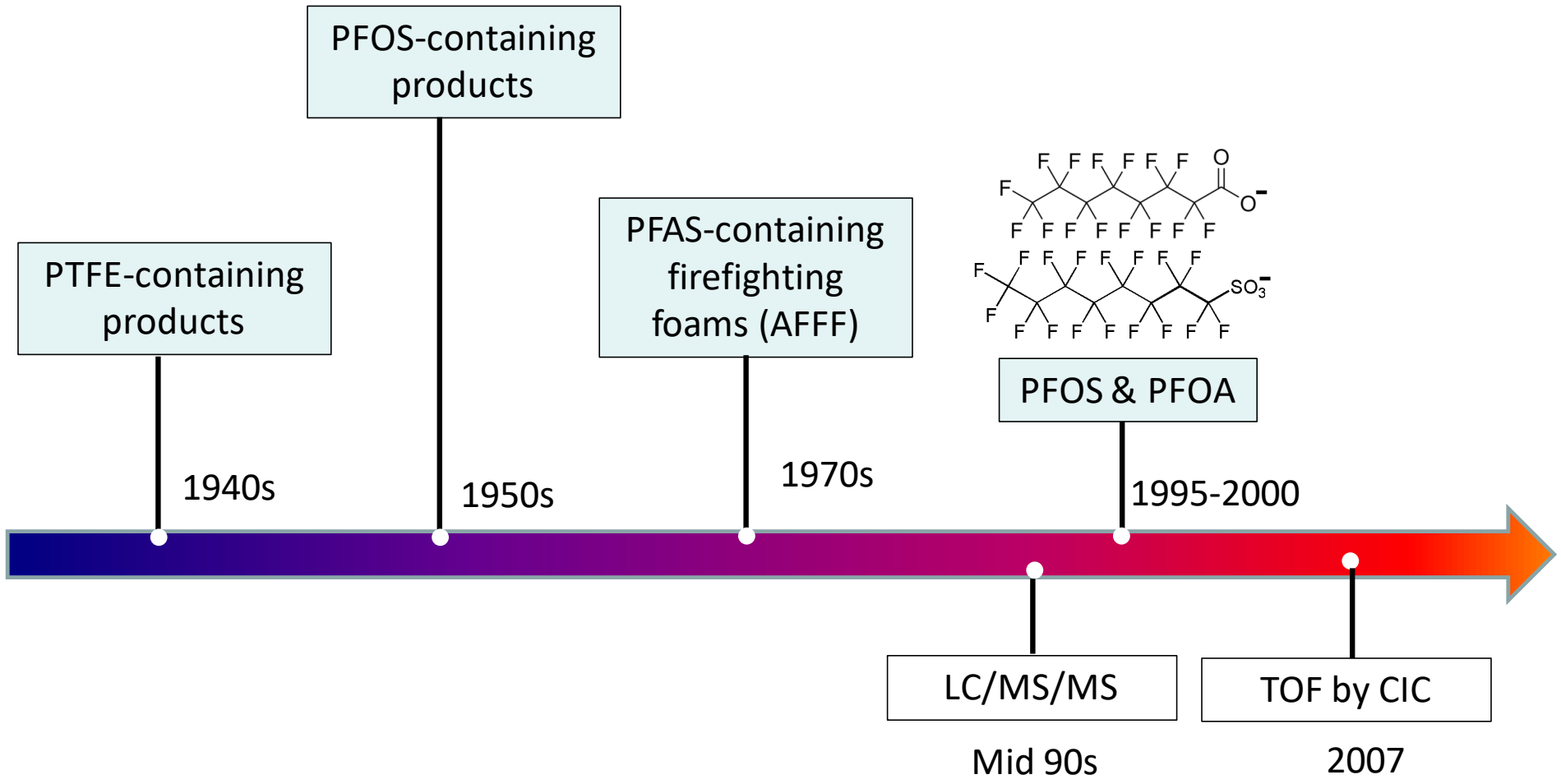
How Current Analytical Methodologies Affect Our Ability to Investigate the Occurrence and Fate of PFAS

Anh Pham

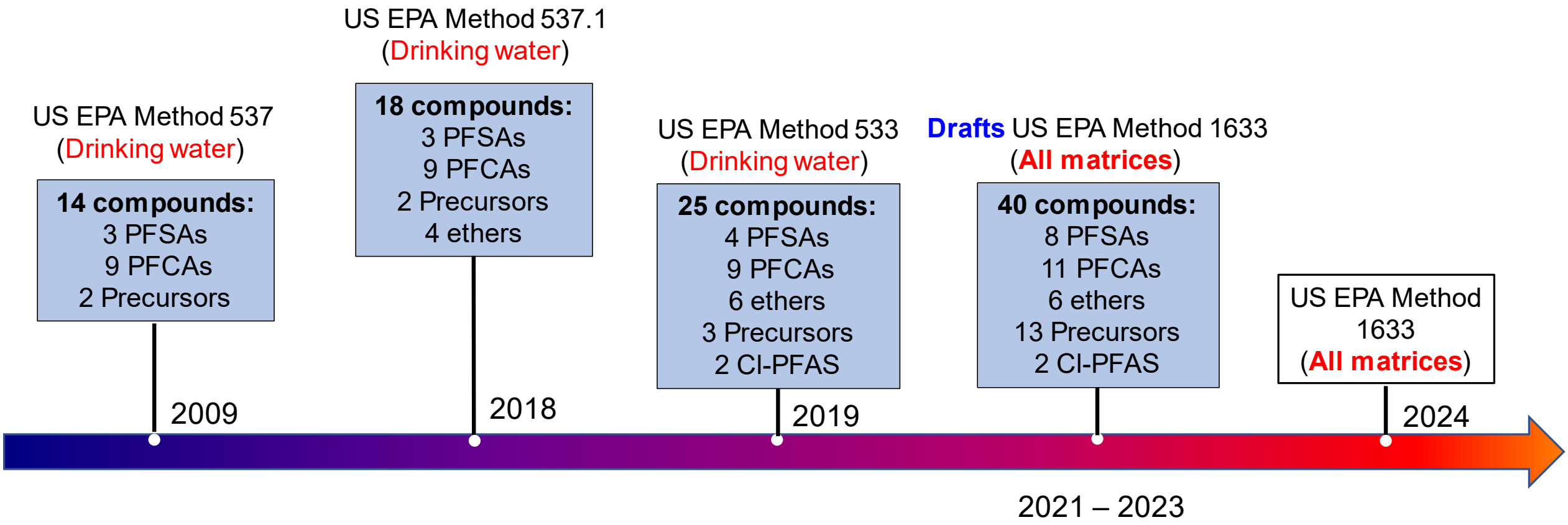
Department of Civil & Environmental Engineering
University of Waterloo

PFAS – “Emerging” Contaminants

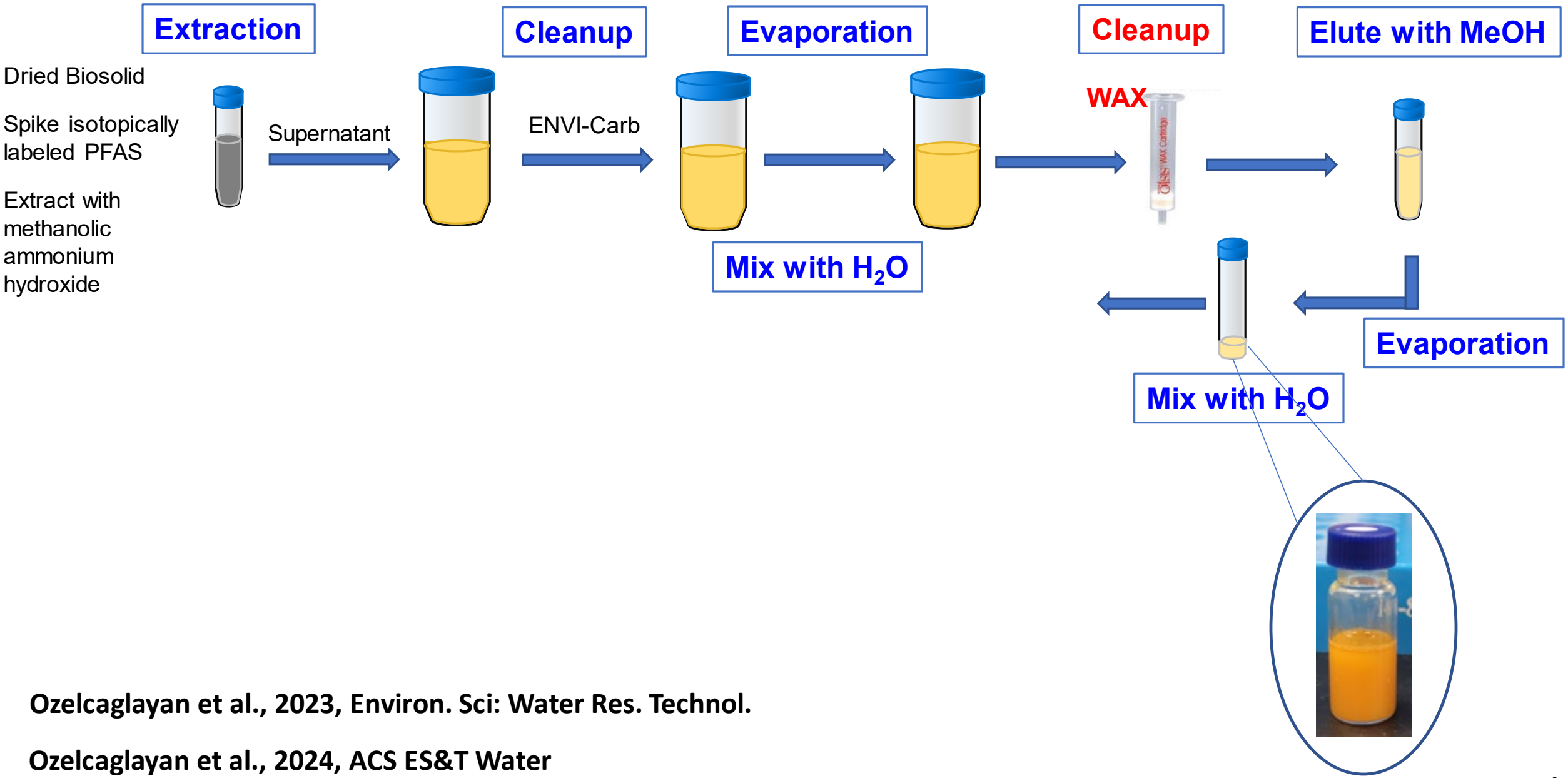


PFAS Analysis: The New Wild West

PFAS analytical methods are still evolving



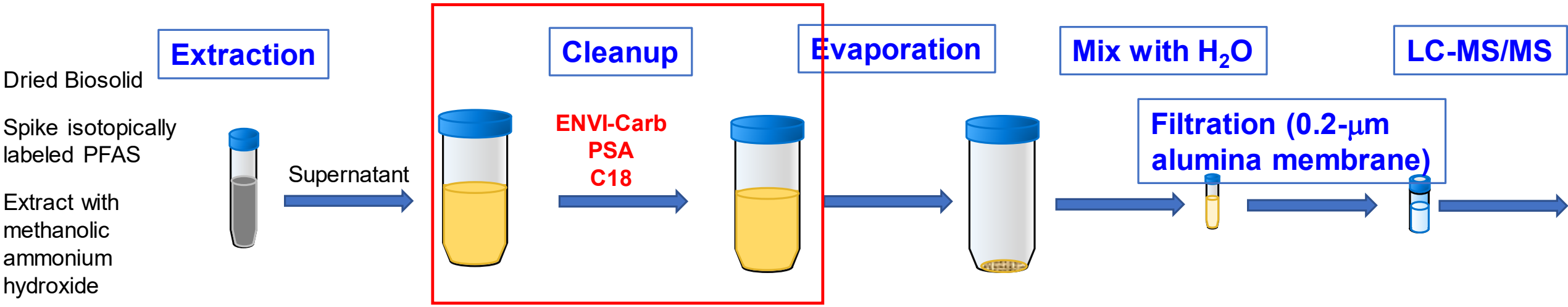
Analysis of PFAS in Biosolids by US EPA Method 1633



Ozelcaglayan et al., 2023, Environ. Sci: Water Res. Technol.

Ozelcaglayan et al., 2024, ACS ES&T Water

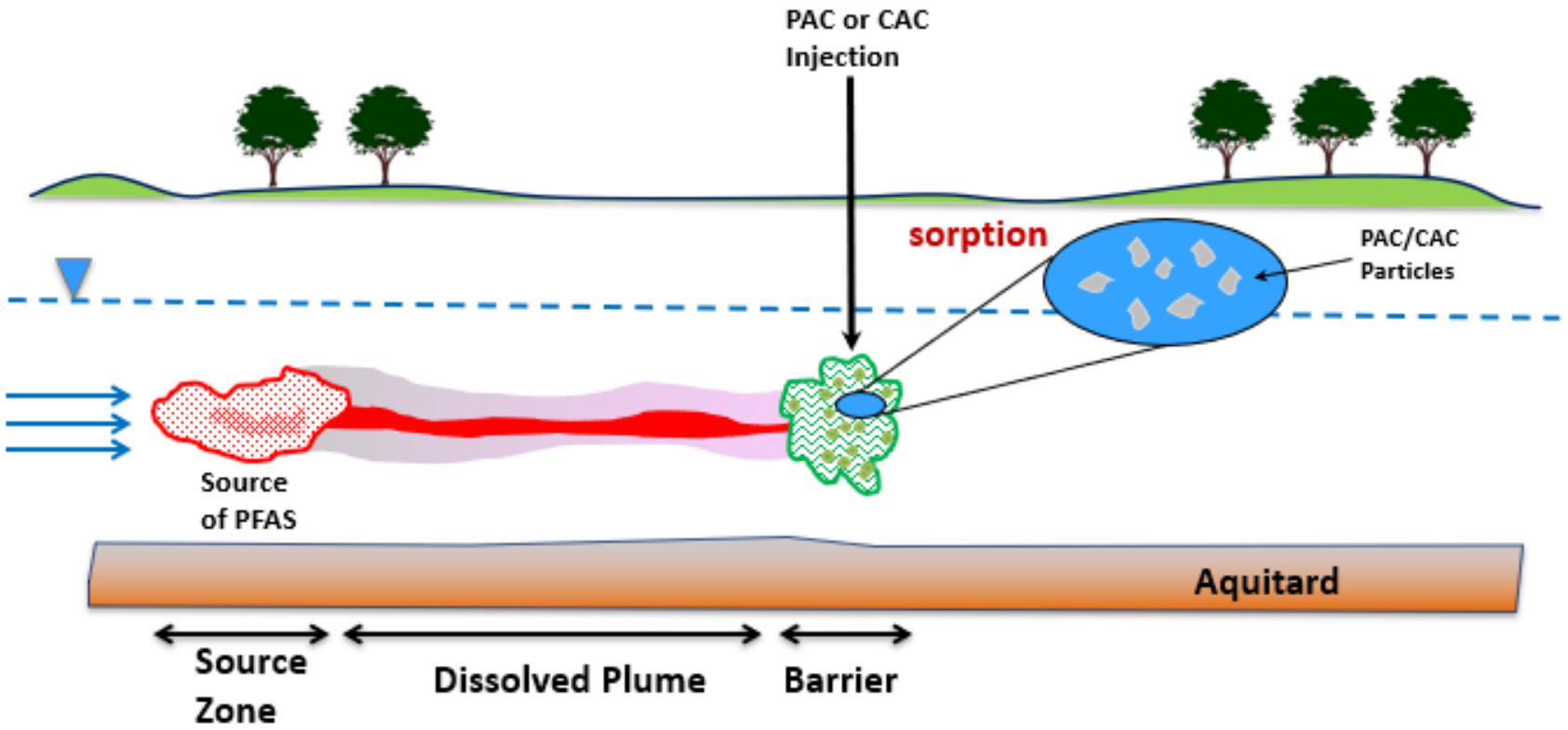
PFAS in Biosolids Analytical Workflow

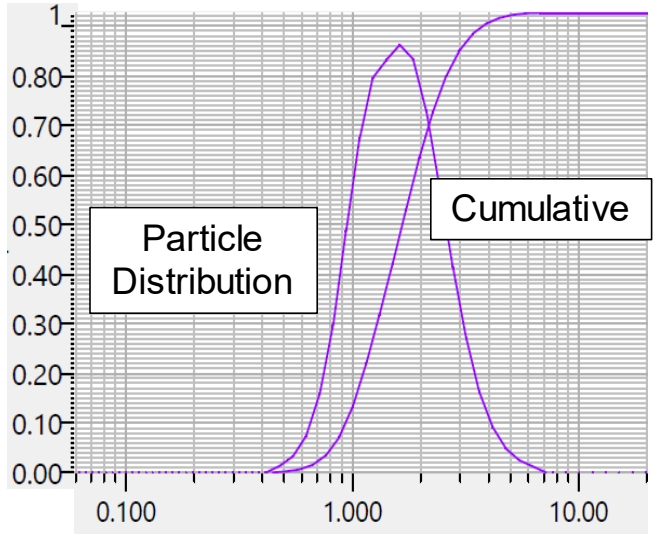


Adsorbents used in the cleanup step	Type of organics that can be removed
Graphitized non-porous carbon (ENVI-Carb)	Planar, non-polar compounds
C18-functionalized silica (C18)	Non-polar compounds
Primary-secondary amine-functionalized silica (PSA)	Hydrophilic compounds: fatty acids, sugar, pigments
Hydrophilic-lipophilic balance (HLB) resin	Anionic & neutral compounds
Weak anion exchange resin (WAX)	Anionic compounds

Ozelcaglayan et al., 2023, Environ. Sci: Water Res. Technol.

An Investigation of Factors Affecting In Situ PFAS Immobilization by Activated Carbon





SERDP
DOD ▪ EPA ▪ DOE

Project ER21-3959

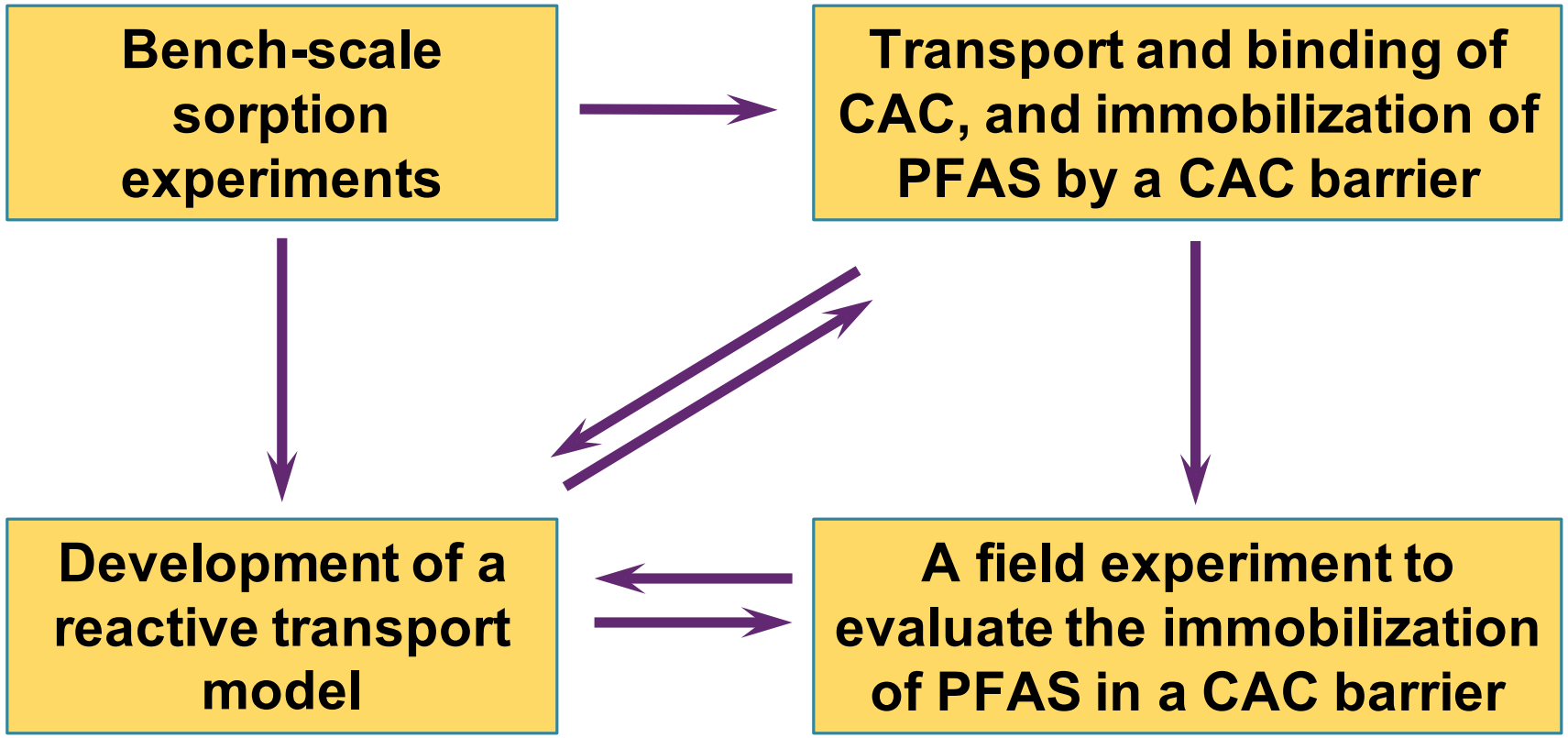
An Investigation of Factors Affecting In Situ PFAS Immobilization by Activated Carbon

The unknown: How long will AC barriers last?

Specific objectives

- Investigate factors affecting sorption of PFAS on CAC
- Evaluate the transport and binding of CAC in porous media
- Assess long-term adsorption capacity and potential for PFAS re-release

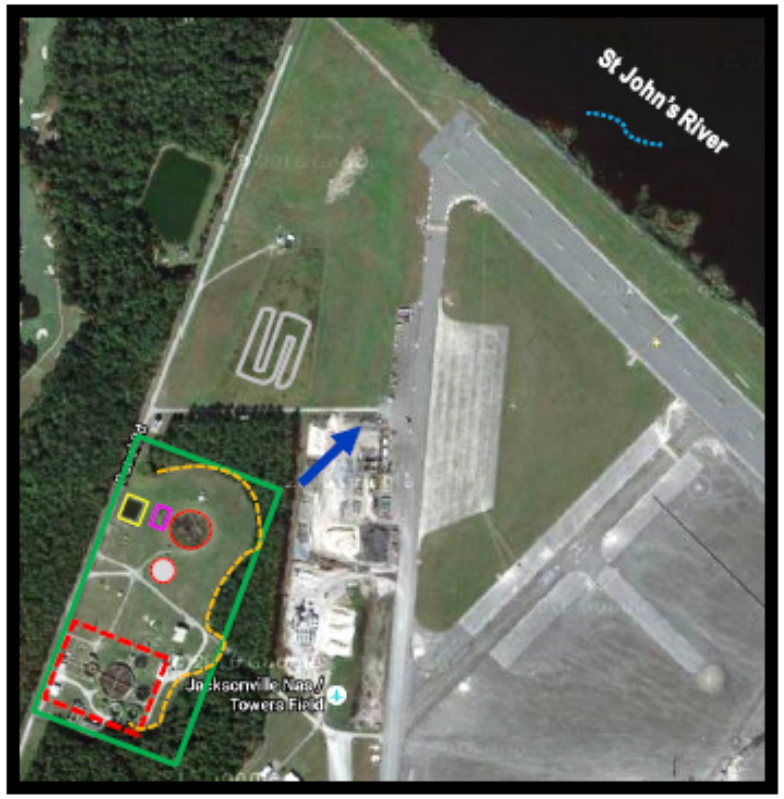
An Investigation of Factors Affecting In Situ PFAS Immobilization by Activated Carbon



An Investigation of Factors Affecting In Situ PFAS Immobilization by Activated Carbon

Naval Air Station, Jacksonville, FL

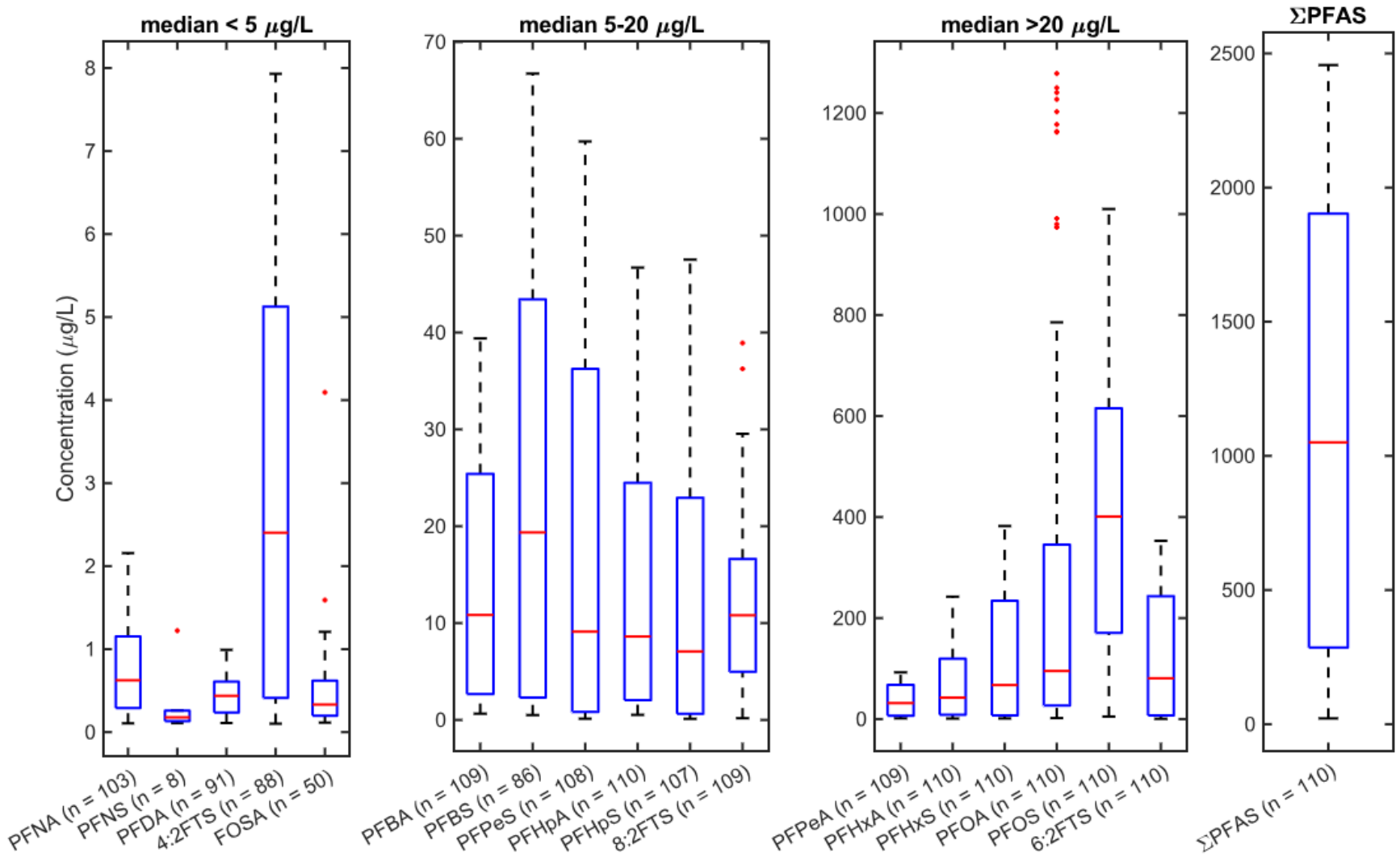
- Firefighter Training Area (FT-02)
- PCA 15 – FFTF (PCA 15)



Firefighter Training Area (FT-02)

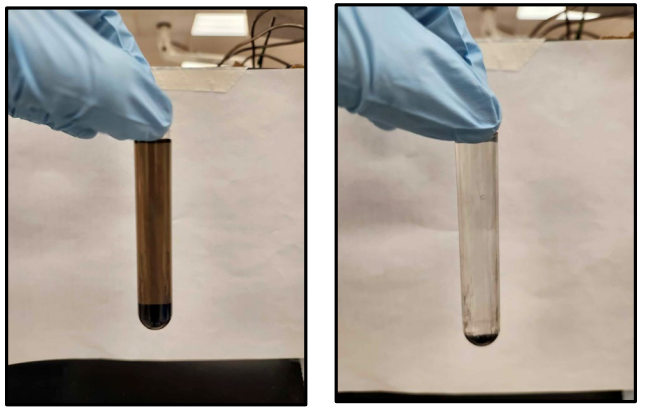
	Former Training Area (in use 1968-1991)
	Current Fire Training Area
	Pond/Pump Station
	Wastewater Treatment Plant
	Unlined Polishing Pond
	OW Separator
	St. John's River
	Tree Line
	GW: Primarily N/NE

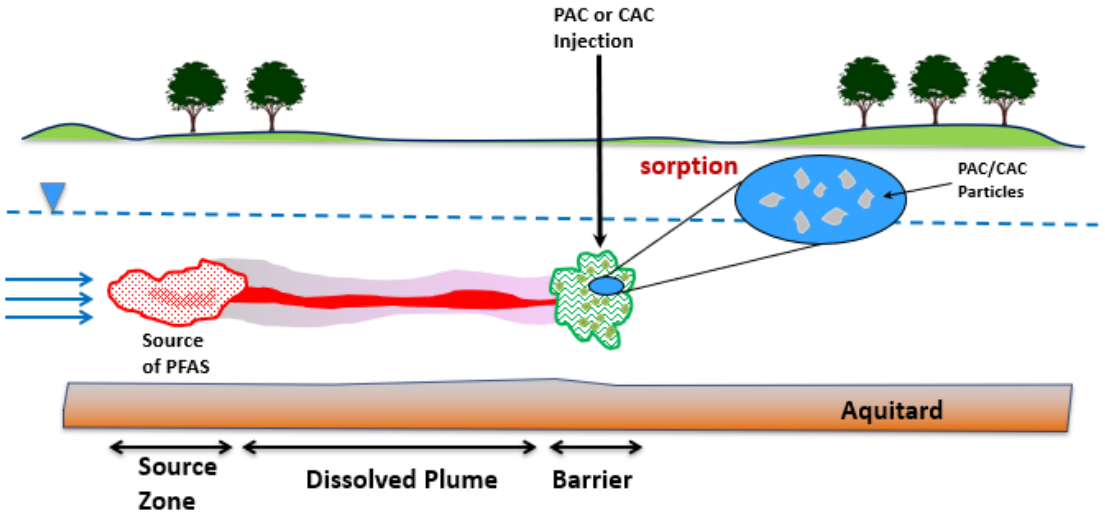
An Investigation of Factors Affecting In Situ PFAS Immobilization by Activated Carbon



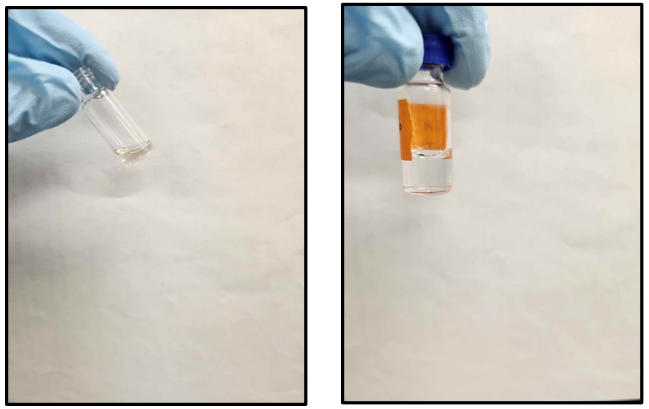
An Investigation of Factors Affecting In Situ PFAS Immobilization by Activated Carbon

230,000xg

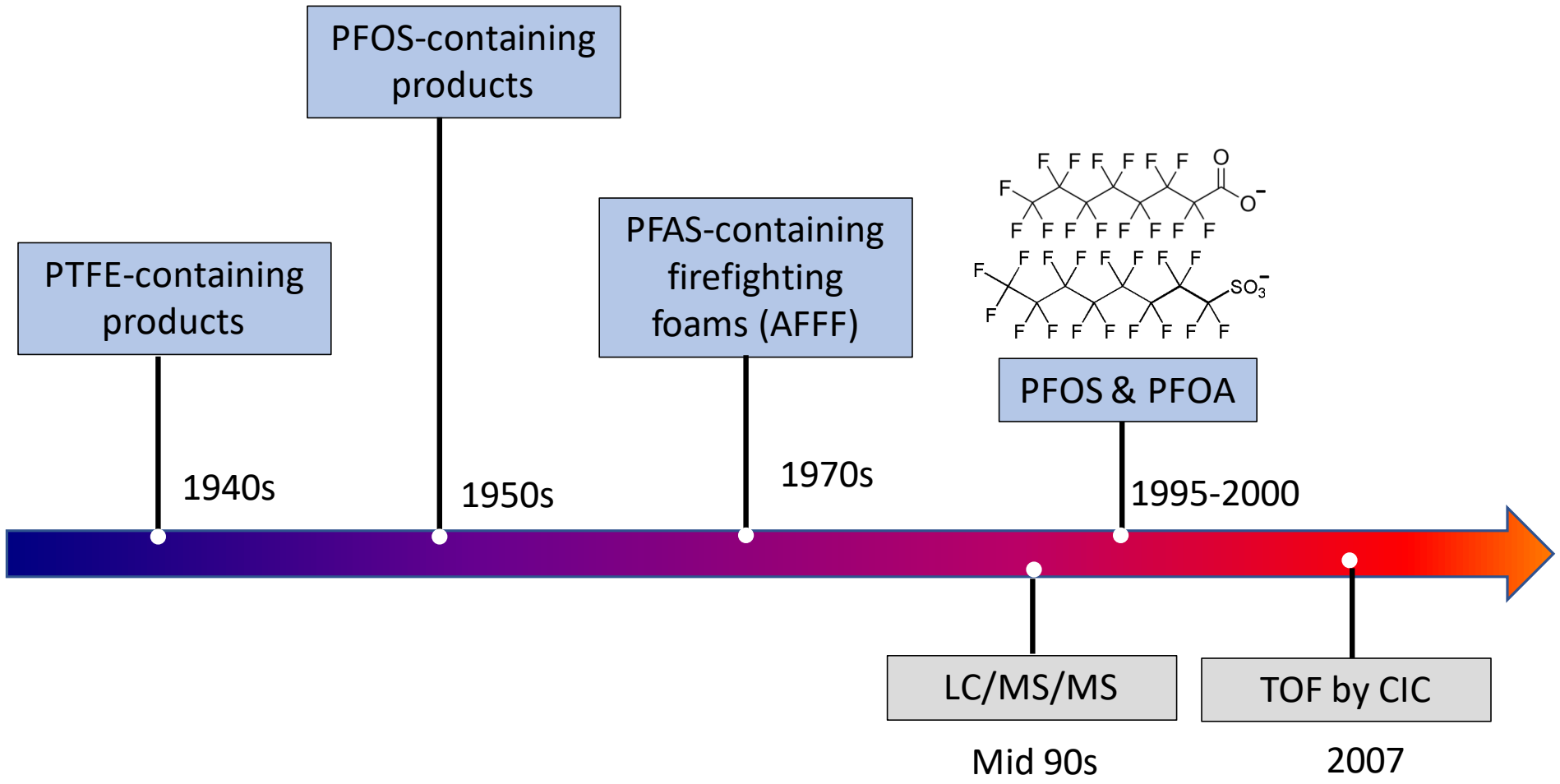




0.02 μm Al_2O_3 filter



PFAS – “Emerging” Contaminants



US EPA Method 537
(Drinking water)

14 compounds:
3 PFSAs
9 PFCAs
2 Precursors

2009

US EPA Method 537.1
(Drinking water)

18 compounds:
3 PFSAs
9 PFCAs
2 Precursors
4 ethers

2018

US EPA Method 533
(Drinking water)

25 compounds:
4 PFSAs
9 PFCAs
6 ethers
3 Precursors
2 Cl-PFAS

2019

Drafts US EPA Method 1633
(**All matrices**)

40 compounds:
8 PFSAs
11 PFCAs
6 ethers
13 Precursors
2 Cl-PFAS

2021 – 2023

US EPA Method
1633
(**All matrices**)

2024

2007

2022

Draft Method 1621
(**AOF in Aqueous matrices**)

Method 1621
(**AOF in Aqueous matrices**)

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JOURNAL OF CHROMATOGRAPHY A
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Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: A mass balance approach to determine individual perfluorinated chemicals in water

Yuichi Miyake[a], Nobuyoshi Yamashita[a,*], Pawel Rostkowski[a,b], Man Ka So[a,c], Sachi Taniyasu[a], Paul K.S. Lam[c], Kurunthachalam Kannan[d,e,**]

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[c] Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China
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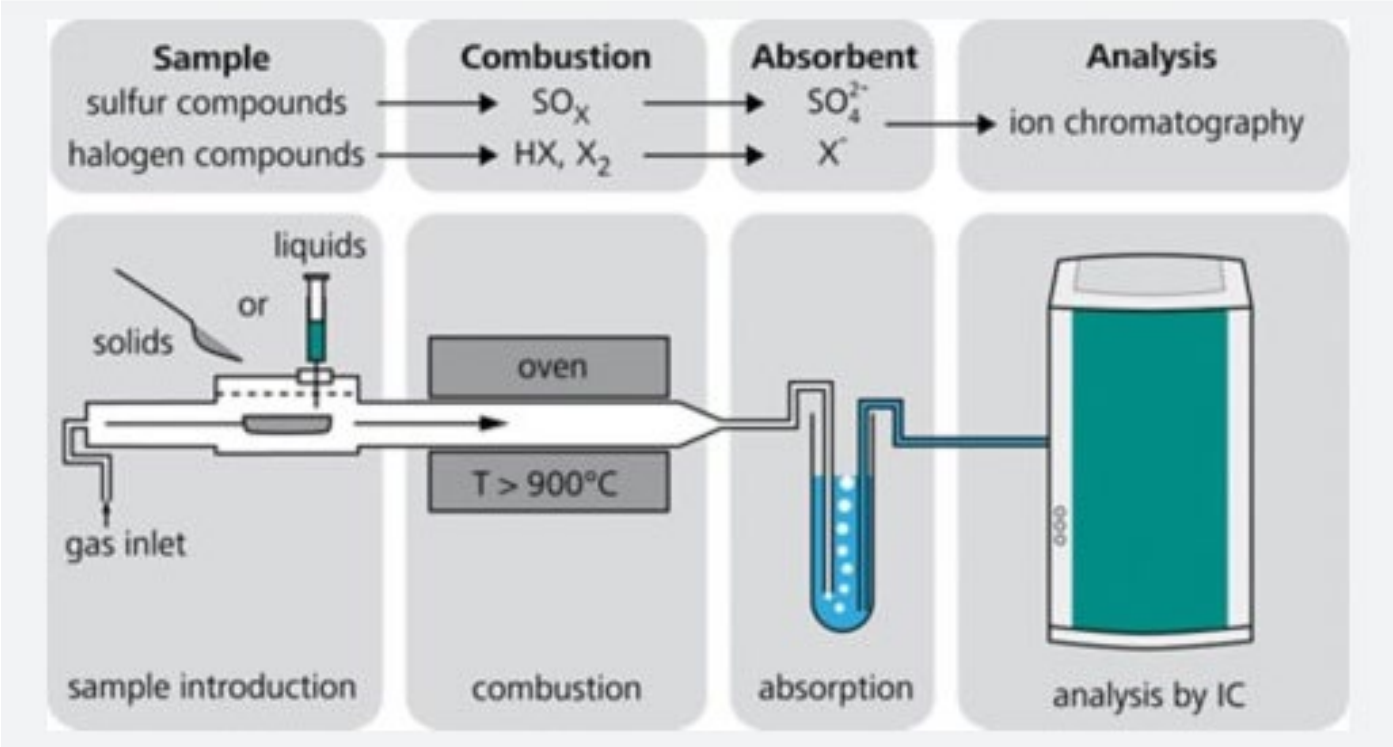
Available online 23 December 2006

Analysis of Total Organic Fluorine (TOF) by CIC

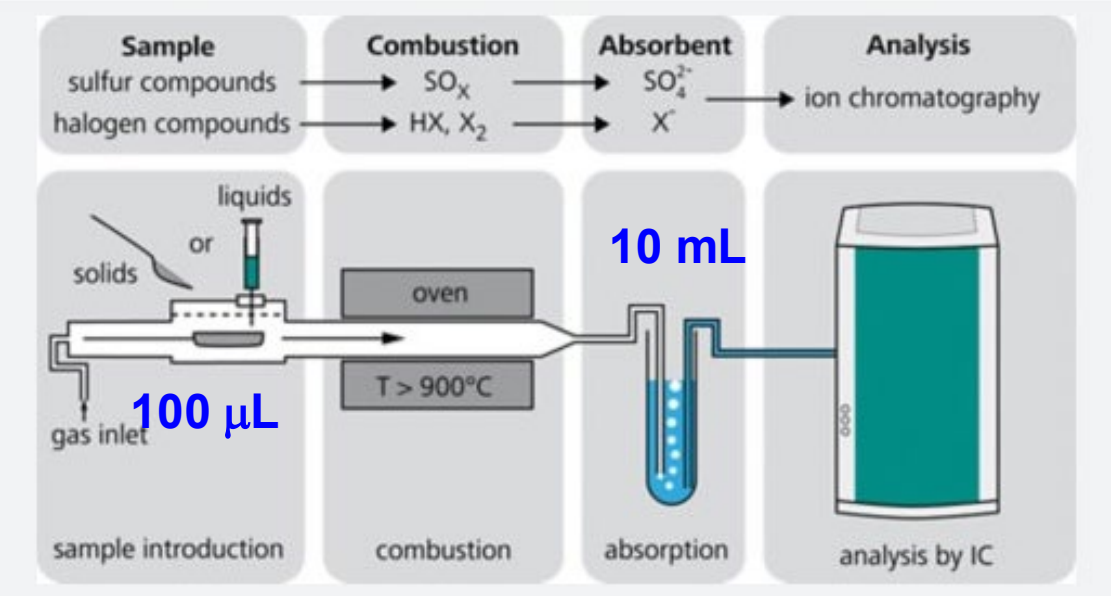
PFAS **PFAS→ HF** **F^-**



- Complementary to LCMS analysis
- Cheaper (?)

Challenge #1: Instrument LOD & LOQ

PFAS **PFAS→ HF** **F^-**



IC LOQ: ~ 1 µg/L

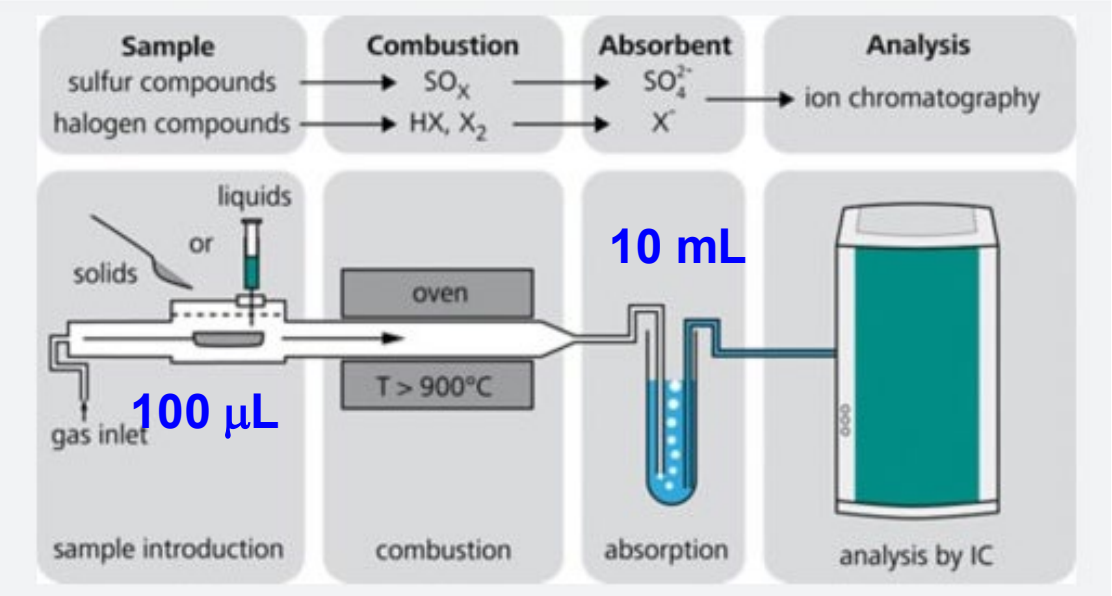
Instrument LOQ (best-case scenario): **~ 100 µg/L**

Challenge #1: Instrument LOD & LOQ

Boat blank	F^- peak area ((µS/cm)×min)	Instrument LOQ
May 2022	0.20 – 0.35	~ 750 ppb
March 2023	0.04 – 0.06	~ 100 ppb

(with a 1-mL injection loop)

PFAS **PFAS→ HF** **F^-**

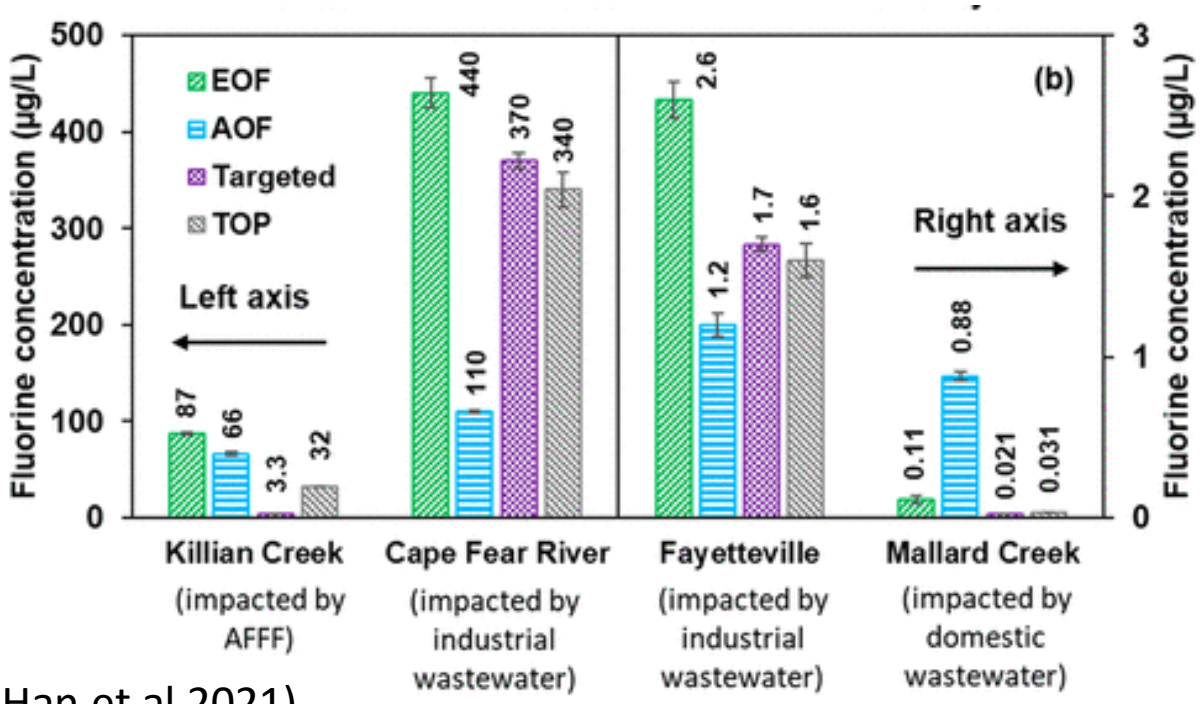


IC LOQ: ~ 1 µg/L

Instrument LOQ (best-case scenario): **~ 100 µg/L**

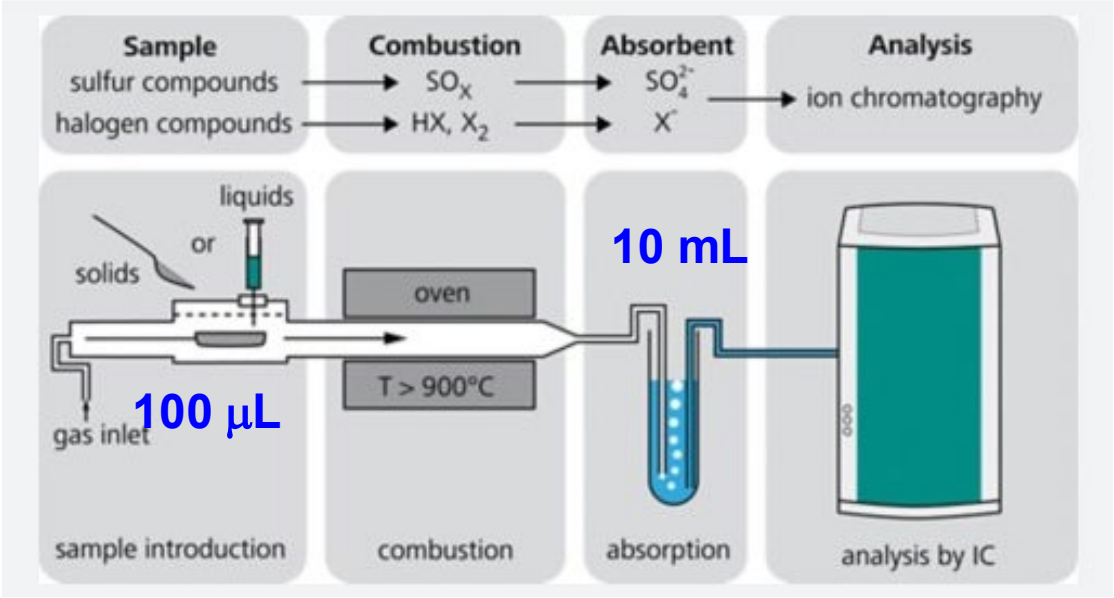
(Lesson learned: bake it till you make it)

Challenge #1: Instrument LOD & LOQ



(Han et al 2021)

PFAS **PFAS→ HF** **F^-**



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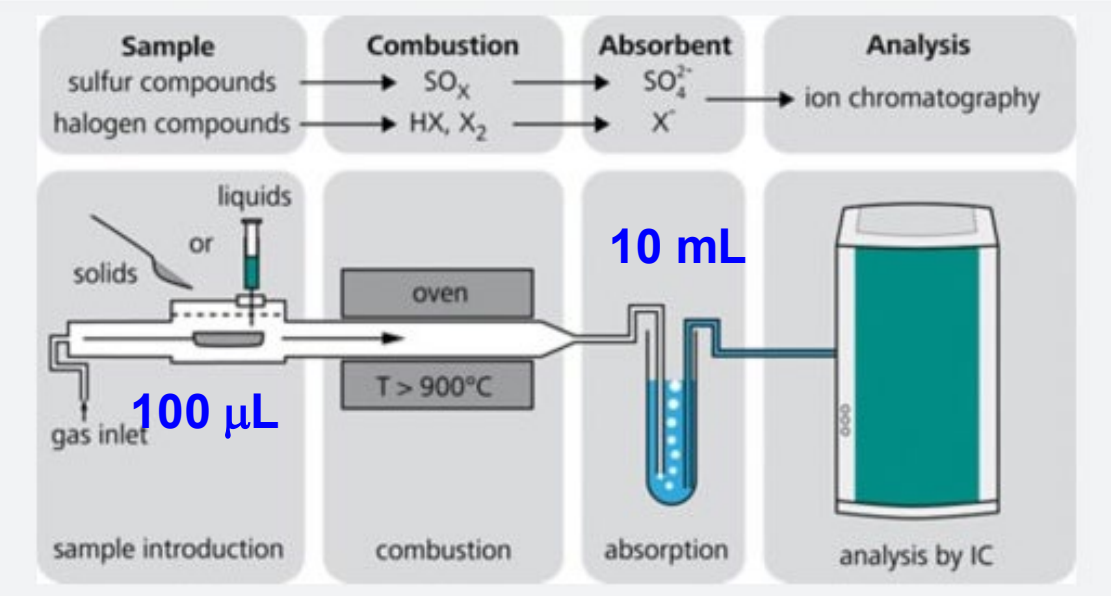
Challenge #1: Instrument LOD & LOQ

PFAS PFAS→ HF F^-

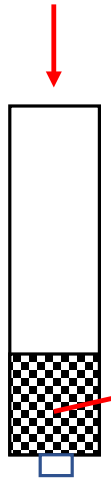


- Load more sample on the boat

  (max ~ 0.5 mL liquid or 50 mg solid)

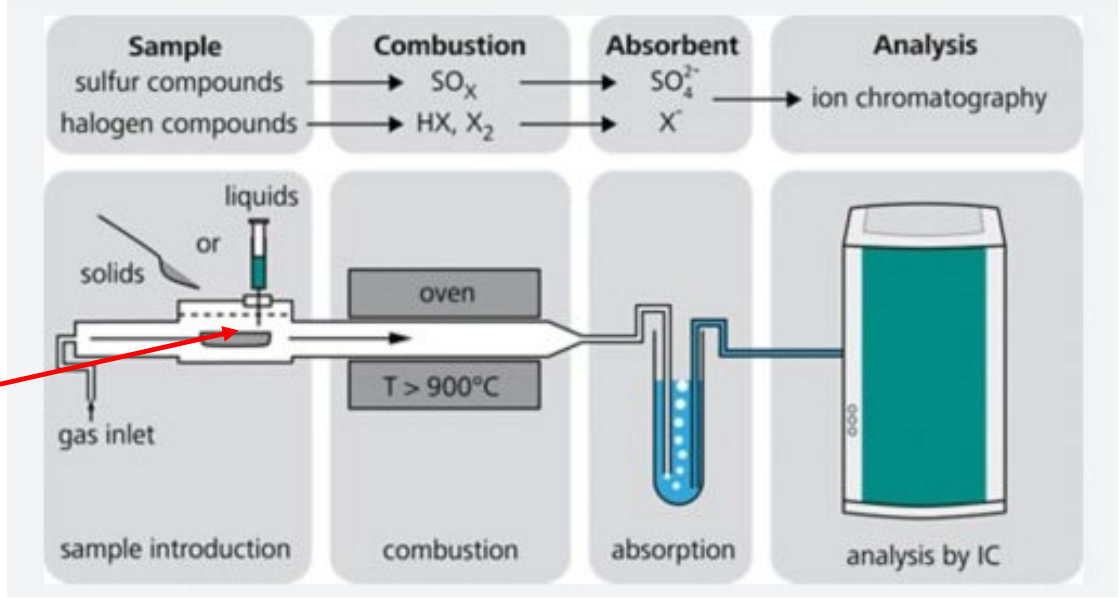
Challenge #1: Instrument LOD & LOQ

Aqueous sample



Sorbent that retains TOF

PFAS PFAS→ HF F^-



Ion Exchange: Extractable Organic Fluorine (EOF)
Activated Carbon: Adsorbable Organic Fluorine (AOF)

- Load more sample on the boat

  (max ~ 0.5 mL liquid or 50 mg solid)

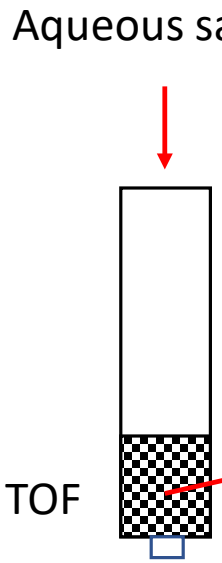
Best case scenario: lower LOQ by ~200,000

- **SPE extraction of aqueous samples**
- **Use a larger injection loop (1 – 2 mL)**

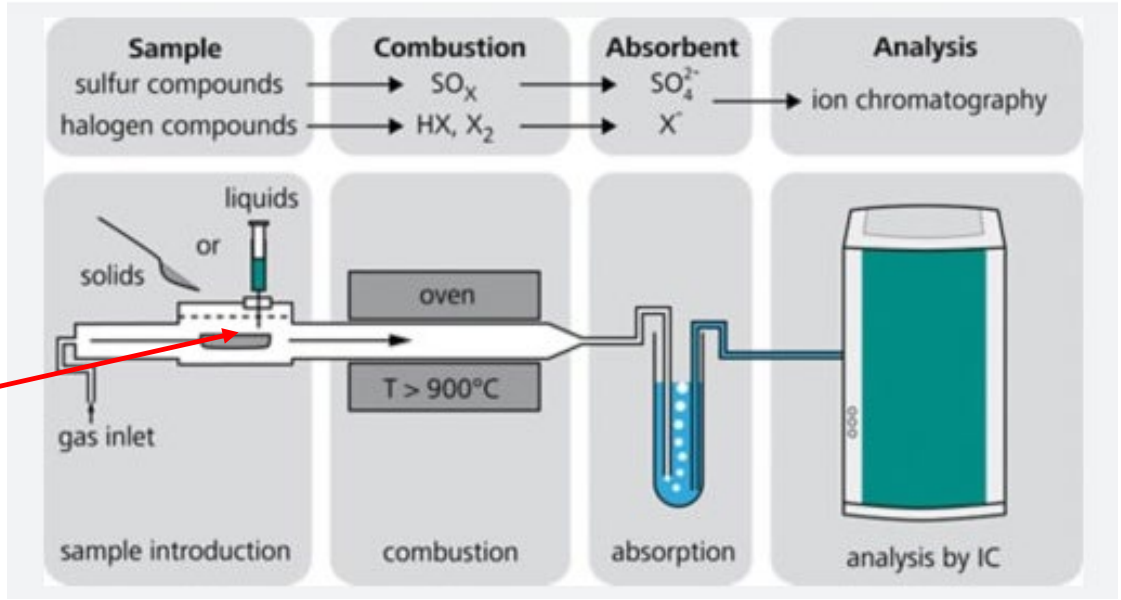
Challenge #2: Separating F^- from Organic Fluorine

TF = TOF + IF

< 1% > 99%



PFAS **PFAS→ HF** **F^-**



Ion Exchange: Extractable Organic Fluorine (EOF)
Activated Carbon: Adsorbable Organic Fluorine (AOF)

Do these adsorbents contain inorganic fluorine?

- Load more sample on the boat

  (max ~ 0.5 mL liquid or 50 mg solid)

Best case scenario: lower LOQ by 200,000 (!)

- **SPE extraction of aqueous samples**
- **Use a larger injection loop (1 – 2 mL)**

Challenge #2: Separating F^- from Organic Fluorine

Type	Sorbents with vendor and feedstock material information	Native Fluorine level (µg/g) (n≥2)	Remarks
Polymer resins	AMBERSORB 560 • Dow Chemical Co • Sulfonated styrene-divinylbenzene	0.92 ± 0.01	Interference with fluoride analysis in IC
	DOWEX TAN-1 • Dow Chemical Co • Polystyrene-divinylbenzene	0.16 ± 0.01	Poor PFAS recovery under the sample loading conditions
	DOWEX-1 • Dow Chemical Co • Polystyrene-divinylbenzene	Data not valid	Incomplete combustion
	Purofine PFA694E • Purolite Corp • Polystyrene-divinylbenzene	0.47 ± 0.04	Interference with fluoride analysis in IC
	Purolite A592E • Purolite Corp • Polystyrene-divinylbenzene	5.7 ± 0.3	Native F level too high
	AmberLite IRA67 • Sigma-Aldrich • Polyacrylic	2.8 ± 0.1	Native F level too high
	AmberLite IRA958 • Sigma-Aldrich • Polyacrylic	0.15 ± 0.01	Poor PFAS recovery under the sample loading conditions
	AmberLite IRA910 • Sigma-Aldrich • Polystyrene-divinylbenzene	0.34 ± 0.14	Poor PFAS recovery under the sample loading conditions
	Waters WAX SPE resin • Waters Corp • Co-polymer of hydrophilic N-vinylpyrrolidone & lipophilic divinylbenzene functionalized with a piperazine ring	Data not valid	Incomplete combustion
	Waters HLB SPE resin • Waters Corp • Co-polymer of hydrophilic N-vinylpyrrolidone & lipophilic divinylbenzene	Data not valid	Incomplete combustion

(Han et al 2021)

Challenge #2: Separating F^- from Organic Fluorine

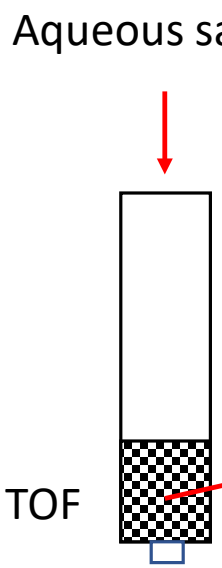
Type	Sorbents with vendor and feedstock material information	Native Fluorine level (µg/g) (n≥2)	Remarks
Granular activated carbon	Ujotit AK-200-1200 • Dr. Felgenträger & Co. Öko.-chem. and pharma GmbH, Germany • Polystyrene-divinylbenzene	0.28 ± 0.02 (Data from Wagner *et al.* 2013)	Product out of market
	Analytik Jena activated carbon • Analytik Jena US LLC • Unknown feedstock material	0.37 ± 0.01	The best sorbent in this study
	Cosa Xentaur prepacked carbon • COSA Xentaur Crop • Unknown feedstock material	1.9 ± 0.1	Native F level too high
	FILTRASORB400 • Calgon Carbon Corp • Bituminous coal	3.2 ± 0.2	Native F level too high
Activated carbon fiber	ACF-15 • Nippon Kynol Inc • Phenolic-resin	40.4 ± 5.8	Native F level too high

(Han et al 2021)

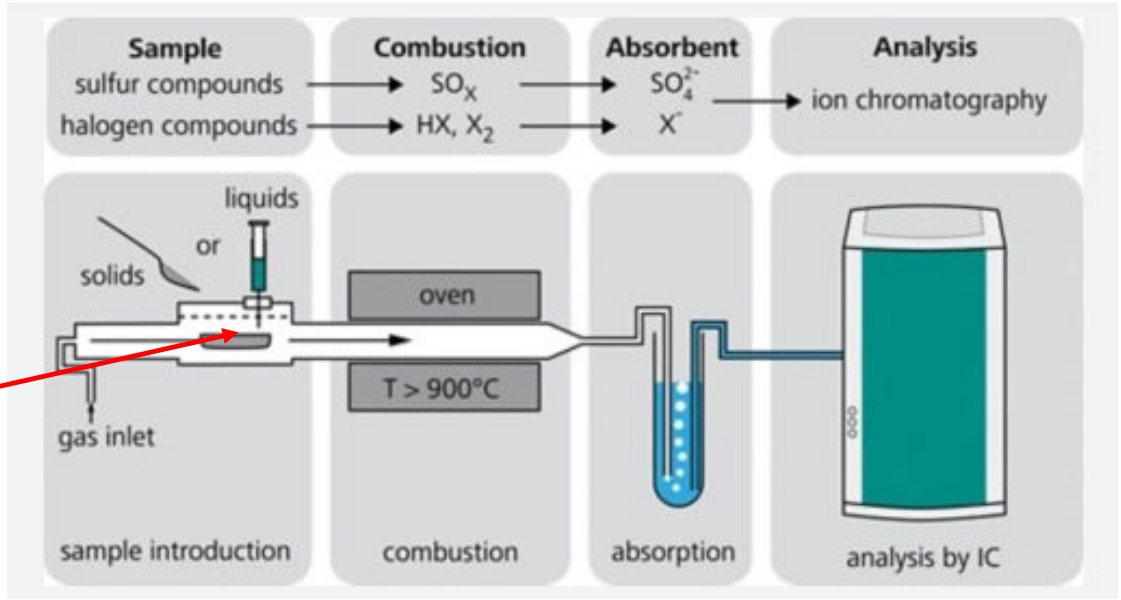
Challenge #2: Separating F^- from Organic Fluorine

TF = TOF + IF

< 1% > 99%



PFAS **PFAS→ HF** **F^-**



Ion Exchange: Extractable Organic Fluorine (EOF)
Activated Carbon: Adsorbable Organic Fluorine (AOF)

Do these adsorbents contain inorganic fluorine?

MDL is controlled in part by the concentration of F in the sorbent and the IF concentration in the sample

- Load more sample on the boat
  (max ~ 0.5 mL liquid or 50 mg solid)
- Decrease the absorber volume (min 10 mL)
- **SPE extraction of aqueous samples**
- **Use a larger injection loop (1 – 2 mL)**

Challenge #3: Analysis of TOF in solid samples

TF = TOF + IF

< 1% > 99%

How about solid samples?

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How about solid samples?

- Direct analysis of solid samples → TF, not TOF

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How about solid samples?

- Direct analysis of solid samples → TF, not TOF
- Separating IF from solid samples: methods?

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- Separating IF from solid samples: methods?
- Extracting TOF without extracting IF?

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TF = TOF + IF

< 1% > 99%

How about solid samples?

- Direct analysis of solid samples → TF, not TOF
- Separating IF from solid samples: methods?
- Extracting TOF without extracting IF?

NaF solubility in MeOH: ~4 mmol/L

J. Chem. Eng. Data **1996,** *41,* 1111−1113

Solubilities of Various Alkali Metal and Alkaline Earth Metal Compounds in Methanol

Vernon A. Stenger

Analytical Sciences Laboratory, The Dow Chemical Company, 1108 East Park Drive, Midland, Michigan 48640

NaF solubility in MeOH: ~50 mmol/L

Journal of the Franklin Institute

Volume 212, Issue 3, September 1931, Pages 343-349

THE SOLUBILITIES OF ALKALI BROMIDES AND FLUORIDES IN ANHYDROUS METHANOL, ETHANOL, AND BUTANOL.

BY

FREDERICK G. GERMUTH,

Division of Research, Bureau of Standards, City of Baltimore.

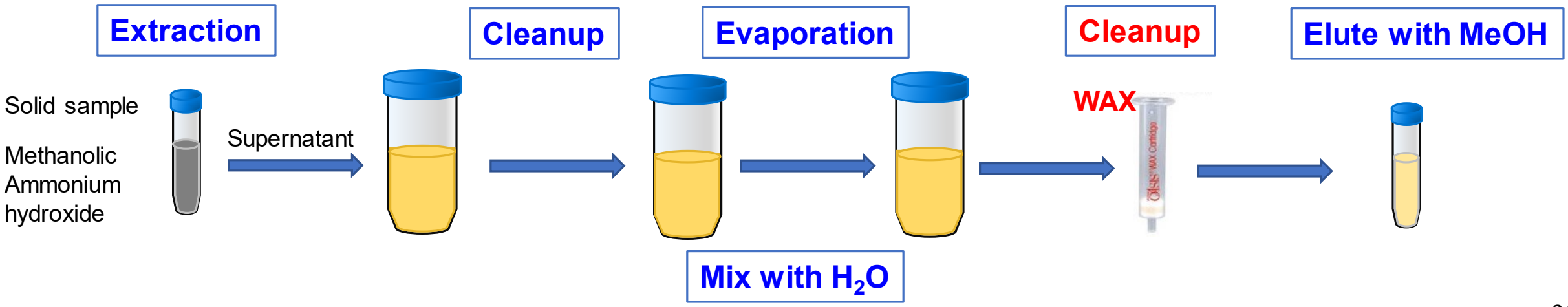
Challenge #3: Analysis of TOF in solid samples

TF = TOF + IF

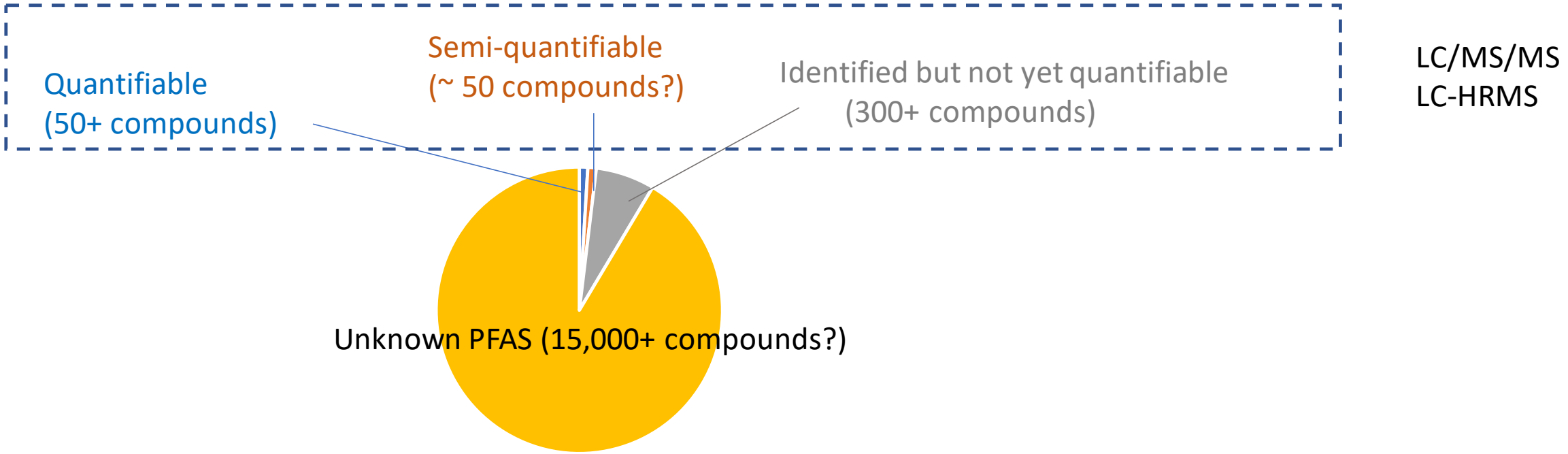
< 1% > 99%

How about solid samples?

- Direct analysis of solid samples → TF, not TOF
- Separating IF from solid samples: methods?
- Extracting TOF without extracting IF?
- Extracting TF, followed by IF separation

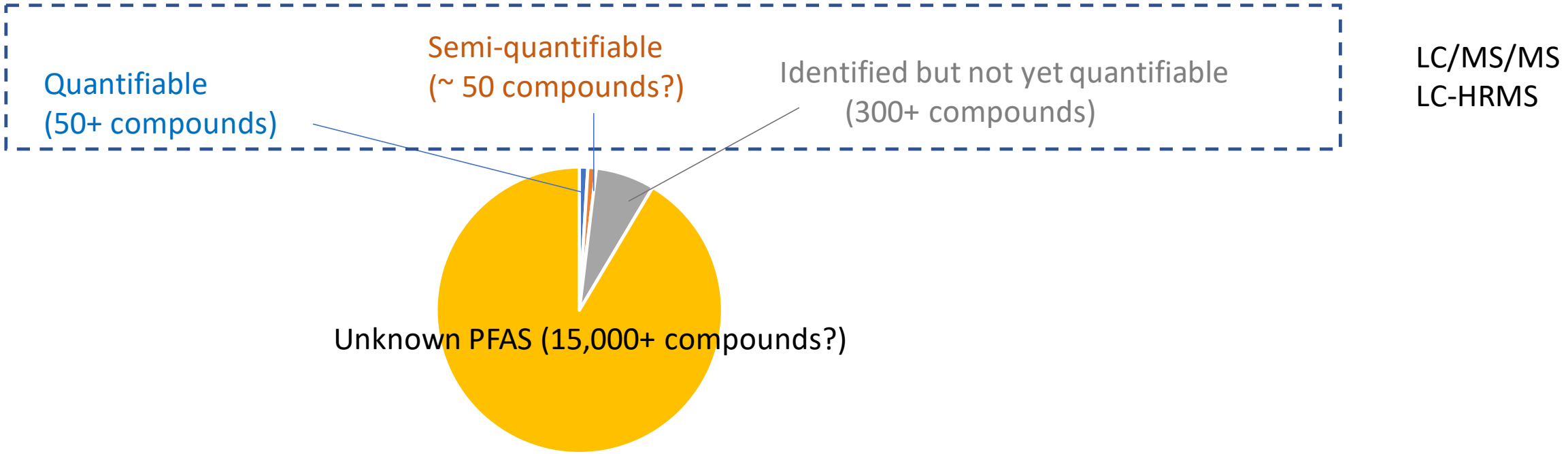


Summary



PFAS analysis by LC/MS/MS: expensive; many compounds; analytical methods are still evolving

Summary



PFAS analysis by LC/MS/MS: expensive; many compounds; analytical methods are still evolving

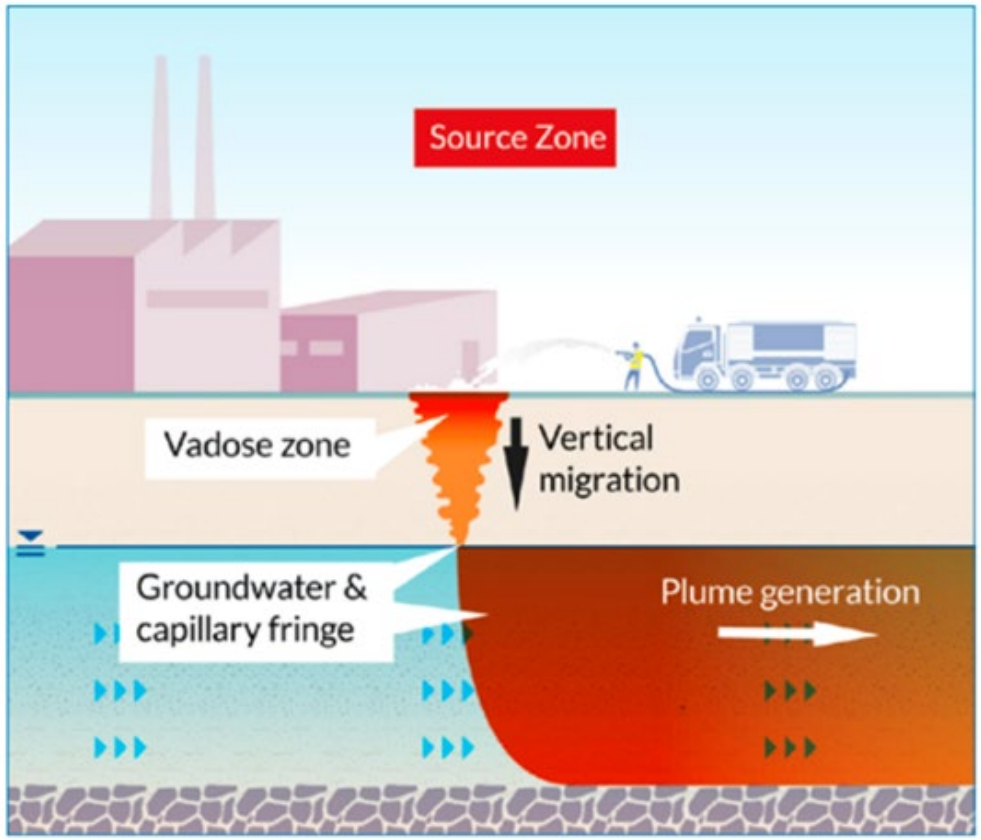
TOF analysis by CIC: methods are less developed

- Not all TOF are PFAS (e.g., Teflon)
- How can we use TOF results for risk assessment?

REMTEC & EMERGING CONTAMINANTS SUMMIT

OCTOBER 15-17, 2024

We need solutions that treat PFAS contamination at the source

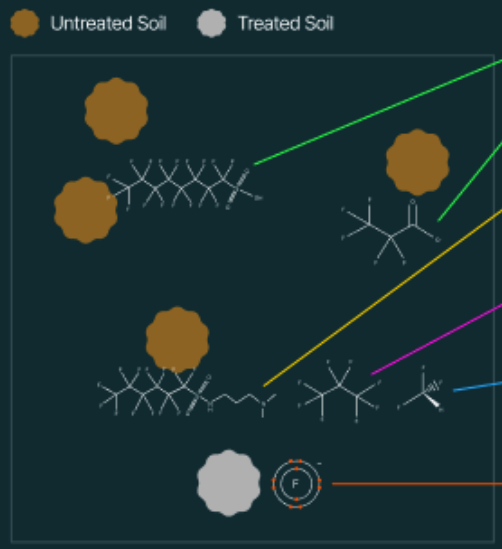


Mass Balance in Solid-Phase Destruction Processes

$$F_{tot} = \bullet F_{target\ PFAS\ (s)} + \blacklozenge F_{non\text{-}target\ PFAS\ (s)} + \blacktriangle F_{target\ PFAS\ (g)} + \hexagon F_{non\text{-}target\ PFAS\ (g)} + \blacksquare F_{fluoride\ ion\ (s)}$$

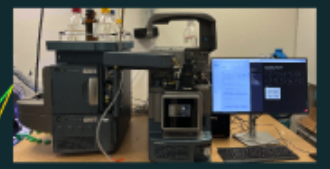
Methods for PFAS Contamination and Destruction Verification in Soil

Ball Milling of Contaminated Soil



Flourine Measured	Analytical Method(s)	Rationale
● Target PFAS (s)	EPA 1633[2] or similar	Isotope dilution tandem mass spectrometry is required for target PFAS quantitation
◆ Non-target PFAS (s)	Total Oxidizable Precursor (TOP) Assay,[3] ^{19}F-NMR[4]	"Total PFAS" measurements have complex tradeoffs so redundant methods are included
▲ Target PFAS (g)	OTM-45,[5] OTM-50[6]	EPA has recently developed methods specifically targeting volatile PFAS
⬢ Non-target PFAS (g)	TF_g[7]	Speciation of potential volatile products is likely more diverse than target list of target GC-MS methods
■ Fluoride ion (s)	^{19}F-NMR[4]	Unlike ISE or IC, NMR can detect some complexed inorganic fluoride

LC-MS/MS



NMR Spectroscopy

GC-MS/MS

Custom Instrumentation by Ye et al. (2024)