SGS Environment Health and Safety

Per-and Polyfluoroalkyl Substances (PFAS): State of Science and Regulation in Air and Industrial Hygiene

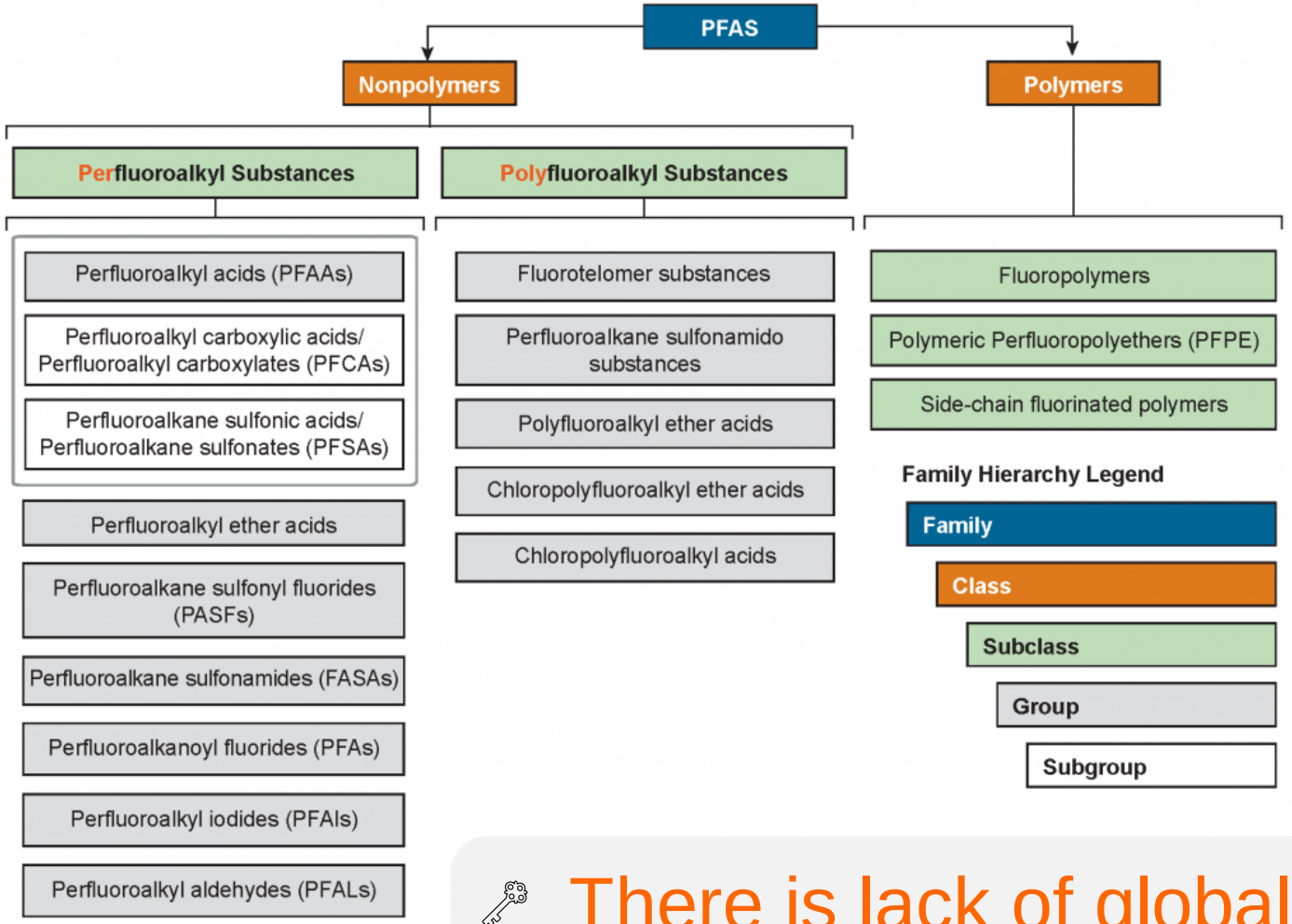
AIHA Webinar: October 10 2023 Bharat Chandramouli

Learning Objectives

- What are PFAS? Why are they a concern? IH Implications
- Overall Regulatory Picture
- Measuring PFAS
- Exposure scenarios and studies

Background and Regulation

PFAS terminology and family tree

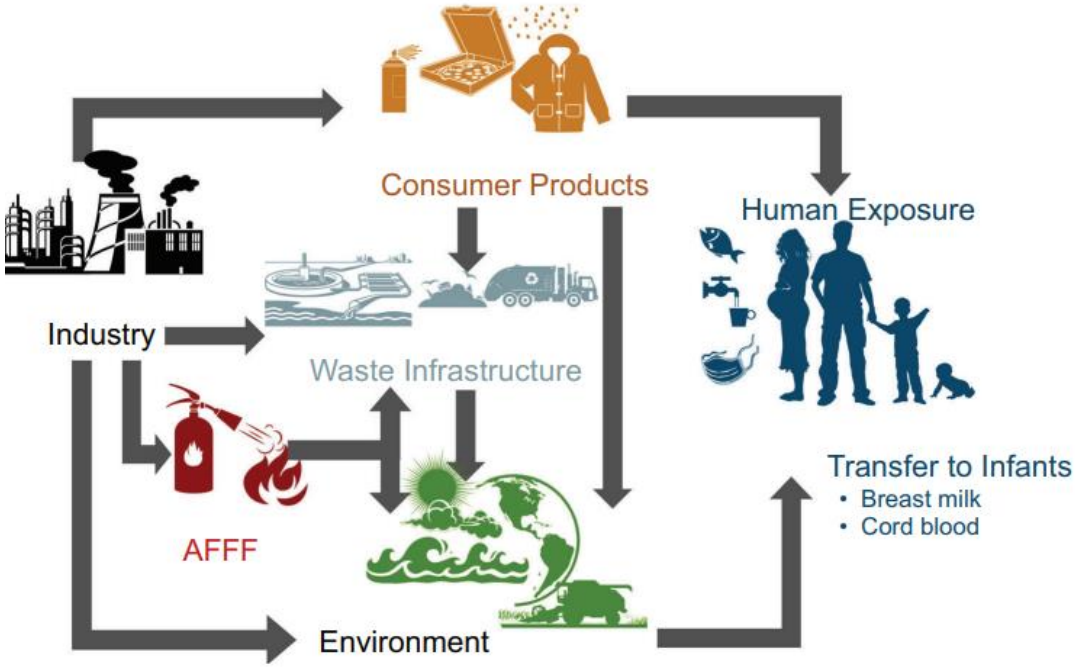


- EPA: At least two continuous carbons containing fluorine where one carbon is fully fluorinated and the other is at least partially fluorinated. **Also, case by case (August 2023)!**
- OECD: Atleast one fully fluorinated CF3 or CF2

There is lack of global consensus on what constitutes a PFAS

PFAS (itrcweb.org)

PFAS Exposure



PFAS	Diet	Dust	Tap water	Food Pkg.	Inhalation	Dermal	Other	Reference
PFOA	16	11		56	14		2[a]	Trudel et al. [25]
PFOA	85	6	1	3[b]			4[c]	Vestergren and Cousins [74]
PFOA	77	8	11		4			Haug et al. [23]
PFOA	66	9	24		<1	<1		Lorber and Egeghy [76]
PFOA	41		37				22[d]	Tian et al. [163]
PFOA	99		<1					Shan et al. [164]
PFOS	66	10	7		2		16[d]	Gebbink et al. [165]
PFOS	72	6	22		<1	<1		Egeghy and Lorber [75]
PFOS	96	1	1		2			Haug et al. [23]
PFOS	81	15					4[a]	Trudel et al. [25]
PFOS	93		4				3[d]	Tian et al. [163]
PFOS	100		<1					Shan et al. [164]
PFBA		4	96					Gebbink et al. [165]
PFHxA	38	4	38		8		12[d]	Gebbink et al. [165]
PFOA	47	8	12		6		27[d]	Gebbink et al. [165]
PFDA	51	2	4		15		28[d]	Gebbink et al. [165]
PFDoDA	86	2	2		4		5[d]	Gebbink et al. [165]

[a]Carpet
[b]Consumer goods
[c]Precursors
[d]Indirect

Sunderland et al. - 2019

A review of the pathways of human exposure to poly- and perfluoroalkyl substances (PFASs) and present understanding of health effects

- Most exposure through diet
- Inhalation and dust significant

EPA releases Health Advisory Levels June 2022

What are the HAs for the four PFAS?

PFOA Interim Updated Health Advisory – Input Parameters and HA Value			
Parameter	**Value**	**Units**	**Source**
Chronic RfD	1.5E-9	mg/kg/day	U.S. EPA, 2021a. *Draft* RfD based on developmental immune health outcome (suppression of tetanus vaccine response in 7-year-old children). Human epidemiological studies.
DWI-BW	0.0701	L/kg-day	U.S. EPA, 2019. 90th percentile direct and indirect consumption of community water, consumers-only population, two-day average, for children ages 0 to <5 years based on 2005–2010 National Health and Nutrition Examination Survey (NHANES).
RSC	0.2	N/A	U.S. EPA, 2021a. RSC based on a review of the current scientific literature.
***PFOA Interim Updated Lifetime Health Advisory = 4E-09 mg/L or 0.004 ppt* (EPA 2022a)**			

PFOS Interim Updated Health Advisory – Input Parameters and HA Value			
Parameter	**Value**	**Units**	**Source**
Chronic RfD	7.9E-09	mg/kg/day	U.S. EPA, 2021b. *Draft* RfD based on developmental immune health outcome (suppression of diphtheria vaccine response in 7-year-old children). Human epidemiological studies.
DWI-BW	0.0701	L/kg-day	U.S. EPA, 2019. 90th percentile direct and indirect consumption of community water, consumers-only population, two-day average, for children ages 0 to <5 years based on 2005–2010 NHANES.
RSC	0.2	N/A	U.S. EPA, 2021b. RSC based on a review of the current scientific literature.
***PFOS Interim Updated Lifetime Health Advisory = 2E-08 mg/L or 0.02 ppt* (EPA 2022b)**			

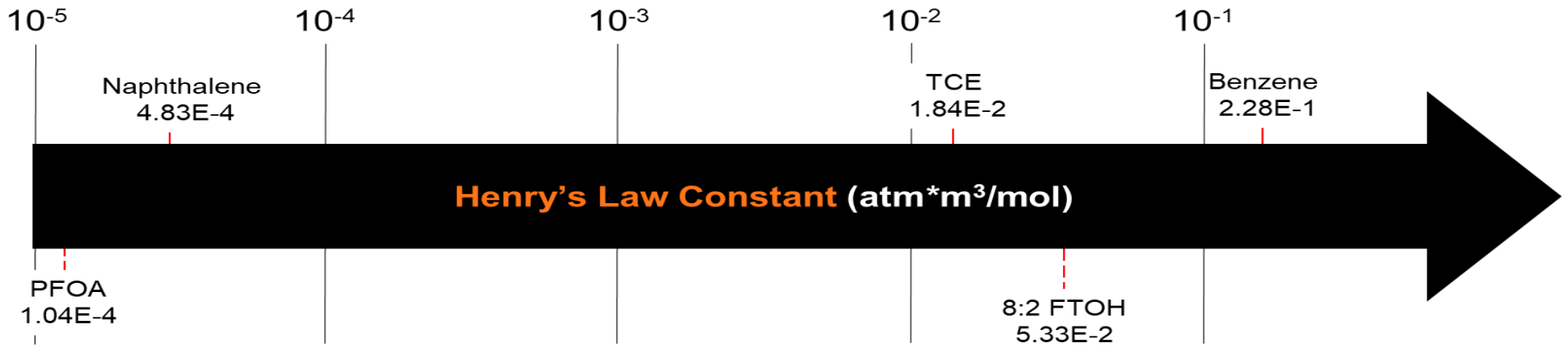
$$\text{Lifetime HA} = \left(\frac{\text{RfD}}{\text{DWI-BW}}\right) * \text{RSC}$$

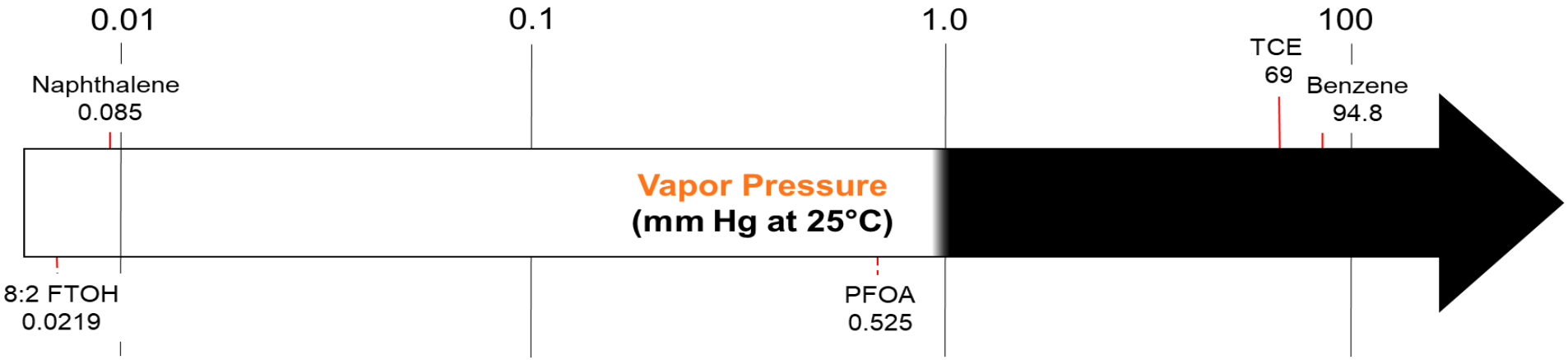
EPA's Acceptable PFOA/PFOS level is essentially zero, like lead

Volatility

EPA Volatility Criteria (EPA, 2017):
Henry's Law Constant of 10^{-6}
AND/OR
1 mm Hg

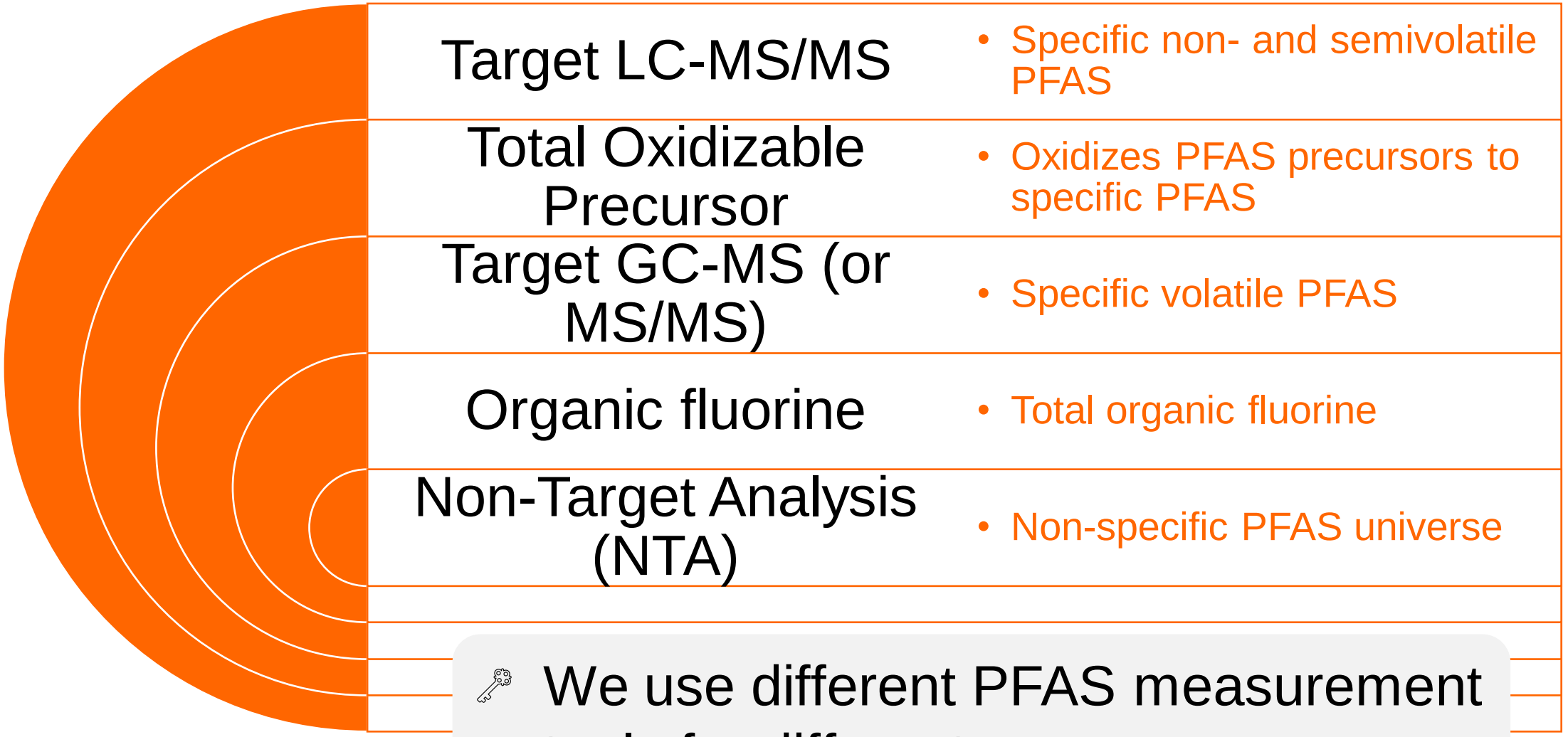
PFAS volatility is complicated by ionization state and water





PFAS Measurement

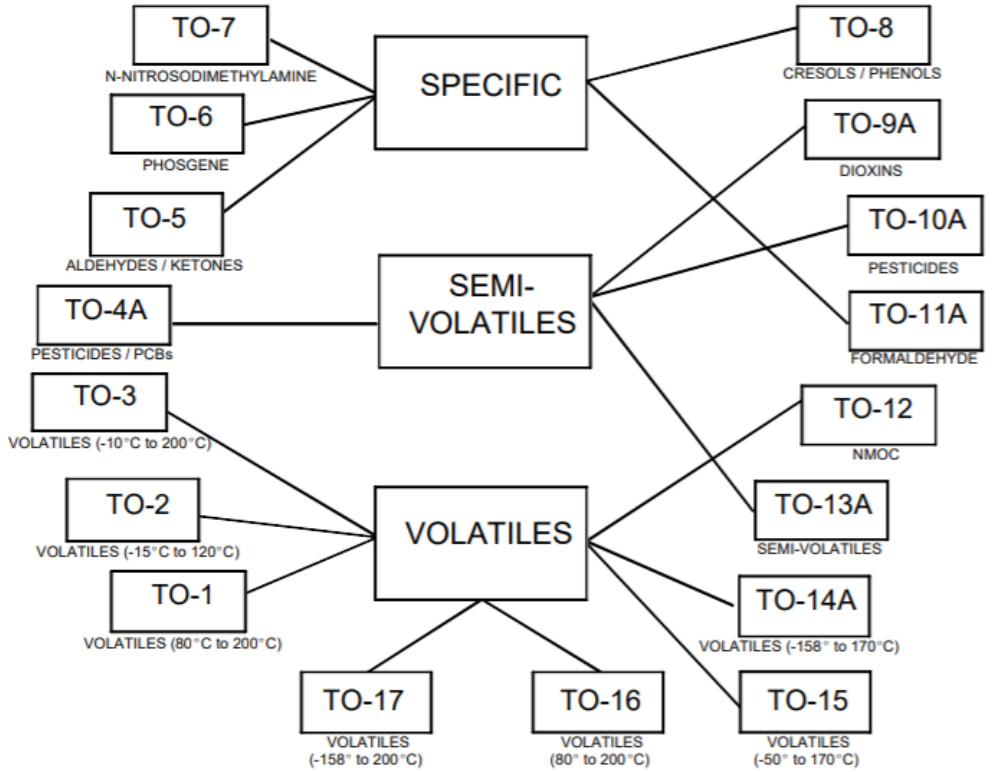
Measuring PFAS

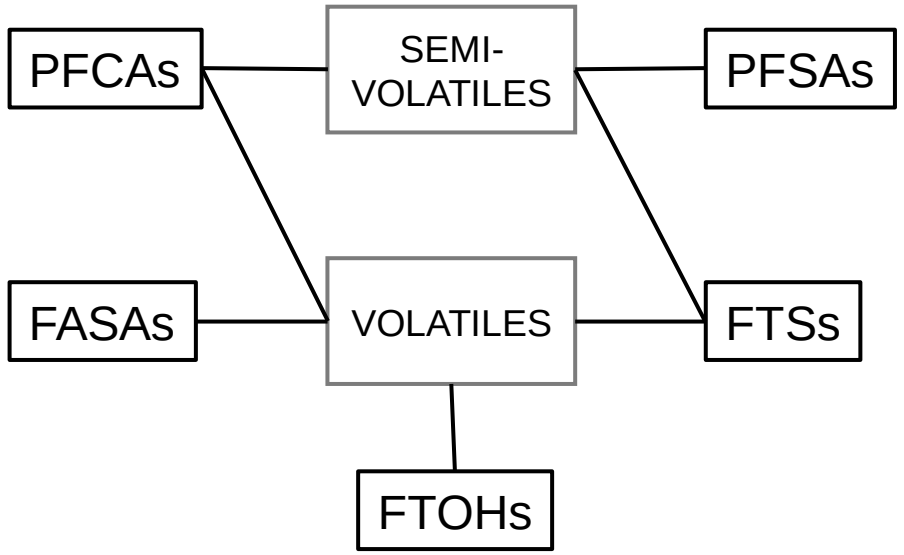


Target LC-MS/MS	• Specific non- and semivolatile PFAS
Total Oxidizable Precursor	• Oxidizes PFAS precursors to specific PFAS
Target GC-MS (or MS/MS)	• Specific volatile PFAS
Organic fluorine	• Total organic fluorine
Non-Target Analysis (NTA)	• Non-specific PFAS universe

We use different PFAS measurement tools for different purposes

Thousands of Compounds with Complex Chemistry

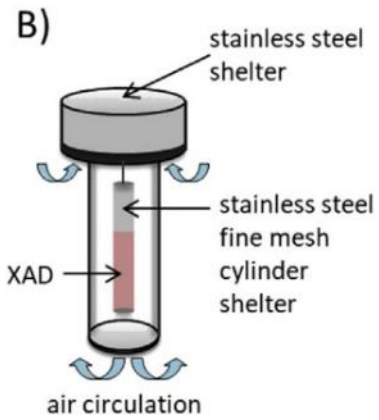


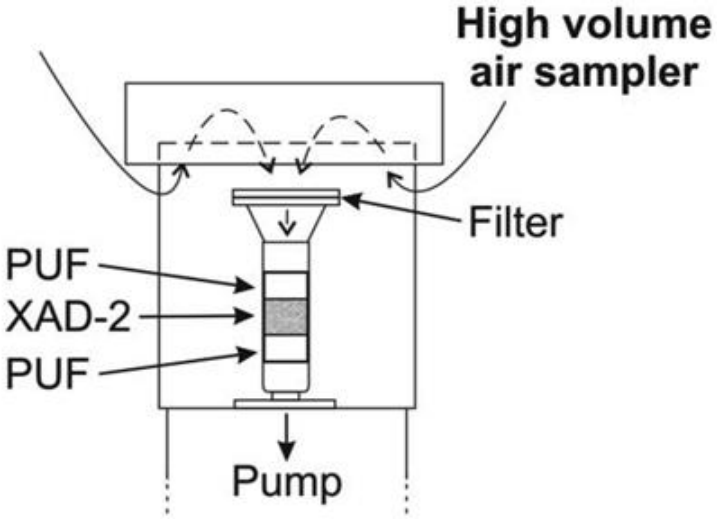


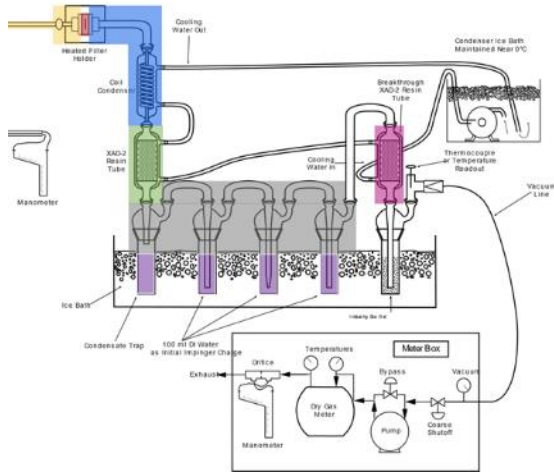
With thousands of PFAS and complex chemistry there will need to be more than one technique to cover PFAS in air

Current Air Sampling Methods

SUMMA TD Tubes Passive XAD/PUF/Filter Emissions







Approximately by decreasing volatility

Available EPA Methods Summary

Method	Matrix	Instrument	Remarks
537.1	Drinking Water	LC-MS/MS	18 targets
533	Drinking Water	LC-MS/MS	24 Targets
1633	NPW, solids, tissue, waste	LC-MS/MS	40 targets
8327	Water	LC-MS/MS	24 targets
1621	Water	Combustion Ion Chromatography	“Total” organic fluorine screening
OTM-45	**Air** Stack Emissions	LC-MS/MS	Up to 49 targets

PFAS Analytical Methods Development and Sampling Research | US EPA

EPA 1633 standardizes PFAS methods (except air)

United States Environmental Protection Agency

Menu

Search EPA.gov

News Releases from Headquarters > Water (OW)

CONTACT US

EPA Announces First Validated Laboratory Method to Test for PFAS in Wastewater, Surface Water, Groundwater, Soils

September 2, 2021

US EPA

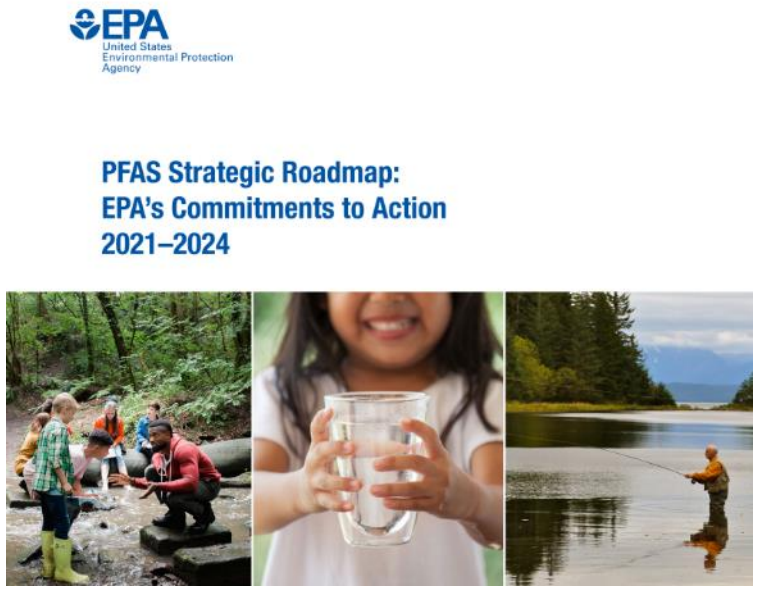
EPA 1633 Draft (finalized 2024) was developed and validated at SGS for the US EPA

EPA: Air Methods in Progress

Matrix/Application	Details	When?
Source air Semi/nonvolatile PFAS	Like OTM-45, but using GC/MS targeted/non-targeted	TBD
Source and ambient air Volatile PFAS Modified Method TO-15	Uses SUMMA canisters for GC-MS targeted/non-targeted	TBD
Ambient/near source volatile	Field/Real-time Mass Spectrometry	“Coming Soon”
Semivolatiles/Ambient air	Based on TO-13A High volume sampling	“Coming Soon”
Volatile PFAS in ambient/occupational	SUMMA Canisters and sorbent traps	“Coming Soon”

PFAS Analytical Methods Development and Sampling Research | US EPA

The Federal PFAS Action Plan 2021-2024

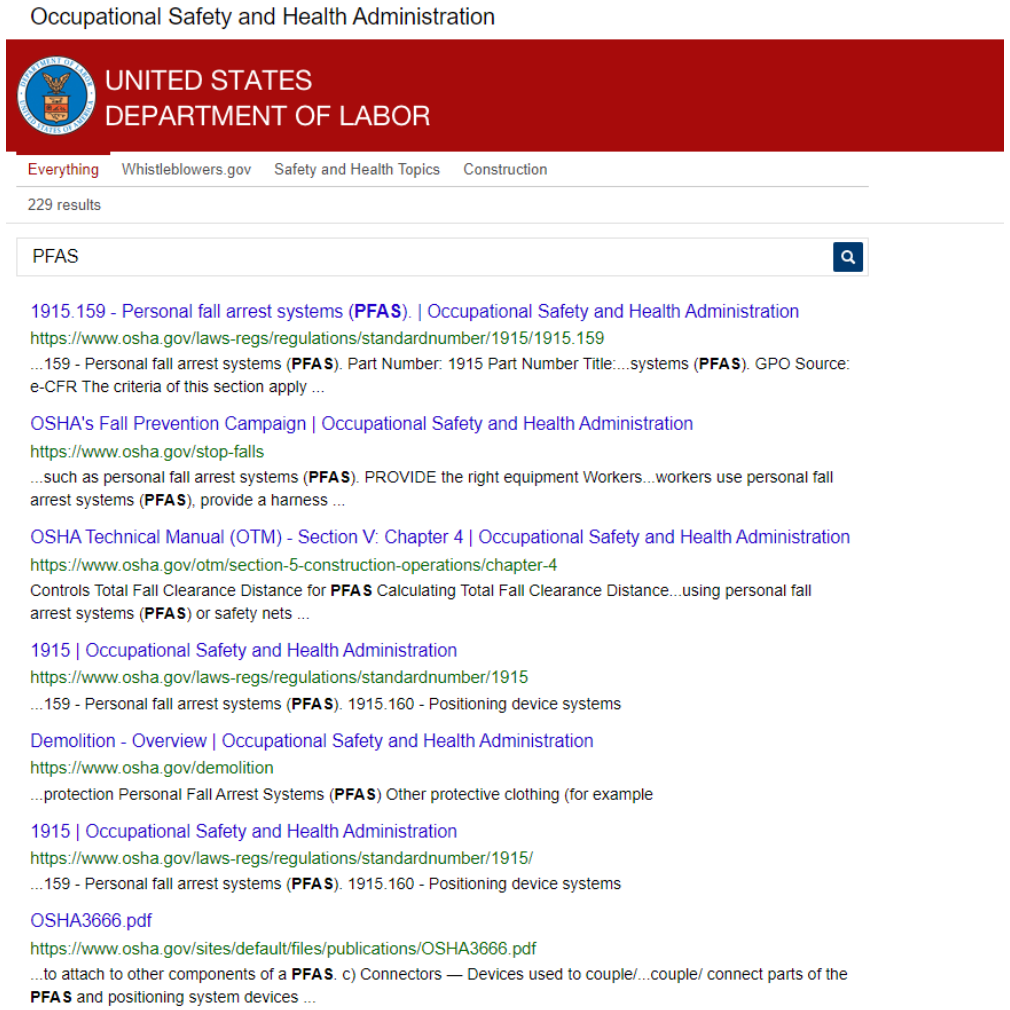


"EPA's PFAS strategic roadmap is our plan to deliver tangible public health benefits to all people who are impacted by these chemicals — regardless of their zip code or the color of their skin."

Michael S. Regan
EPA Administrator

- National PFAS testing strategy
- **MCL** Establish a national primary drinking water regulation for PFOA and PFOS by 2023
- **NPDES** Restrict PFAS discharges from industrial sources through a multi-faceted Effluent Limitations Guidelines program – 2022
- **AIR and Radiation** Build framework for air emissions monitoring and mitigation

OSHA and PFAS



OSHA has not pivoted from Personal Fall Arrest Systems to Forever Chemicals

NIOSH and PFAS

Per- and polyfluoroalkyl substances (PFAS)

Print

Photo: Port of Seattle Fire Department

PFAS is often a component of Aqueous Film Forming Foam (AFFF), a class B firefighting foam used for suppression of liquid fuel fires.

On This Page

NIOSH PFAS Website is a good introduction to PFAS occupational risks

PFAS | NIOSH | CDC

Safe Drinking Water Act Maximum Contaminant Levels

The Safe Drinking Water Act (SDWA) was passed by Congress in 1974, with amendments added in 1986 and 1996, to protect our drinking water. Under the SDWA, EPA sets the standards for drinking water quality and monitors states, local authorities, and water suppliers who enforce those standards.

News Releases: Headquarters | Water (OW)

CONTACT US

Biden-Harris Administration Proposes First-Ever National Standard to Protect Communities from PFAS in Drinking Water

March 14, 2023

Contact Information

What are the proposed MCLs?

Compound	Health Advisory Level (ng/L)	Proposed MCLG (health based not enforceable)	Proposed MCL (enforceable levels) (ng/L or ppt or unitless)
PFOA	0.004	Zero	4.0
PFOS	0.02	Zero	4.0
PFNA	Not yet finalized (using 9 from ATSDR)	1.0 (unitless) Hazard Index	1.0 (unitless) Hazard Index
PFHxS	Not yet finalized (using 10 from ATSDR)		
PFBS	2000		
HFPO-DA (commonly referred to as GenX Chemicals)	10		

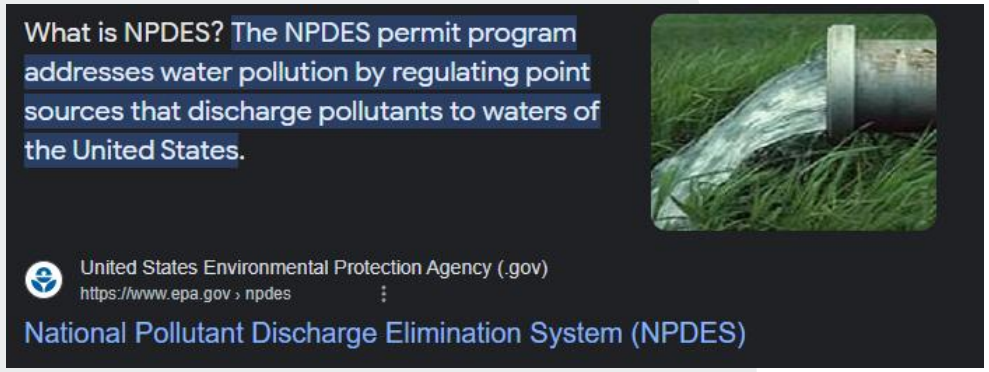
What's a hazard index?

- The hazard index is a combined unitless calculation for PFHxS, HFPO-DA, PFNA and PFBS
- Uses the toxicologically derived HBWCs (essentially the HALs/equivalent) as the denominator to weight the contributions of these 4 PFAS by relative toxicity
- NDs are zero!

PFAS	Health Based Water Concentration (HBWC ng/L)
PFHxS	9
HFPO-DA	10
PFNA	10
PFBS	2000

$$HI\ MCLG = \left(\frac{[GenX_{water}]}{[GenX_{HBWC}]}\right) + \left(\frac{[PFBS_{water}]}{[PFBS_{HBWC}]}\right) + \left(\frac{[PFNA_{water}]}{[PFNA_{HBWC}]}\right) + \left(\frac{[PFHxS_{water}]}{[PFHxS_{HBWC}]}\right) = 1.0$$

The National Pollution Discharge Elimination System (NPDES)



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF WATER

December 5, 2022

MEMORANDUM

SUBJECT: Addressing PFAS Discharges in NPDES Permits and Through the Pretreatment Program and Monitoring Programs

FROM: Radhika Fox
Assistant Administrator

TO: EPA Regional Water Division Directors, Regions 1-10

- Addressing PFAS discharges from POTWs and industrial sources
- Quarterly monitoring for 40 targets

  Organic fluorine using EPA 1621

  Include biosolids as well

State-Level Regulations (ITRC and Paris-Devila et al)

TABLE 2 The derived RfCs and the calculated worker noncarcinogenic screening level using default exposure assumptions.[21]

PFAS	Acronym	CASRN	ECHA data (mg/m^3)	MI DEQ air RfC (mg/m^3)	MN DOH RfC (mg/m^3)	NJ DEP RfC (mg/m^3)	TX CEQ RfC (mg/m^3)	ECHA indoor worker SL ($\mu g/m^3$)	MI indoor worker SL ($\mu g/m^3$)	MN indoor worker SL ($\mu g/m^3$)	NJ indoor worker SL ($\mu g/m^3$)	TX indoor worker SL ($\mu g/m^3$)
Perfluorododecanoic acid	PFDoDA	307-55-1					4.20E−05					1.84E−01
Perfluorodecanoic acid	PFDA	335-76-2					5.30E−05					2.32E−01
Perfluorononanoic acid	PFNA	375-95-1					2.80E−05					1.23E−01
Perfluorooctanoic acid	PFOA	335-67-1		7.00E−05	6.30E−05	7.00E−06	4.10E−06		3.07E−01	2.76E−01	3.07E−02	1.80E−02
Perfluorobutanoic acid	PFBA	375-22-4			0.01		1.00E−02			4.38E+01		4.38E+01
Perfluorooctanesulfonic acid	PFOS	1763-23-1		7.00E−05	1.10E−05	6.00E−06	8.10E−05		3.07E−01	4.82E−02	2.63E−02	3.55E−01
Perfluorohexanesulfonic acid	PFHxS	355-46-4			3.40E−05		1.30E−05			1.49E−01		5.69E−02
Perfluorobutanesulfonic acid	PFBS	375-73-5			0.002		4.90E−03			8.76E+0		2.15E+01
Perfluorooctanesulfonamide	PFOSA	754-91-6					4.10E−06					1.80E−02
Fluorotelomer alcohol 6:2	FTOH 6:2	647-42-7	0.015					6.52E+01				

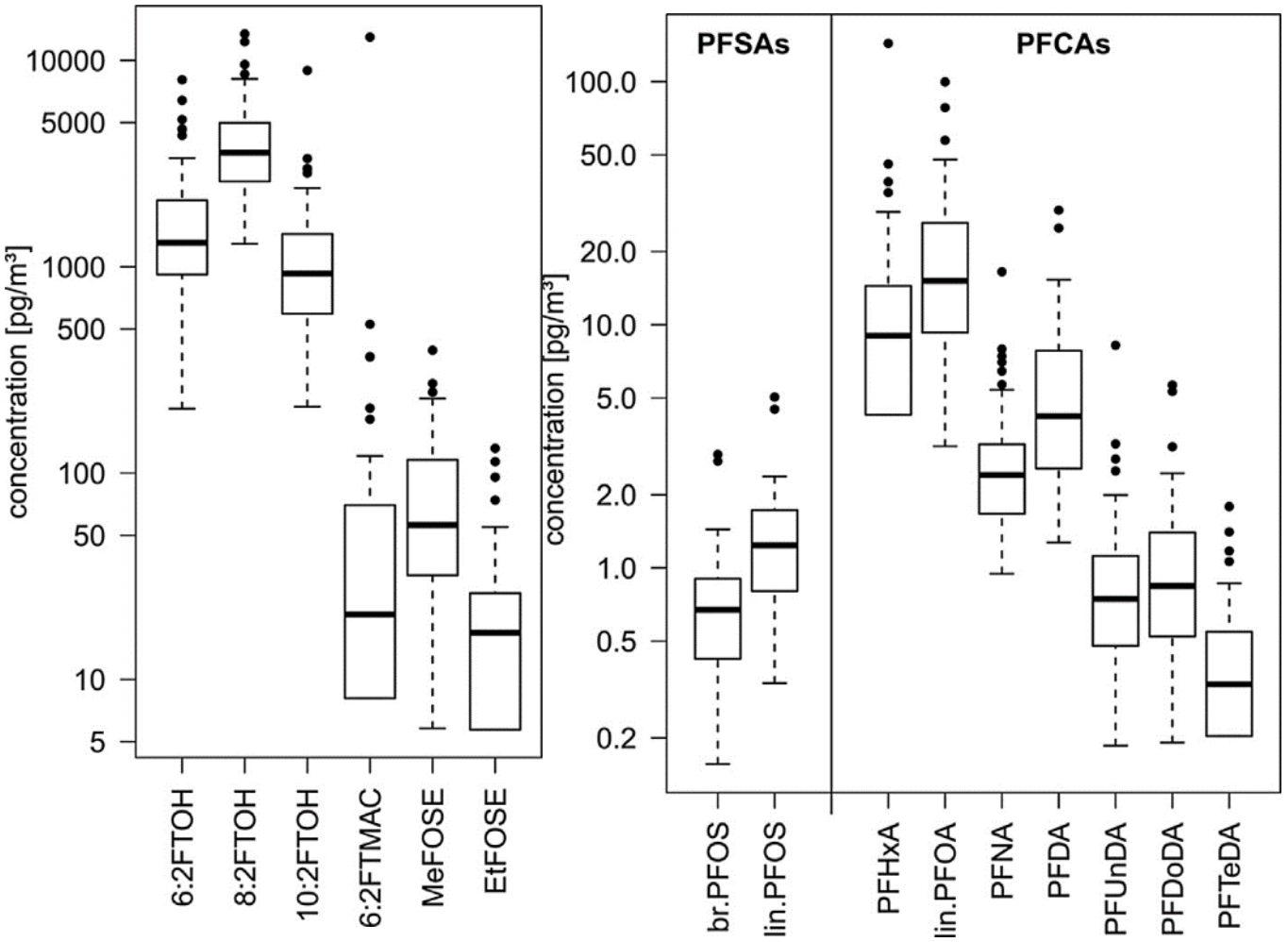
Note: The default composite worker exposure scenario assumes that a worker is exposed 250 days a year for eight hours a day for 25 years. A target hazard quotient of 1 was used for this screening level calculation.

- Ever evolving and complex, changes monthly
- Regulations primarily in Water (potable/non-potable) and Soil
- Inhalation
  - Minnesota, Michigan New Jersey and Texas have Inhalation RfCs using route-to-route extrapolation from oral RfD

Residential Air Exposure

Indoor Environments (Children's Bedrooms)

(Winkens et al., 2017)

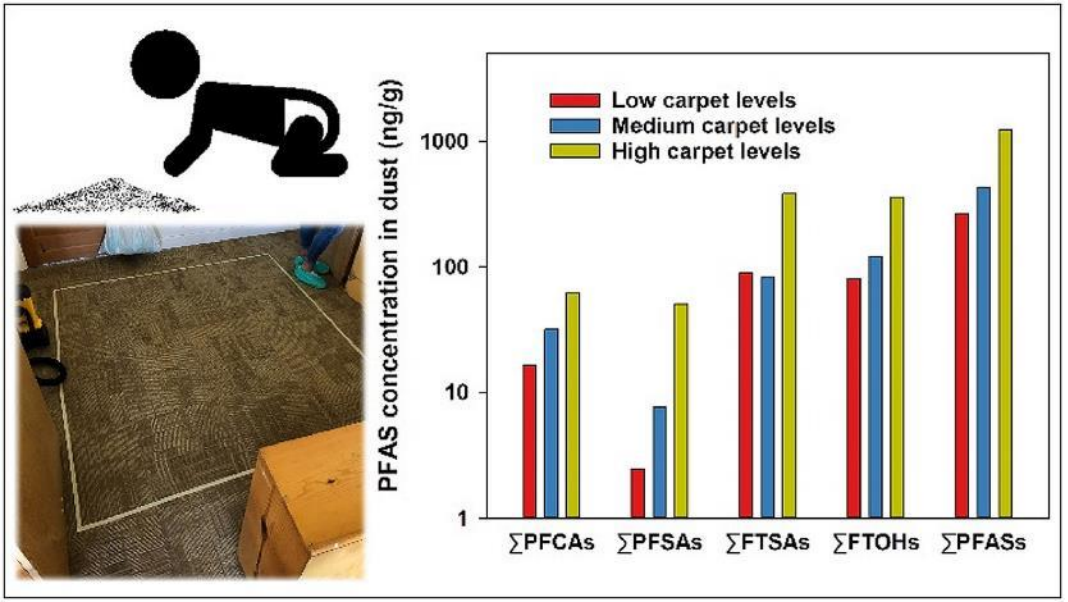


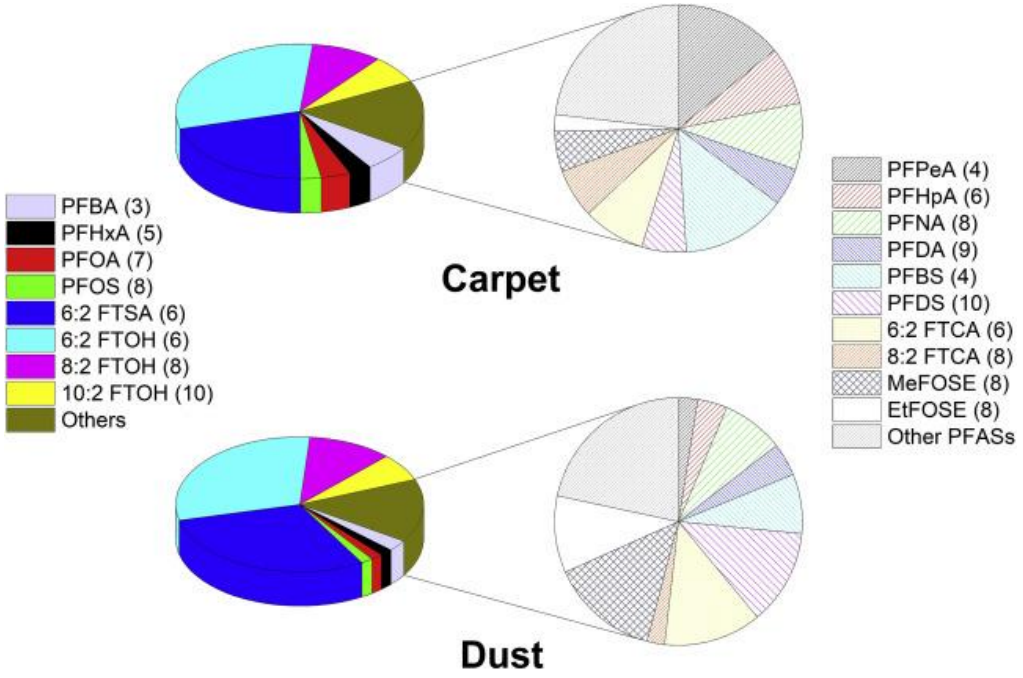
- More carboxylates than sulfonates in indoor air
- FTOH predominate
- High variability due to varied sources

When measurement includes gas phase, volatile PFAS are predominant

Indoor Environments (Carpets at Daycares)

(Wu et al., 2020)



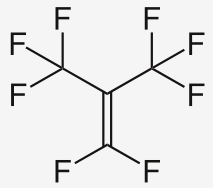
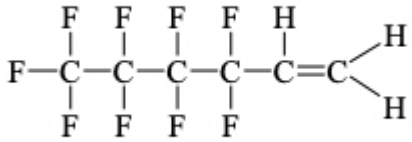
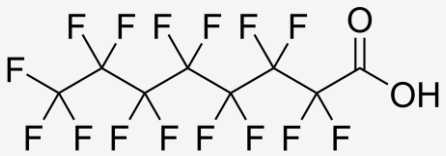


https://doi.org/10.1016/j.chemosphere.2020.126771

Dust represents particulate exposure, hence semi- and non-volatile PFAS also predominant

Worker Exposure

ACGIH TLVs

PFAS	Structure	TLV	Notes
Perfluoroisobutylene (PFIB)		0.082 mg/m^3 (0.01 ppm) Ceiling	Highly toxic perfluorocarbon arising from PTFE pyrolysis
Perfluorobytlethylene		1023 mg/m^3 (100 ppm) 8 hr TWA	Solvent used in polymer manufacture, food contact packaging
Ammonium Perfluorooctanoate aka PFOA		0.01 mg/m3 8 hr TWA	Multiple uses including polymer processing. Phased out in NA

Occupational Exposure Still Emerging

Received: 22 July 2022 | Revised: 13 January 2023 | Accepted: 17 January 2023
DOI: 10.1002/ajim.23461

REVIEW ARTICLE

AMERICAN JOURNAL OF INDUSTRIAL MEDICINE WILEY

Occupational exposures to airborne per- and polyfluoroalkyl substances (PFAS)—A review

Tamara Paris-Davila[1] | Linda G. T. Gaines[2] | Katherine Lucas[1] | Leena A. Nylander-French[1]

doi:10.1002/ajim.23461

Journal of Exposure Science & Environmental Epidemiology www.nature.com/jes

REVIEW ARTICLE

Check for updates

Occupational exposure to per- and polyfluoroalkyl substances: a scope review of the literature from 1980–2021

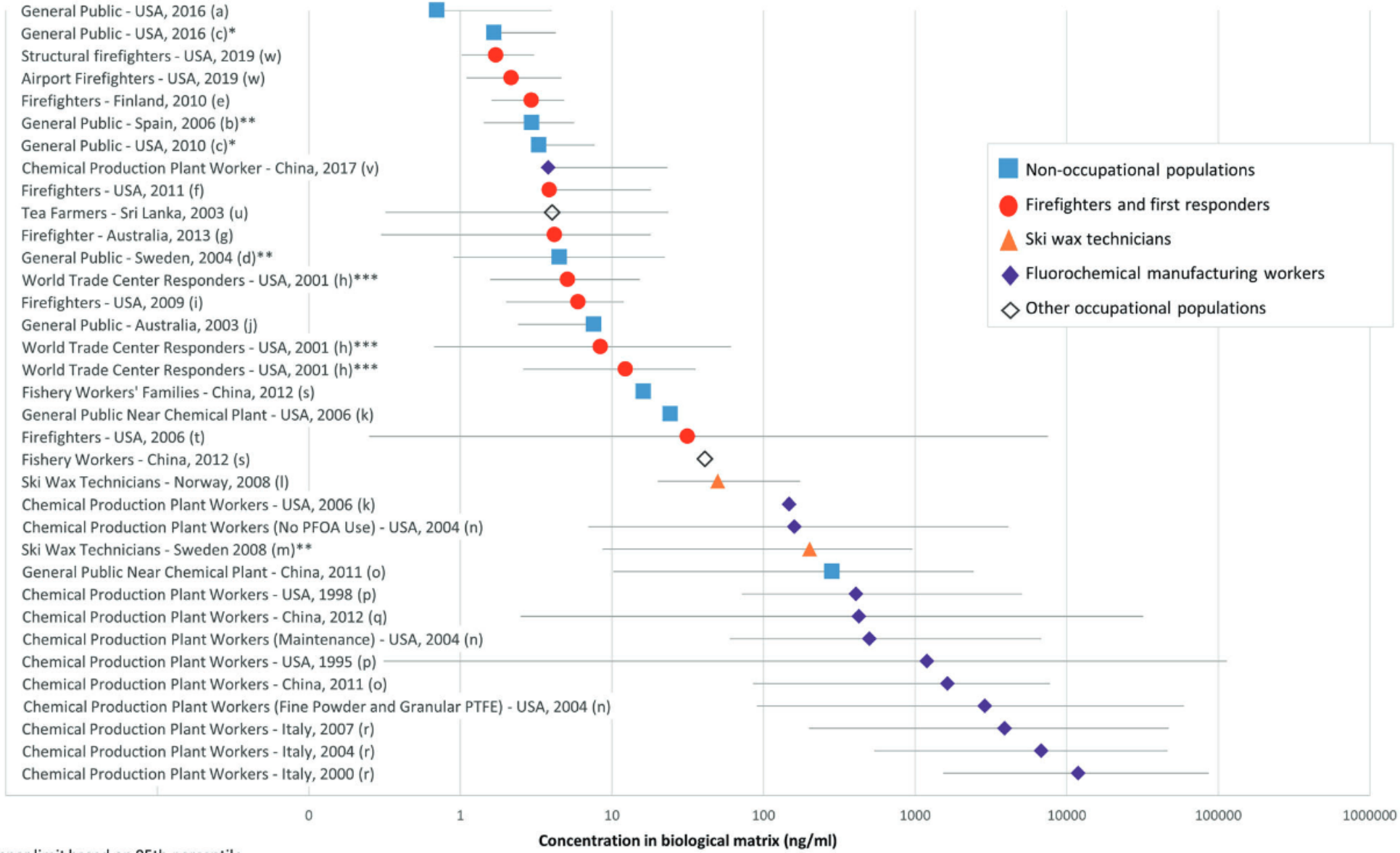
Brian T. Christensen[1] and Miriam M. Calkins[1]

https://doi.org/10.1038/s41370-023-00536-y

- Two recent review articles provide some context and identify gaps
- Most studies focused on
  - Fluorochemical workers (early)
  - Firefighters
  - Ski-wax technicians
- Most work has been on serum monitoring aggregate exposure
- Air/Dust monitoring in workplace air, not necessarily breathing zone
- Which PFAS to measure?
- What other populations are vulnerable?

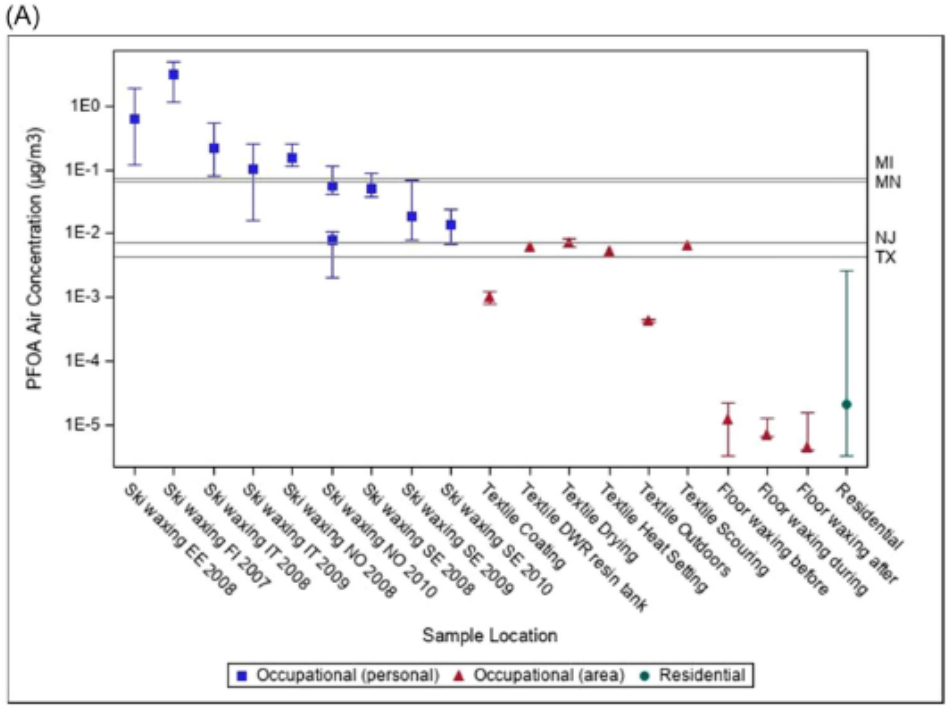
Worker Exposure Serum Consolidated

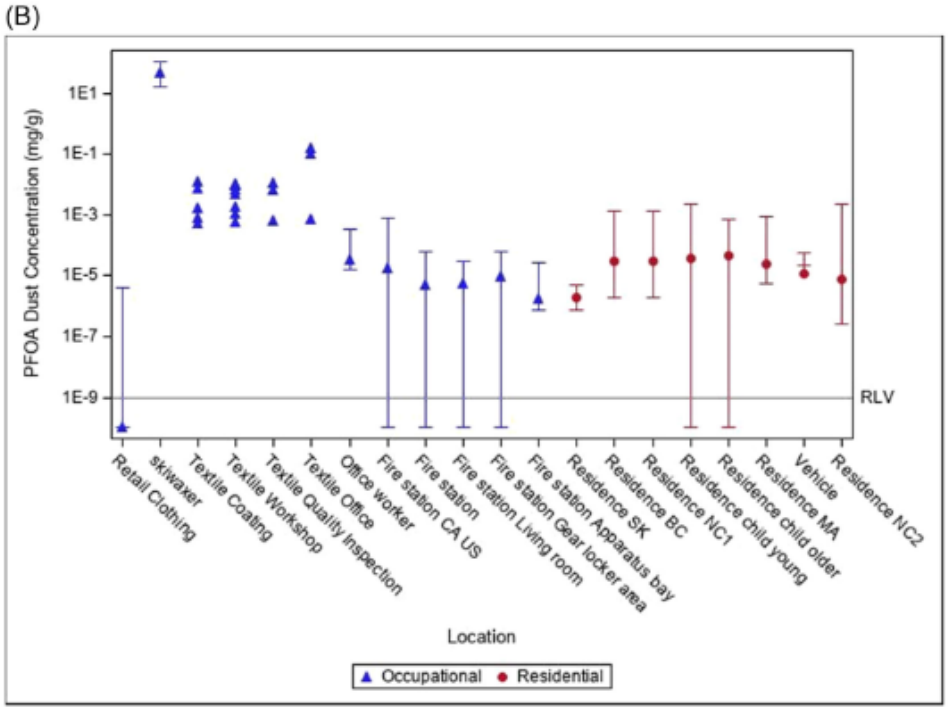
Christensen & Calkins 2023



*Upper limit based on 95th percentile

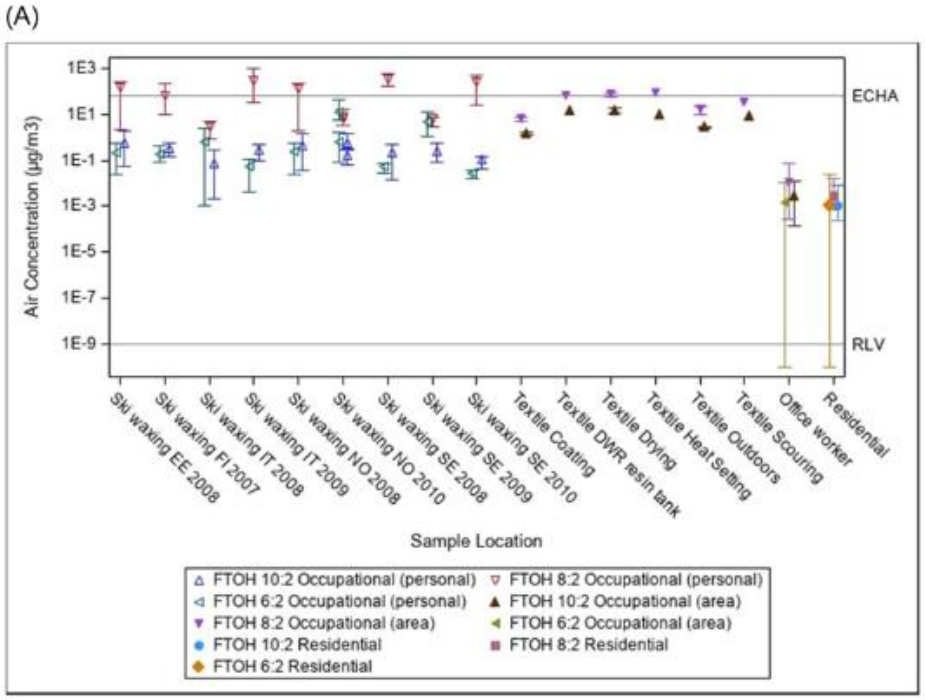
PFOA Dust and Air Concentrations Paris-Devlia et al, 2023

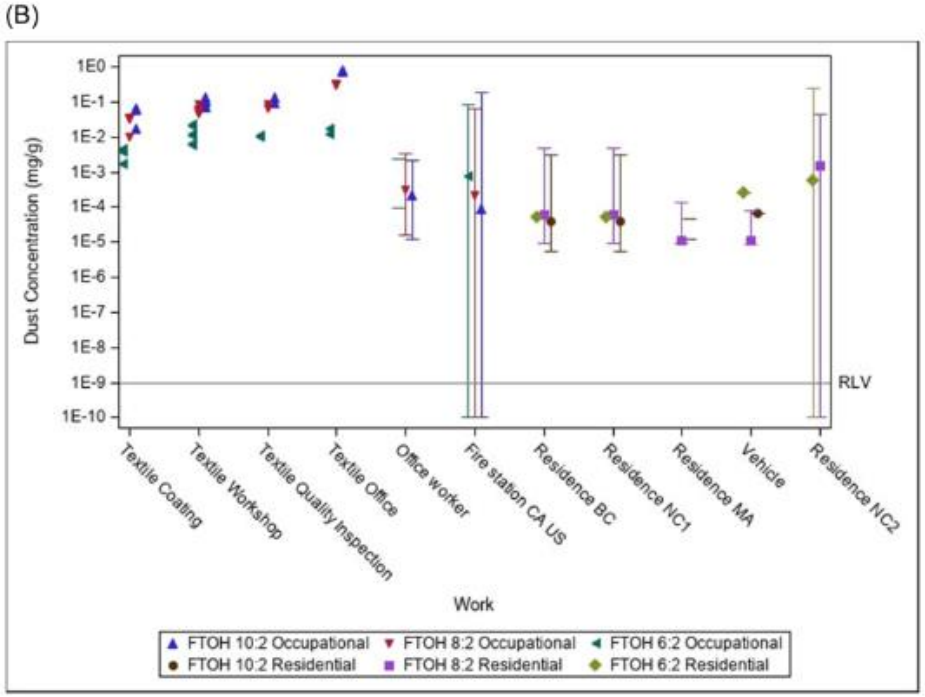




- Overall, Ski wax techs have the highest PFOA exposure based on fairly old data, but other air exposures textiles etc. may exceed RfC
- With phaseout of longer-chain PFAS, we would expect these to decline
- Are these the appropriate PFAS to monitor?

FTOH Dust and Air Concentrations Paris-Devila et al, 2023

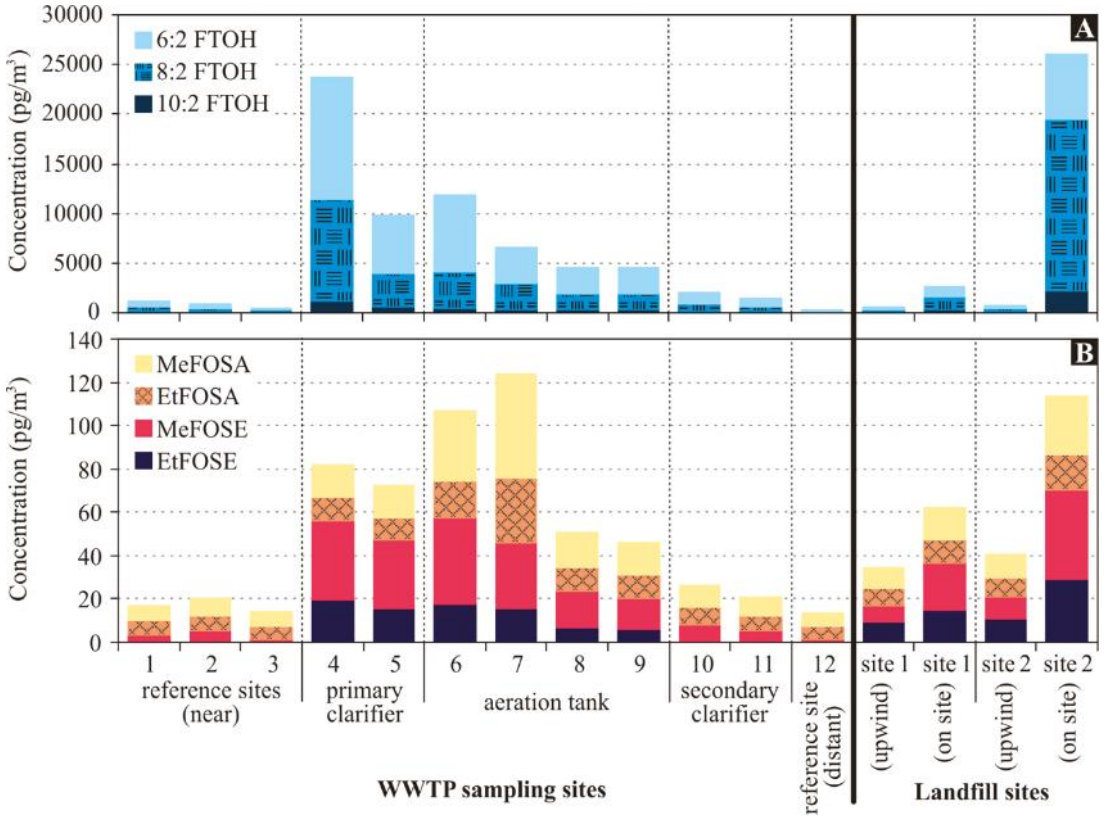


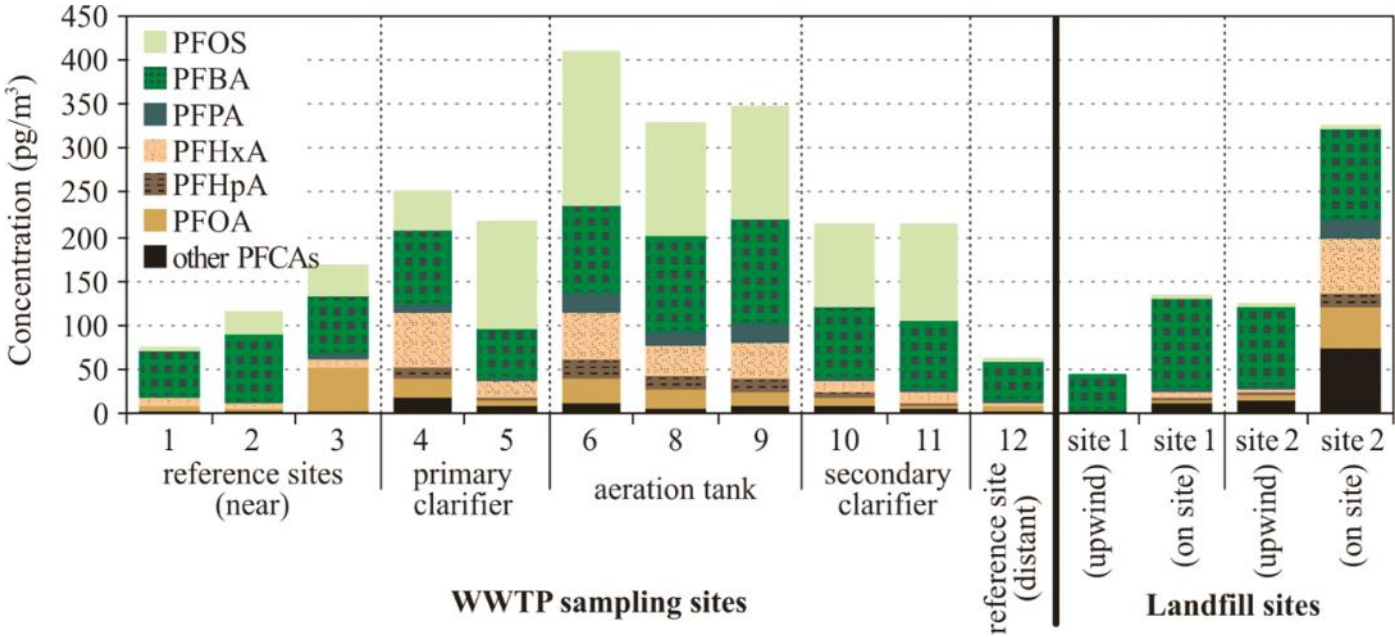


- Fluorotelomer alcohols are volatile and are present at much higher concentrations than the semivolatile PFAS
- FTOHs can transform to perfluorinated carboxylic acids in-vivo and in the environment
- ECHA has RfCs for 6:2 FTOH which is still in active use
- No standard reference methods for FTOHs developed yet, in progress
- The volatile PFAS universe is still very poorly mapped, so there is a lot of uncertainty

Wastewater Treatment Plan and Landfill Sources

(Ahrens et al, 2011)





Of target PFAS, fluorotelomer alcohols two orders of magnitude higher

To conclude

PFAS is being regulated on multiple fronts

Drinking water and waste are ahead of Industrial Hygiene and Indoor Exposure

PFAS of focus in air are volatile/neutral and haven’t been measured frequently

Methods for air monitoring are still in development, but other matrices are becoming standardized

Questions?

For more information, visit https://www.sgs-ehsusa.com/pfas-analysis/

- Bharat Chandramouli, Ph. D
- Find me on LinkedIn