Evaluation of the Vapor Intrusion Potential of Volatile Per- and Polyfluoroalkyl Substances

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Agenda

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- Background
- Henry's Law Constants
- Evaluation of VI Potential
- Wrap-up

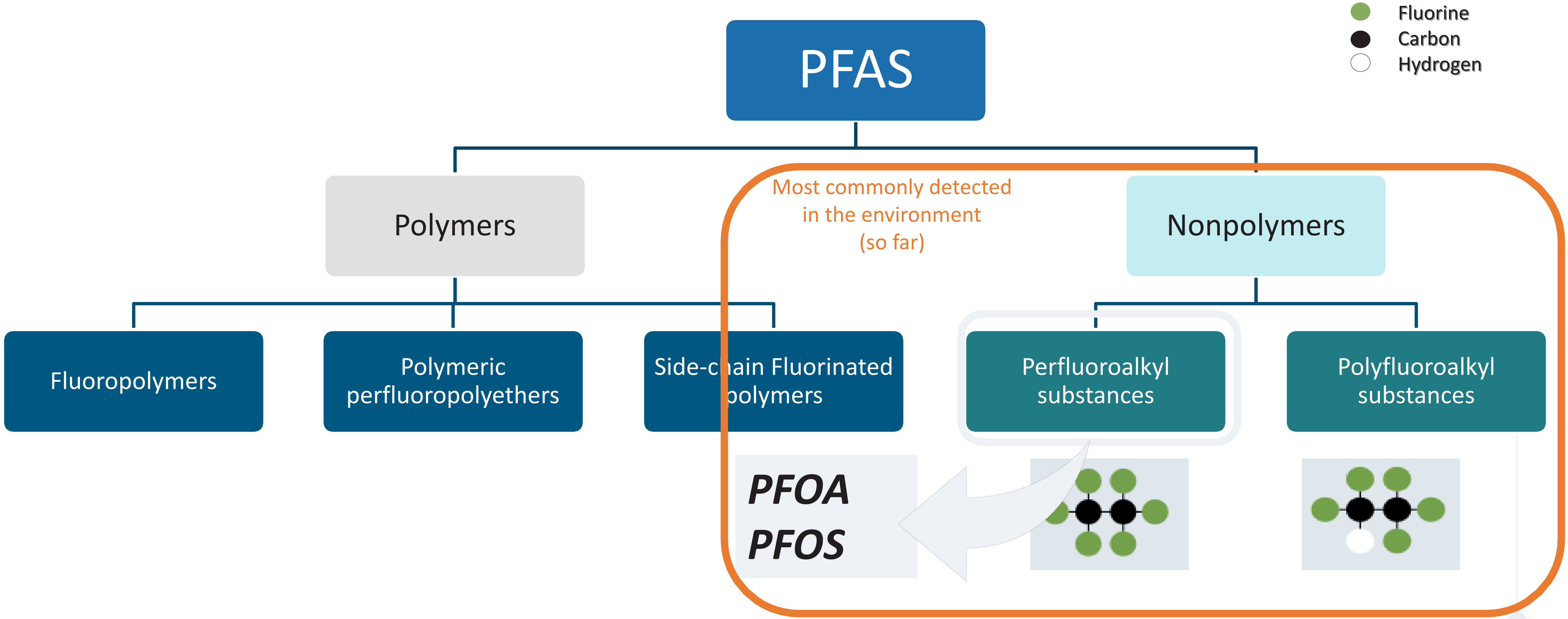
What are Per- and Polyfluoroalkyl Substances (PFAS)?

- ✓ Large class of surfactants used since 1940s
- ✓ Found in wide range of consumer and industrial applications
- ✓ Unique chemical & physical properties
- ✓ Extremely persistent and mobile in the environment





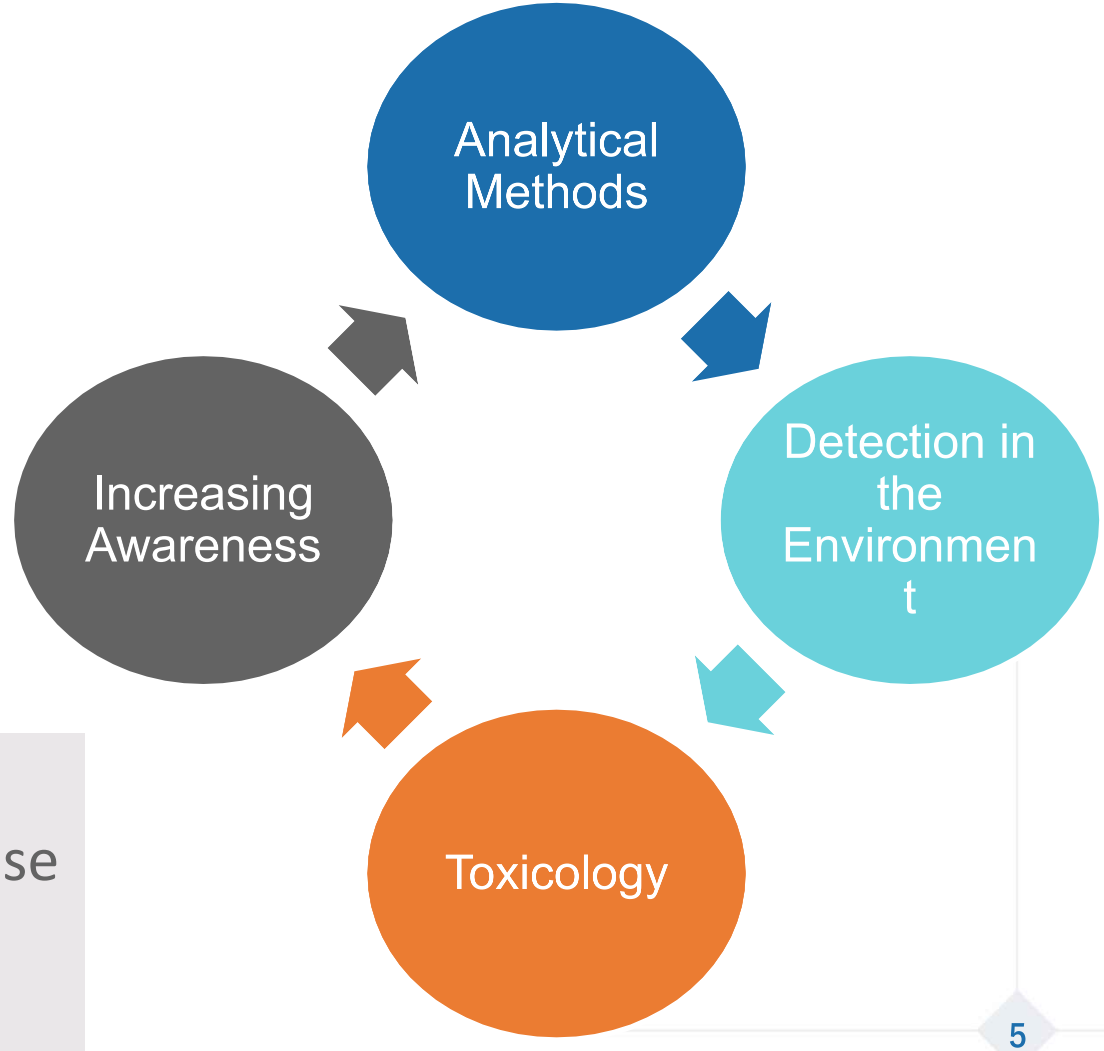

12,000 PFAS Grouped by Chemistry:
All Very Different Chemistries and Uses



PFOA = perfluorooctanoic acid
PFOS = perfluorooctane sulfonic acid

PFAS in the Environment?

- Understanding of PFAS has evolved over time
- Initial focus on solids, liquids
- Less emphasis on gas



KEY POINT

Based on characteristics of early-studied PFAS, volatility & vapor-phase transport not expected.

PFAS in Ambient Air: *Example Study*

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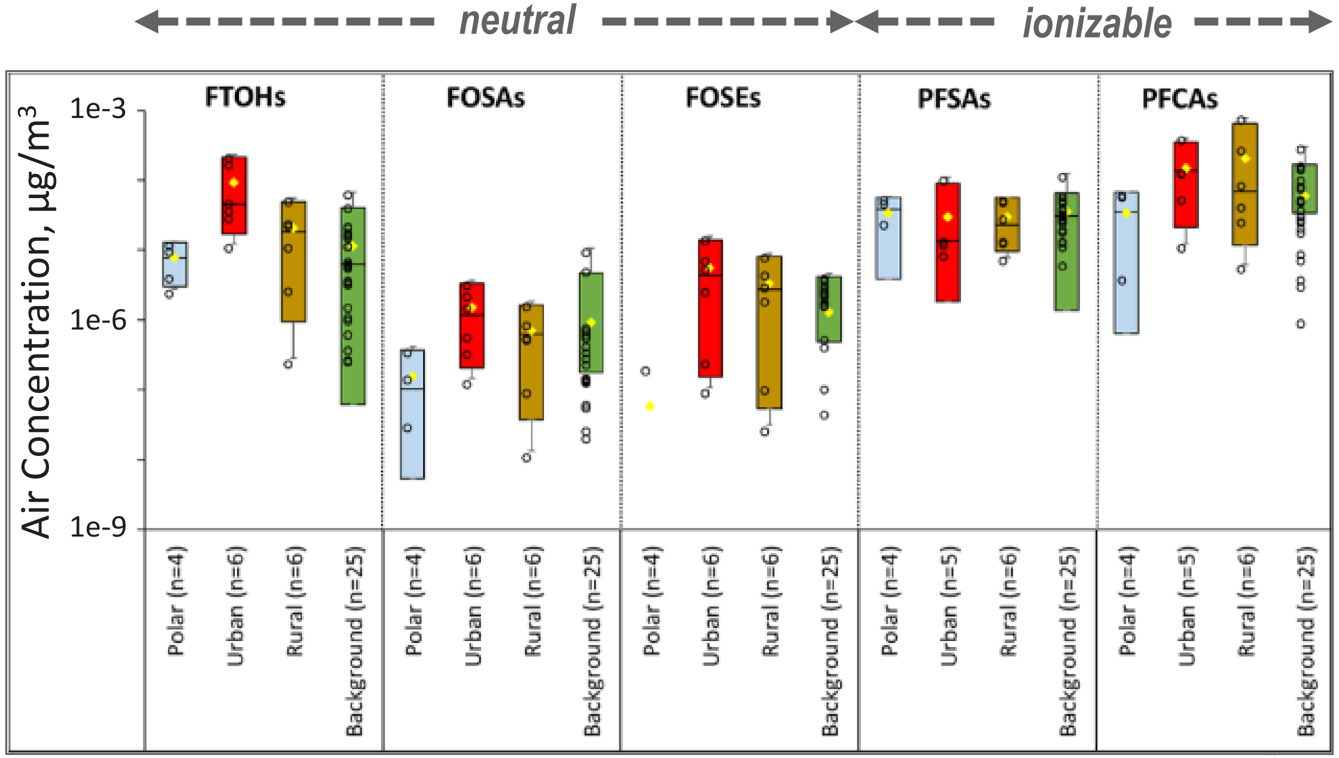
- 9 year study at 41 global sites – polar, urban, rural
- PFAS found at all sites
- Used sorbent-impregnated PUF samplers
- Measured **neutral** PFAS (gas-phase) and **ionizable** PFAS (sorbed to water vapor/particles)



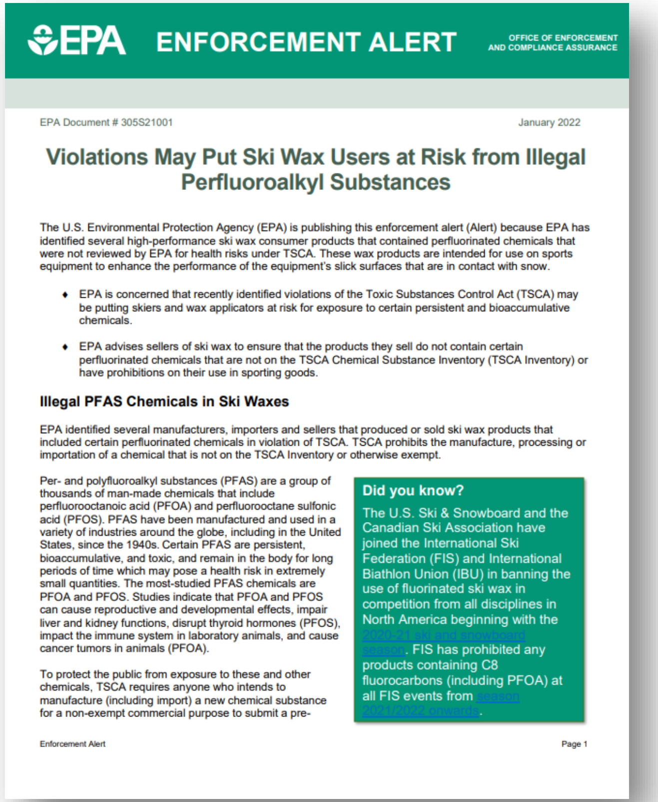
Adapted from Figure 1, Saini et al., 2023, Environmental Pollution

KEY POINT	**Airborne PFAS** are globally distributed and found in ambient air at sub ng/m³ levels

Neutral PFAS = not expected to be charged at environmentally relevant pH; Ionizable PFAS = expected to be charged

PFAS in Indoor Air

- FTOHs ubiquitous in indoor air
  - Classrooms, residences, workplaces
  - Sub nanogram/m^3 (10-4 $\mu g/m^3$) to hundreds of micrograms/m^3 (250 $\mu g/m^3$)
- Highest indoor air concentrations of FTOHs reported in occupational settings
  - 8:2 FTOH up to 250 $\mu g/m^3$ (Nilsson et al., 2010)
- Ski tuners & other studies – potential impact of volatile PFAS on human health?


EPA ENFORCEMENT ALERT
OFFICE OF ENFORCEMENT AND COMPLIANCE ASSURANCE

EPA Document # 305S21001 January 2022

Violations May Put Ski Wax Users at Risk from Illegal Perfluoroalkyl Substances

The U.S. Environmental Protection Agency (EPA) is publishing this enforcement alert (Alert) because EPA has identified several high-performance ski wax consumer products that contained perfluorinated chemicals that were not reviewed by EPA for health risks under TSCA. These wax products are intended for use on sports equipment to enhance the performance of the equipment's slick surfaces that are in contact with snow.

- EPA is concerned that recently identified violations of the Toxic Substances Control Act (TSCA) may be putting skiers and wax applicators at risk for exposure to certain persistent and bioaccumulative chemicals.
- EPA advises sellers of ski wax to ensure that the products they sell do not contain certain perfluorinated chemicals that are not on the TSCA Chemical Substance Inventory (TSCA Inventory) or have prohibitions on their use in sporting goods.

Illegal PFAS Chemicals in Ski Waxes

EPA identified several manufacturers, importers and sellers that produced or sold ski wax products that included certain perfluorinated chemicals in violation of TSCA. TSCA prohibits the manufacture, processing or importation of a chemical that is not on the TSCA Inventory or otherwise exempt.

Per- and polyfluoroalkyl substances (PFAS) are a group of thousands of man-made chemicals that include perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). PFAS have been manufactured and used in a variety of industries around the globe, including in the United States, since the 1940s. Certain PFAS are persistent, bioaccumulative, and toxic, and remain in the body for long periods of time which may pose a health risk in extremely small quantities. The most-studied PFAS chemicals are PFOA and PFOS. Studies indicate that PFOA and PFOS can cause reproductive and developmental effects, impair liver and kidney functions, disrupt thyroid hormones (PFOS), impact the immune system in laboratory animals, and cause cancer tumors in animals (PFOA).

To protect the public from exposure to these and other chemicals, TSCA requires anyone who intends to manufacture (including import) a new chemical substance for a non-exempt commercial purpose to submit a pre-

Did you know?

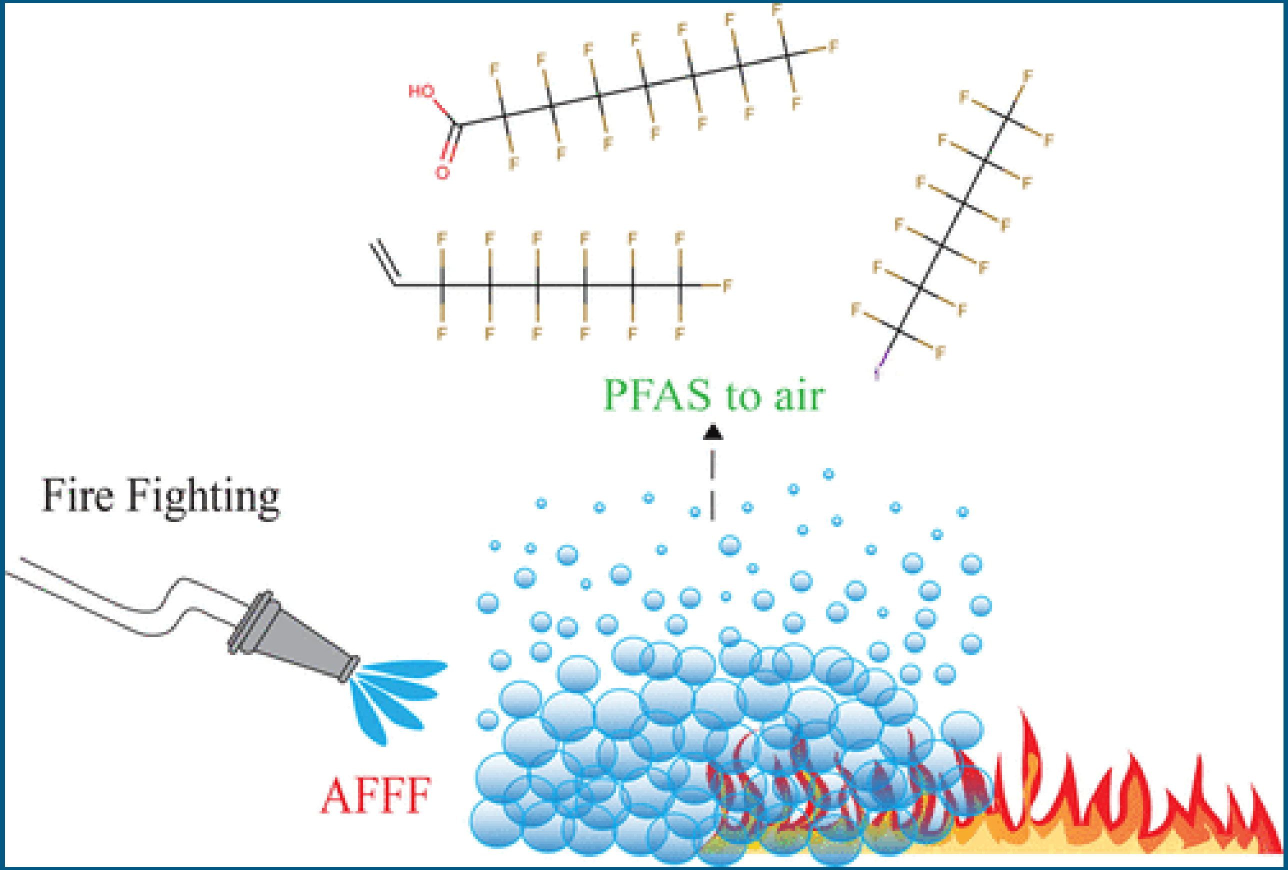
The U.S. Ski & Snowboard and the Canadian Ski Association have joined the International Ski Federation (FIS) and International Biathlon Union (IBU) in banning the use of fluorinated ski wax in competition from all disciplines in North America beginning with the 2020-21 ski and snowboard season. FIS has prohibited any products containing C8 fluorocarbons (including PFOA) at all FIS events from season 2021/2022 onwards.

Enforcement Alert Page 1

Enforcement Alert, USEPA, 2022

References: Nilsson et al., 2010; Freberg et al., 2010; Morales-McDevitt et al., 2021; Kissel et al., 2023

PFAS in Sources:
Headspace of Aqueous Film Forming Foam

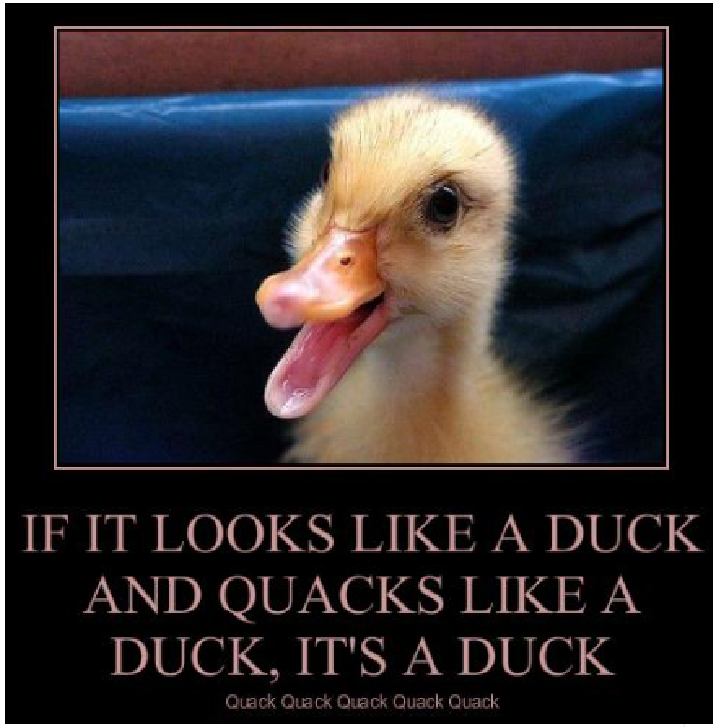


PFAS Detected in Headspace	
Group	**Concentration Range (µg/m3)**
Fluorotelomer alcohols (5)	0.5−38.1 µg/m3
Perfluorinated carboxylic acids (10)	0.4−13670 µg/m3
Fluorotelomer sulfonate (1)	72.1 µg/m3

Roth et al., 2020, Environmental Science & Technology Letters

Vapor Intrusion?

- Vapor-phase PFAS understudied, but growing evidence of presence in outdoor air, indoor air, and headspace
- Suggests potential for VI, though more confidence in evaluation if volatility is better understood
- Per USEPA's Vapor Intrusion Guidance 2015, chemical is "volatile" if:
  - (1) Vapor pressure is greater than 1 mm Hg ***or*** (2) Henry's Law constant is greater than 10^{-5} atm-m^3/mol.



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ISSUE	Limited availability of Henry's Law Constants for PFAS.

Agenda

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Compilation of Henry's Law Constants

- Measured Values
  - Abusallout et al. (2022)
- Modeled Values
  - Studies published 2006-2022

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Henry's Law constants of 15 per- and polyfluoroalkyl substances determined by static headspace analysis

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ABSTRACT

While it is thought that some per- and polyfluoroalkyl substances (PFAS) may volatilize from aqueous solutions, experimentally measured Henry's Law constants (k_H, synonymous with air : water partition coefficient) are scarce. This leads to a lack of understanding of the partitioning of PFAS and an inability to predict concentrations above contaminated groundwater (e.g., vapor intrusion). We measured k_H for 27 PFAS via headspace analysis and manipulations of the gas to liquid phase ratio. Fifteen PFAS produced mass spectrometry signals suitable for k_H measurements. At 25 °C the experimentally measured dimensionless k_H were: 0.31 – 2.82 for four fluorotelomer alcohols (FTOHs), 0.09 – 0.18 for three fluorotelomer sulfonates (FTSs), 0.30 – 1.01 for three iodinated PFAS, 0.43 – 0.92 for two sulfonamides, 3.86 for 6:2 fluorotelomer olefin, 0.69 for 8:2 fluorotelomer carboxylic acid, and 0.32 for 8:2 fluorotelomer acrylate. Longer fluoroalkyl chain length resulted in increased k_H for FTOHs and FTSs, the only two groups in which chain length was studied. Perfluorinated sulfonates and carboxylates were generally not volatile enough to be measured, even at pH as low as 1, although fluorotelomers of both functional groups were measurably volatile. Temperature effects were well described by the van't Hoff equation. k_H was not significantly different in various environmentally relevant matrices demonstrating the broad applicability of the produced constants.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are fluorinated organic chemicals that have unique chemical and mechanical attributes, including chemical and thermal stability. Thus, they have been used in a variety of industrial and commercial applications (Kissa, 2001). However, they are difficult to destroy, resulting in the nearly ubiquitous occurrence of PFAS across the globe, from the deep sea to arctic air (Yamashita et al., 2008; Shoeib et al., 2006), and human blood at microgram per liter concentrations (Worley et al., 2017; Hansen et al., 2001; Wang et al., 2018; Kwok et al., 2013; Munoz et al., 2017; Rahman et al., 2014; Xiao, 2017; Sinclair and Kannan, 2006). Exposure to PFAS has been shown to lead to adverse health outcomes in humans (Sunderland et al., 2019) and other ecological endpoints(Rericha et al., 2021), which is thought to be at least partially due to PFAS binding with serum albumin and proteins, causing interference with the binding of fatty acids and other endogenous ligands (Shi et al., 2012; Martin et al., 2003; Ahrens et al., 2009; Luebker et al., 2002).

A significant amount of research has focused on aqueous occurrence and transport of PFAS, but less is known about their release and occurrence to/in air. Among the published research focusing on gas-phase PFAS, indoor household air samples contained a total concentration of 3308 pg m^{-3} of four gas phase PFAS (Shoeib et al., 2011). In another study, the concentration of PFAS in indoor household air samples (gas and particle phase) was 100 times higher than that found in outdoor urban air samples (Shoeib et al., 2004). Certain professions are also at greater risk of gas-phase PFAS exposure. For example, PFAS are used in some ski waxes and 19 perfluorinated carboxylic acids (PFCAs) and sulfonates (PFSAs) were present in the serum of 13 professional ski tuners. Perfluorooctanoic acid (PFOA) was present at the greatest concentration in the tuners' blood and ranged between 50 and 80,000 ng mL^{-1} serum, potentially through the transformation of other PFAS in the air (Nilsson et al., 2010; Freberg et al., 2010). For example, the room air in which the employees worked contained 830 – 255,000 ng m^{-3} 8:2 fluorotelomer alcohol (FTOH) from the wax powder. Furthermore, our team recently published an investigation of PFAS present in the

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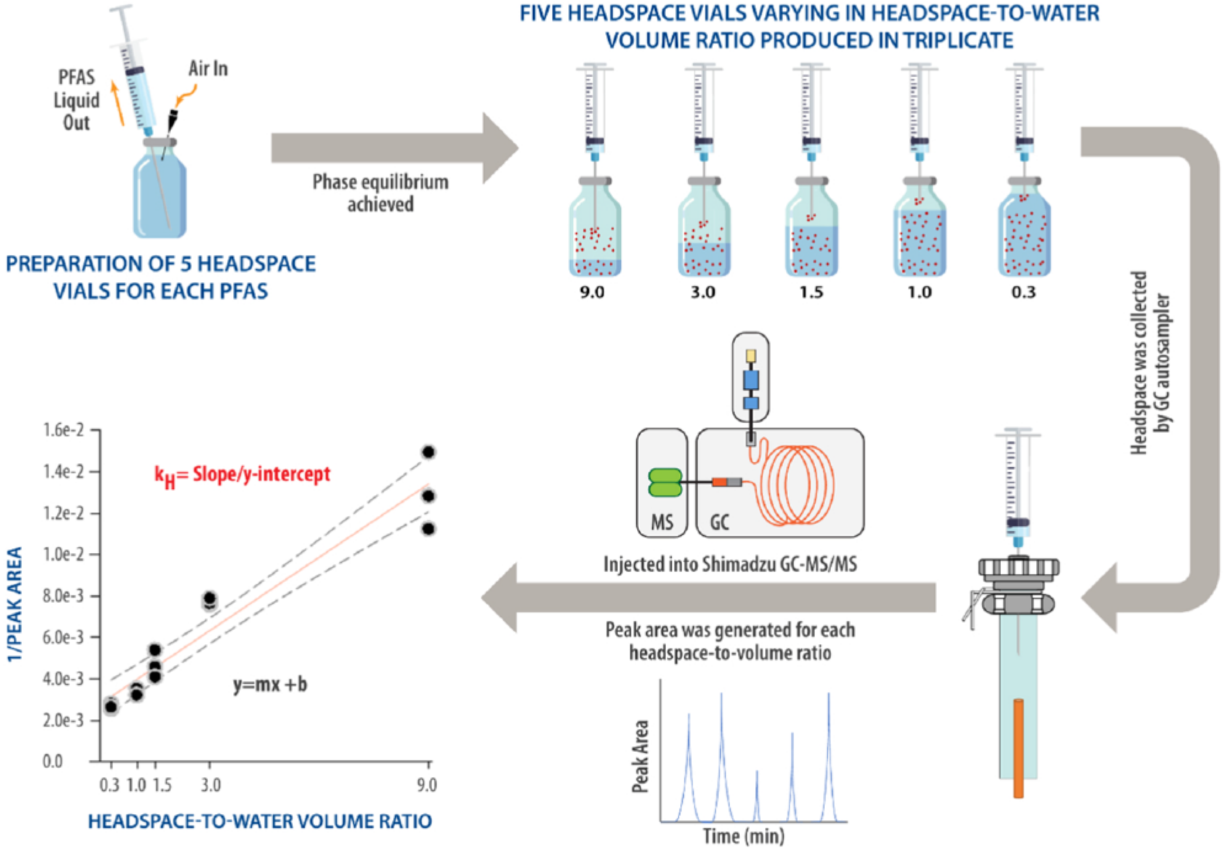
Measurement of Henry's Law Constants

- Selected **27 PFAS** based on potential volatility or prevalence in the subsurface
- Used validated test method for HLC determination
- Outcome:
  - Developed HLC for **15** compounds
  - **12** not volatile enough to measure



Adapted from Figure 1, Abusallout et al., 2022, Journal of Hazardous Materials Letters

Selected Results

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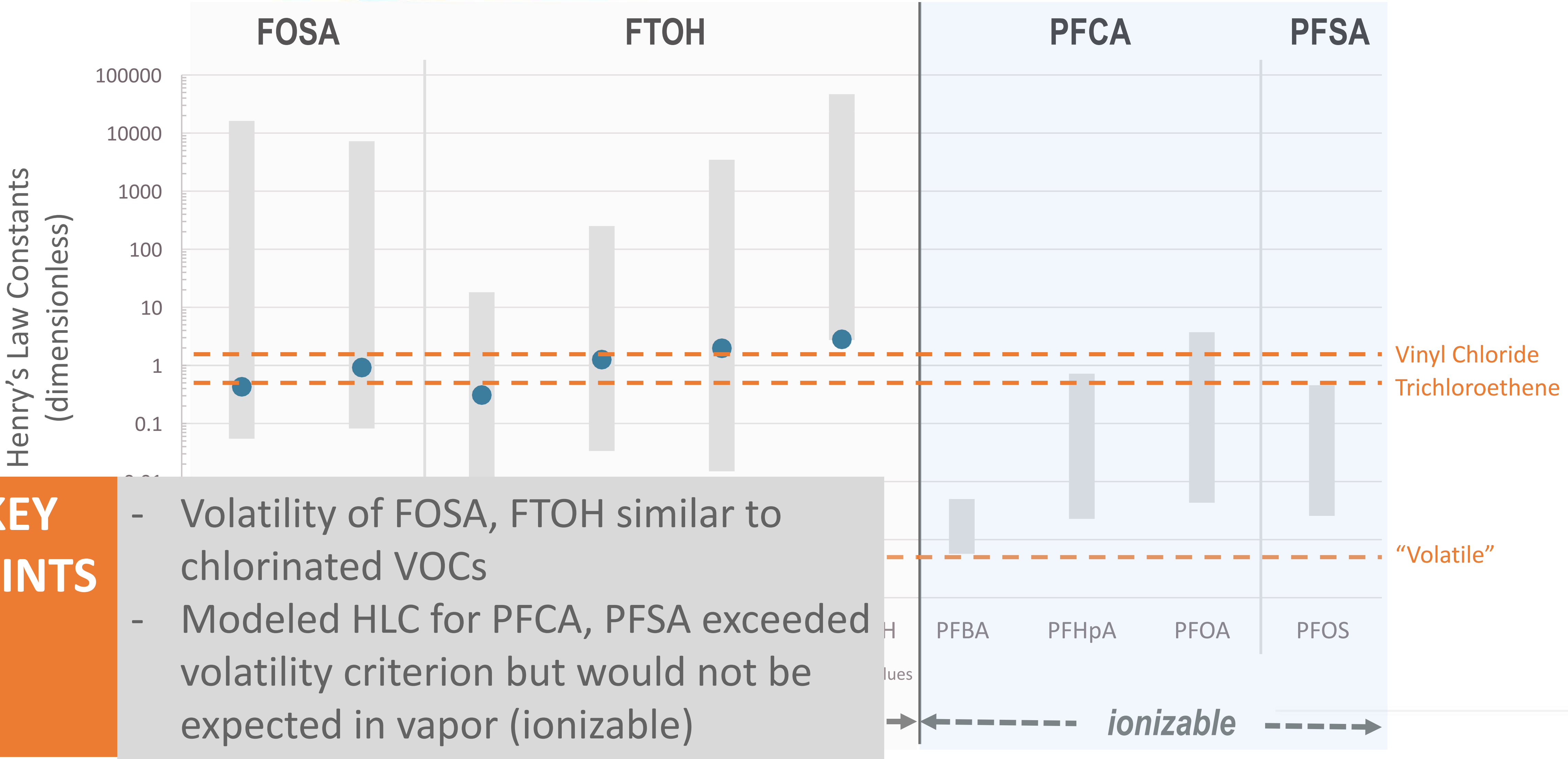
Group	PFAS Compound	HLC (dimensionless) (Abusallout et al. 2022)
Perfluorooctane sulfonamide (FOSA)	EtFOSA MeFOSA	0.43 0.92
Fluorotelomer Alcohols (FTOH)	4:2 FTOH 6:2 FTOH 8:2 FTOH 10:2 FTOH	0.31 1.26 1.98 2.82
Perfluorocarboxylic Acids (PFCAs)	PFBA PFHpA PFOA	NVE NVE NVE
Perfluorosulfonic Acids (PFSAs)	PFOS	NVE

KEY POINT

PFCAs and PFSAs generally not volatile enough to be measured.

Notes: 1) NVE = not volatile enough; 2) USEPA Henry's Law volatility threshold of 1x10-5 atm m^3 mol^{-1} = 0.00041 at 25C (dimensionless)

Measured and Modeled Henry's Law Constants



KEY POINTS

- Volatility of FOSA, FTOH similar to chlorinated VOCs
- Modeled HLC for PFCA, PFSA exceeded volatility criterion but would not be expected in vapor (ionizable)

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Vapor Intrusion Potential?

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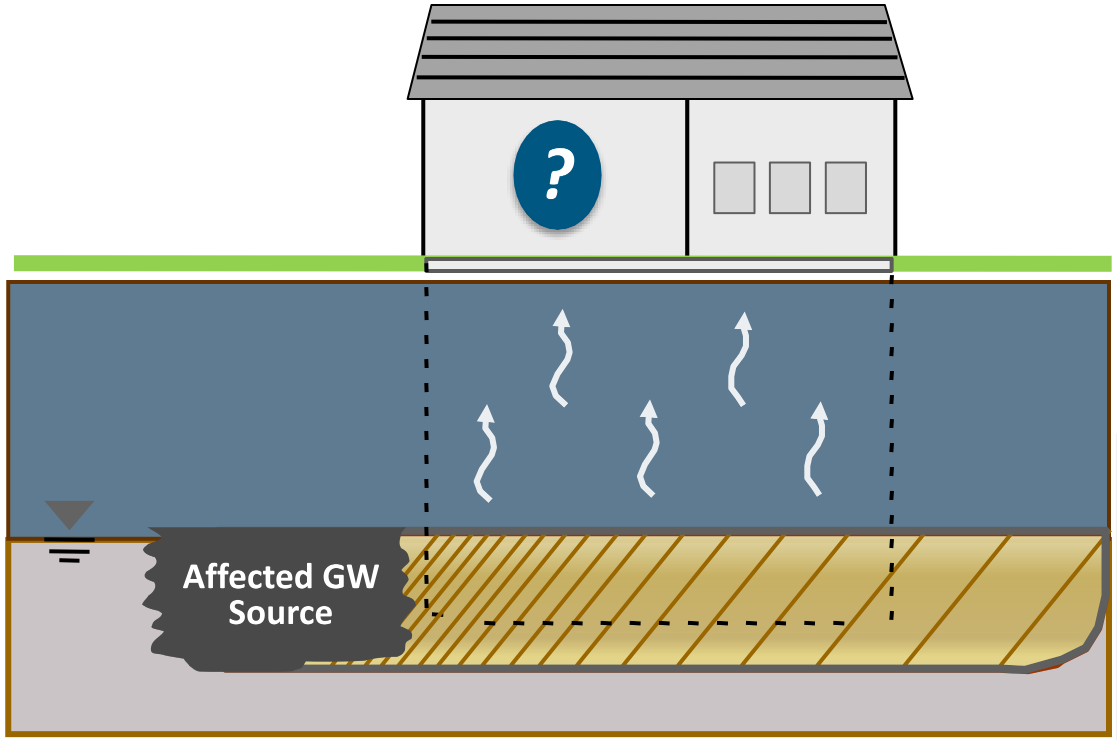
- All measured/modeled Henry's Law constants exceed USEPA "volatility criteria"
- Screening-level model of simulated AFFF release
  - 8:2 FTOH



8:2 FTOH Concentration in Indoor Air?

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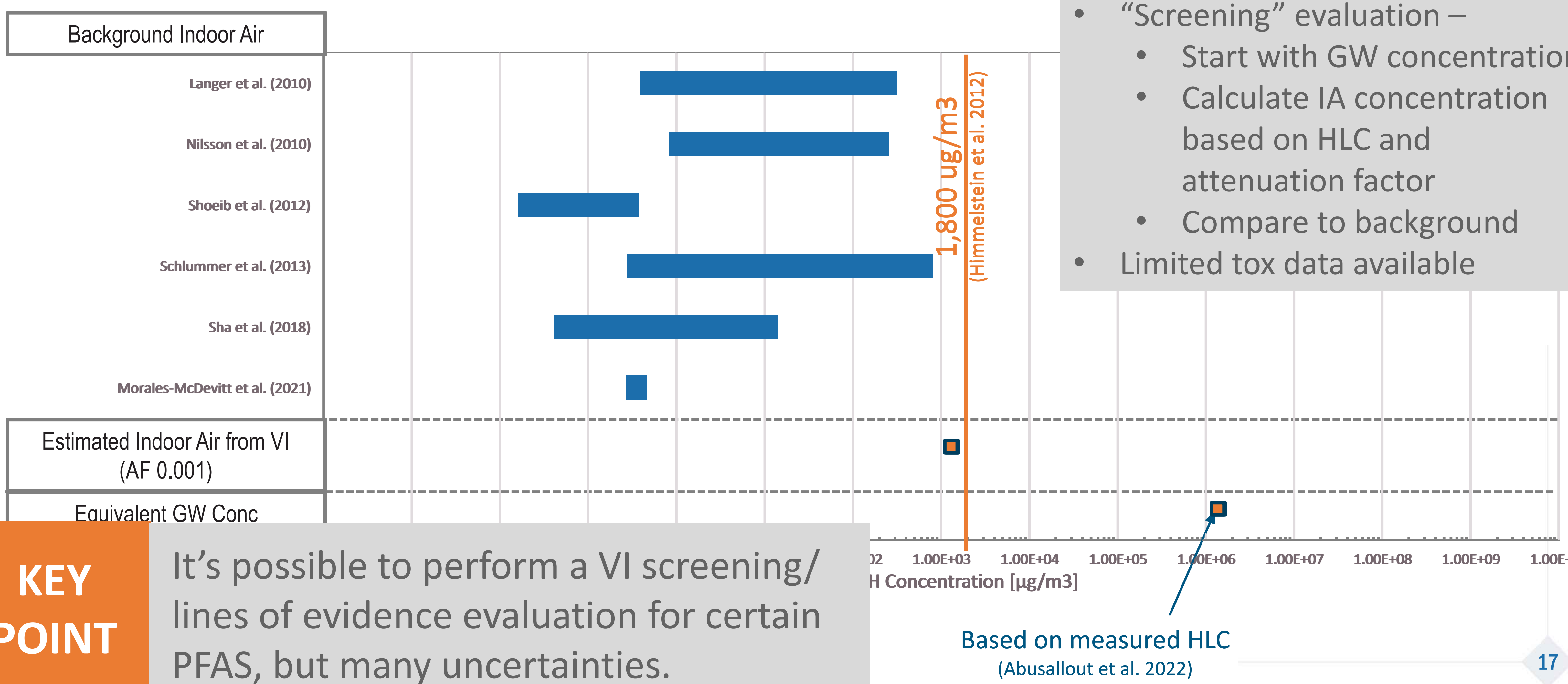

- "Screening" evaluation –
  - Start with GW concentration
  - Calculate IA concentration based on HLC and attenuation factor
  - Compare to background
- Limited tox data available

KEY POINT

It's possible to perform a VI screening/ lines of evidence evaluation for certain PFAS, but many uncertainties.

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Wrap-up

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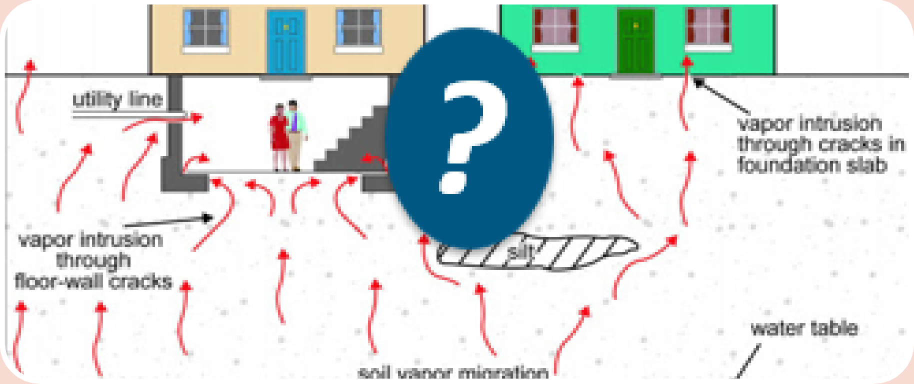

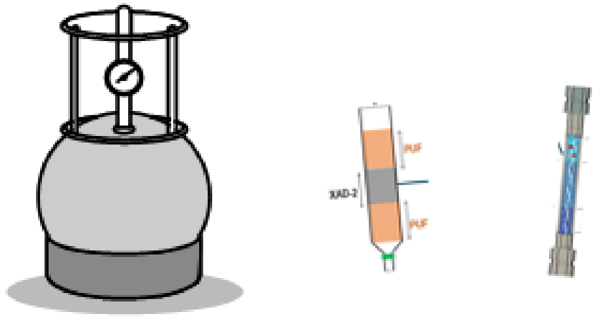

Are PFAS a VI Problem?

- Depends which PFAS
- Traditional volatility criteria and screening methods may apply for <u>some</u> PFAS, but not others
- Updated conceptual model needed

Challenges Ahead

- Availability & range of Henry’s Law Constants
- Limited inhalation tox data
- Analytical issues
- Analytical methods under development

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  - David Hanigan, Ph.D., P.E. (UNR)
  - Chase Holton, Ph.D., P.E. (GSI)
  - Ibrahim Abusallout, Ph.D. (Fraunhofer)
  - Junli Wang, Ph.D. (UC Riverside)
  - Seth McCoy (UNR)

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Award # 2128407

Thank You

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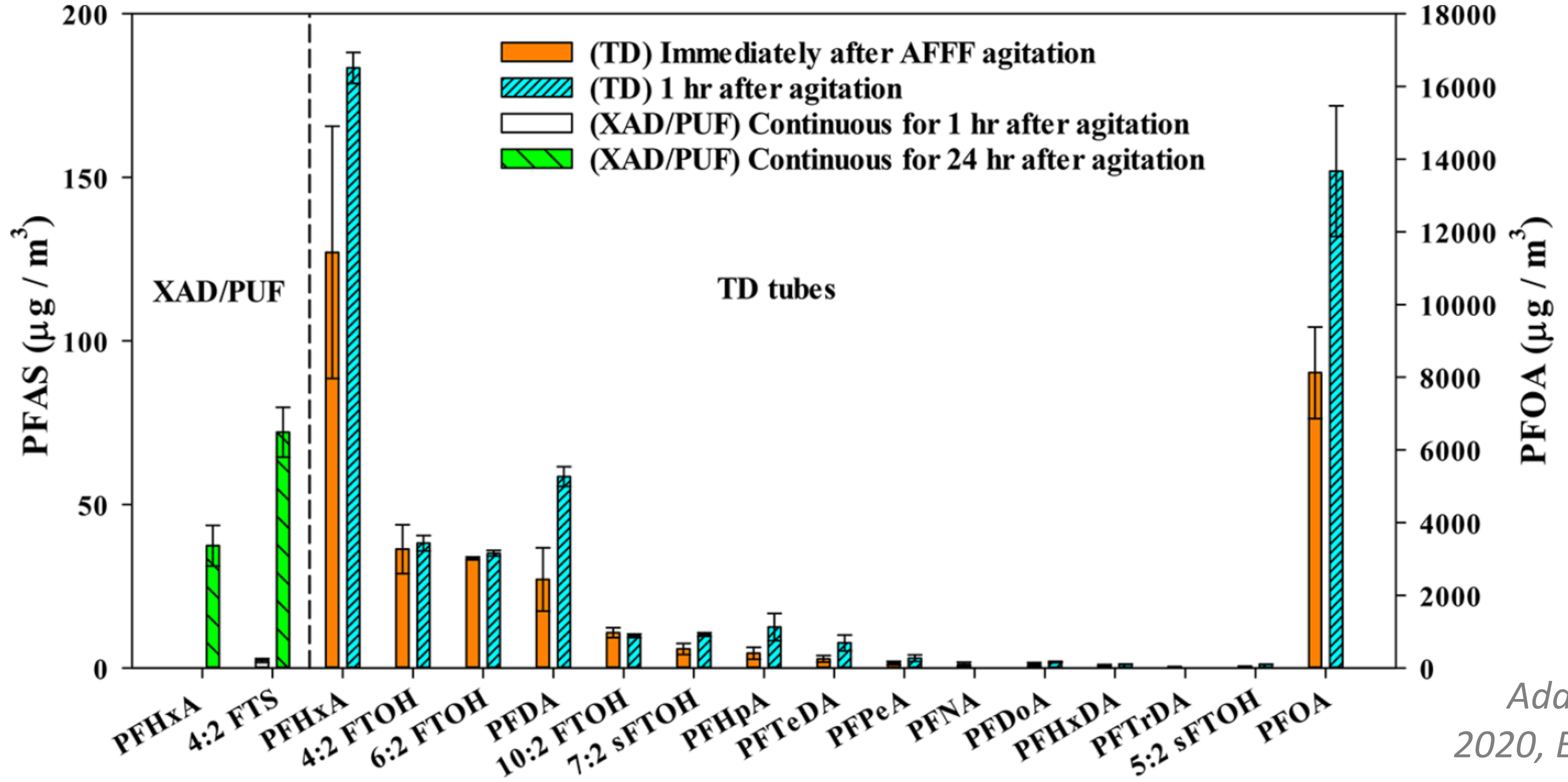
Extra Slides

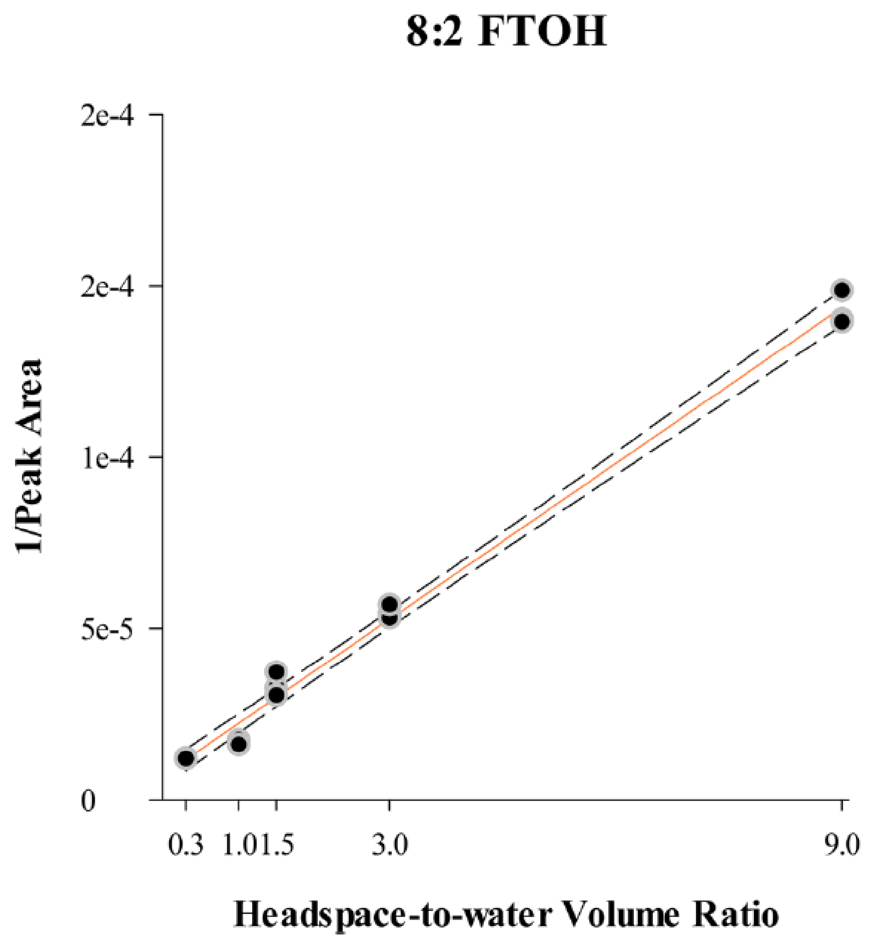
PFAS in AFFF Headspace



Adapted from Roth et al., 2020, Environmental Science & Technology Letters

KEY POINT Sixteen PFAS detected in AFFF headspace but unclear why PFCAs detected by GC/MS.

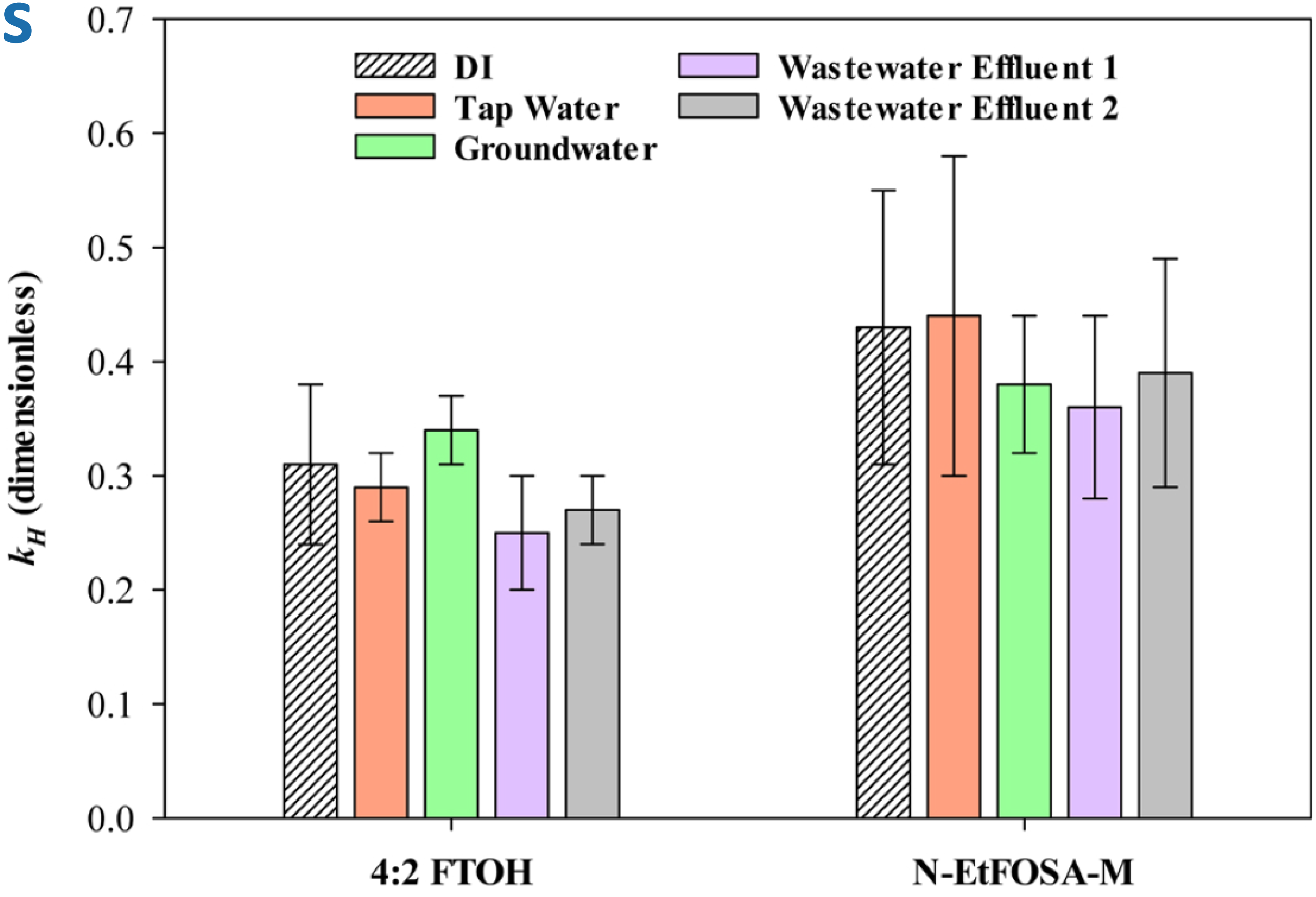
Results



PFAS	k_H	Slope	Intercept	R^2
4:2 FTOH	0.31 ± 0.07	2.77 ± 0.39 × 10^{-5}	8.91 ± 1.70 × 10^{-5}	0.920
6:2 FTOH	1.26 ± 0.40	5.18 ± 0.29 × 10^{-6}	4.12 ± 1.20 × 10^{-6}	0.986
8:2 FTOH*	1.98 ± 0.69	1.51 ± 0.06 × 10^{-5}	7.66 ± 2.60 × 10^{-6}	0.993
10:2 FTOH*	2.82 ± 1.12	6.92 ± 0.22 × 10^{-4}	2.45 ± 0.96 × 10^{-4}	0.995
4:2 FTS	0.09 ± 0.02	4.11 ± 0.88 × 10^{-4}	4.33 ± 0.38 × 10^{-3}	0.833
6:2 FTS	0.16 ± 0.01	2.37 ± 0.17 × 10^{-4}	1.48 ± 0.08 × 10^{-3}	0.976
8:2 FTS	0.18 ± 0.02	8.55 ± 0.65 × 10^{-5}	4.75 ± 0.28 × 10^{-4}	0.975

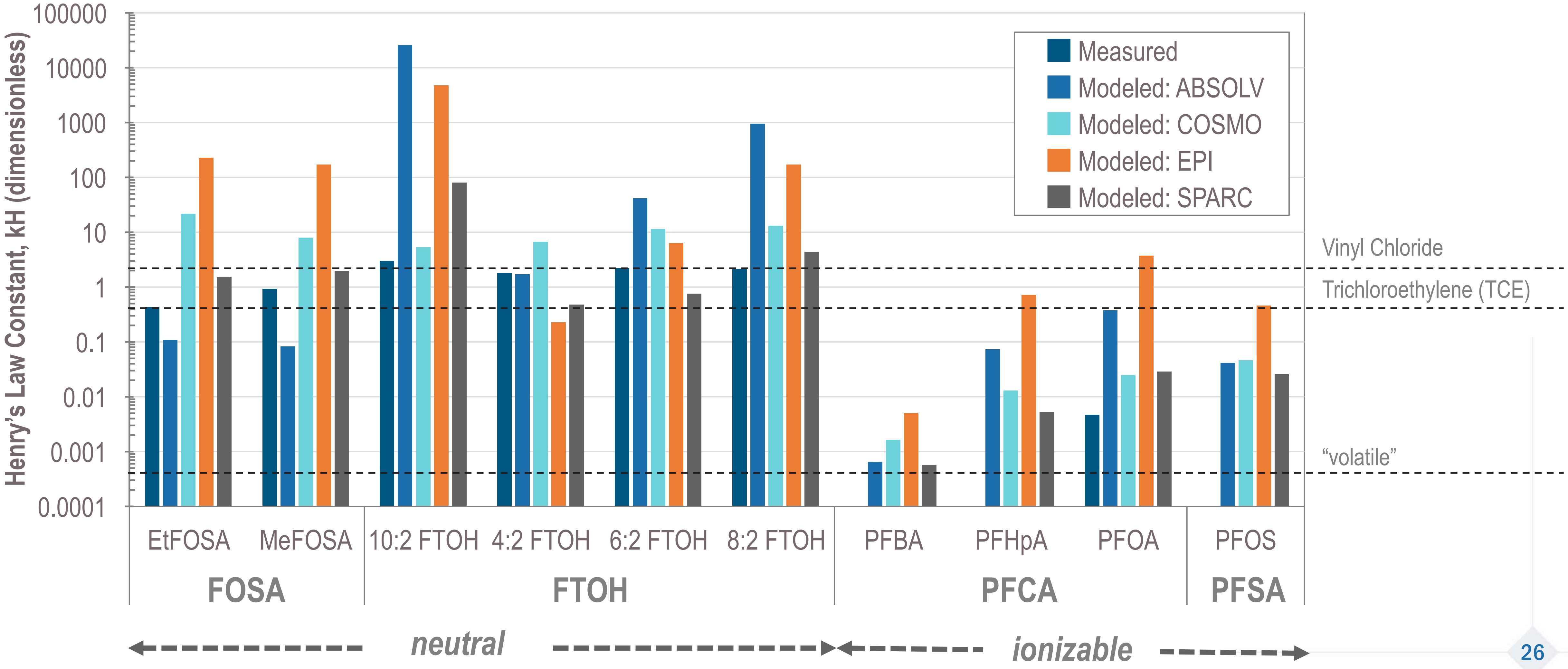
Adapted from Figure 2 and Table 1, Abusallout et al., 2022, Journal of Hazardous Materials Letters

Results



Adapted from Figure 3, Abusallout et al., 2022, Journal of Hazardous Materials Letters

Measured and Modeled Henry's Law Constants (Averages)



Measured values include multiple studies