Is Atmospheric Partitioning and Transport of PFAS a Global Issue?

Julia Roth | April 5, 2022


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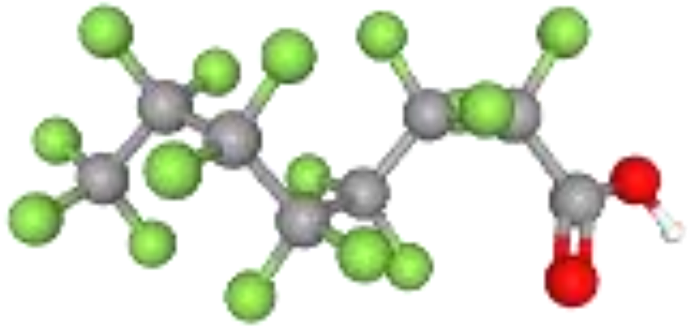
Presentation Summary

- PFAS Background and Sources
- PFAS Partitioning
- Global Case Study #1
- Global Case Study #2
- Global Case Study #3
- Conclusions

PFAS Background and Sources



Global Atmospheric Sources

Manufacturing

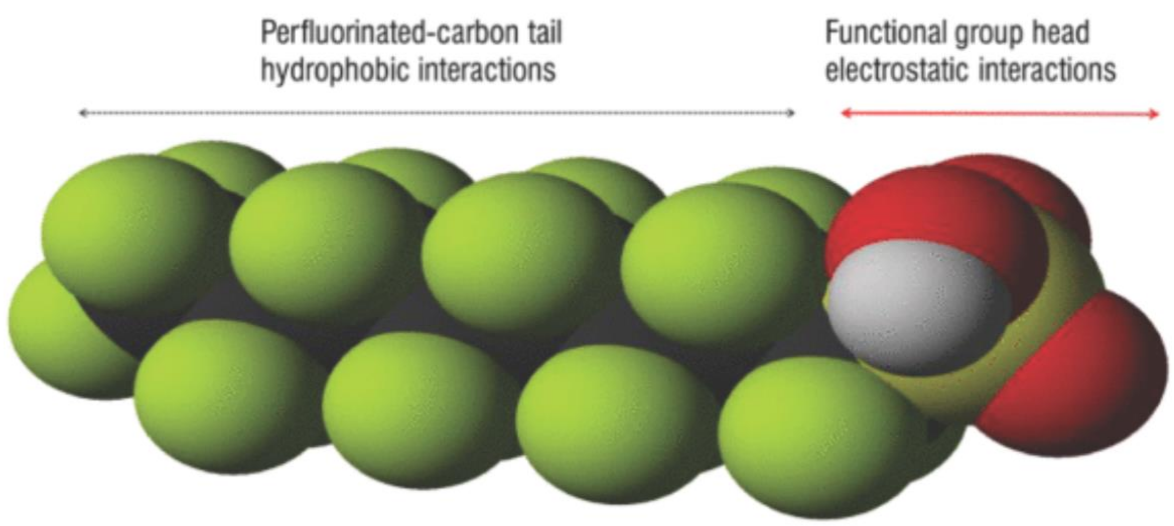
Wastewater Treatment Plants

Landfills

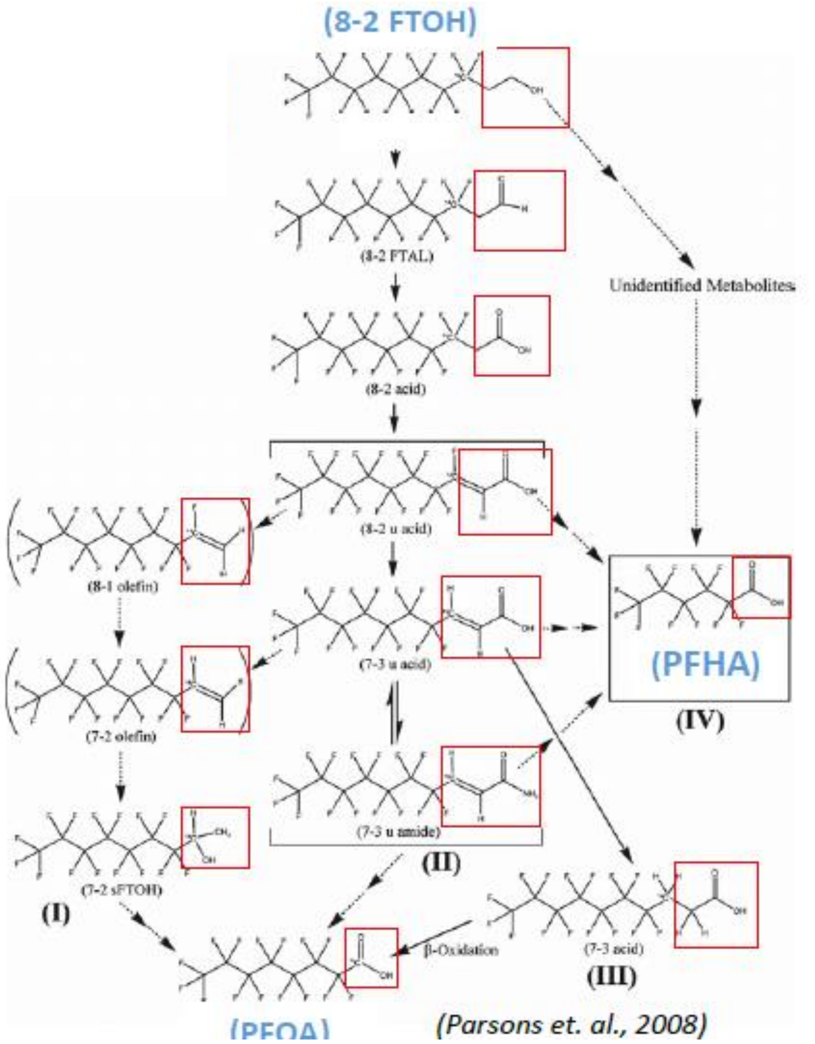
Incinerators

SGS

PFAS Structure

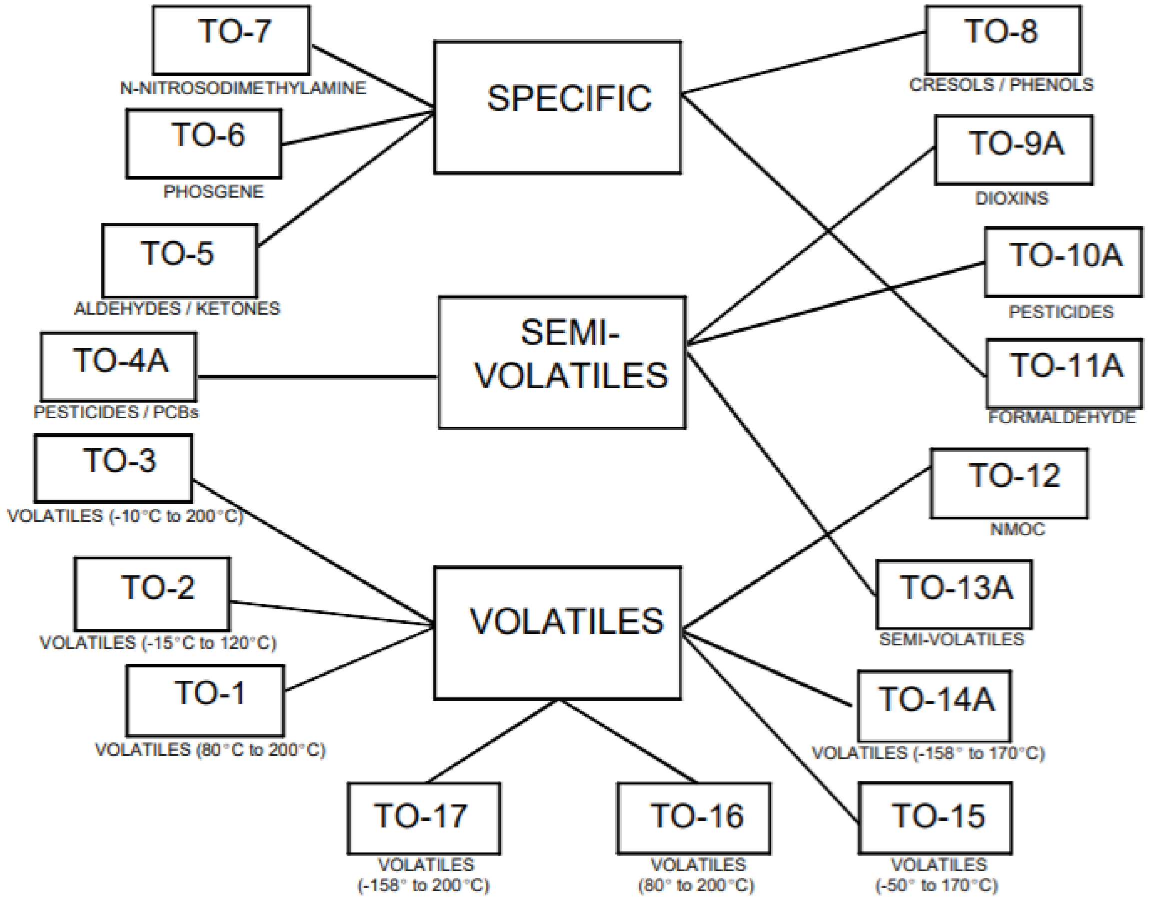


(National Academies of Sciences, Engineering, and Medicine, 2017)

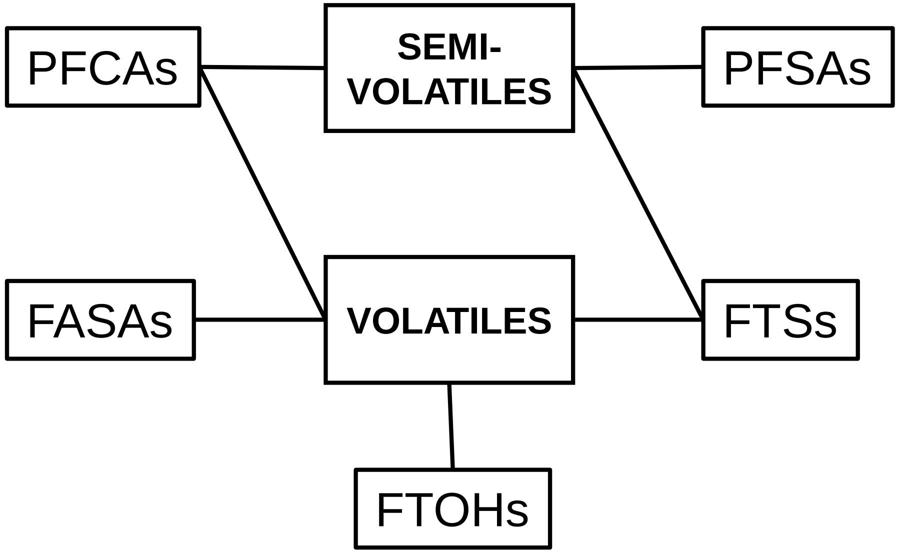


Key Takeaway	The functional group can suggest volatility. Chain length and structure also affect volatility.

Volatile vs Semi-Volatile



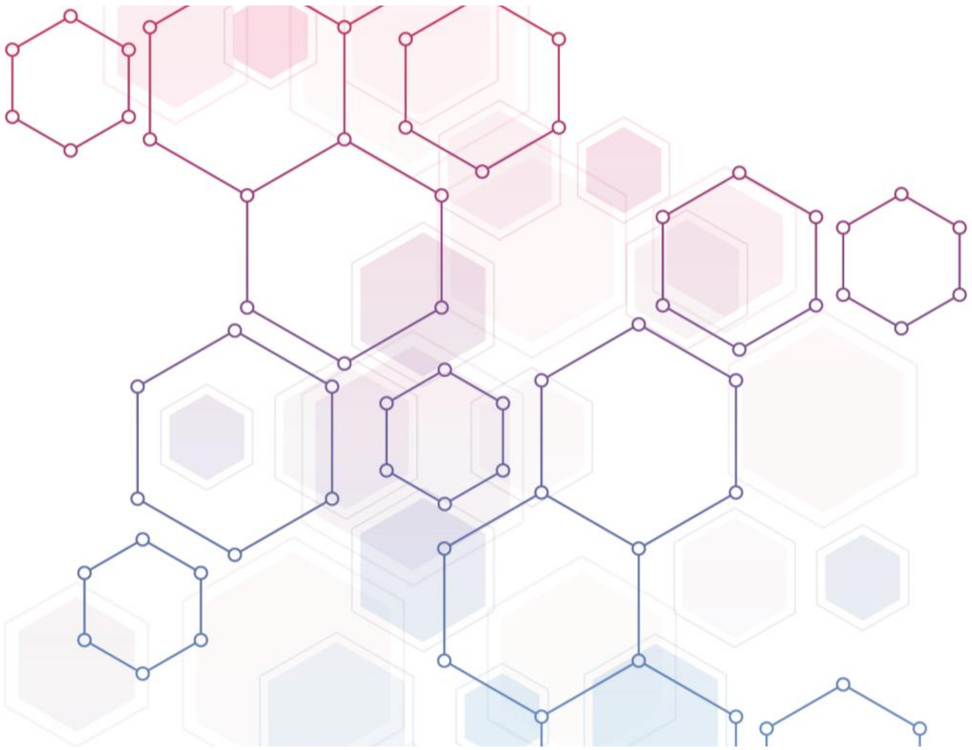
To Be Further Developed…



Key Takeaway

With thousands of PFAS compounds, there will likely need to be more than one analytical method to determine volatile and semi-volatile PFAS concentrations in air and samplers will vary based on application.

PFAS Partitioning



Volatility Criteria

Substance	Aqueous Solubility (g/L)	P_{vapor} (PA)	Henry's Law Constant (atm m^3 mol^{-1})
PFOS (K^+)	5.19 E-1	3.31 E-4	3.4 E-9
PFOA (H+)	9.5	7.0 E1	4.6 E-6
PFOA (NH4+)	>5.00 E2	<1.3 E-3/9.2 E-3	<1.1 E-11/7.8 E-11
N-EtFOSE	1.51 E-4	5.4 E-1	1.9 E-2
N-EtFOSEA	8.9 E-4	N.A.	--
6:2 FTOH	1.2-1.7 E-2	N.A.	1 E -2
8:2 FTOH	1.40 E-4	2.93	9.6 E-2

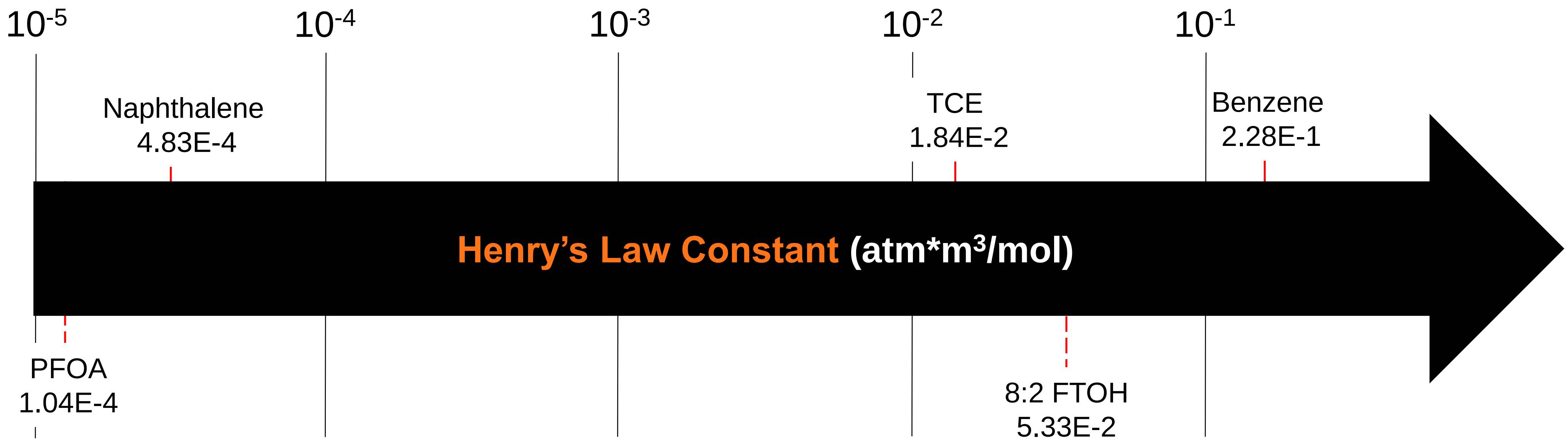
Meets USEPA's 2015 volatility criteria:

1. Henry's Law Constant $>10^{-5}$ atm*m^3/mol
2. P_{vapor} > 1 mm HG

Key Takeaway

Most models consider FTOHs and FOSEs/FOSAs volatile. Some theoretical calculations also suggest that some FTSs and PFCAs are volatile.

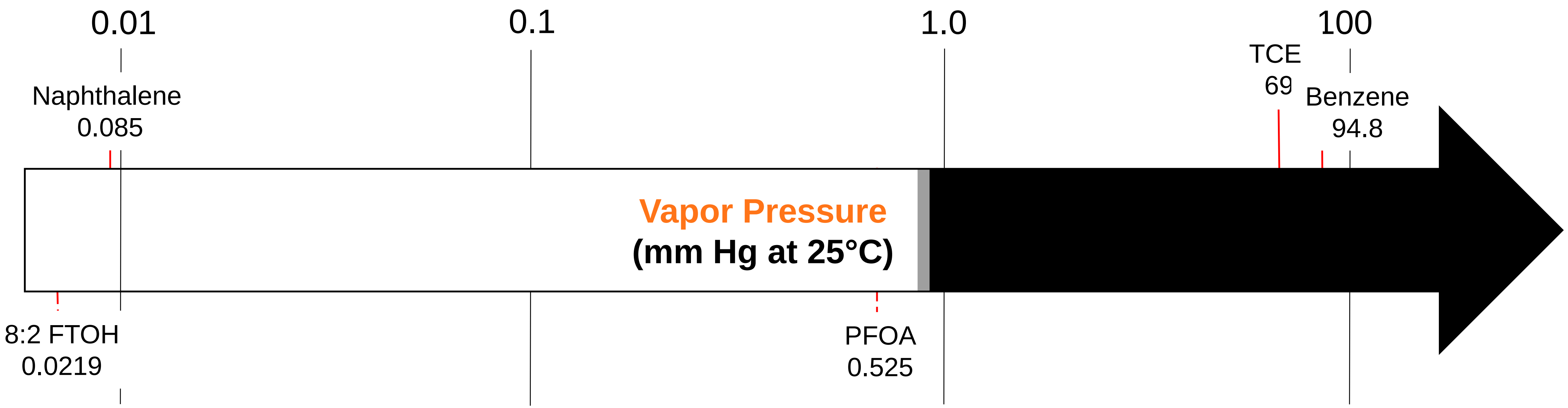
Henry’s Law Constants



Key Takeaway	Both theoretical and experimental Henry’s Law Constants vary greatly for PFAS and commonly documented constituents like TCE. Values for PFOA and 8:2 FTOH have been averaged in the figure above.

Citations Used in Figure:
Naphthalene, TCE, and Benzene Henry’s Law Constants: https://www.nj.gov/dep/srp/guidance/rs/chemproperties.pdf
Measured Henry’s Law Constant for 8:2 FTOH (Average of Wu and Chang, 2011; Lei et all, 2004): http://satellite.mpic.de/henry/casrn/678-39-7
Measured Henry’s Law Constant for PFOA (Average of Kutsuna and Hori, 2008; Li et all, 2006): http://satellite.mpic.de/henry/casrn/335-67-1

Vapor Pressures



Key Takeaway

Theoretical and experimental values vary based on the study/model. Field data is key to better understanding these compounds.

Citations Used in Figure:
Naphthalene Vapor Pressure (*Ambrose D et al; J Chem Soc Trans 71: 35-41 (1975))*: https://pubchem.ncbi.nlm.nih.gov/compound/Naphthalene#section=Vapor-Pressure
TCE Vapor Pressure
(*Boublik, T., Fried, V., and Hala, E., The Vapour Pressures of Pure Substances. Second Revised Edition. Amsterdam: Elsevier, 1984., p. 87):https://pubchem.ncbi.nlm.nih.gov/compound/Trichloroethylene#section=Vapor-Pressure*
Benzene Vapor Pressure:
*(Daubert, T.E., R.P. Danner. Physical and Thermodynamic Properties of Pure Chemicals Data Compilation. Washington, D.C.: Taylor and Francis, 1989., p. 361):*https://pubchem.ncbi.nlm.nih.gov/compound/241#section=Vapor-Pressure
Measured for PFOA (Hekster et al. (2003); HSDB (2012); SRC (2016) ATSDR (2015); Kaiser et al. (2005): https://clu-in.org/contaminantfocus/default.focus/sec/Per-_and_Polyfluoroalkyl_Substances_(PFASs)/cat/Chemistry_and_Behavior/p/2

Global Case Study #1

Distribution of perfluoroalkyl compounds and mercury in fish liver from high-mountain lakes in France originating from atmospheric deposition

Ahrens et al., 2010

Background – Ahrens et al., Study

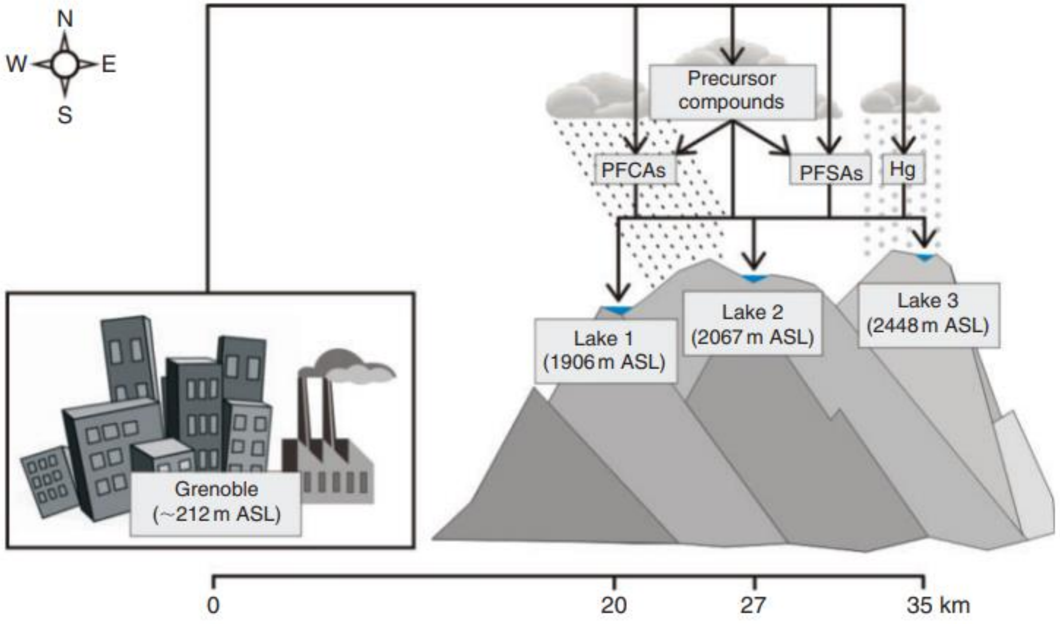


Figure 3 (Ahrens et al., 2010)

PFC Source:
Manufacturing in Grenoble France

Altitudes Converted:
- Grenoble: 696 ft above sea level
- Lake 1: 6253 ft above sea level
- Lake 2: 6781 ft above sea level
- Lake 3: 8031 ft above sea level

Distances Converted:
- Lake 1: 12.4 miles
- Lake 2: 16.7 miles
- Lake 3: 21.7 miles

Results 1 – Ahrens et al., Study

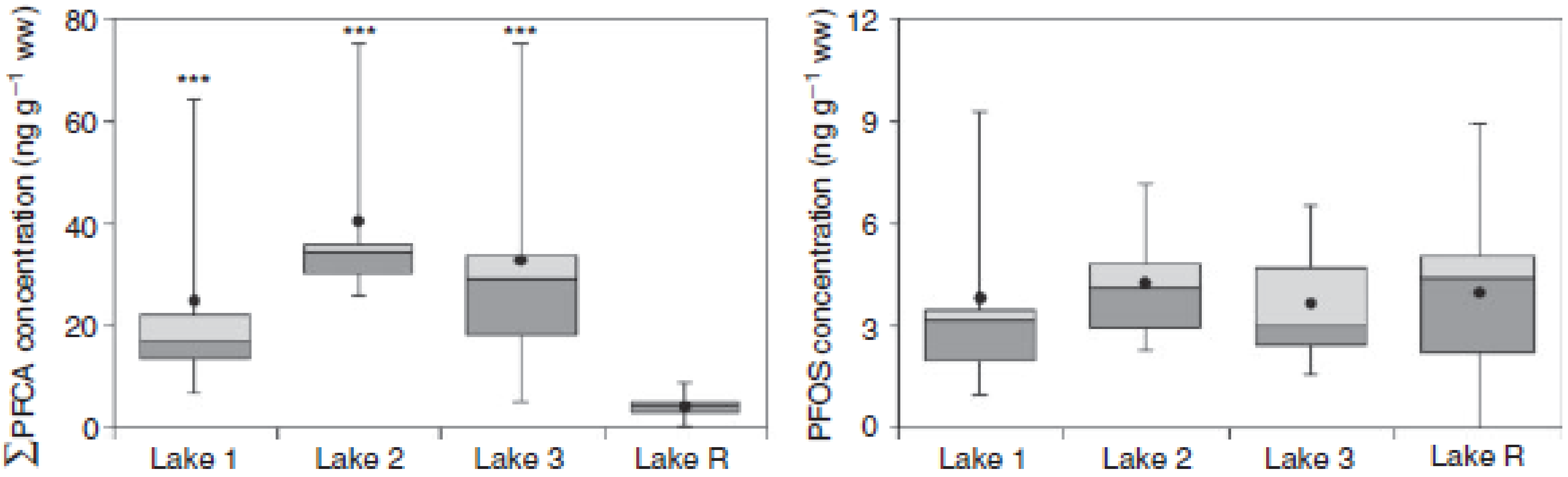


Figure 1 (Ahrens et al., 2010)

Key Takeaway	Total PFCAs were higher than the reference lake. PFOS was found at a lower concentration than PFCAs and were similar concentrations to the reference lake.

Results – Ahrens et al., Study

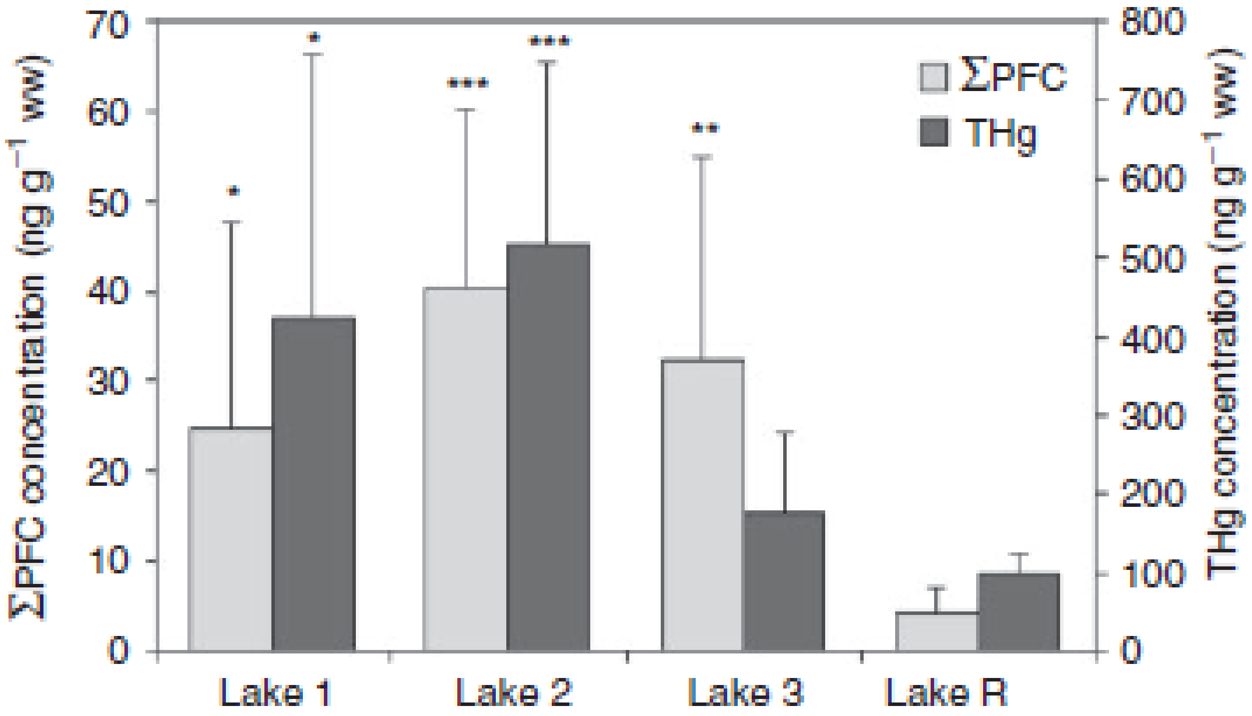


Figure 2 (Ahrens et al., 2010)

Key Takeaway

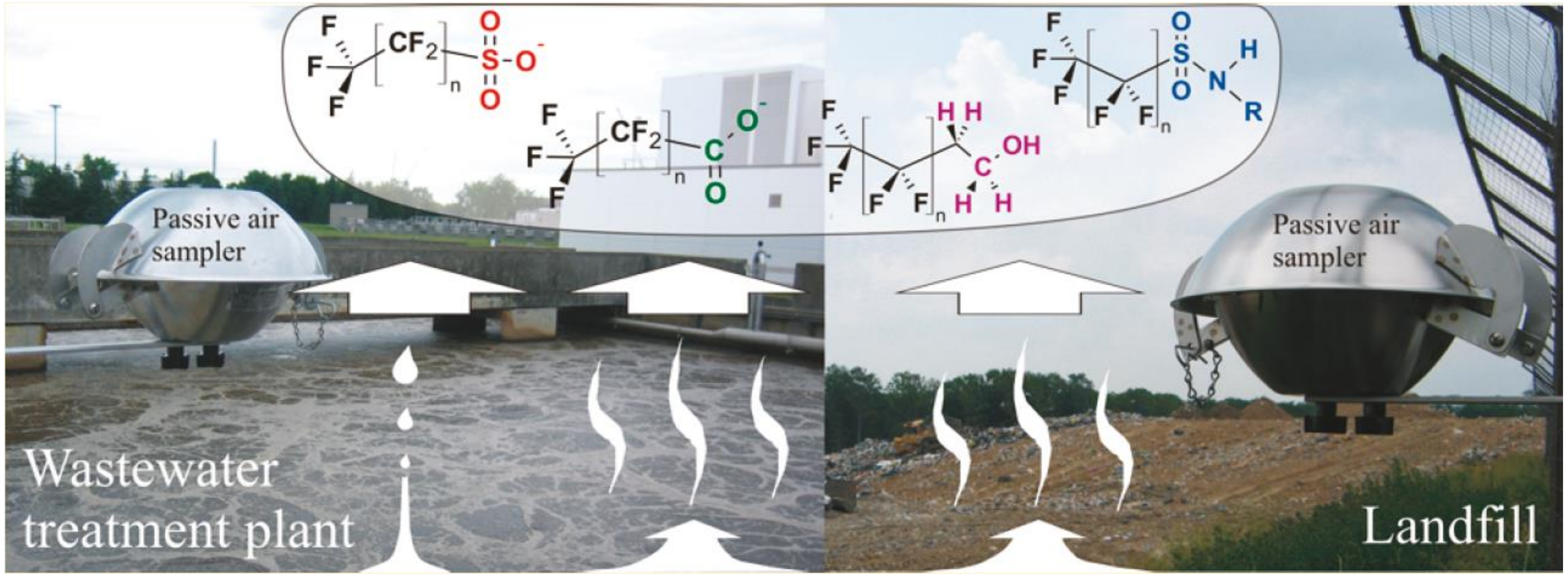
Total PFCs (PFOS and PFCAs) and were detected at higher levels in Lakes 1-3 compared to the reference lake suggesting atmospheric deposition and bioaccumulation in the fish liver.

Global Case Study #2

Wastewater Treatment Plant and Landfills as Sources of Polyfluoroalkyl Compounds to the Atmosphere

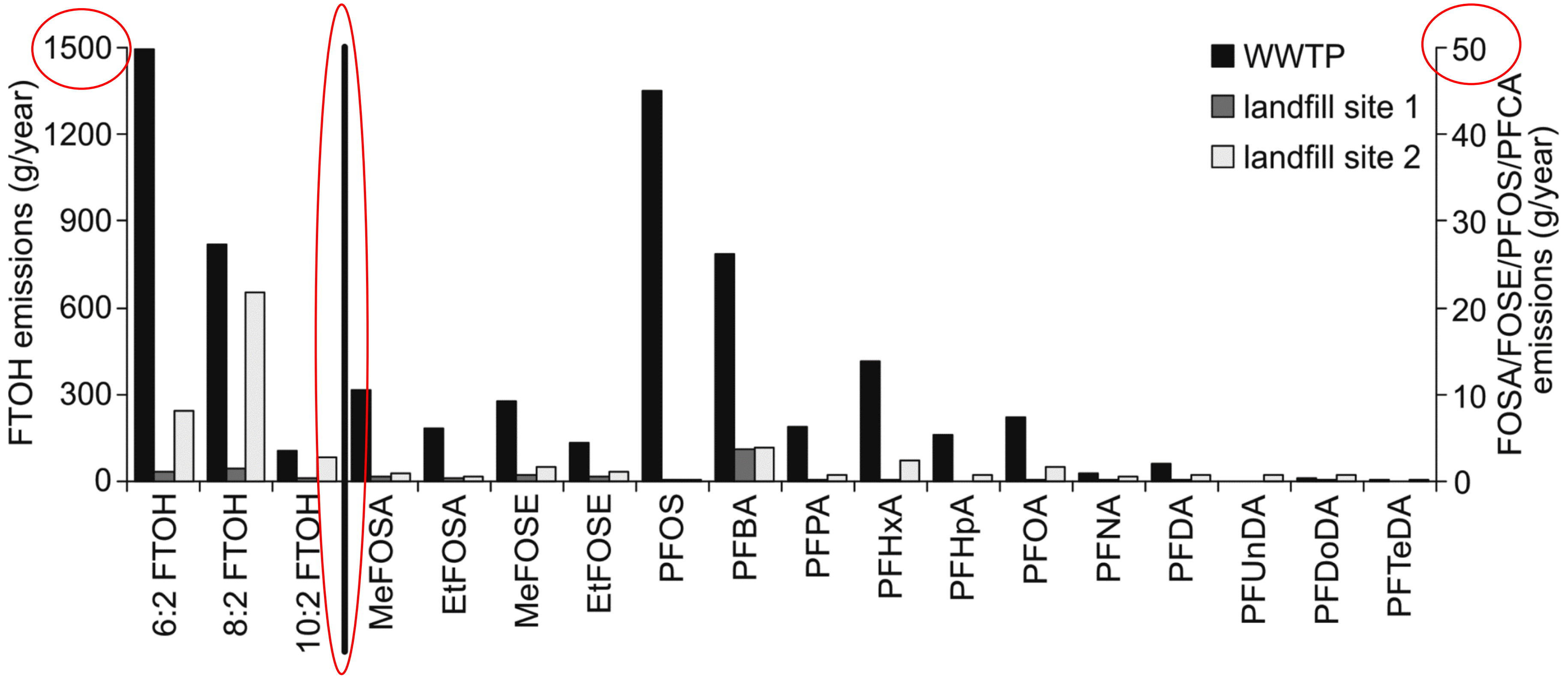
Ahrens et al., 2011

Background - Ahrens et al., 2011



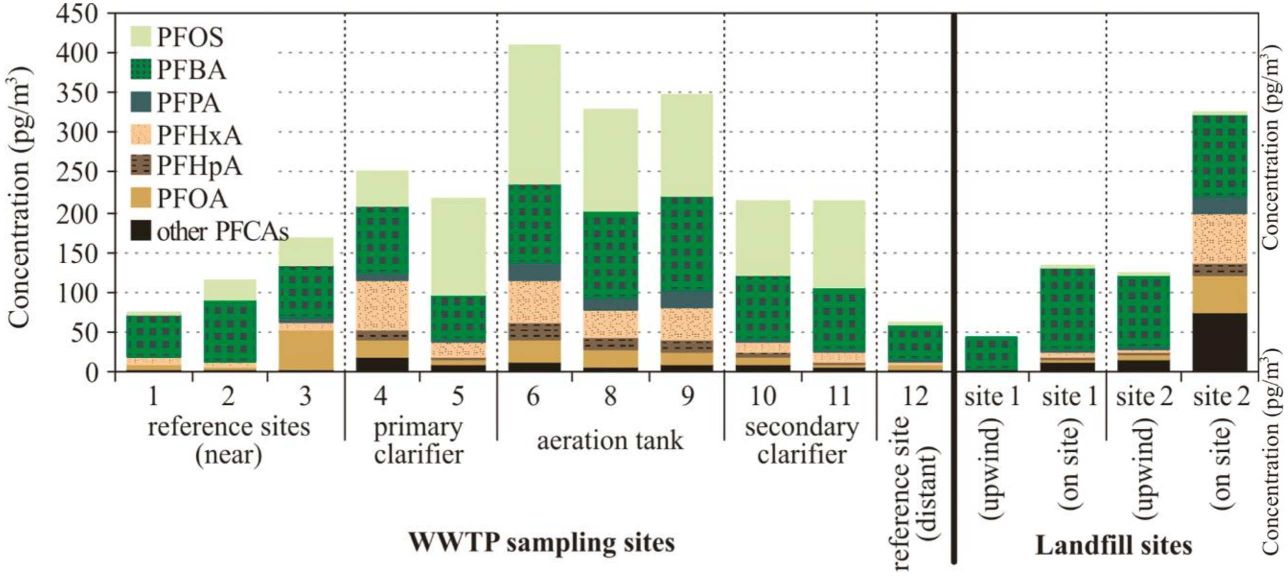
- 5 PFAS Subgroups Analyzed: FTOHs, FOSAs, FOSEs, PFCAs, and PFSAs
- Wastewater and landfill sites were compared to a reference site
  - The landfill sites had 5-30 times greater concentrations

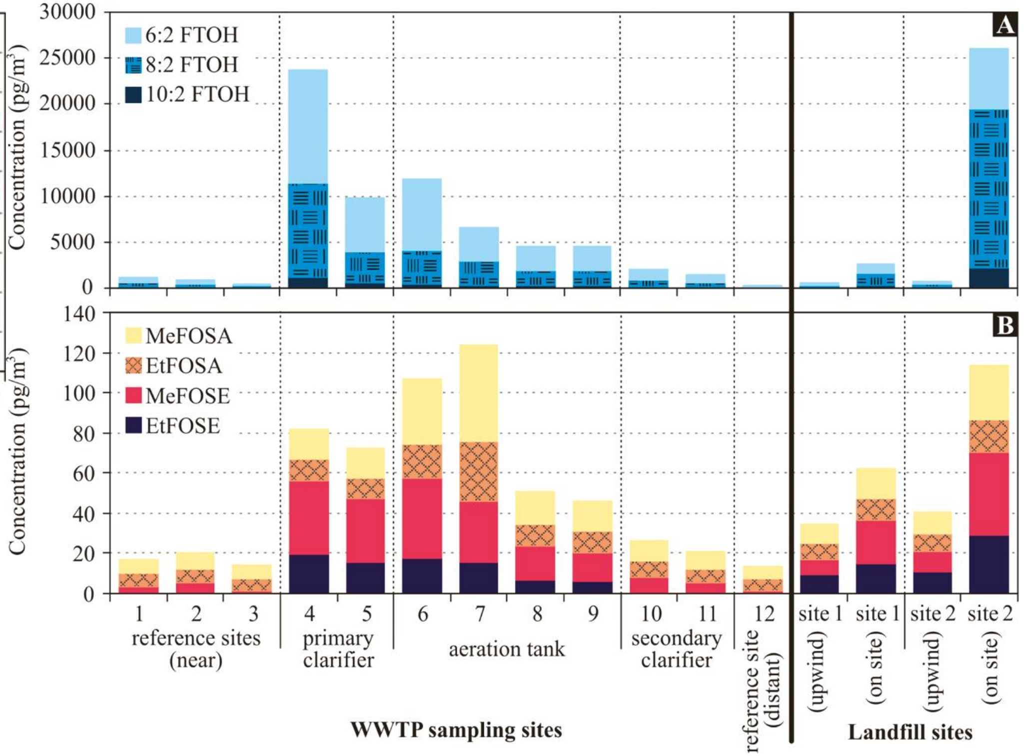
Results 1 - Ahrens et al., 2011



- Drastic differences in concentrations from 2 landfill sites with the same sampling and analysis
- Temperature, humidity, elevation, composition, and landfill gas treatment can affect PFAS concentrations in air, leading to large concentration differences between sites

Results 2 - Ahrens et al., 2011





- Of target PFAS, fluorotelomer alcohols 2 orders of magnitude higher than other PFAS subgroups evaluated
- FTOHs are volatile so this could have inhalation and atmospheric deposition implications

Global Case Study #3

Perfluorinated Chemicals in the Arctic Atmosphere

Shoeib et al., 2006

Background - Shoeib et al, 2006

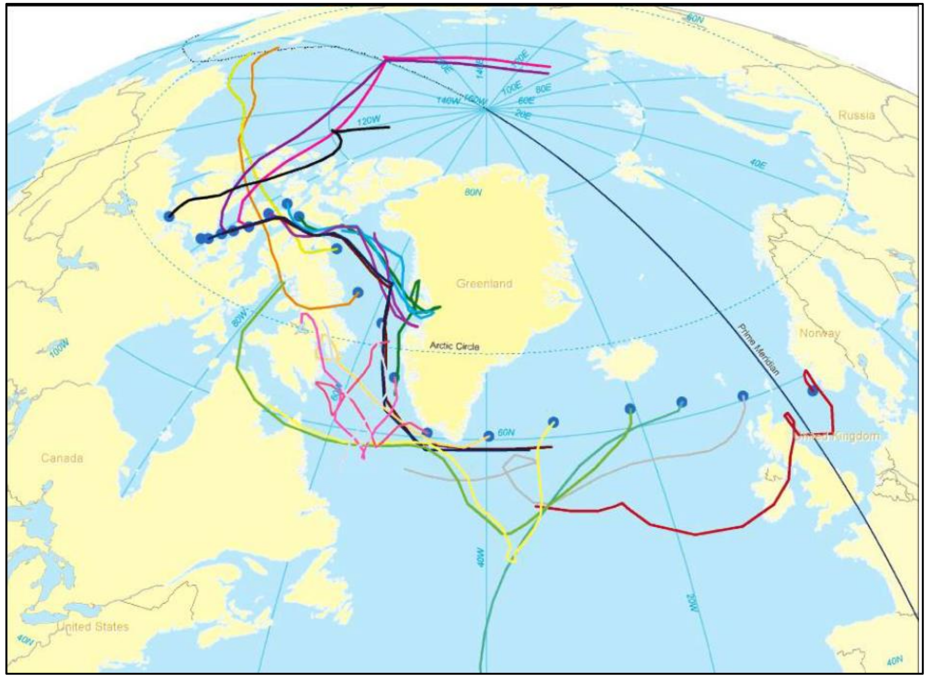


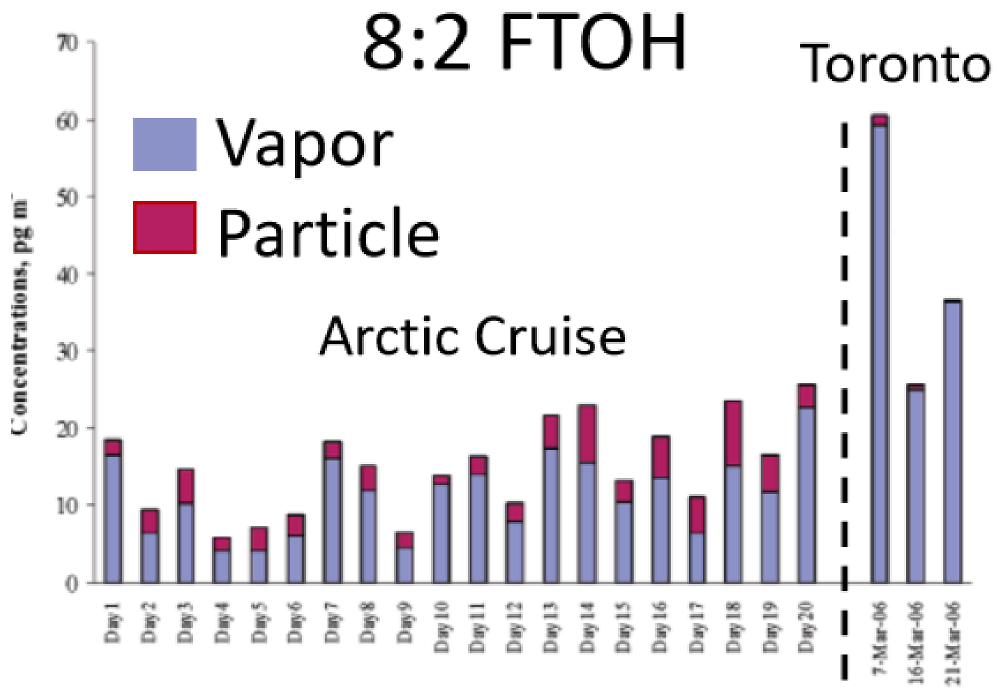
Figure 1 (Shoeib et al., 2006)

- Twenty high volume arctic PFAS samples were collected
- Analysis focused on precursors believed to degrade into PFCAs and PFOS
- Arctic results were compared to urban results collected from Toronto to evaluate long-range transport

Results - Shoeib et al, 2006

		6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSE	EtFOSE
Arctic Gas Phase Air Concentration	Arithmetic Means (pg/m3)	2.65	11.4	6.57	8.3	1.87
Arctic Particle Phase Air Concentration	Arithmetic Means (pg/m3)	BDL	3.5	0.8	3.53	1.05
Toronto Gas Phase Air Concentration	Arithmetic Means (pg/m3)	17.7	40.2	21.2	8	2.33
Toronto Particle Phase Air Concentration	Arithmetic Means (pg/m3)	0.31	0.71	1.09	4.2	0.96
Arctic Particle Phase	Percentage	BDL	23%	15%	32%	22%
Toronto Particle Phase	Percentage	BDL	2% ± 1%	5% ± 3%	30% ± 16%	30% ± 16%

Notes:
1) BDL = Below Detection Levels
2)MeFOSEA was analyzed for, but below detection levels



(Shoeib et al., 2006)

Key Takeaway	FTOH and FOSE/FOSA concentrations are present in ambient air samples and were predominantly measured in the gas phase, not sorbed to particles. These results support model predictions of efficient, long-range atmospheric transport and widespread distribution.

Conclusions

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- PFAS Precursor samples indicate long range transport and wide spread distribution in the atmosphere making atmospheric PFAS a global issue
- Transformation of precursors and deposition has been demonstrated
- Long chain PFAS (mainly PFOS and PFOA) have largely been phased out in the US, however, imports still frequently contain long chain PFAS
- While PFOA and PFOS concentrations can be found in American's blood in the ppb range, there has been a reduction in concentrations that corresponds with these chemicals being phased out between 1999 and 2014
  - 70% reduction for PFOA and 84% for PFOS
- More research is needed on short chain PFAS and fluorinated PFAS replacements

References

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1. Slide 5 Image: https://pubchem.ncbi.nlm.nih.gov/compound/Perfluorooctanoic-acid
2. Slide 6, Image 1: *National Academies of Sciences, Engineering, and Medicine, 2017*
3. Slide 6, Image 2: Parsons et. al, 2008
4. Slide 7 Image: *https://www.epa.gov/sites/default/files/2019-11/documents/tocomp99.pdf*
5. *Slide 10-11,* Naphthalene, TCE, and Benzene Henry's Law Constants: https://www.nj.gov/dep/srp/guidance/rs/chemproperties.pdf
6. Slide 10, Measured Henry's Law Constant for 8:2 FTOH (Average of Wu and Chang, 2011; Lei et all, 2004): http://satellite.mpic.de/henry/casrn/678-39-7
7. Slide 10, Measured Henry's Law Constant for PFOA (Average of Kutsuna and Hori, 2008; Li et all, 2006): http://satellite.mpic.de/henry/casrn/335-67-1
8. Slide 11, Naphthalene Vapor Pressure (*Ambrose D et al; J Chem Soc Trans 71: 35-41 (1975))*: https://pubchem.ncbi.nlm.nih.gov/compound/Naphthalene#section=Vapor-Pressure
9. Slide 11, TCE Vapor Pressure (*Boublik, T., Fried, V., and Hala, E., The Vapour Pressures of Pure Substances. Second Revised Edition. Amsterdam: Elsevier, 1984., p. 87):https://pubchem.ncbi.nlm.nih.gov/compound/Trichloroethylene#section=Vapor-Pressure*
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11. Slides 12-15: "Shoeib et al. - 2006 - Perfluorinated Chemicals in the Arctic Atmosphere.Pdf," 2006.
12. Slides 16-19: Lutz Ahrens et al., "Wastewater Treatment Plant and Landfills as Sources of Polyfluoroalkyl Compounds to the Atmosphere," Environmental Science & Technology 45, no. 19 (October 1, 2011): 8098–8105, accessed January 8, 2020, https://doi.org/10.1021/es1036173.
13. Slide 20-22: M. Shoeib, T. Harner, and P. Vlahos, "Perfluorinated Chemicals in the Arctic Atmosphere," Environmental Science & Technology 40, no. 24 (December 1, 2006): 7577–7583, accessed March 18, 2019, https://doi.org/10.1021/es0618999.