US EPA Advances in PFAS Air Science

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US EPA Office of Research and Development

Association of Air Pollution Control Agencies
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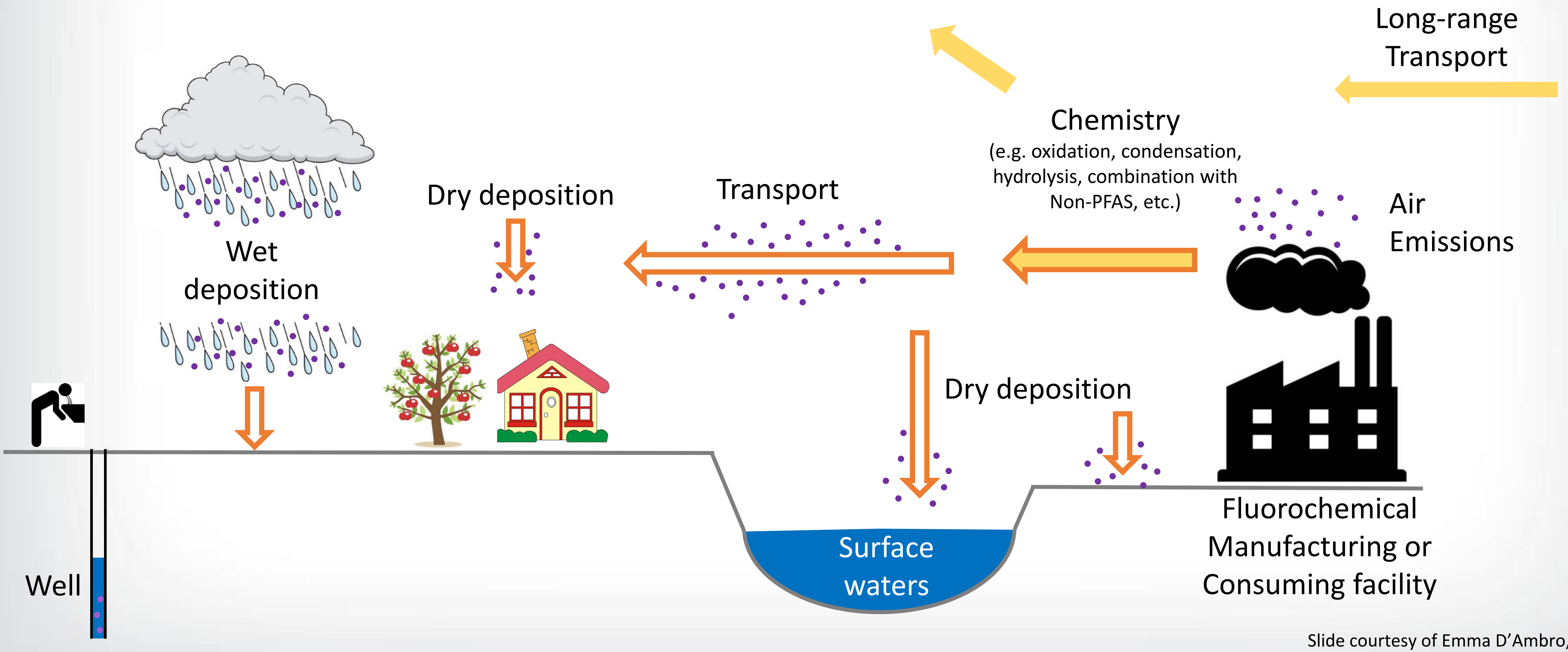
PFAS in Air

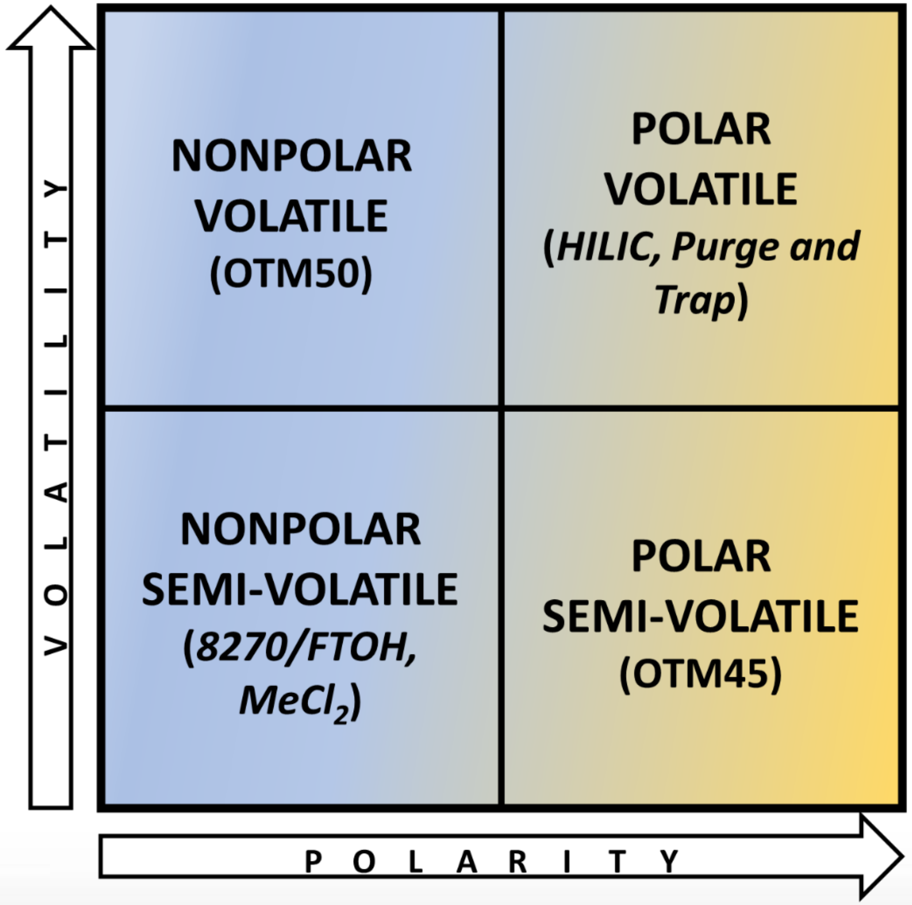


Slide courtesy of Emma D'Ambro, US EPA

PFAS Air Measurement Methods

- **Canister sampling (OTM-50) with GC/MS analysis**
- 30 target C1-C8 PFAS
- PIC/PIDs, industrial PFAS
- End of 2023?

- **Method 0010 sampling with GC/MS analysis (OTM-55)**
- FTOHs, select 8270 compounds and potential PICs
- Potential compounds of concern



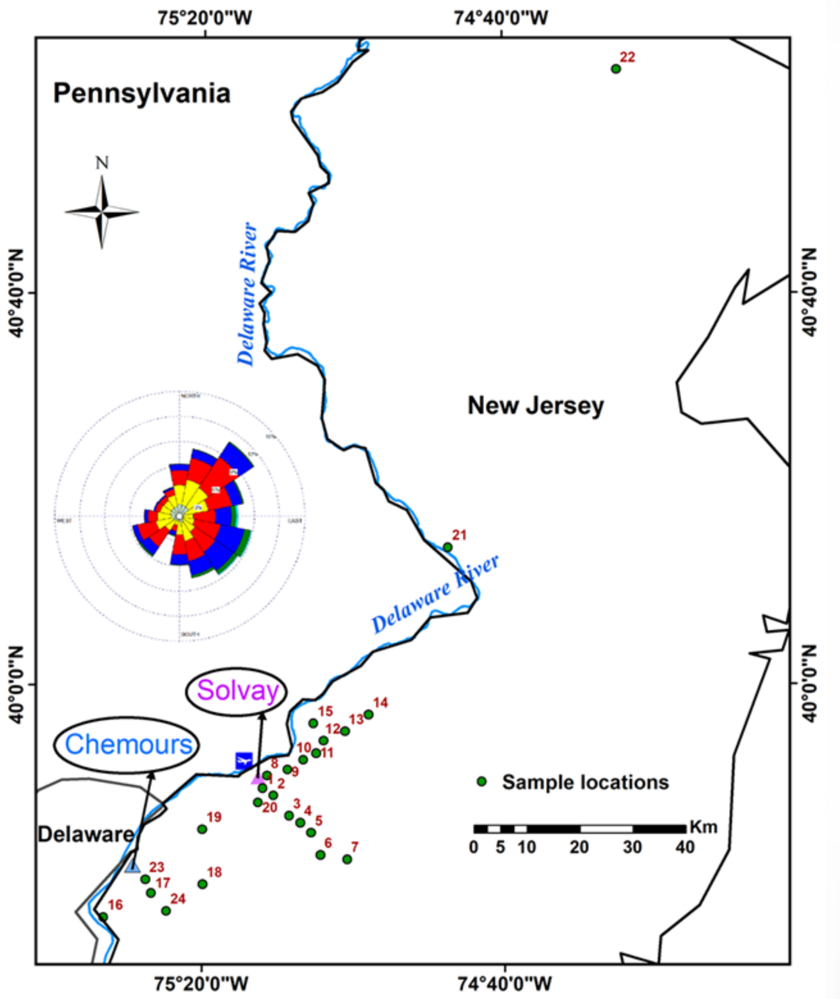
- **Not a current focus**
- Impinger sampling?
- LC analysis?
- Limited number of PFAS in this class

- **OTM-45 sampling with LC/MS analysis**
- 49 target PFAS (C4 and larger)
- Revision expected end of 2023

Slide courtesy of Ariel Wallace US EPA

PFAS in Environmental Samples

- NJDEP approached EPA requesting assistance to investigate PFAS distribution in the state
- NJDEP initially collected soil, vegetation & water samples
- Targeted PFAS & non-targeted mass-spectral analysis on all sample matrices



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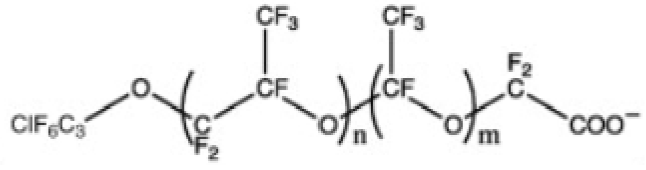
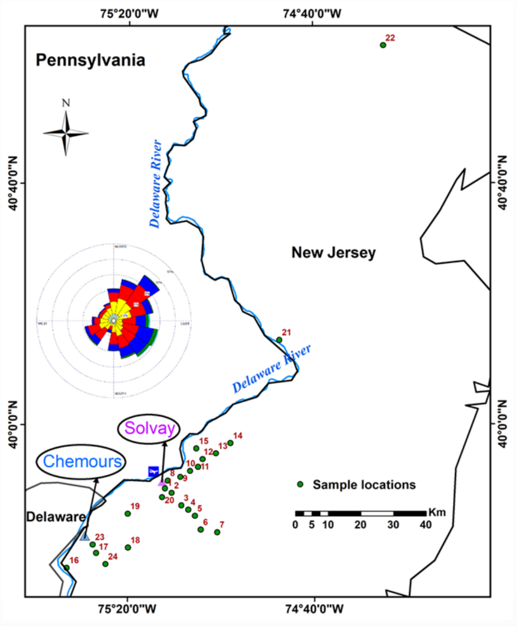
Nontargeted Analytical Results

- Initial non-targeted analyses identified a family of **previously unknown PFAS** in soil & water
- Family name: chloro perfluoropolyether carboxylates ClPFPECAs
- A subsequent literature search found the existence of these **compounds had been identified in literature as "Solvay's product"** (Wang et al. 2013. Environ. Int.)
- Solvay had a plant in NJ.

Solvay's product (CAS No. 329238-24-6)





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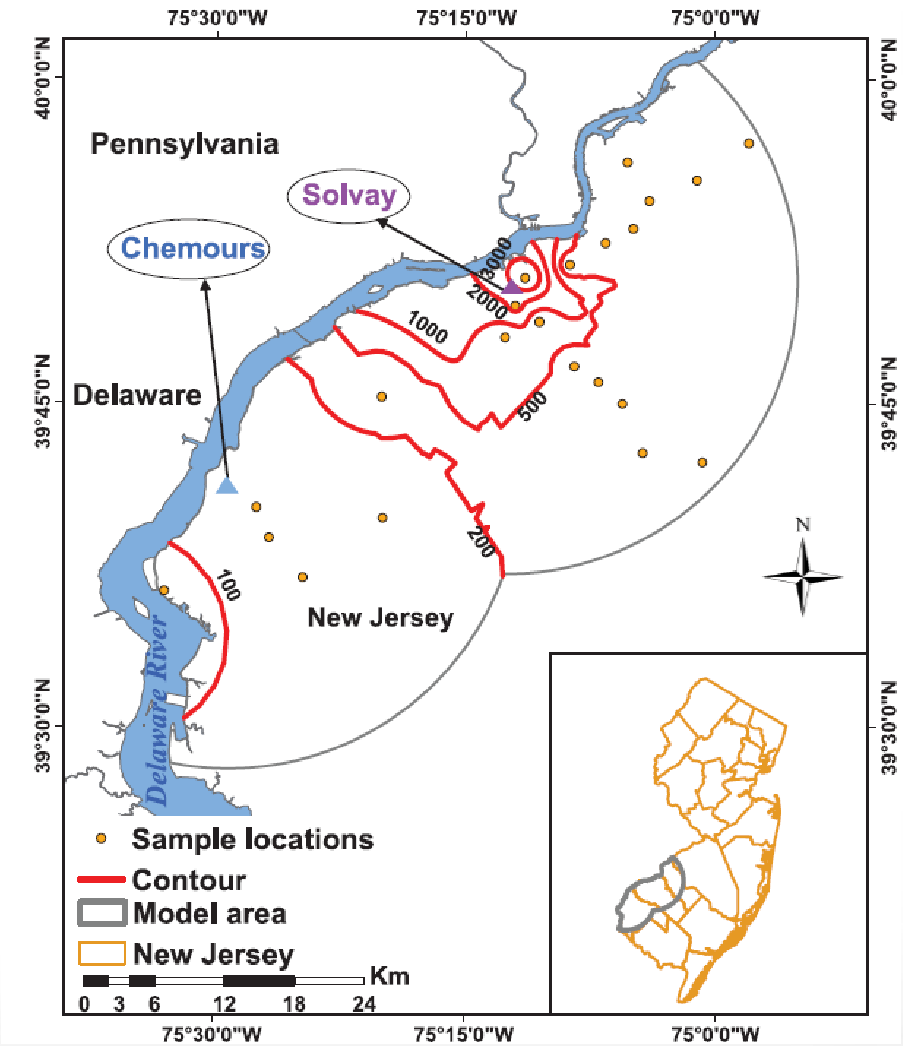
ClPFPECA Geographic Distribution

- Based on literature ID as "Solvay's product" soil concentrations were plotted against distance from Solvay
- When slopes with distance plotted against congener mass, also a significant relationship
- So smaller congeners dispersed more widely than larger congeners
- When contoured, the contours graded to high values at samples closest to Solvay



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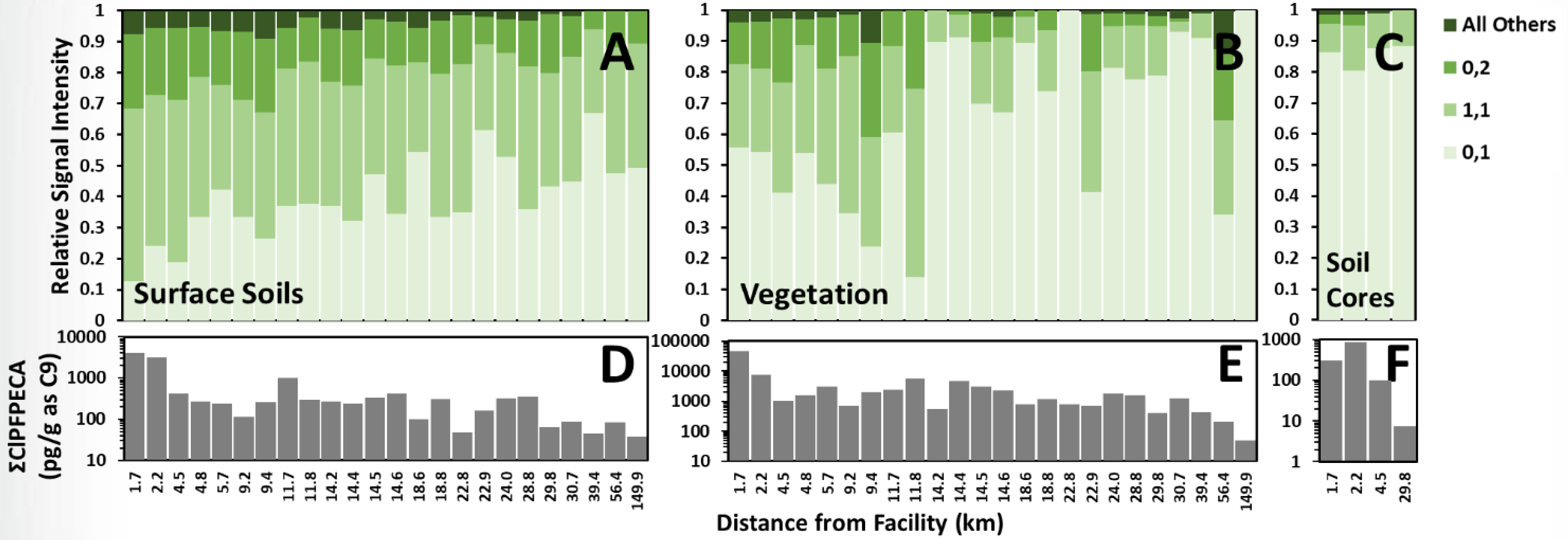
Concentration and Distribution of ClPFPECAs and PFCAs in Surface Soils, Vegetation and Subsoils



- ≥2 ClPFPECA congeners detected in all matrices
- Decrease in concentration with distance to facility ; ~ 6-fold higher in vegetation than surface soils
- Signal dominated by smallest congeners represent 91% of the total signal in surface soil samples, 96% in vegetation samples, and 98% in subsoil samples

Slide courtesy of Marina Evich and John Washington, US EPA

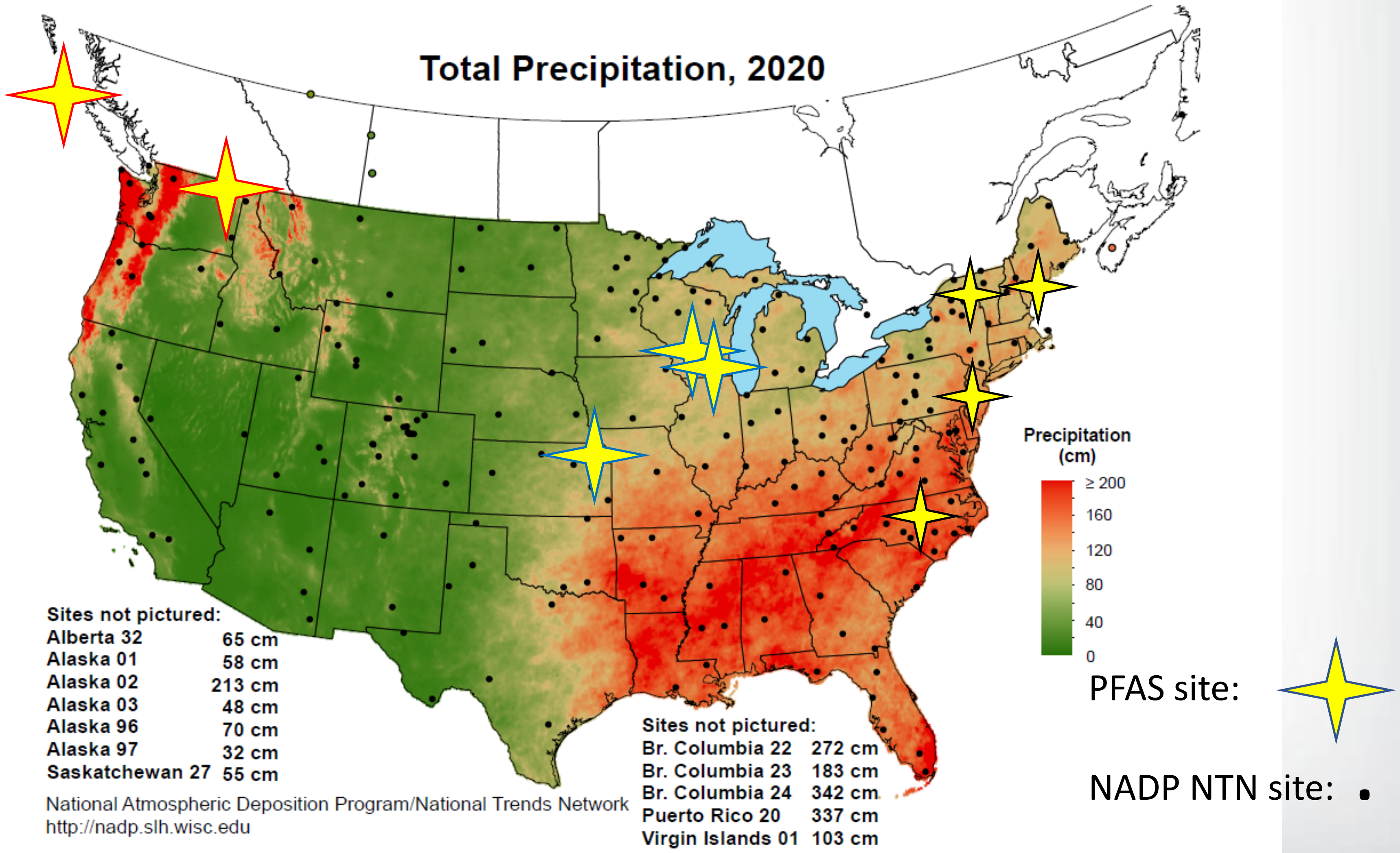
PFAS in Wet Deposition: Sampling Began September 2020

National Atmospheric Deposition Program (NADP)

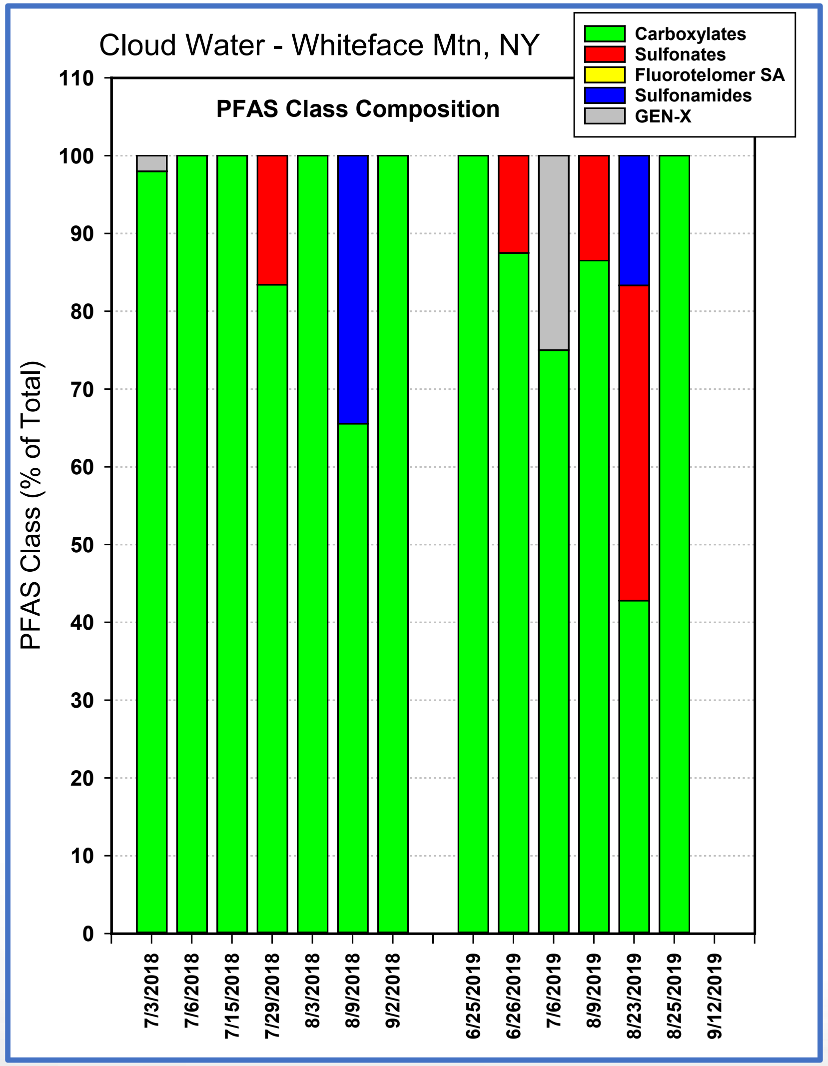
National Trends Network (NTN)

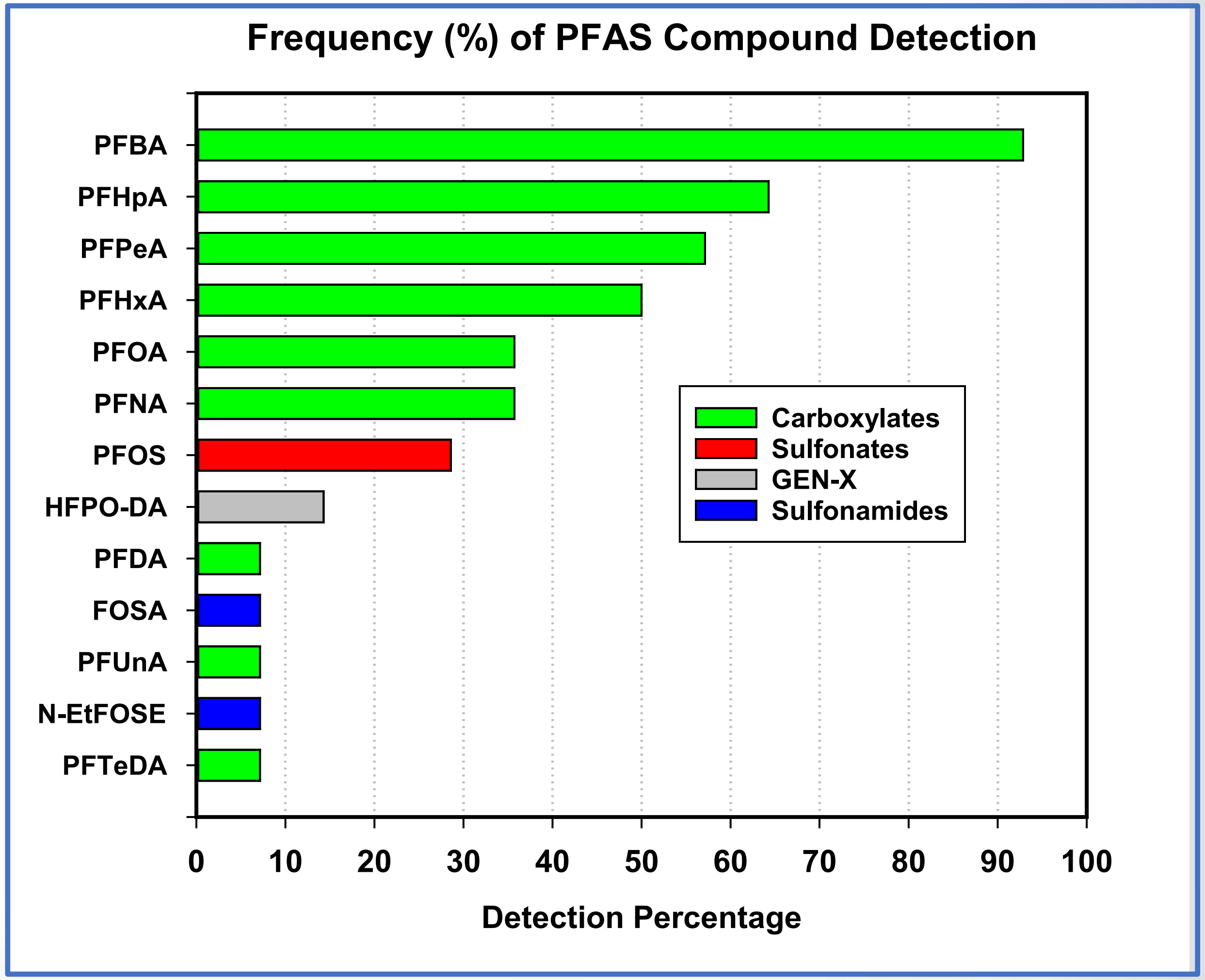
Current PFAS Sites
(NADP NTN Locations)
10 sites across US

Open to partnering with other NADP sites/operators



PFAS in Wet Deposition

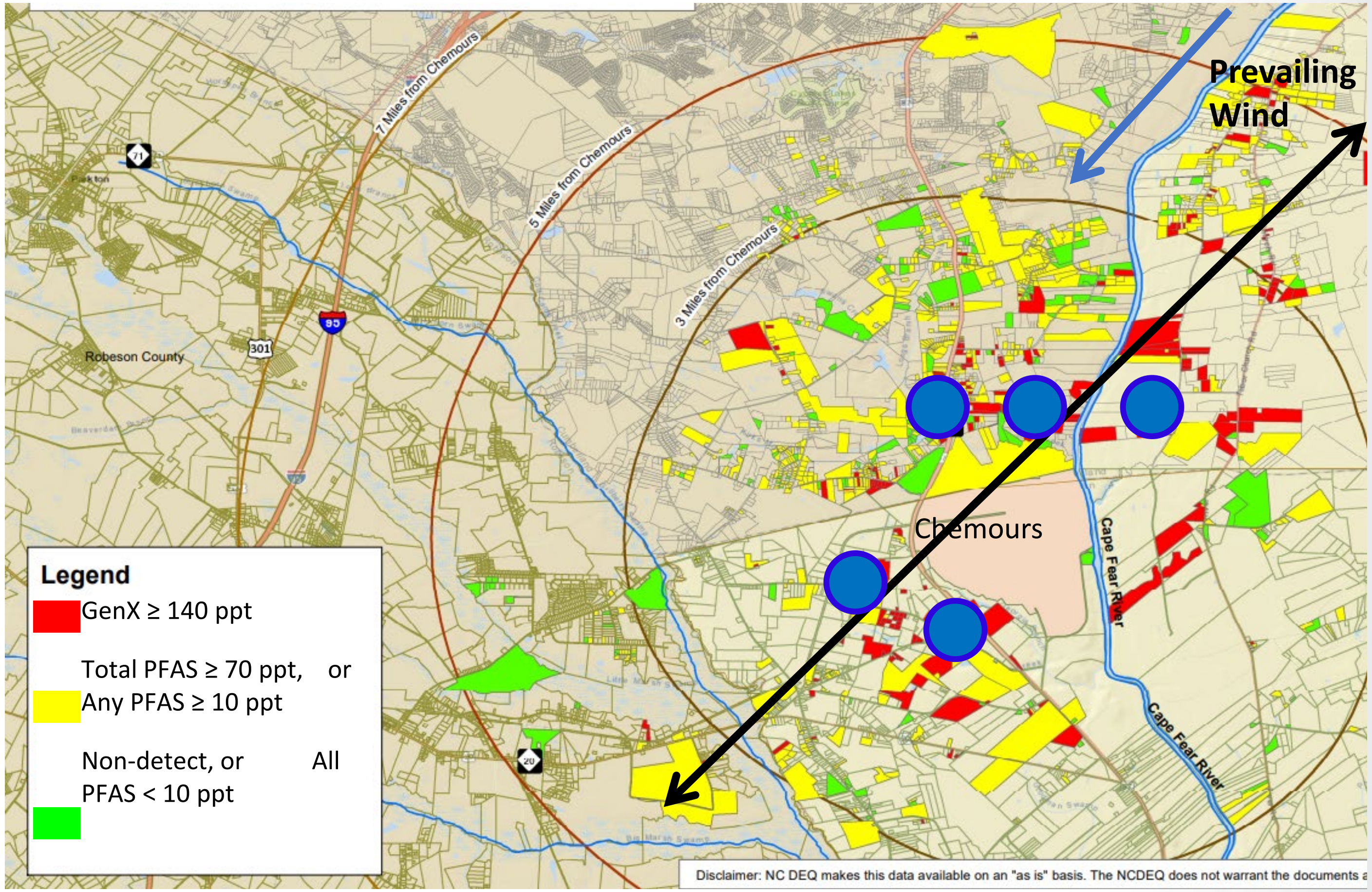




Offenberg 2023 (in prep)

Modeling PFAS Air Fate and Transport

- High levels of PFAS have been found in water wells near production facilities
- Some of these wells are ***upstream* and *across*** the river
- NC Department of Environmental Quality measurements have confirmed deposition of GenX from air
- Influence of air emissions have been corroborated with **qualitative** plume dispersion modeling (NCDEQ). *See also: Galloway et al., EST, 2020*



NC Department of Environmental Quality

D'Ambro et al, US EPA, 2022 AWMA presentation

Community Multiscale Air Quality (CMAQ) Model

CMAQ *(see-mak)* is an active open-source development project of the U.S. EPA that consists of a suite of programs for conducting air quality model simulations.

For over two decades, EPA and states have used EPA's Community Multiscale Air Quality (CMAQ) Modeling System, a powerful computational tool for air quality management.

CMAQ brings together three kinds of models:

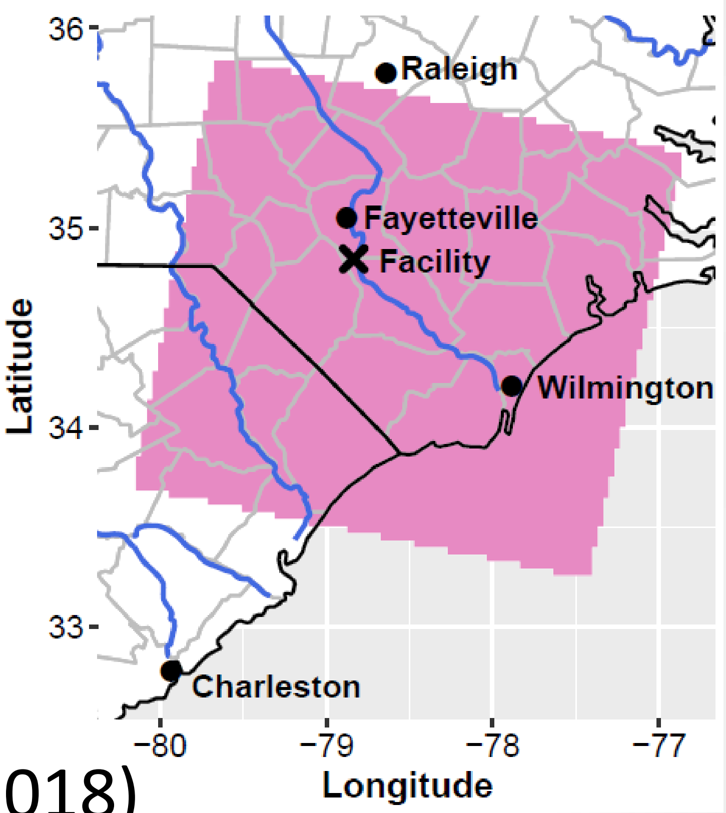
- **Meteorological models** to represent atmospheric and weather activities.
- **Emission models** to represent man-made and naturally-occurring contributions to the atmosphere.
- An **air chemistry-transport model** to predict the atmospheric fate of air pollutants under varying conditions.

CMAQ Fact Sheet October 2022 (pdf)

Slide courtesy K. Wyat Appel US EPA, 2023

CMAQ-PFAS

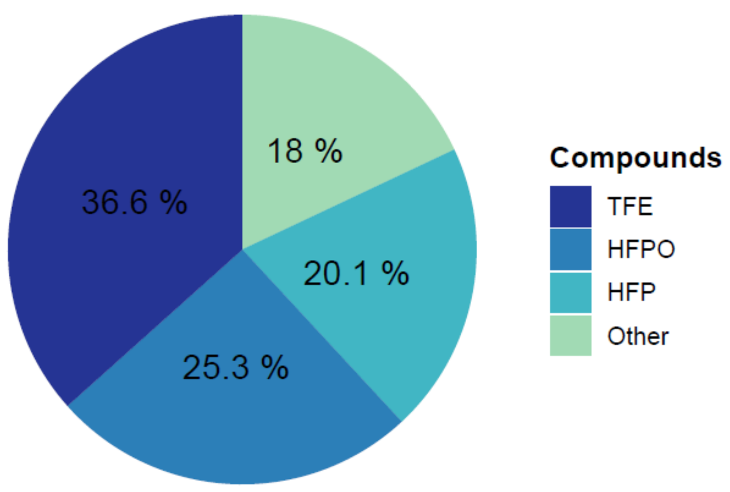
- Domain:
  - Eastern NC/ Northeast SC
  - 1 km x 1 km
- Simulation details:
  - CMAQ v. 5.3.2 for 2018
  - WRF 4.0.1 (meteorology)
  - CB6 (chemistry module)
  - NEI 2014 (standard emissions, projected to 2018)
  - PFAS emissions from Chemours Fayetteville-Works
  - No PFAS oxidative chemistry included (yet!)

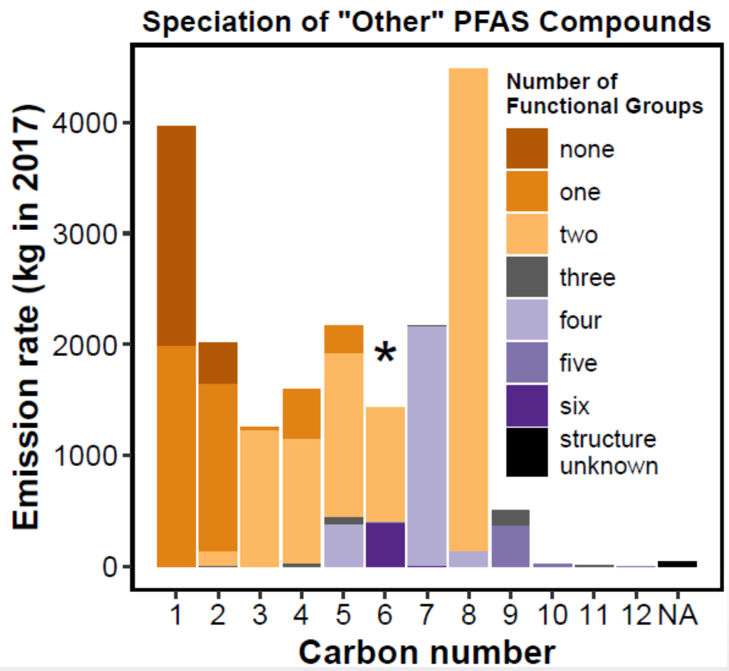


D'Ambro et al, US EPA, 2022 AWMA presentation

Facility-Specific PFAS Emissions

- 109,393 kg emissions in 2017
- 53 individual PFAS compounds
- Specific temporal profile of emissions based on production processes

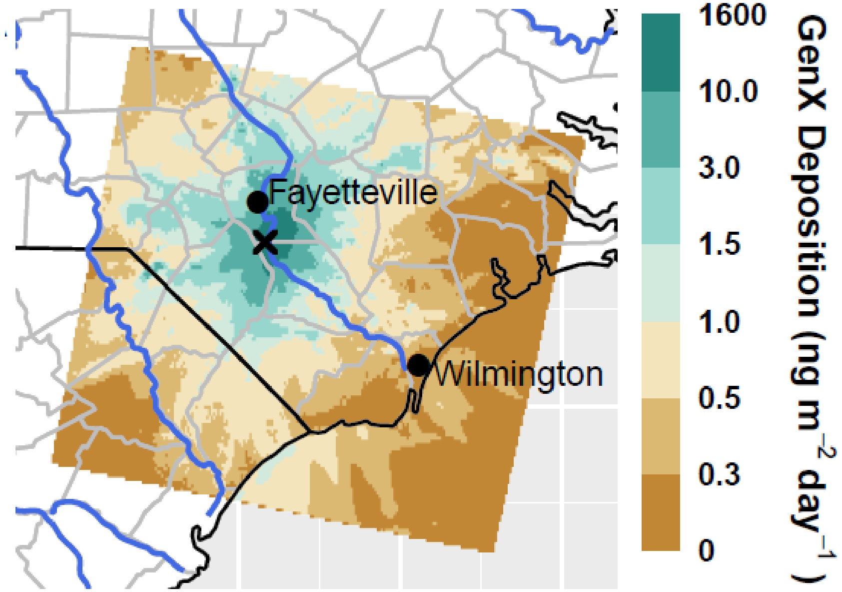


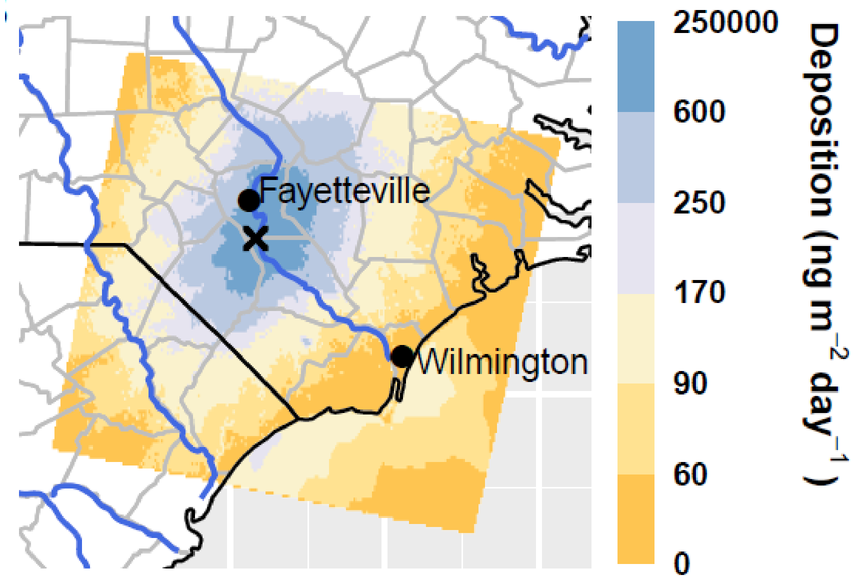


- ~80% of emissions are from 3 small, volatile (c* ~10^{10} µg m^3), insoluble (Henry's Law constants ~1E-3 – 10 M atm^{-1}) compounds

D'Ambro et al, US EPA, 2022 AWMA presentation

CMAQ-PFAS: Domain-Wide Deposition





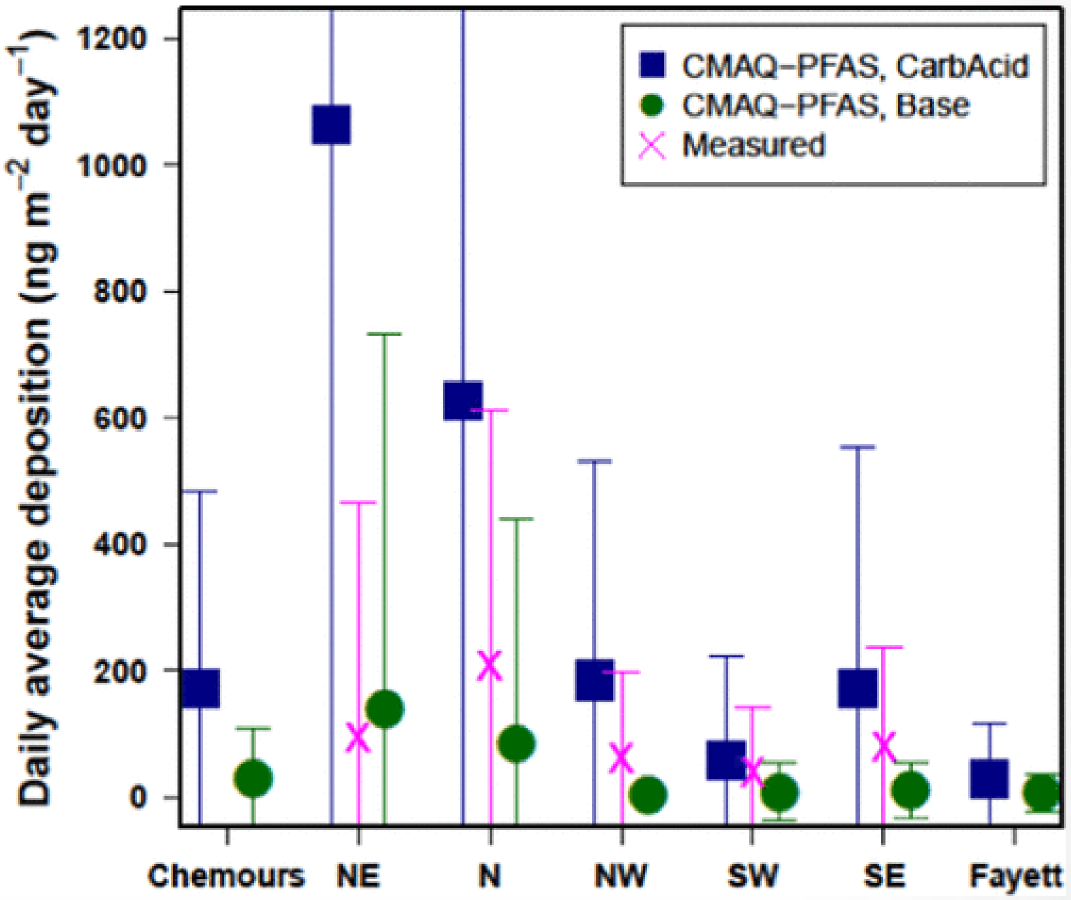
- Maximum annual deposition, *GenX*: 1,550 ng m^{-2} day^{-1}
- Maximum annual deposition, *total PFAS*: 245,000 ng m^{-2} day^{-1}
- 90^{th} percentile is 2 orders of magnitude lower for both

D'Ambro et al, US EPA, 2022 AWMA presentation

CMAQ-PFAS: GenX Predicted vs. Measured

CMAQ-PFAS predicted track reasonably well with NC DEQ sample measurements

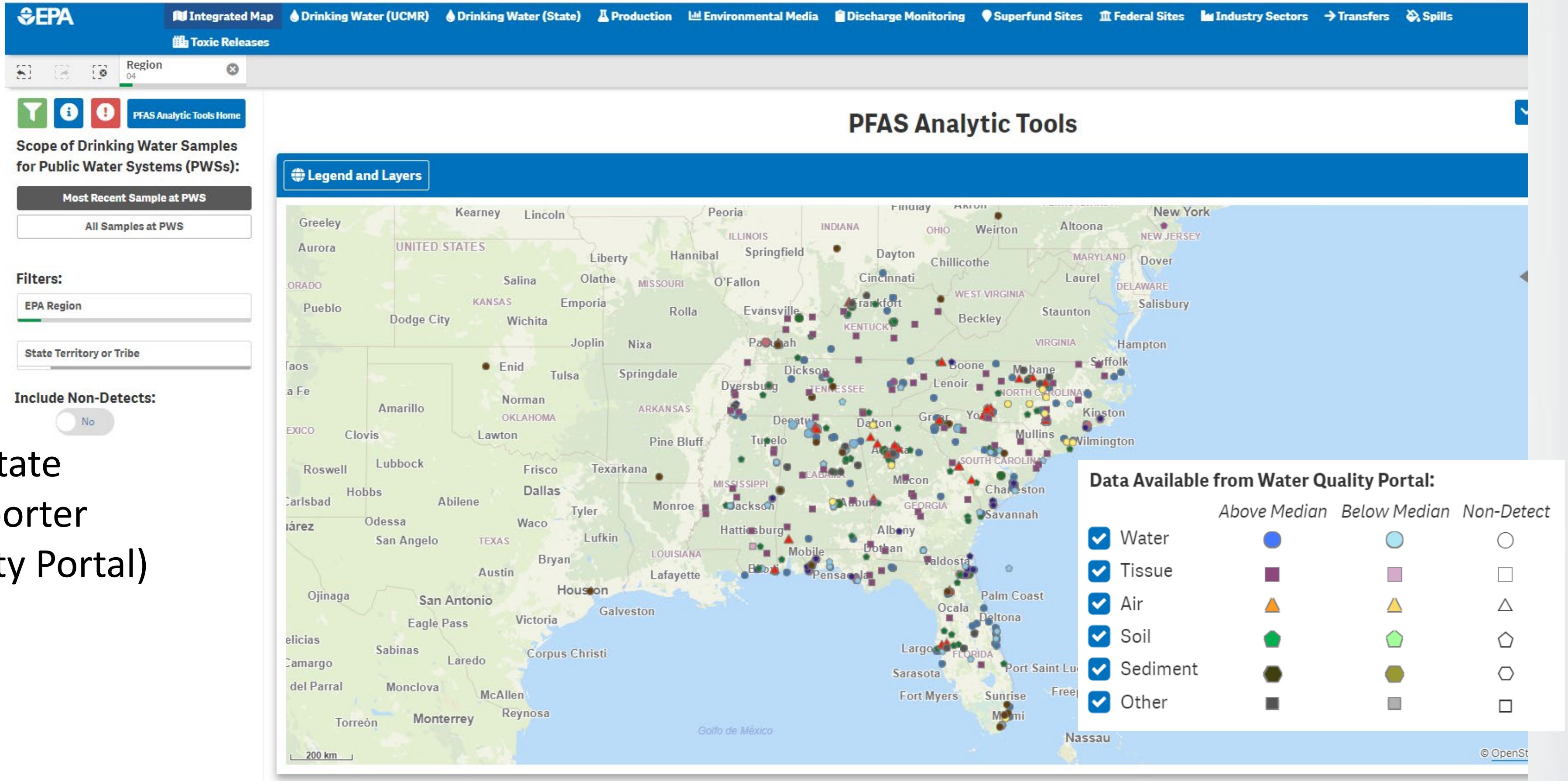
CMAQ-CarbAcid shown as a 'bounding scenario' for GenX



D'Ambro et al 2021

PFAS Analytic Tools

Web-based geospatial analysis tool, presents publicly available information on PFAS presence



Data layers:

- Drinking Water: UCMR3 + State
- Chemical Manufacturer/Importer
- Environmental (Water Quality Portal)
- Discharge Monitoring
- Superfund sites
- Federal Facilities
- Industry Sectors
- Spills
- Toxic Releases

Available online at echo.epa.gov => Analyze Trends

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References

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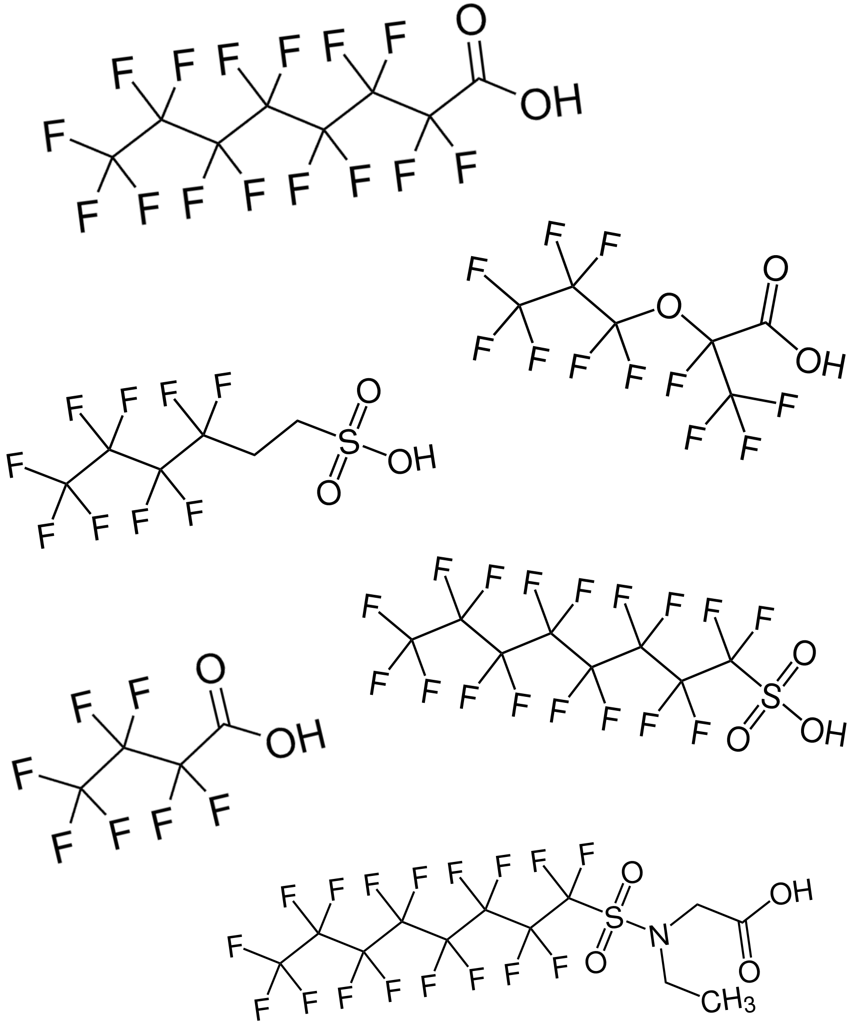
- Emma L. D'Ambro, Havala O. T. Pye, Jesse O. Bash, James Bowyer, Chris Allen, Christos Efstathiou, Robert C. Gilliam, Lara Reynolds, Kevin Talgo, and Benjamin N. Murphy. 2021. Characterizing the Air Emissions, Transport, and Deposition of Per- and Polyfluoroalkyl Substances from a Fluoropolymer Manufacturing Facility. *Environmental Science & Technology* 2021 *55* (2), 862-870 DOI: 10.1021/acs.est.0c06580
- Emma L. D'Ambro, Benjamin N. Murphy, Jesse O. Bash, Robert C. Gilliam, Havala O.T. Pye, Predictions of PFAS regional-scale atmospheric deposition and ambient air exposure, Science of The Total Environment, Volume 902, 2023, 166256, ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2023.166256 .

Additional Slides

OTM-45 Target Compounds

- Perfluorinated carboxylic acids (PFCAs)
- Perfluorinated sulfonic acids (PFSAs)
- Perfluorinated sulfonamides (FOSAs)
- Perfluorinated sulfonamide ethanols (FOSEs)
- Perfluorinated sulfonamido acetic acids (FOSAAs)
- Fluorotelomer sulfonates (FTSs)
- Fluorotelomer acrylates (FTACs)
- Fluorinated replacement chemicals



Slide courtesy of Ariel Wallace US EPA

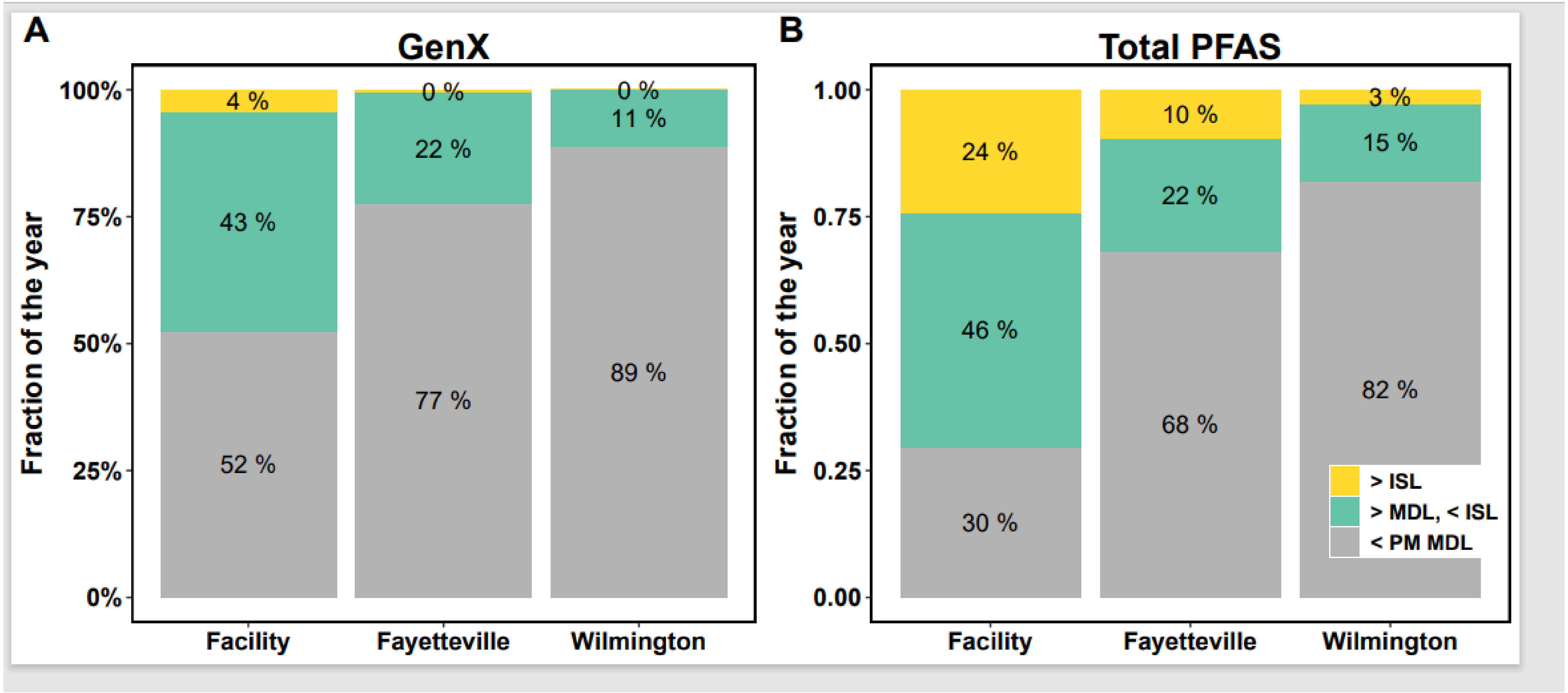
OTM-50 Target Compounds

Name	MDL 1X dilution		PQL 1X dilution	
	ppbv	ug/m^3	ppbv	ug/m^3
Tetrafluoromethane	1.02	3.73	49.19	179.95
Hexafluoroethane	0.03	0.18	0.49	2.81
Chlorotrifluoromethane	0.03	0.12	0.49	2.14
Fluoroform	0.05	0.15	0.49	1.43
Octafluoropropane	0.02	0.17	0.49	3.85
Difluoromethane	0.05	0.12	0.49	1.06
Pentafluoroethane	0.03	0.15	0.49	2.42
Octafluorocyclobutane	0.03	0.22	0.49	4.11
Fluoromethane	0.04	0.06	0.49	0.69
Tetrafluoroethylene	0.01	0.06	0.49	2.06
Hexafluoropropene	0.02	0.14	0.49	3.08
1,1,1-trifluoroethane	0.05	0.18	0.49	1.71
Hexafluoropropene Oxide	0.1	0.72	0.49	3.4
Chlorodifluoromethane	0.03	0.12	0.49	1.75
1,1,1,2-tetrafluoroethane	0.04	0.17	0.49	2.07

Name	MDL 1X dilution		PQL 1X dilution	
	ppbv	ug/m^3	ppbv	ug/m^3
Perfluorobutane	0.03	0.32	0.49	4.82
1H-Heptafluoropropane	0.03	0.19	0.49	3.48
Octafluorocyclopentene	0.04	0.34	0.49	4.35
Trichlorofluoromethane	0.03	0.18	0.49	2.78
Dodecafluoro-n-pentane	0.03	0.4	0.49	5.9
1H-Nonafluorobutane	0.02	0.21	0.5	4.53
Tetradecafluorohexane	0.02	0.32	0.49	6.91
1H-Perfluoropentane	0.02	0.24	0.5	5.56
Heptafluoropropyl-1,2,2,2-tetrafluoroethylether (E1)	0.01	0.17	0.49	5.84
Hexadecafluoroheptane	0.01	0.22	0.49	7.9
1H-Perfluorohexane	0.01	0.18	0.49	6.53
Perfluorooctane	0.02	0.28	0.49	8.98
1H-Perfluoroheptane	0.01	0.21	0.49	7.6
1H-Perfluorooctane	0.01	0.19	0.49	8.63
2H-Perfluoro-5-methyl-3,6-dioxanonane (E2)	0.01	0.26	0.49	9.22

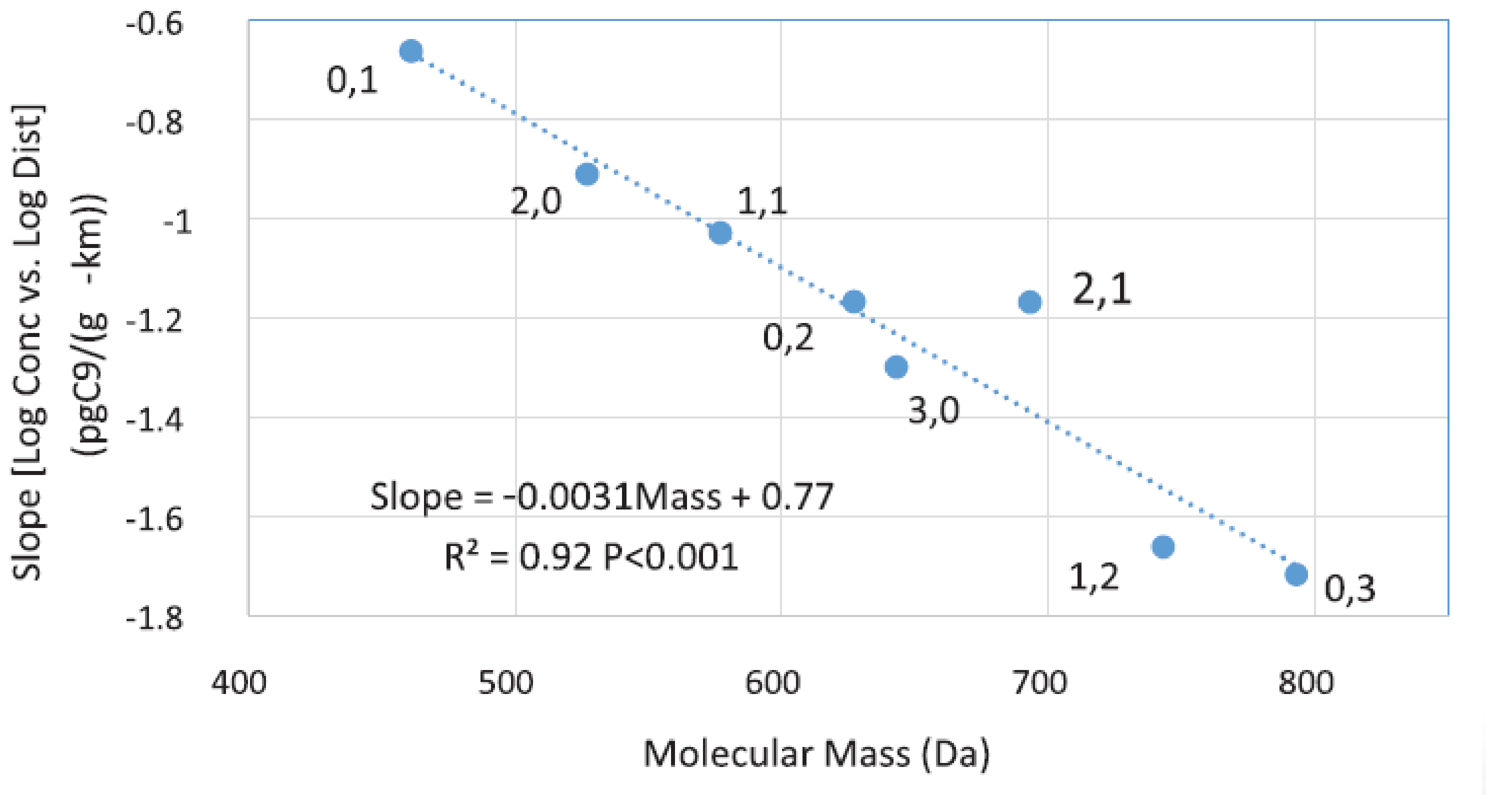
Slide courtesy of Ariel Wallace US EPA

Predicted PFAS air concentrations by Inhalation Screening Level (ISL)



D'Ambro et al, 2023

Lower-mass PFAS dispersed from a stack point-source more widely than higher-mass.
Dispersion as a function of mass (note mass might be a proxy for another directly functional cause):



Washington et al 2020