Session 5: Source Emissions Measurement Methods and Modeling Air Emissions, Transport and Deposition

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US EPA Office of Research and Development

PFAS Science Webinars for Region 1 and New England States & Tribes

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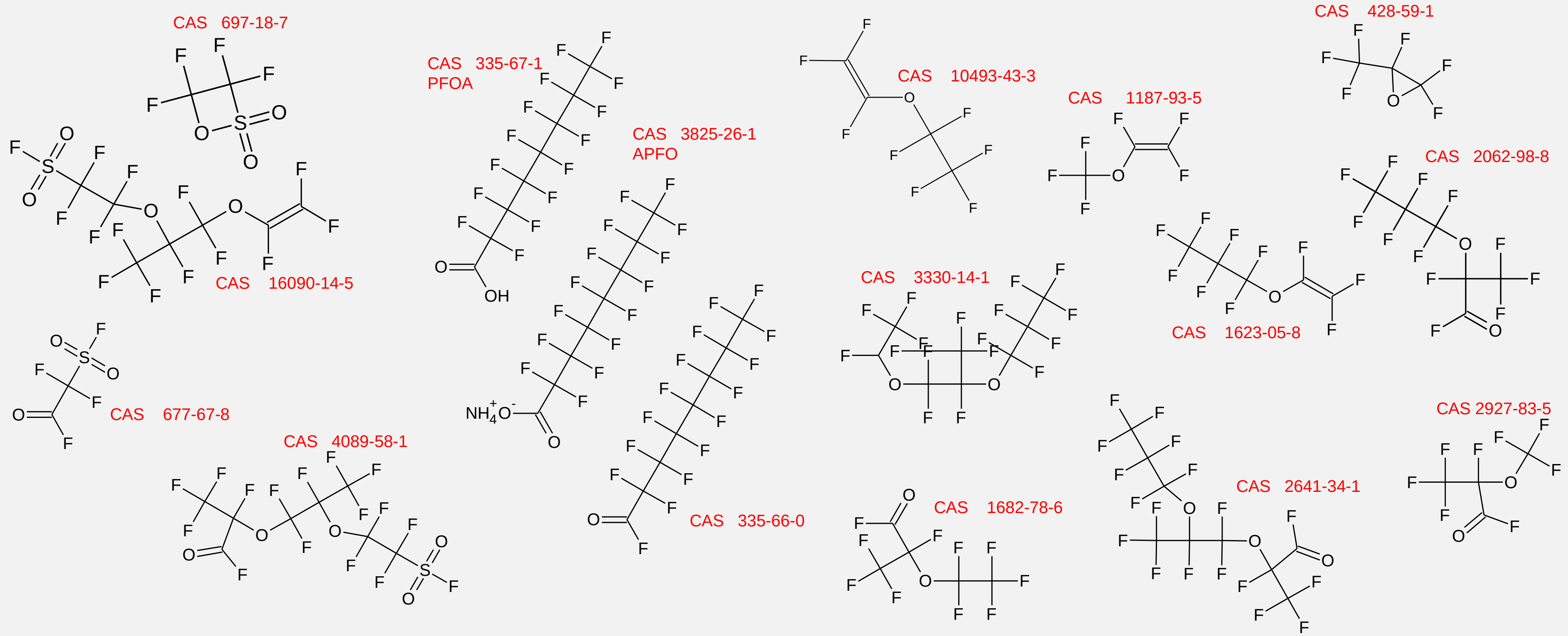
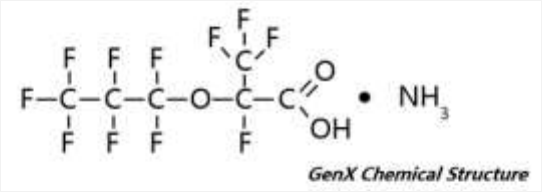
EPA PFAS Air-Related Research

- **Analytical Methods** to detect, identify and quantify PFAS in emissions and ambient air
- **Chemical Transport Modeling** to predict atmospheric dispersion and deposition associated with air sources
- **Effectiveness of Thermal Treatments** for destroying PFAS materials

So many PFAS compounds!

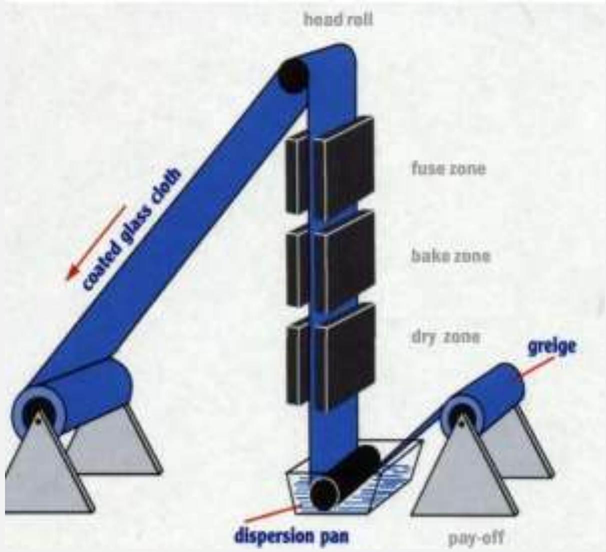


So how do we measure them?

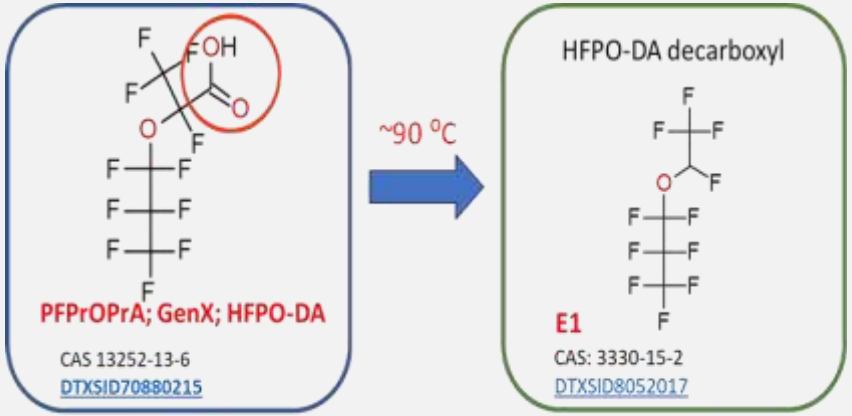


Emissions Measurement Considerations/Challenges

- Emission sources are diverse:
  - PFAS chemical manufacturers
  - PFAS used in commercial applications
  - PFAS emitted during thermal treatment of waste (e.g., AFFF, biosolids, municipal)
  - Products of Incomplete Combustion (PICs)
- Process can alter emission composition
- Validated source and ambient air methods for PFAS do not exist, but some research methods are available
- Current emissions tests often target only a small number of PFAS compounds for analysis while significantly more may be present



Example Coating Process



ORD PFAS Emissions Measurement Activities

- Supporting multiple State emissions testing campaigns
  - States and Regions are those most concerned and looking to EPA for guidance
  - ORD collaborating to provide technical guidance and measurement assistance
  - Providing options for more comprehensive emissions characterizations
  - Analysis of industrial emissions samples for non-targeted PFAS compounds
  - Actively participating or leading field emissions tests
- Supporting EPA Program Offices
  - Office of Air Quality Planning and Standards (OAQPS)
  - Office of Land and Emergency Management (OLEM)
- Methods development research and field evaluations
- Conducting combined methods development and source characterization field testing where possible

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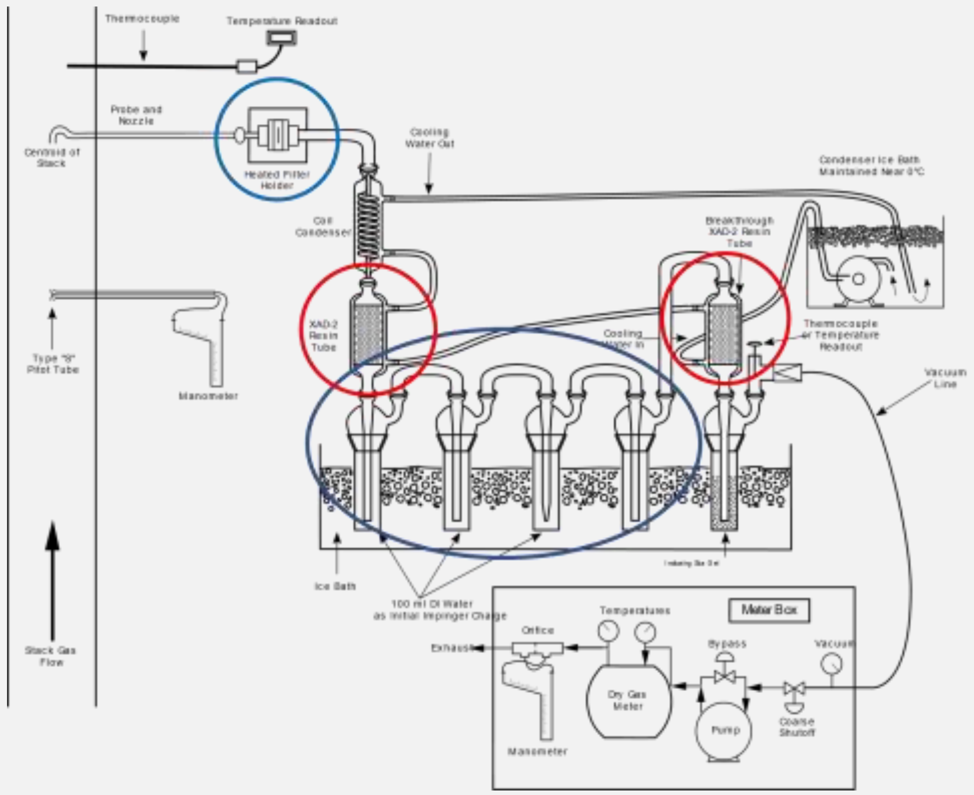
Semivolatile/Nonvolatile Sampling Methods

- Modified SW-846 Method 0010 (MM5) Train for polar and nonpolar PFAS compounds
  - Extra XAD-2 trap for breakthrough
  - Modified glassware rinses
  - Separate solvent extractions for polar and nonpolar compounds
  - Four (4) separate fractions for analysis
- Primary approach for targeted and non-targeted analyses
  - Isotope dilution for targeted analyses
  - Use of internal and pre-sampling surrogate standards (limited by availability of isotopically labeled standards)
  - High resolution mass spec nontargeted analyses
- Other Test Method (OTM)-45 underway for polar PFAS compounds
- Expanding to include fluorotelomer alcohols (FTOHs)

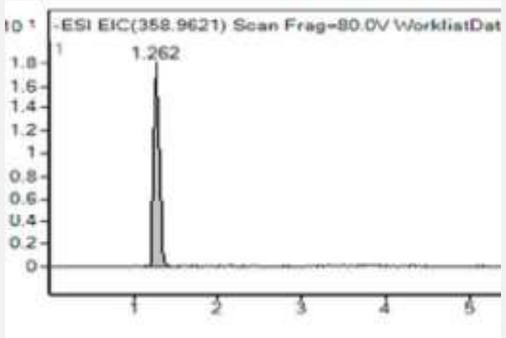


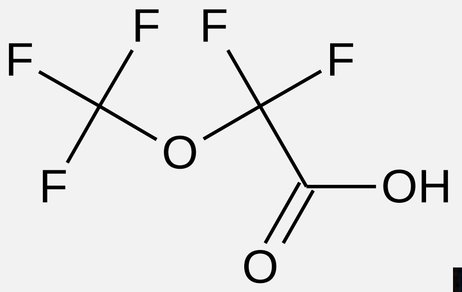
Volatile Sampling Methods

- Using SUMMA canisters (limits use to nonpolars)
- Sorbent traps (suitable for polars and nonpolars)
- Moisture and acid gases a problem for both approaches
- GC/MS analysis for targeted and non-targeted compounds
  - C1-C3 targets
    (e.g., CF_4, CHF_3, C_2F_4,C_2F_6, C_3F_6, C_3F_8, etc)
  - Industrial PFAS
    (e.g., E1, HFPO, FTOHs)
  - High resolution mass spec nontargeted analyses

Non-Targeted Analysis

- High resolution mass spectrometry
- Software calculates exact number and type of atoms needed to achieve measured mass, e.g. $C_3HF_5O_3$
- Software and fragmentation inform most likely structure
- With mass, formula, structure known, potential identities determined by database search

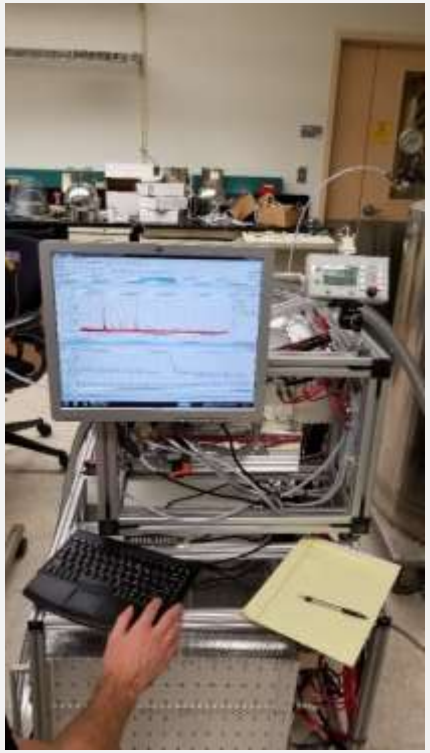




Molecular Formula: $C_3HF_5O_3$
Monoisotopic Mass: 179.984585 Da
[M-H]-: 178.977308 Da

Source: Strynar et al. 2015; Sun et al. 2016

Innovative Measurements Research



Field Deployable, Time of Flight-Chemical Ionization Mass Spectrometer (ToF–CIMS)

- Real-time measurement of polyfluorinated carboxylic acids (PFAS) and FTOHs
- Super sensitive (ppt measurement levels)
- Currently being evaluated as a process emissions analyzer

Total Organic Fluorine

- Combustion/Ion Chromatography?
- Potential technique
- Sample collection an important aspect

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Take Home Messages

- Reliable and comprehensive PFAS and PFAS-related emissions measurement methods are needed for multiple purposes
- Application to thermal treatment/incineration/combustion sources a major focus amongst a host of methods for all media
- Identifying what compounds need to be targeted for measurement is the hard part
- Non-targeted analyses are critical to knowing what compounds are present because you don't find what you don't look for
- Surrogate approaches are needed to know exactly what goes in and what comes out
- Need to have access to actual sources to evaluate methods and conduct comprehensive source characterizations
- ORD collaboration/partnership is integral

Understanding PFAS Air Fate and Transport: A Case Study outside Fayetteville, NC

Acknowledgements:

Emma D'Ambro, Havala O. T. Pye, Jesse Bash, Rob Gilliam and Ben Murphy

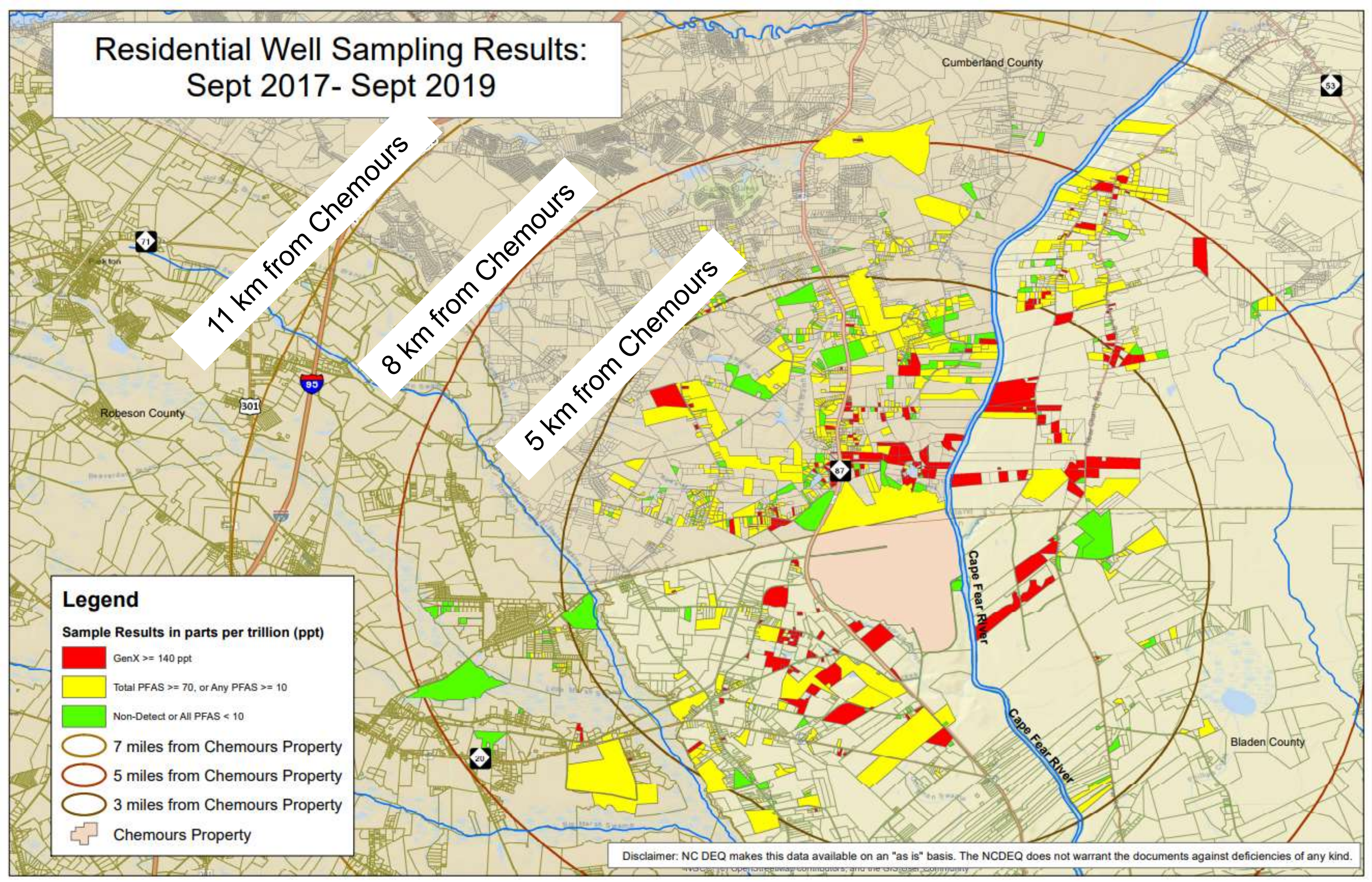
This is a research case study. Focus on specific sources of pollution does not reflect US EPA policy and does not indicate any potential actions or judgements on behalf of the Agency towards those entities.

Case Study: Cape Fear River Basin

- PFAS found along Cape Fear River, into Wilmington, NC and in residents' blood
- Among other compounds, GenX (HFPO-DA) was of primary concern to residents
- Upstream fluoropolymer manufacturer – Chemours, Inc.
- Relatively isolated from other potential PFAS air sources (nearest known producer is 250+ miles away)
- Reductions in Cape Fear River water after water discharge mitigation steps taken at manufacturing facility

References:
Nakayama, S. et al. EST, 2007.
Strynar, M. et al. EST, 2015.
Sun, M. et al. EST, 2016.
McCord, J. et al. EST, 2019.

Near-field well samples suggest multiple pathways to contamination



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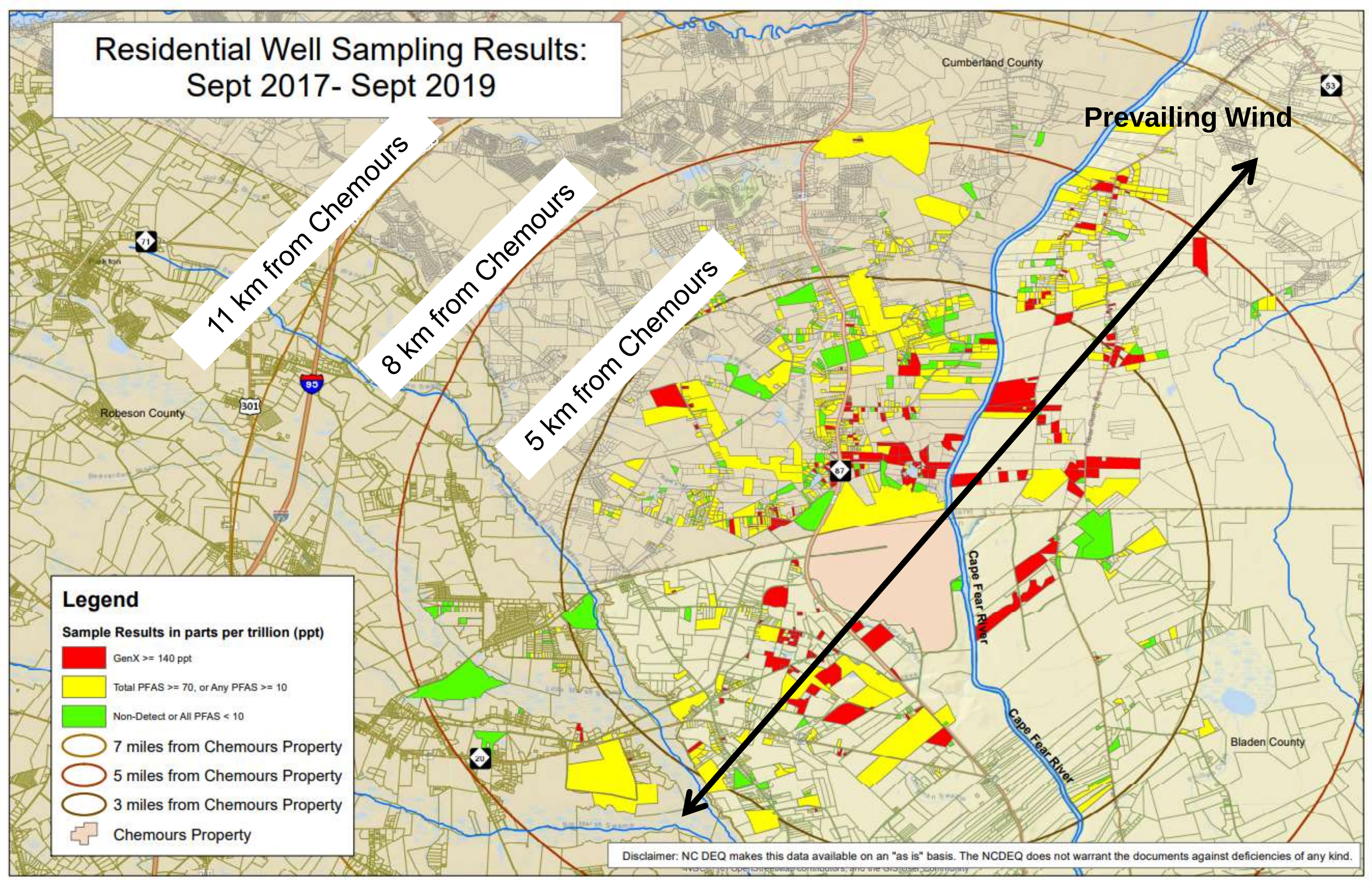
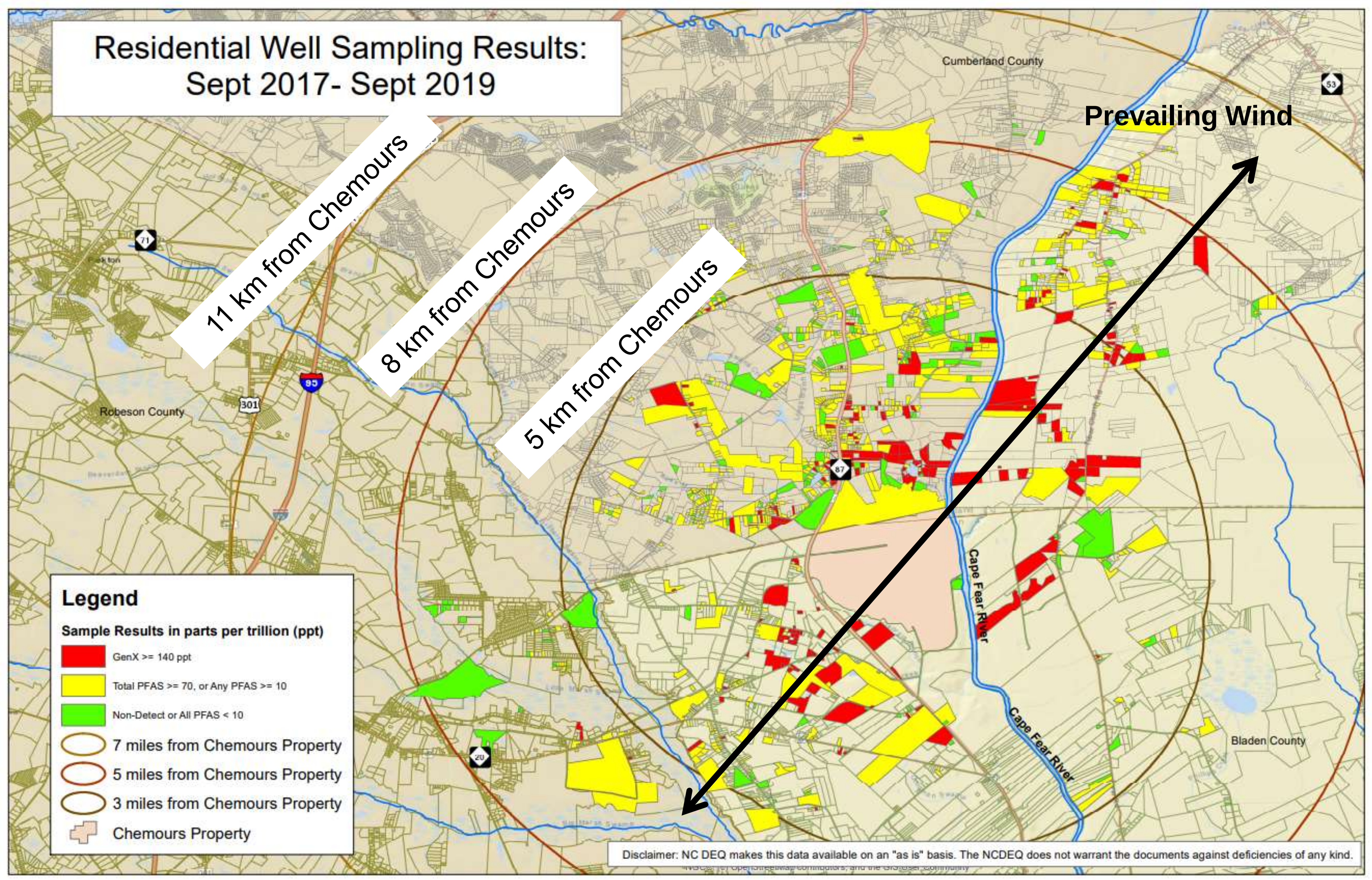


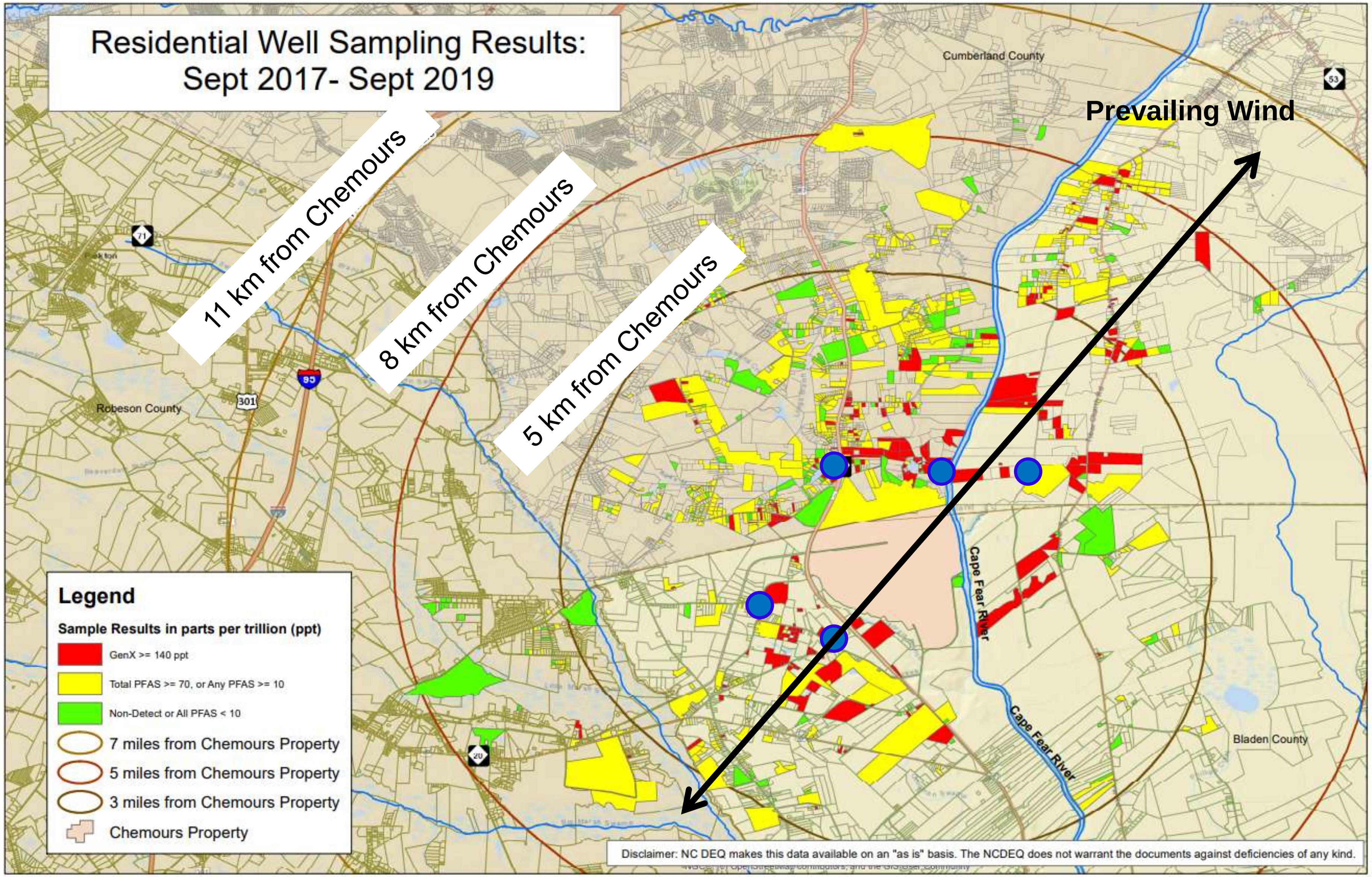
Near-field well samples suggest multiple pathways to contamination

- High levels of PFAS have been found in water wells near production facilities
- Some of these wells are *upstream* and *across* the river



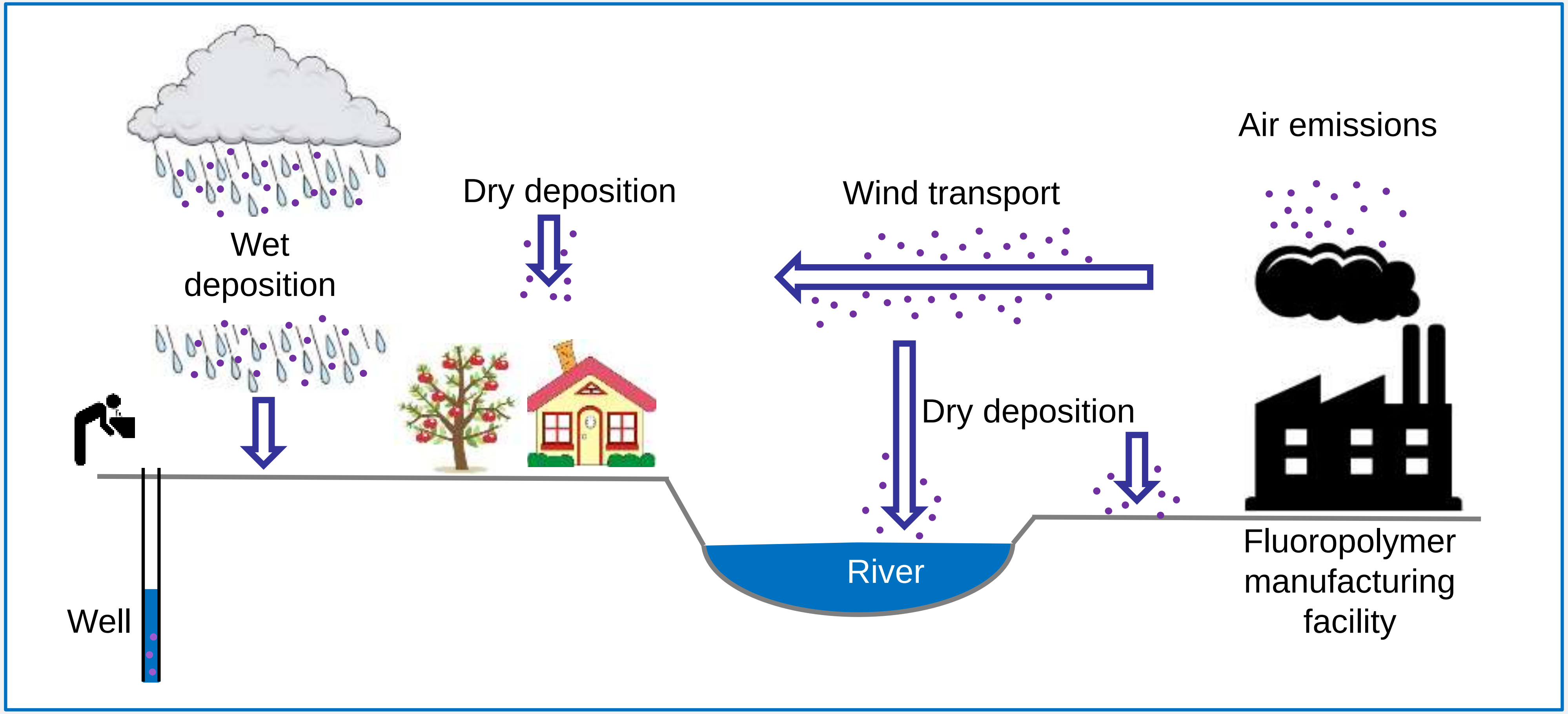
Near-field well samples suggest multiple pathways to contamination

- 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 (DEQ) measurements have confirmed deposition of GenX from air



See recent publication: Galloway et al., EST, 2020

Conceptual explanation of potential role of PFAS air emissions



Adapted from:
Davis, K. et al. Chemosphere, 2007.
See recent publications:
Galloway et al., EST, 2020
Washington et al., Science, *2020*

- Influence of air emissions have been corroborated with **qualitative** plume dispersion modeling (NC DEQ)
- Can we rigorously demonstrate mass closure between expected emissions and measured deposition near the facility?

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Focused Research Objectives

Develop a model of the fate and transport of PFAS ambient air emissions from the Chemours' Inc. Fayetteville-Works facility:

1. Analyze the complete mix of PFAS compounds expected in the air emissions from the facility
2. Assess the importance of PFAS physicochemical properties in determining their fate in ambient air. How complex should our air model be?
3. Evaluate the predicted deposition of GenX (HFPO-DA) against measurements taken by NC DEQ
4. Quantify the ambient air concentration and deposition flux of PFAS in the vicinity of the facility and further downwind

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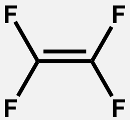
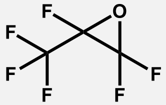
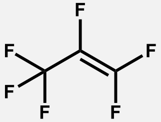
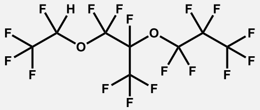
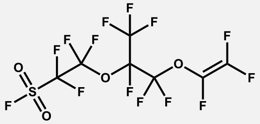
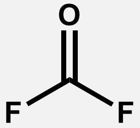
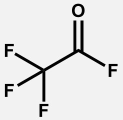
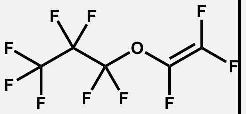
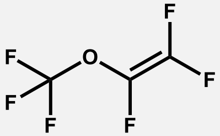
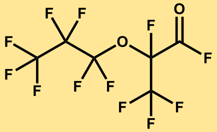
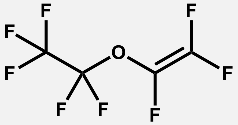
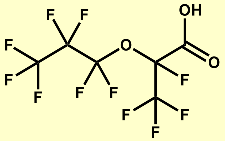
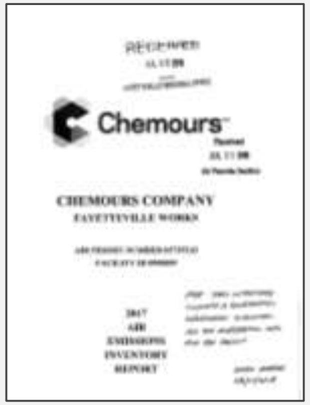
Facility-Wide PFAS Air Emission Rates and Composition

1. TFE		**37%** 88,366 lbs
2. HFPO		**26%** 61,566 lbs
3. HFP		**21%** 48,542 lbs
4. E2		**4%** 9,595 lbs
5. PSEPVE		**2%** 4,736 lbs
6. COF2		**1.8%** 4,404 lbs

7. PAF		**1%** 3,360 lbs
8. PPVE		**1%** 2,846 lbs
9. PMVE		**1%** 2,679 lbs
10. HFPO-DAF		**1%** 1,598 lbs
11. PEVE		**0.6%** 1,536 lbs
18. HFPO-DA		**0.29%** 696 lbs



2017 Inventory
Submitted to NC DEQ

- 49 PFAS compounds reported at total emission of ~240,000 lbs in 2017
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- We estimated compound vapor-pressure and water solubility with the EPA OPERA model:
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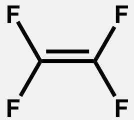
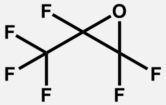
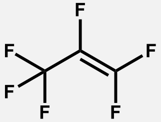
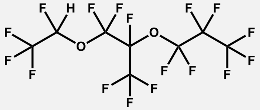
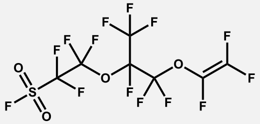
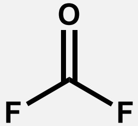
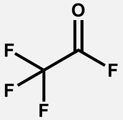
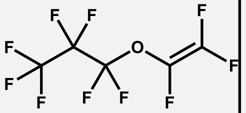
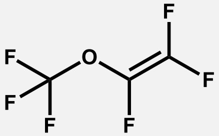
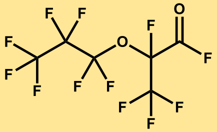
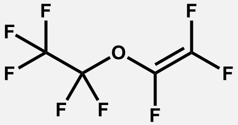
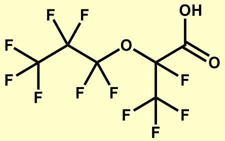
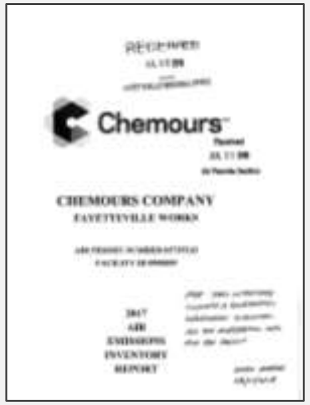
1. TFE		**37%** 88,366 lbs
2. HFPO		**26%** 61,566 lbs
3. HFP		**21%** 48,542 lbs
4. E2		**4%** 9,595 lbs
5. PSEPVE		**2%** 4,736 lbs
6. COF2		**1.8%** 4,404 lbs

7. PAF		**1%** 3,360 lbs
8. PPVE		**1%** 2,846 lbs
9. PMVE		**1%** 2,679 lbs
10. HFPO-DAF		**1%** 1,598 lbs
11. PEVE		**0.6%** 1,536 lbs
18. HFPO-DA		**0.29%** 696 lbs



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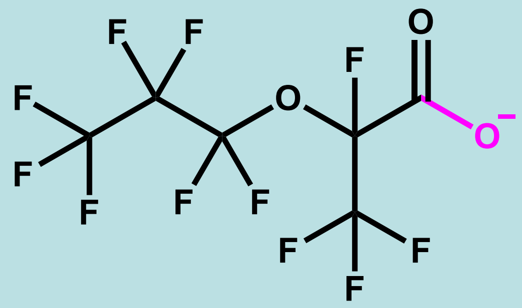
GenX: compound of public concern in Cape Fear River



HFPO-DA anion

Found in water:

e.g. surface and ground water, cloud drops, airborne aqueous particles

HFPO-DA (Hexafluoropropylene oxide – Dimer Acid)
HFPO-DAF (Hexafluoropropylene oxide – Dimer Acid Fluoride)

Strynar, M. et al. EST, 2015.
Hopkins, Z. et al. Journal of Air and Waste Management, 2018.
Guillette, T.C. et al., Environment International, 2019.
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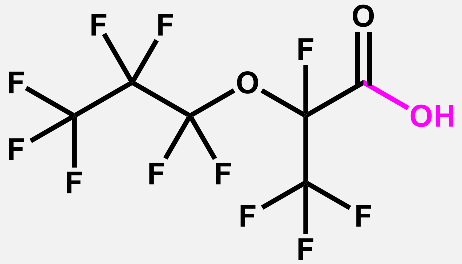
GenX: compound of public concern in Cape Fear River

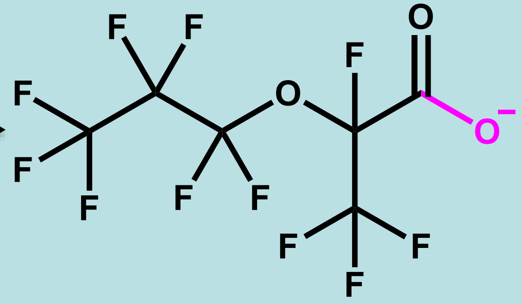
- What's measured in water is not necessarily what's in the air



HFPO-DA

Found in gas phase

Gas/water partitioning



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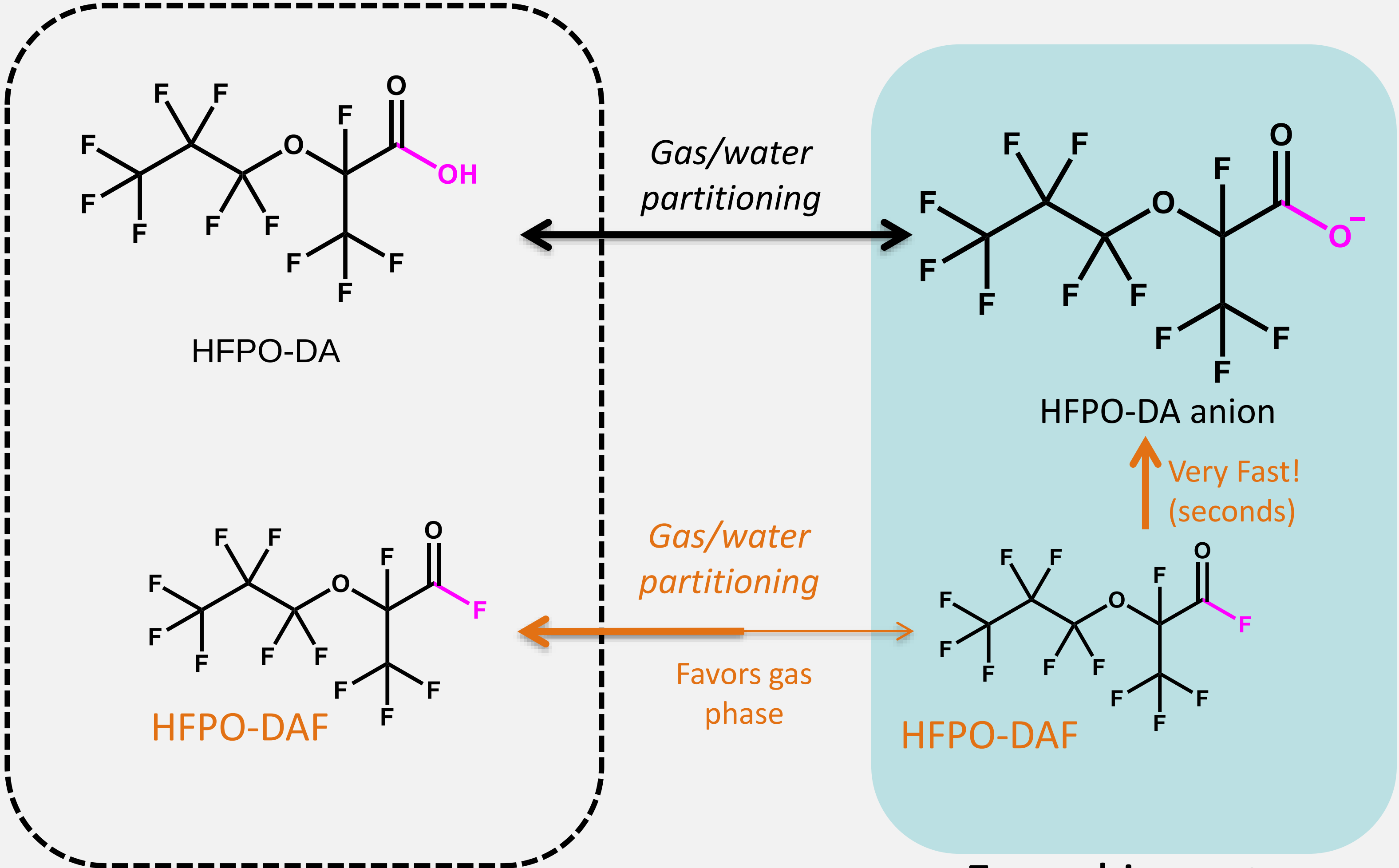
HFPO-DA (Hexafluoropropylene oxide – Dimer Acid)
HFPO-DAF (Hexafluoropropylene oxide – Dimer Acid Fluoride)

GenX: compound of public concern in Cape Fear River

- What's measured in water is not necessarily what's in the air
- HFPO-DAF is a known manufacturing precursor to HFPO-DA, but it is often not quantified



Found in gas phase

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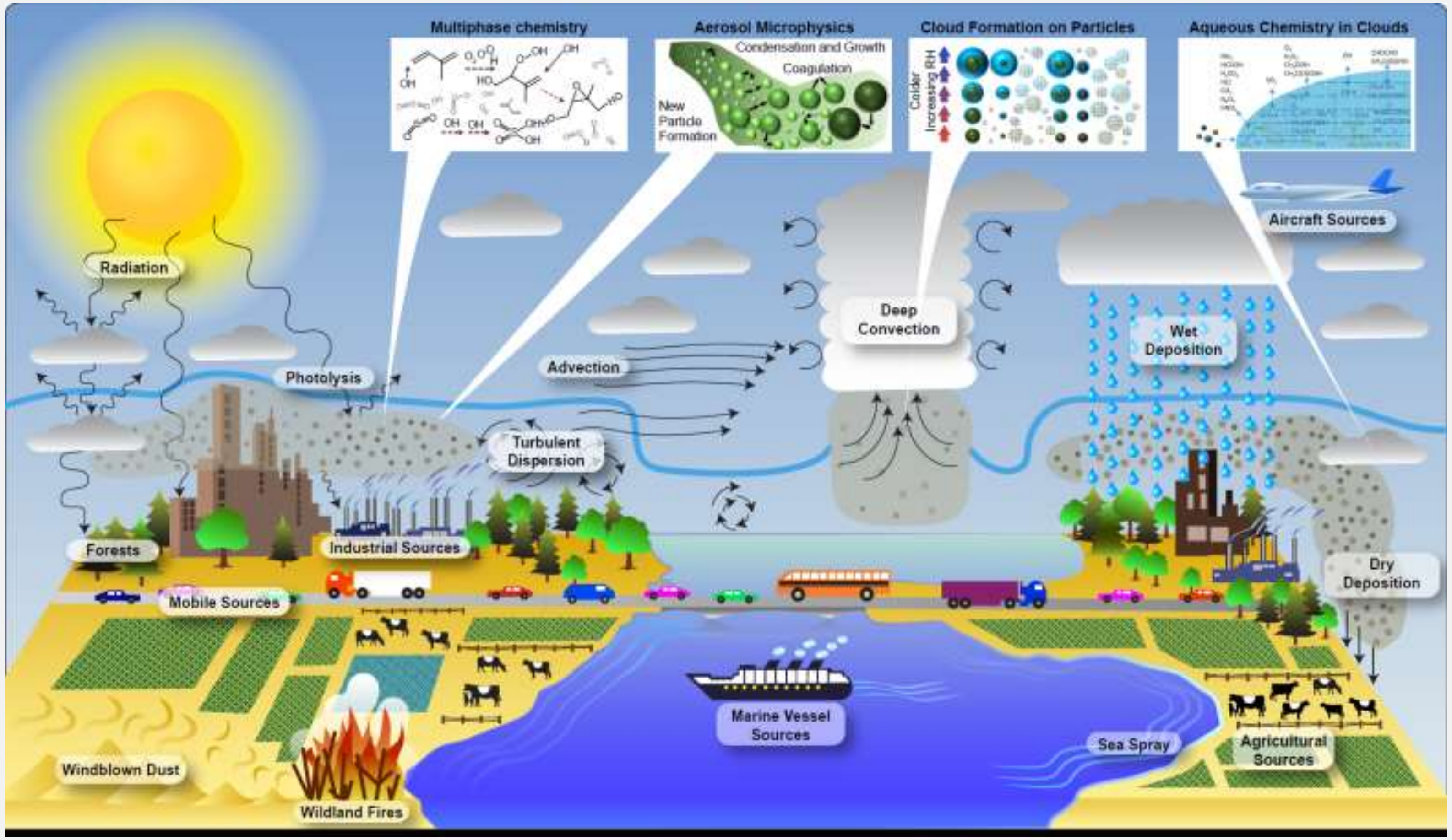
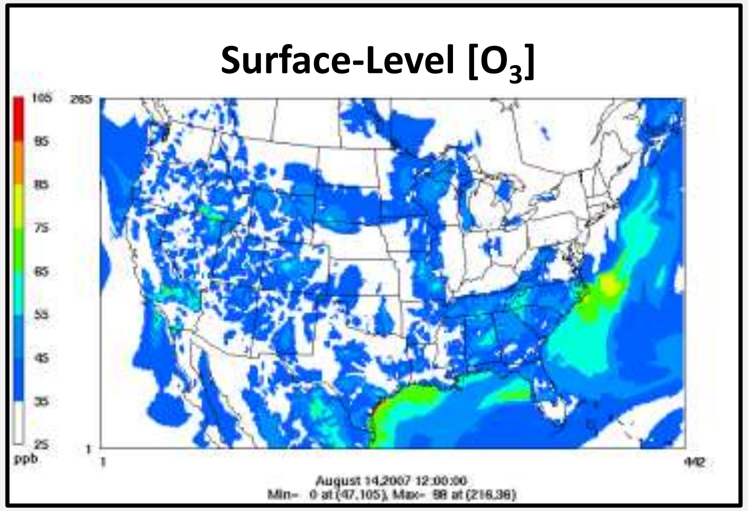
HFPO-DA (Hexafluoropropylene oxide – Dimer Acid)
HFPO-DAF (Hexafluoropropylene oxide – Dimer Acid Fluoride)

Investigate with Regional-Scale Chemical Transport Model

Community Multiscale Air Quality (CMAQ) Model





Model Inputs:

- ~200-300 key pollutants
- Emissions rates
- Chemical reaction rates
- Solubility, vapor pressure
- Land surface properties
- Temperature
- Wind speed/direction
- Precipitation
- …

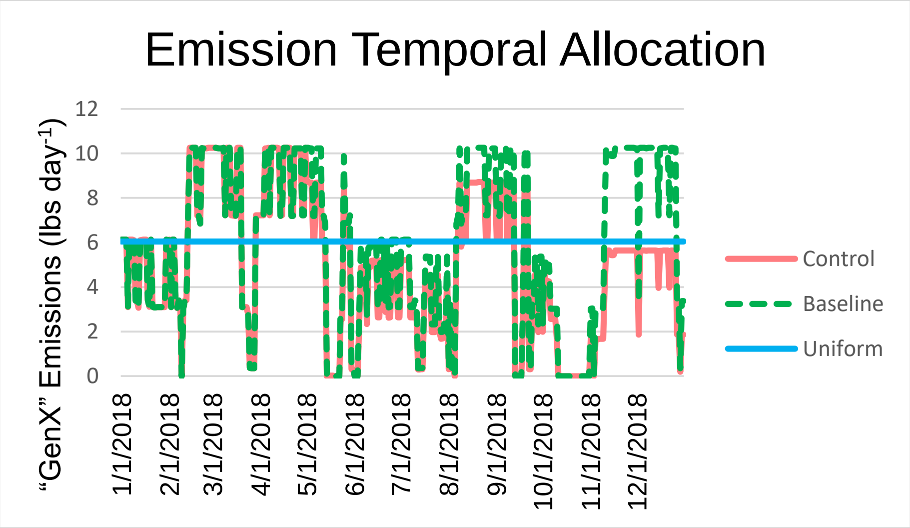
CMAQ

Model Outputs:

- Concentration fields
- Dry Deposition fields
- Wet Scavenging fields
- …

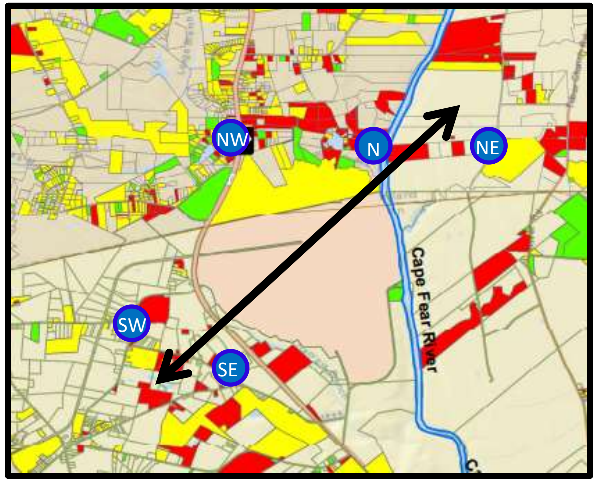
CMAQ-PFAS Development

- PFAS Species
  - 26 explicit
  - 1 lumped “Other PFAS”
- Simulation details:
  - Eastern NC/Northeast SC
  - 1 km x 1 km horizontal resolution
  - Surface → 20+ km altitude
- Scenario details:
  - CY 2018
  - Annual Emission rates from 2017 report
  - 1) Base Case (“*Base*”)
    - Temporal (daily) distribution informed by records shared by facility
    - Some emissions reductions later in 2018 with installation of new controls
  - 2) Carboxylic Acid Case (“*CarbAcid*”): All acyl fluoride compounds (including HFPO-DAF) are assumed to be emitted as carboxylic acids



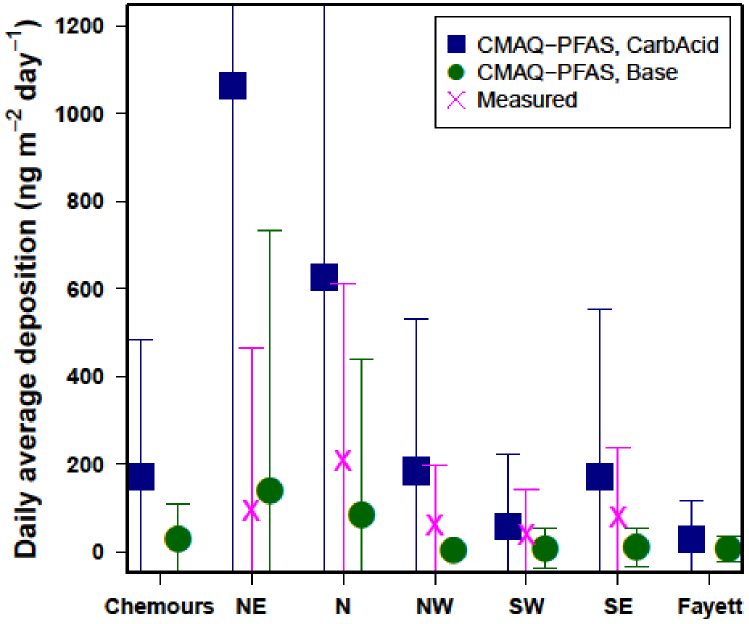
CMAQ-PFAS Evaluation against GenX Measurements

Evaluation Sites

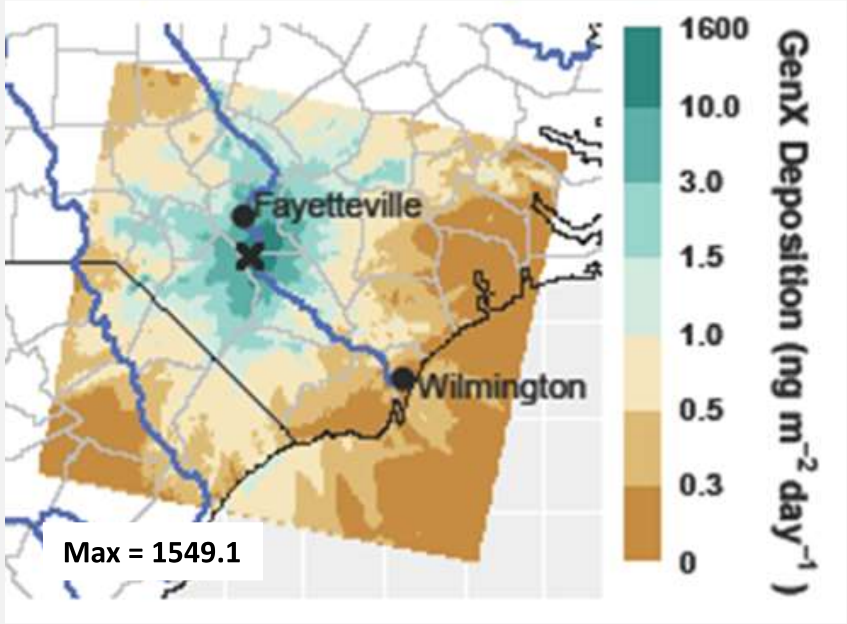


Measured data courtesy of
NC Department of Environmental Quality

"GenX" Deposition Flux (HFPO-DA + HFPO-DAF)



"GenX" Mean Daily Deposition

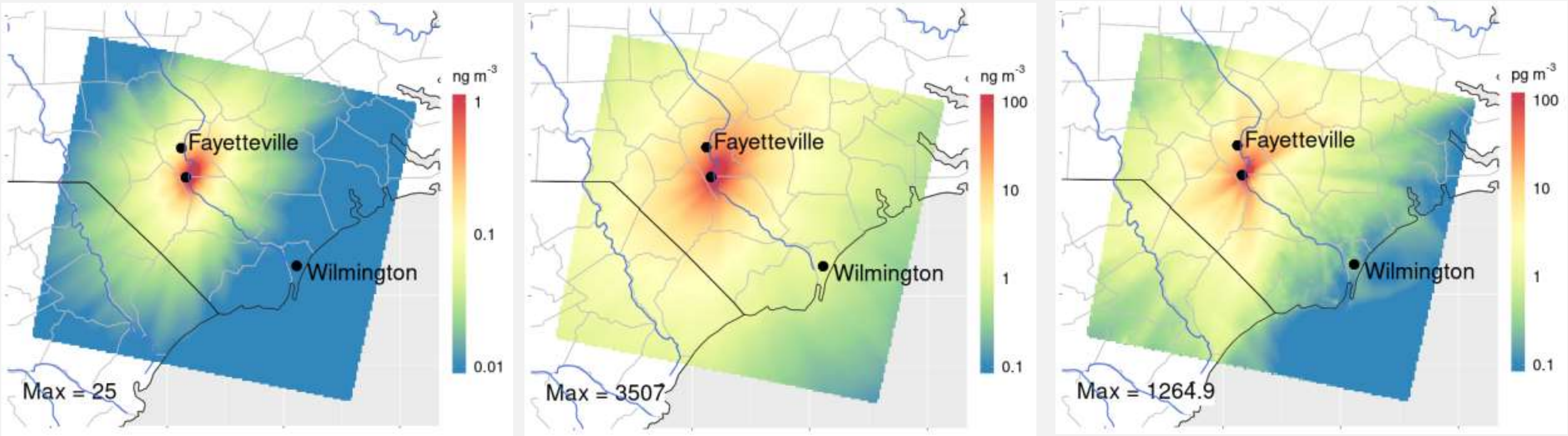


- Model (*"Control"* Case) captures magnitude of deposition observations with some variability within uncertainty of meteorology accuracy and measurement methods
- GenX Deposition is strongly elevated near facility and dispersed throughout the region

$$D_{(<10\ km)} = \sim 50x\ D_{(>50\ km)}$$

Annual Mean Ambient Air Concentration

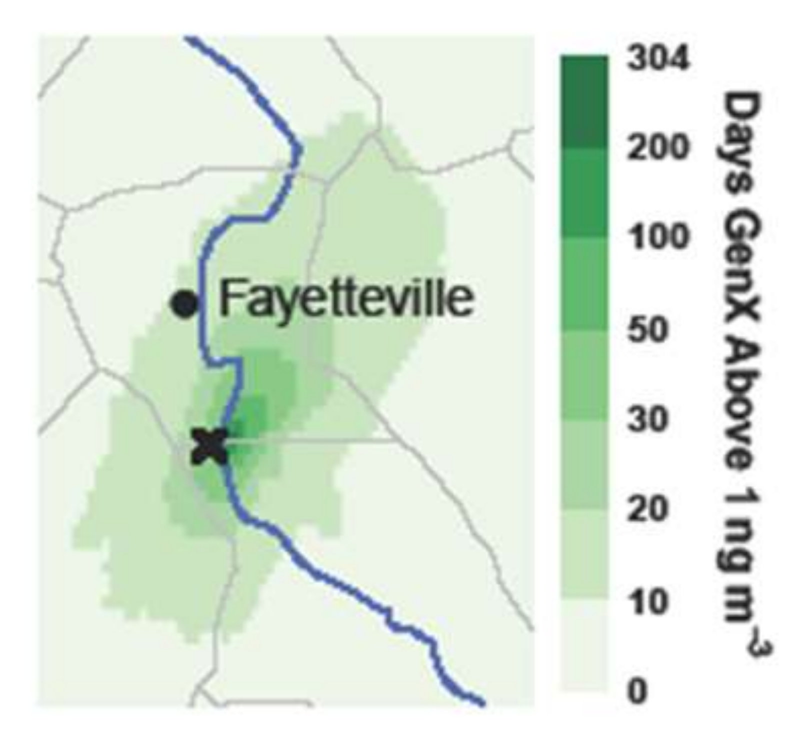
"GenX" ($ng\ m^{-3}$, gas + particle) | **Total PFAS ($ng\ m^{-3}$, gas + particle)** | **Total PFAS Particulate ($pg\ m^{-3}$)**

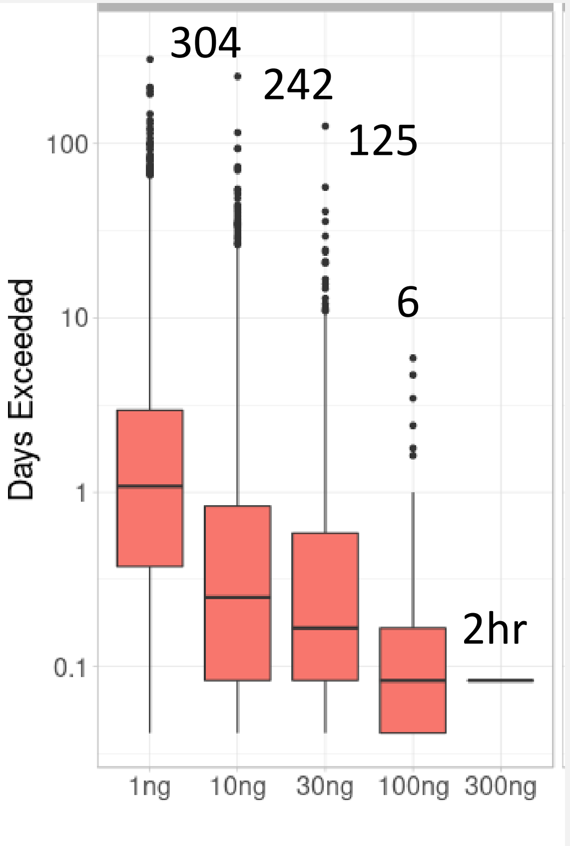


- Ratio Total PFAS / GenX ambient air concentrations mimic emissions ratio (100:1)
- Particulate PFAS concentrations are about 1/1000 Total PFAS and often exceed 100 $pg\ m^{-3}$ near the facility

Emissions Assumptions Affect Peak Air Concentrations

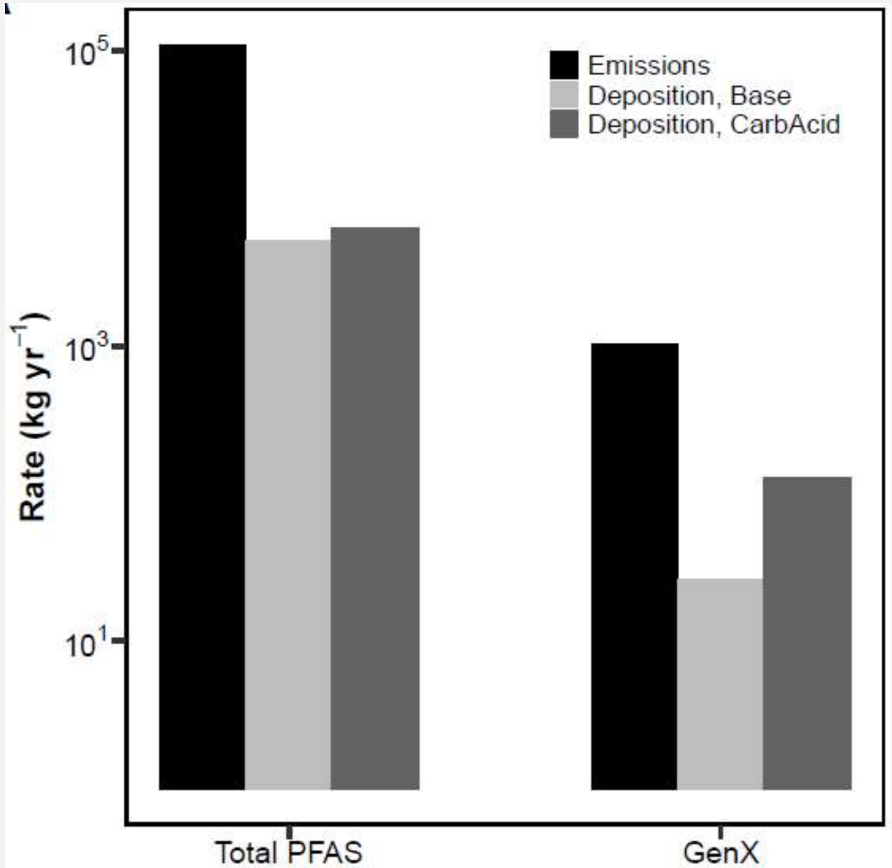
Cumulative Time with "GenX" Concentrations Exceeding 1 ng m^{-3}

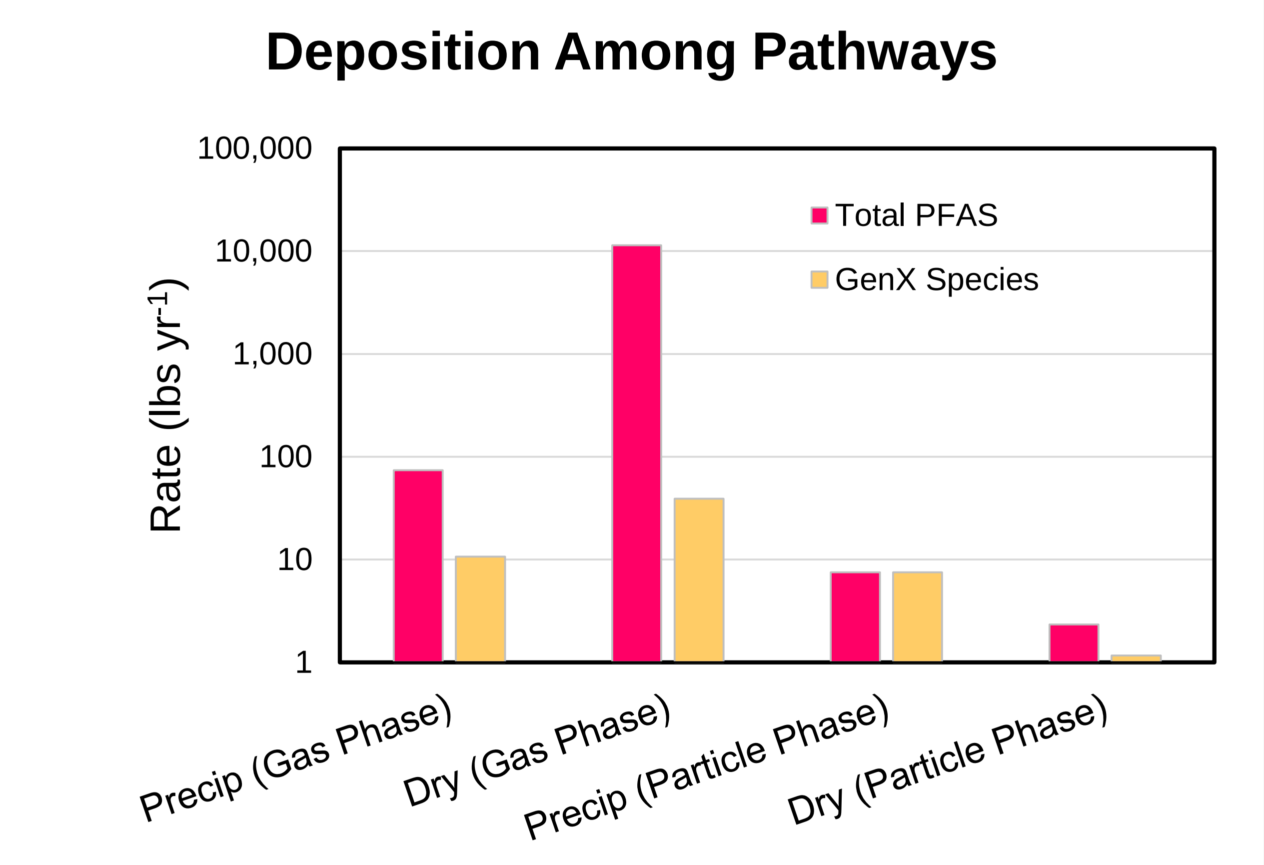




- Locations up to ~30 km away are predicted to experience more than 5 cumulative days of "GenX" air concentrations exceeding 1 ng m^{-3}
- Assumptions about emissions temporal profile impact frequency of exceedances depending on design threshold

Domain-Wide Deposition and Pathway Distribution



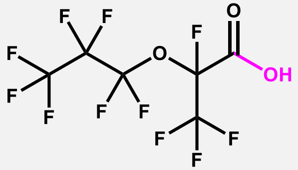


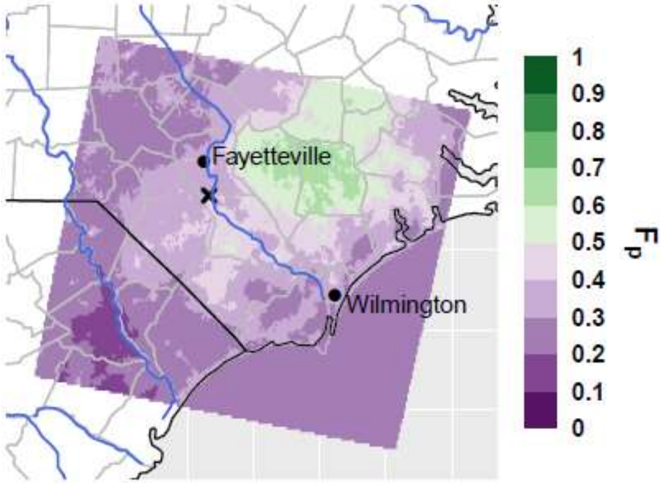
- Only ~5% of total PFAS and 2.5% of "GenX" species deposit inside the domain we have simulated. **95% are transported to the rest of the continent and beyond**
- GenX species are the largest component of PFAS particle deposition from the facility, within this domain

Gas-Particle Partitioning of Semivolatile Species

HFPO-DA

Semivolatile:
Henry's Law (H^{eff}) =
~ 2×10^9 M/atm @ pH=2

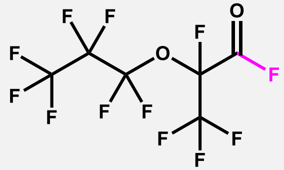


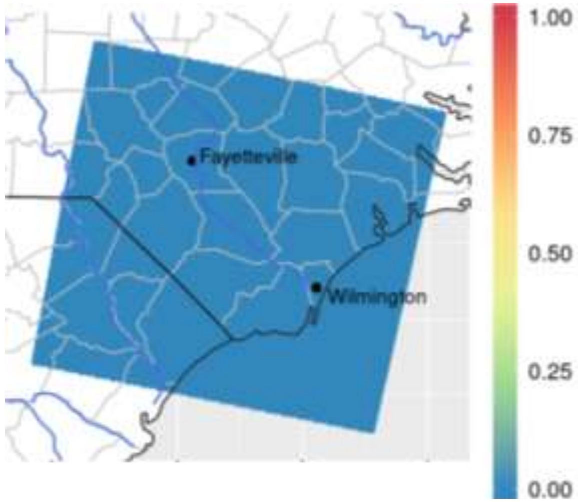


$$\frac{[HFPODA]_{Particle}}{[HFPODA]_{Gas+Particle}}$$

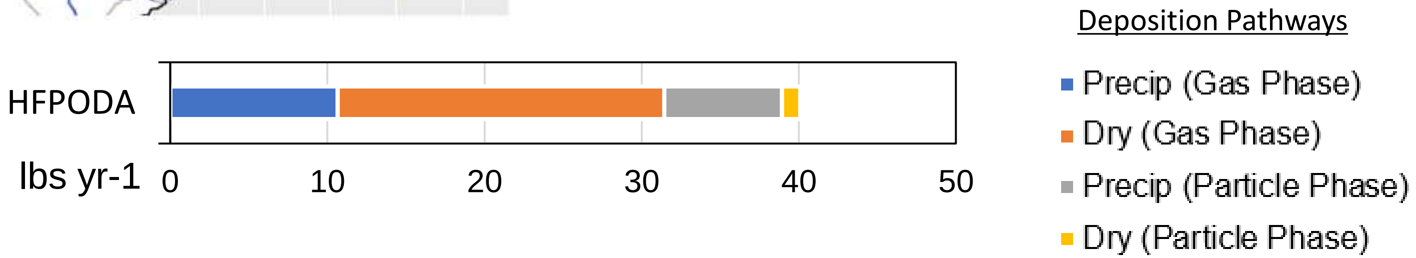
HFPO-DAF

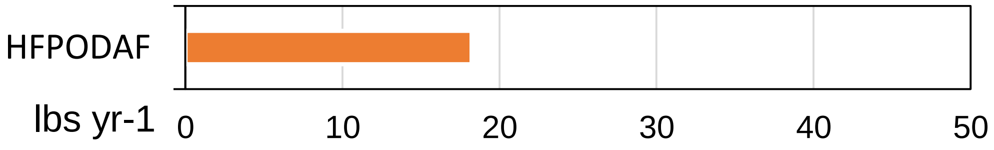
Volatile:
Henry's Law (H^{eff}) =
~ 5×10^{-2} M/atm





$$\frac{[HFPODAF]_{Particle}}{[HFPODAF]_{Gas+Particle}}$$





A full-science chemical model is needed to capture the relative strength of each deposition pathway → likely important for quantifying transfer to other environmental media

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Conclusions

- “GenX” species, while the focus of much attention, contributes 1% of the total PFAS emissions by mass at the NC facility

- CMAQ-PFAS was able to quantitatively capture the magnitude of GenX deposition observed:
  - Suggests that GenX-related species emissions estimates are likely reasonable
  - Required consideration of complex atmospheric phenomena like gas-particle partitioning sensitivity to fine particle pH and liquid water content

- Modeled surface concentrations and deposition are most enhanced near the source, but that’s not the whole story
  - Modeled concentration and point deposition within 10 km of the facility are ~50x higher than those beyond 50 km
  - Modeling estimates that ~97% of GenX and 95% of total PFAS emissions are transported beyond 150 km from the plant

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Future Work and Research Needs

- **Next Steps**
  - Expand analysis to other areas of the US with significant PFAS air emissions and examine longer-range transport (~hundreds-thousands of kilometers)
  - Constrain the gas-phase oxidation of PFAS compounds with reactive functionalities (e.g. alkenes, acid fluorides, ethers, etc.)
- **Comprehensive Research Needs**
  - Emissions rates, composition, and activity data from unconstrained sources like industrial facilities using PFAS, incinerators and AAAF usage
  - Chemical property measurements (vapor pressure, solubility, reactivity) for specific novel PFAS compounds currently in production/use, and refinement of predictive techniques for estimating properties of highly fluorinated species
  - Toxicity for individual species or functionalities to help us better identify problematic inhalation exposures or deposition loads
  - Ambient air and wet/dry deposition PFAS measurements for model evaluation

Collaborations and Stakeholder Engagement

EPA Office of Research and Development
- Stack sampling and method development
- Air sampling method development
- Water and soil sampling
- Property estimation
- Spatial mapping tools

The Chemours Company
- Ongoing collaboration
- Emissions composition, magnitude and temporal variability
- Chemical properties and transformations
- Process control – thermal oxidizer installation

EPA Office of Air and Radiation
- Office of Air Quality Planning and Standards
  - Emission Modeling
  - Fate and Transport Modeling
  - Policy
- Office of Air Programs

North Carolina DEQ
- Preliminary modeling
- Deposition measurements near facility
- Stack sampling
- Process-level understanding

States and EPA Regions
- NH, NJ, NY, MI and VT
- Regions 1, 2, 4 & 5
- Interested in using CMAQ-PFAS to
  - analyze risk
  - understand background levels
  - quantify regional transport

Academic Groups
- UNC (Chapel Hill, Charlotte, Wilmington), North Carolina State, University of Toronto
- National Atmospheric Deposition Program
- Ambient air and deposition sampling
- Human exposure and public health
- Atmospheric chemistry

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For More Information

- The research discussed in this presentation is part of EPA's overall efforts to rapidly expand the scientific foundation for understanding and managing risk from PFAS.

- For more information on EPA's efforts to address PFAS, please visit the following websites
  - EPA PFAS Action Plan – https://www.epa.gov/pfas/epas-pfas-action-plan
  - EPA PFAS Research – https://www.epa.gov/chemical-research/research-and-polyfluoroalkyl-substances-pfas

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