CMAQ-PFAS development for predicting the fate and transport of per- and polyfluoroalkyl substances (PFAS) in the atmosphere

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CMAS 2020

Research-Oriented Presentation

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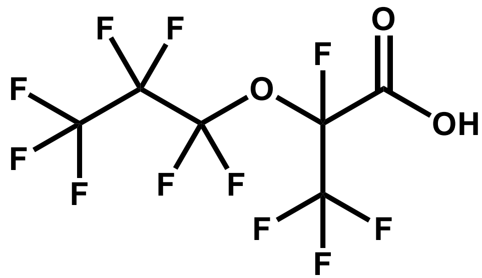
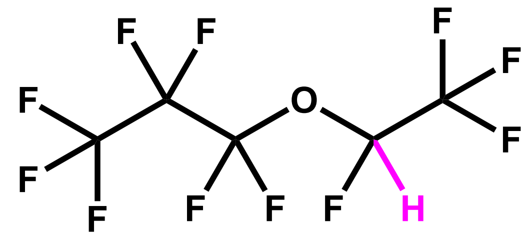
This work has been internally reviewed for technical quality and has been submitted to Environmental Science and Technology

Per- and Polyfluoroalkyl Substances (PFAS)



Perfluoro: carbons are completely fluorinated



Polyfluoro: some hydrogens remain

- **Found in**: food packaging, nonstick products, stain & water repellent fabrics, film-forming foam fire suppressants, and more…

- **Published studies:** individual PFAS have demonstrated impacts on many organs & systems
  - Reproduction: Reduced male fertility & birth weight, preeclampsia
  - Endocrine system
  - Thyroid
  - Elevated cholesterol
  - Ulcerative colitis
  - Cancer: testicular, kidney

OECD Synthesis paper on per- and polyfluorinated chemicals (PFC). 2013

PFAS in the Cape Fear River Basin

- PFAS found along Cape Fear River, into Wilmington, and in Wilmington residents' blood *Kotlarz, et al.* EHP, 2020.

- Fluoropolymer manufacturer (Chemours)

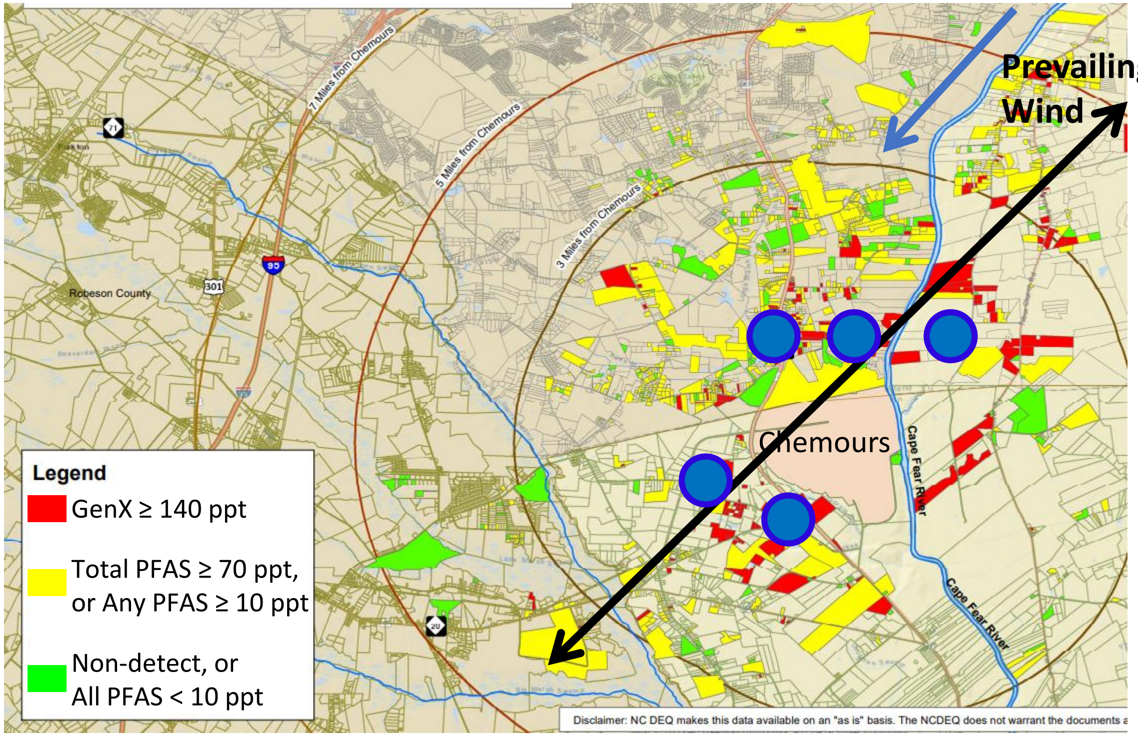
- Relatively isolated from other potential PFAS air sources: nearest known source is 250+ miles away

- Reductions in Cape Fear River water after mitigation steps taken

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

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 measurements have confirmed deposition of GenX from air



NC Department of Environmental Quality

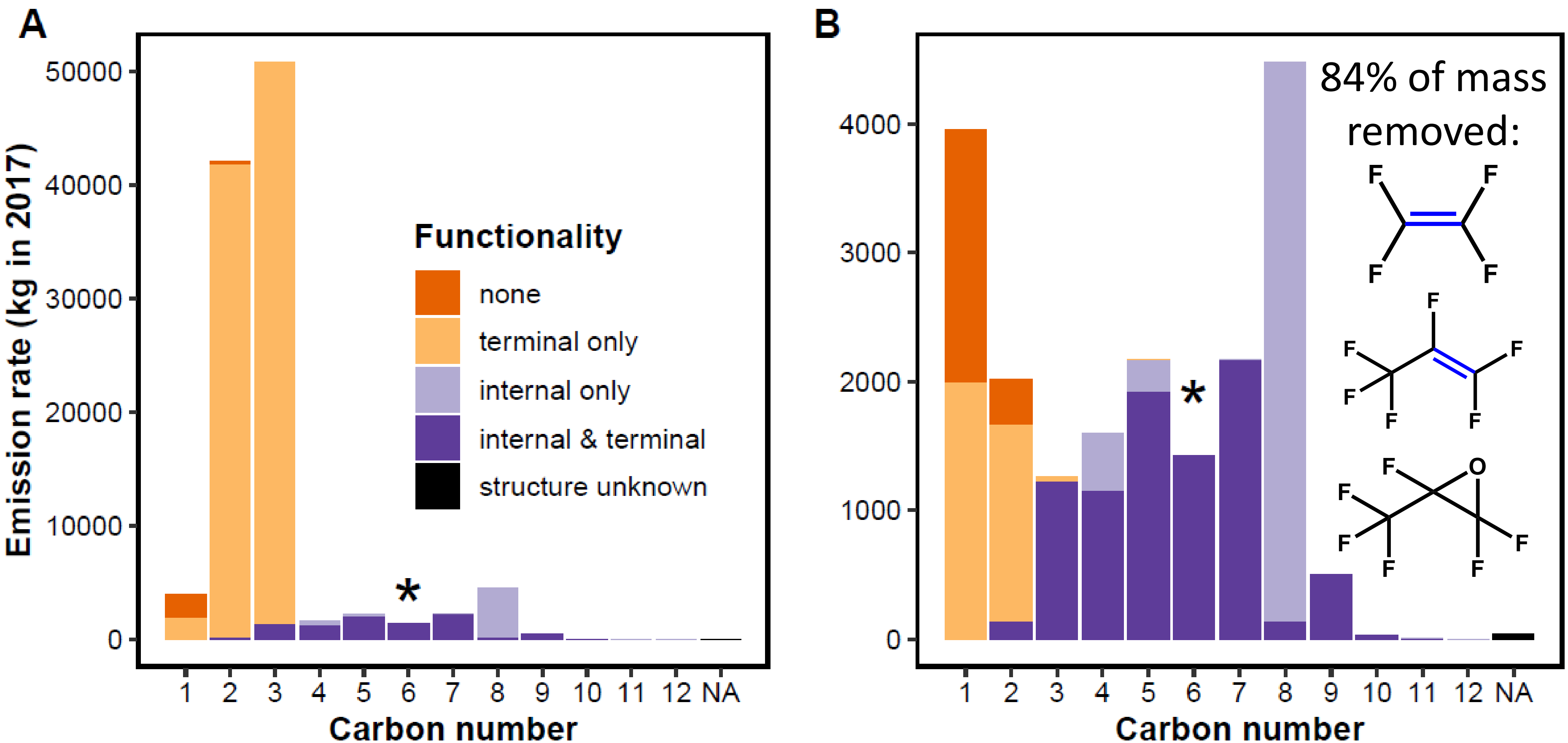
- Influence of air emissions have been corroborated with **qualitative** plume dispersion modeling (NCDEQ).

See also: Galloway et al., EST, 2020

Research Objectives

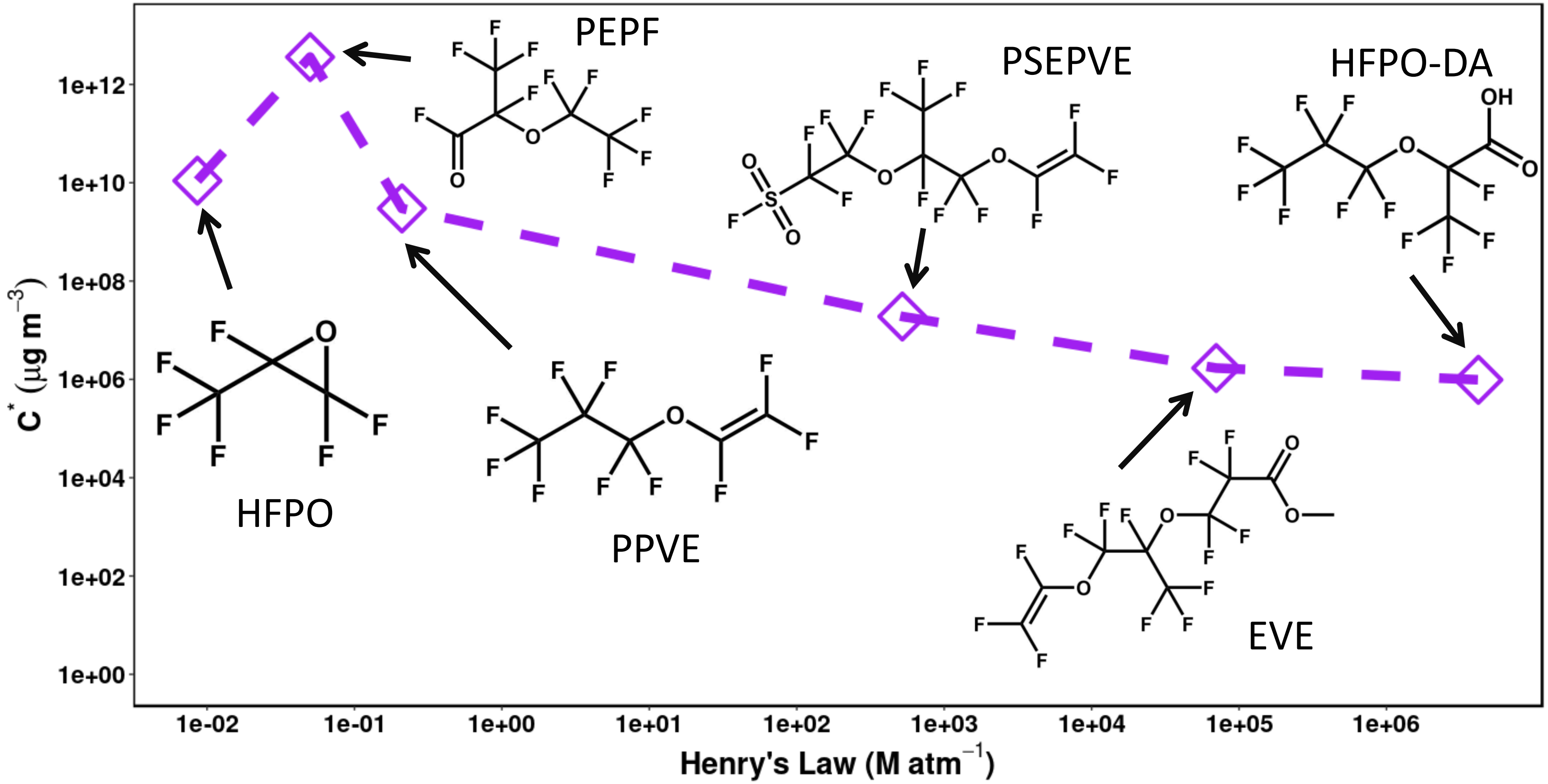
1. Develop a model of the fate and transport of PFAS air emissions from The Chemours’ Company Fayetteville Works facility (CMAQ-PFAS)
2. Evaluate the predicted deposition of one compound (GenX) against measurements taken by North Carolina Department of Environmental Quality (NC DEQ).
3. Quantify the ambient air concentration and deposition flux of PFAS in the vicinity of the facility and further downwind (within 150 km).
4. Assess the importance of PFAS physicochemical properties in determining their fate in ambient air. (How complex should our air model be?)

PFAS Emissions Speciation & Rates



- Detailed air emissions report for 2017 from manufacturer, based primarily on mass balances
- 53 PFAS reported at total emission of 109,393 kg in 2017

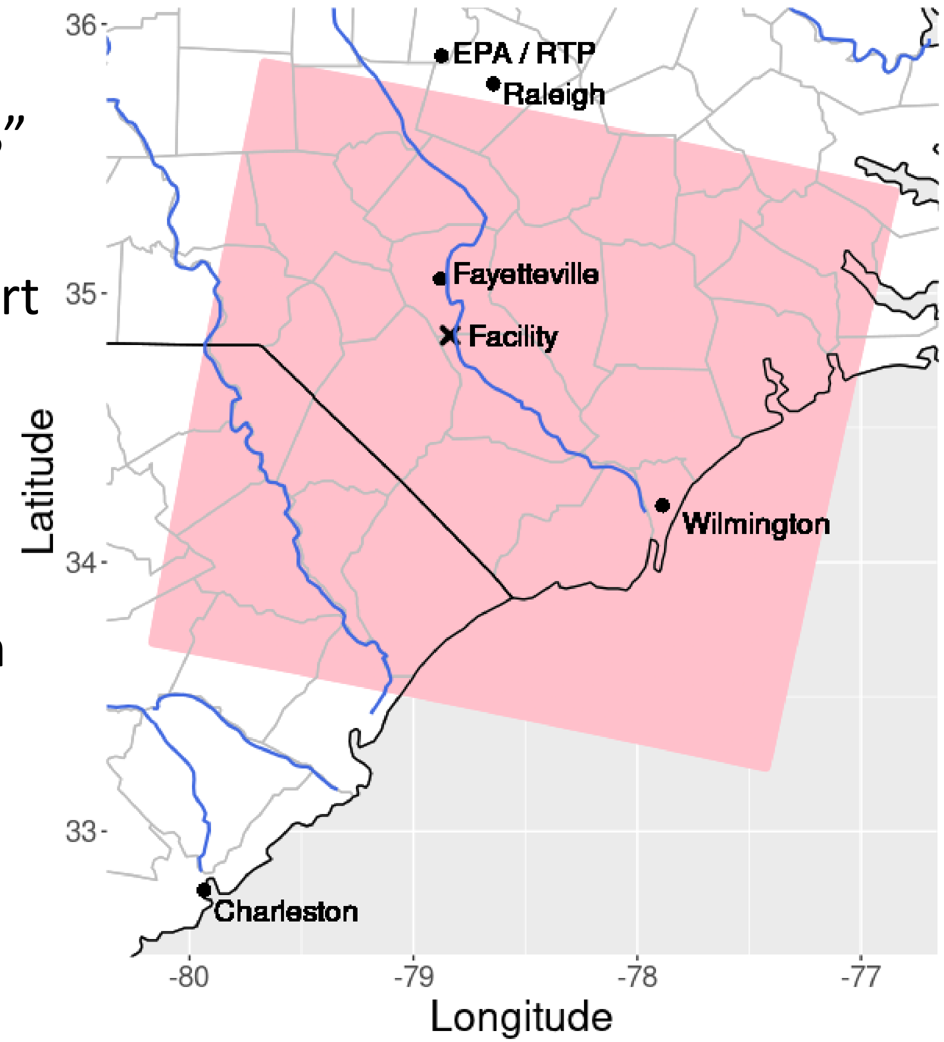
Compounds are diverse in size and functionality



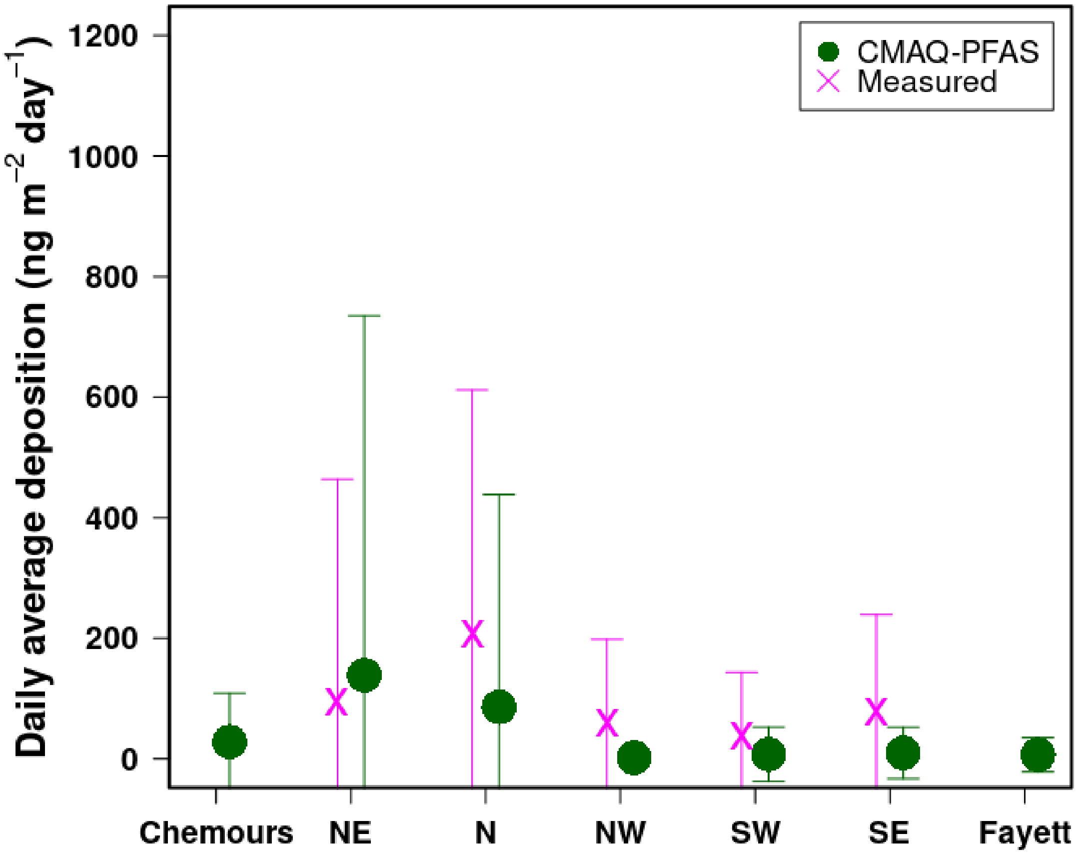
- Physicochemical properties estimated with the EPA OPERA model:
  - Most mass should heavily favor partitioning to gas phase
  - Condensation to airborne particles and cloud drops as well as deposition to surface waters is still important to consider

CMAQ-PFAS development

- PFAS emissions:
  - 26 explicit, 1 lumped "other PFAS"
  - Reductions based on controls
  - Rates from Chemours' 2017 report
- Simulation details:
  - Jan 1st – Dec 31st 2018
  - Eastern NC/ Northeast SC
  - 1 km x 1 km horizontal resolution
  - Surface → 20+ km altitude
  - NEI 2014 (projected to 2018)



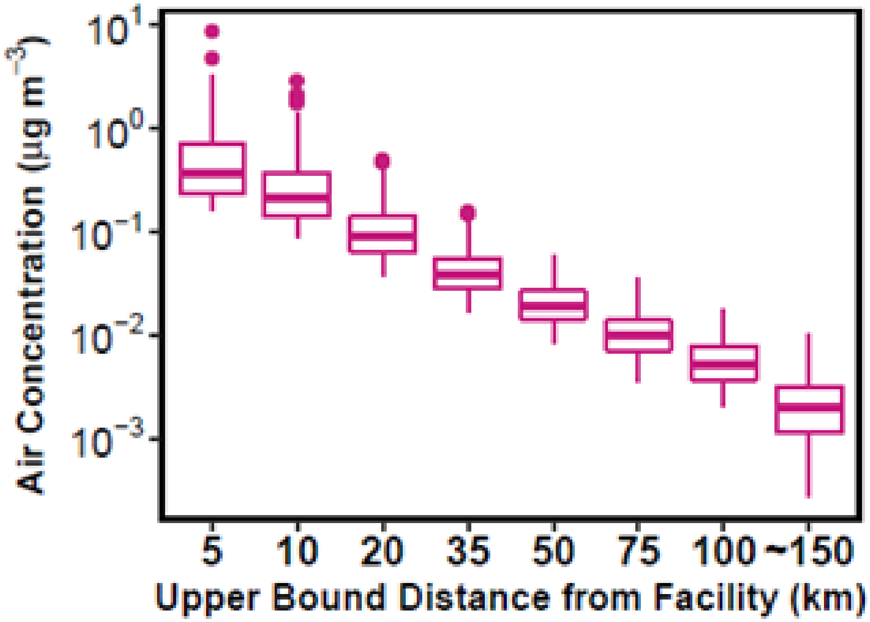
CMAQ-PFAS near-field deposition evaluation

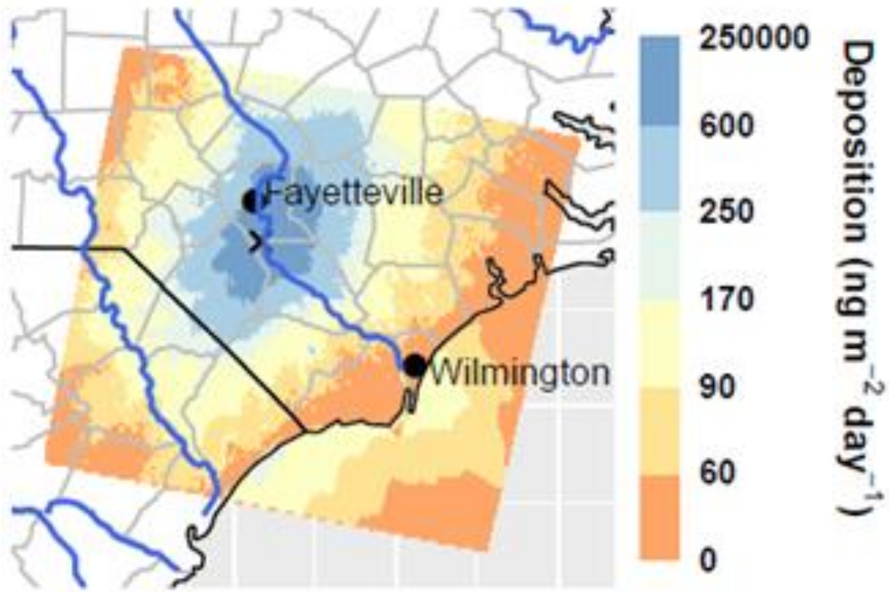


Data courtesy of:
NC Department of Environmental Quality

- All measurements are within 5km of the facility, for one compound (GenX)
- Base model (green circles) captures magnitude of deposition observations (pink x's) with some variability within uncertainty of meteorological predictions and measurement methods.

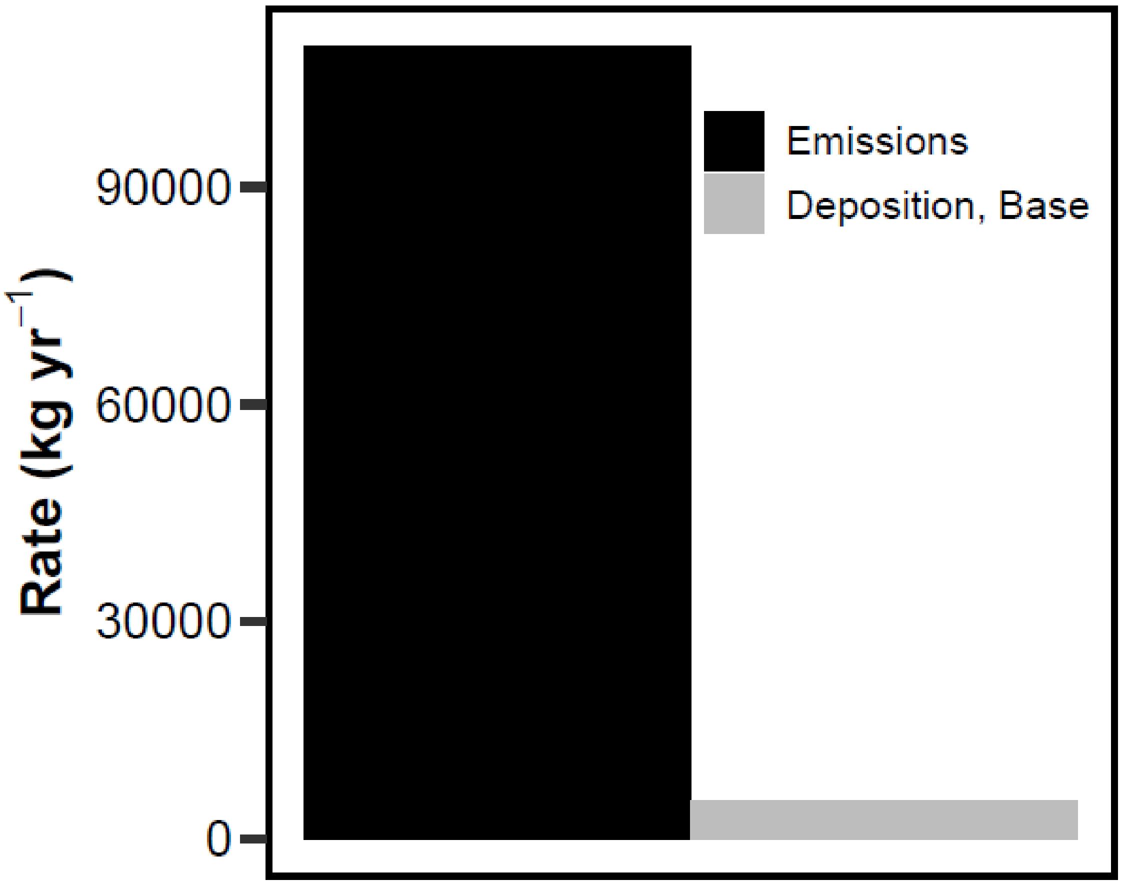
Ambient air concentration & deposition of total PFAS





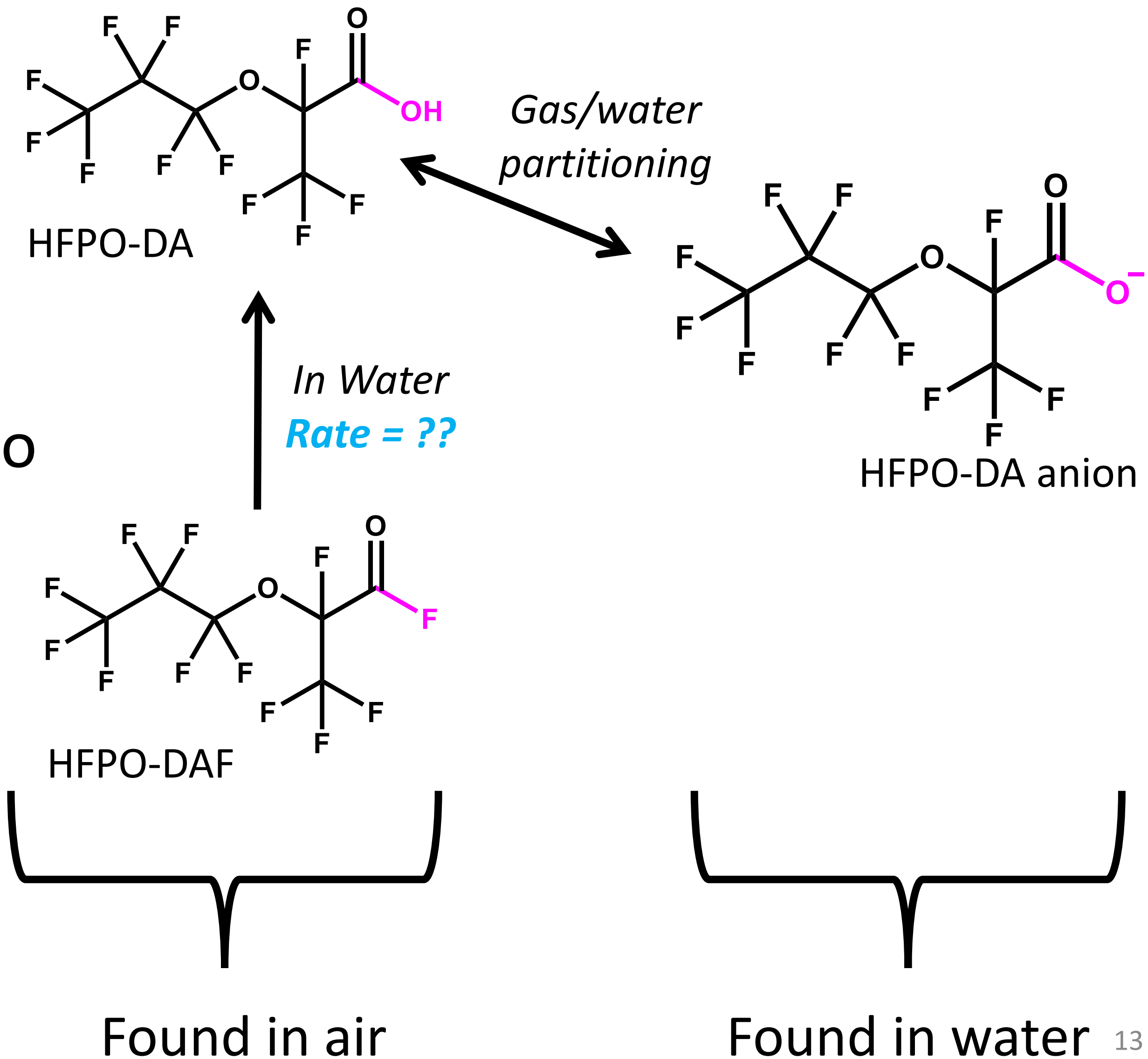
- ➢Max air conc (model)= 8.5 µg m^{-3}, domain-wide median = 0.004 µg m^{-3}
- ➢Max deposition (model)= ~245 µg m^{-2} day^{-1}

Implications



- 4.8% of total PFAS is predicted to deposit within ~150 km of the manufacturer.
- The rest is transported further into the U.S. and beyond

Atmospheric chemical transformations

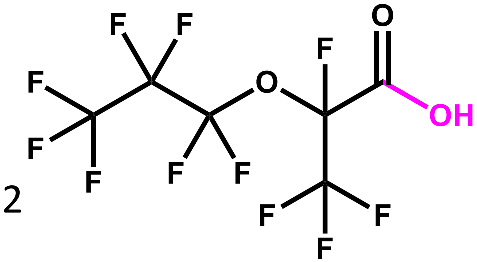


- Acyl fluorides rapidly hydrolyze to carboxylic acids in bulk water

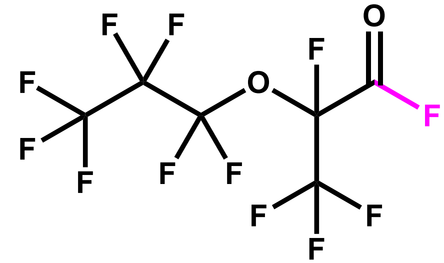
Bunton, C. et al. J. Org. Chem., 1966.

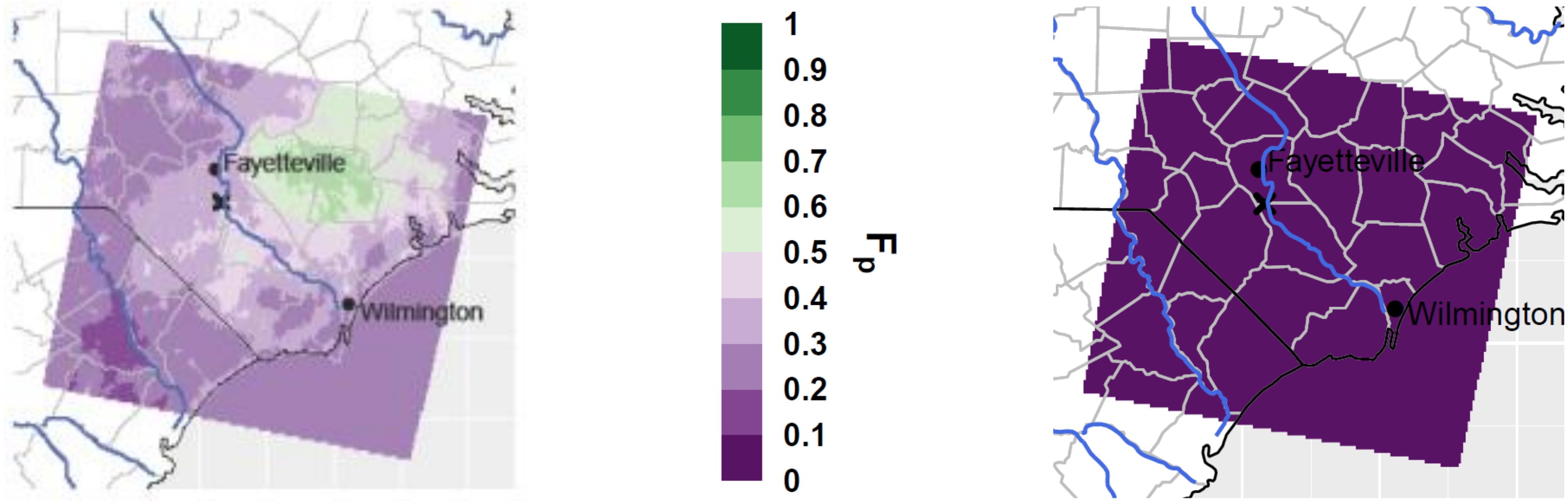
Impact of acyl fluoride hydrolysis: partitioning

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



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





- Structure determines physicochemical properties, and in turn determines phase state
- F_p is highly dependent on aerosol pH and liquid water content

Deposition of semivolatiles

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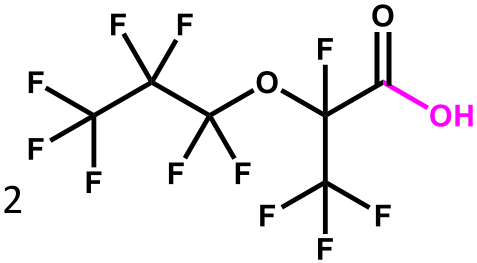
~ $2x10^{9}$ M/atm @ pH=2



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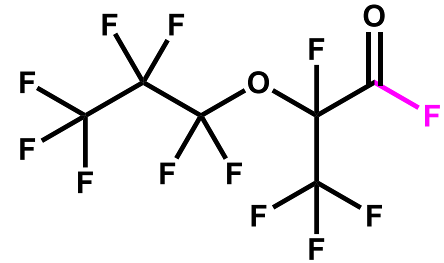
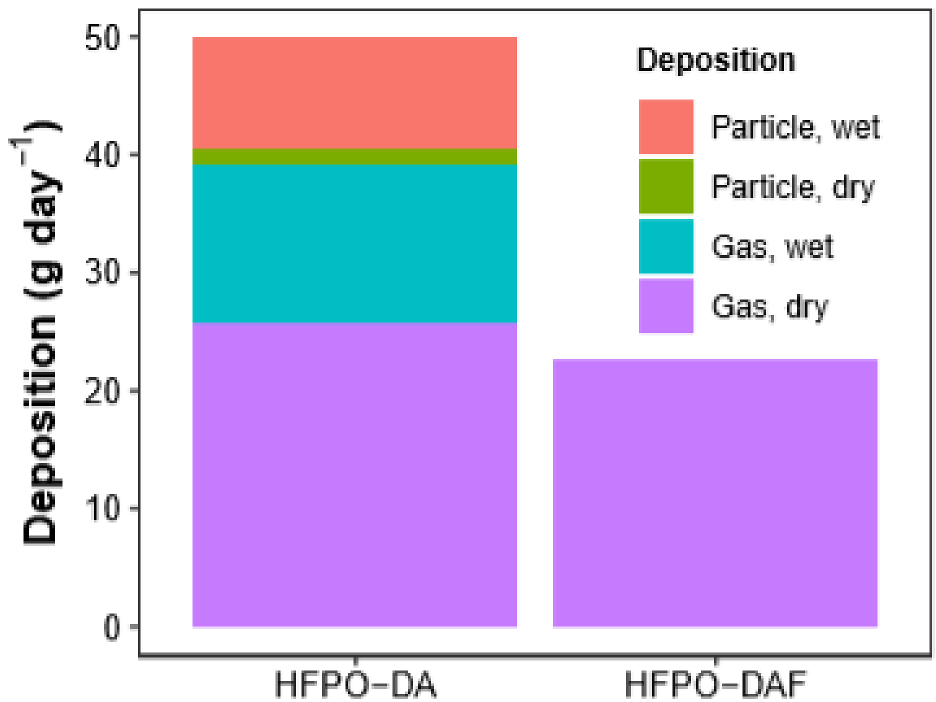
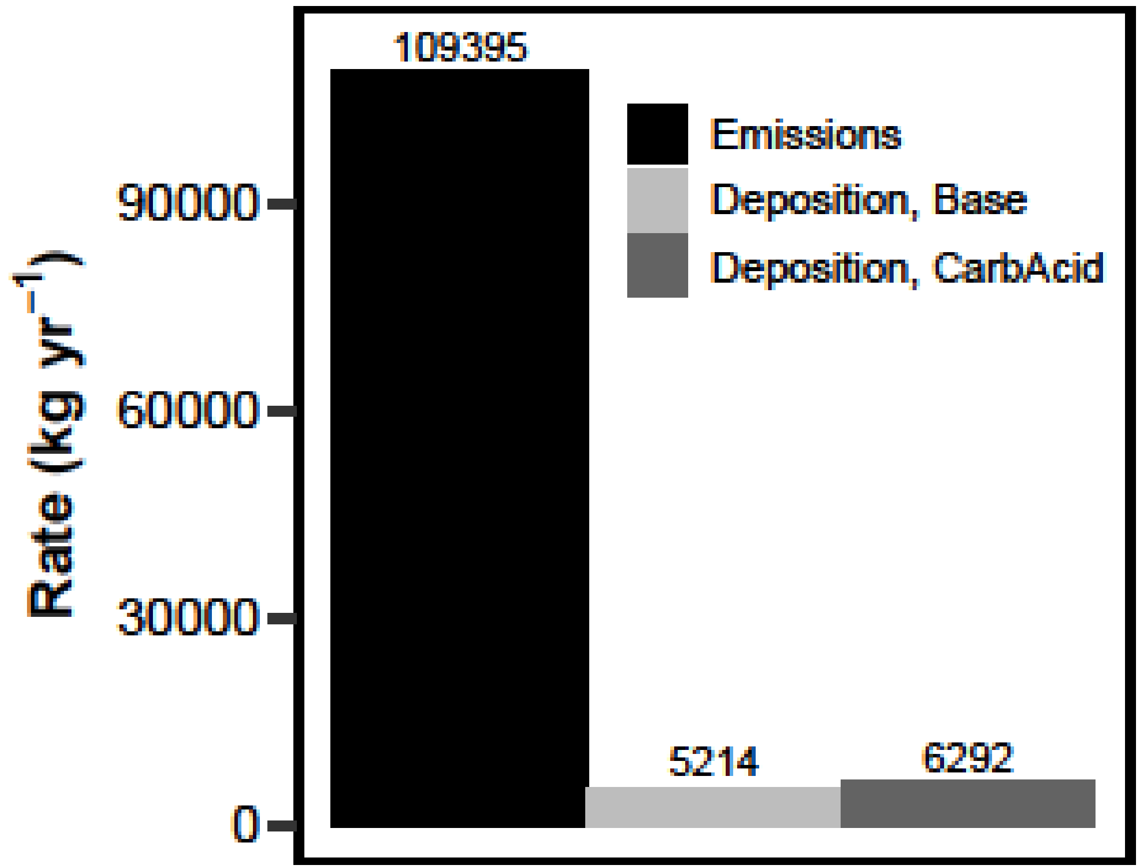




- ➢ Including chemistry and dynamic partitioning is vital for capturing the correct atmospheric behavior

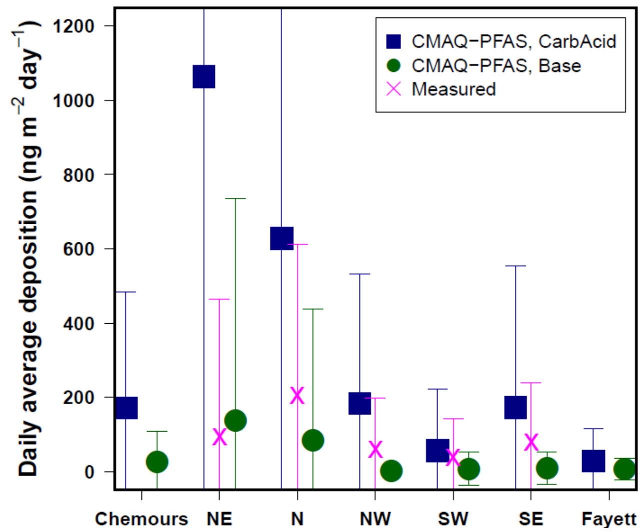
Impact of acyl fluoride hydrolysis: deposition

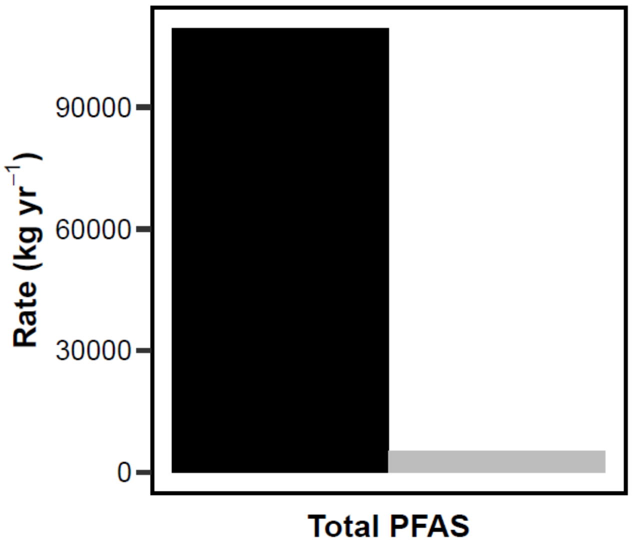


- ➢ Assuming acyl fluorides convert rapidly to carboxylic acids increases their deposition, but does not increase total deposition substantially

Conclusions

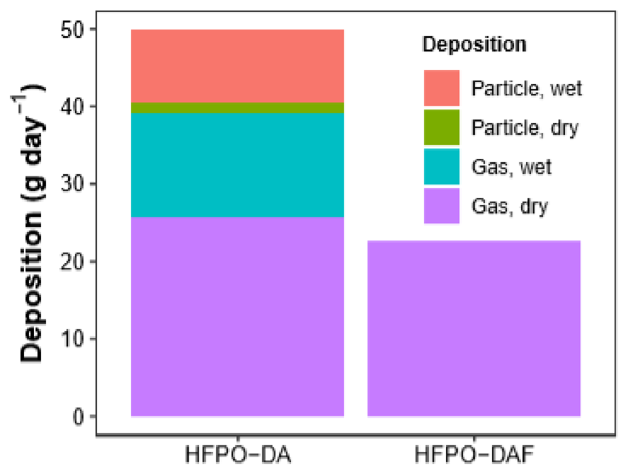
1. A new, state of the science model, CMAQ-PFAS, has been developed to model the air transport and fate of PFAS





2. ~95% of emissions are transported > 150 km downwind

3. Including chemistry and dynamic partitioning is vital for capturing the correct atmospheric behavior



Expansion to Continental Scale PFAS Problem

1. Emission Inventory is critical:
   - Manufacturers, industrial users, incinerators, wastewater treatment facilities, AFFF sites
   - Magnitude and speciation vary widely
   - Present-day vs. recent history vs. historical vs. future

2. Physical-chemical properties: important but tractable with property estimation once we know what compounds are involved.

3. Ambient air and deposition measurements:
   - Irreplaceable for model evaluation
   - But models can help inform what to look for or where to look

4. Toxicity: helpful for narrowing our problem but we can help the toxicologists by predicting which compounds have highest exposure.

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