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# Understanding Processes That Alter PFAS Profiles

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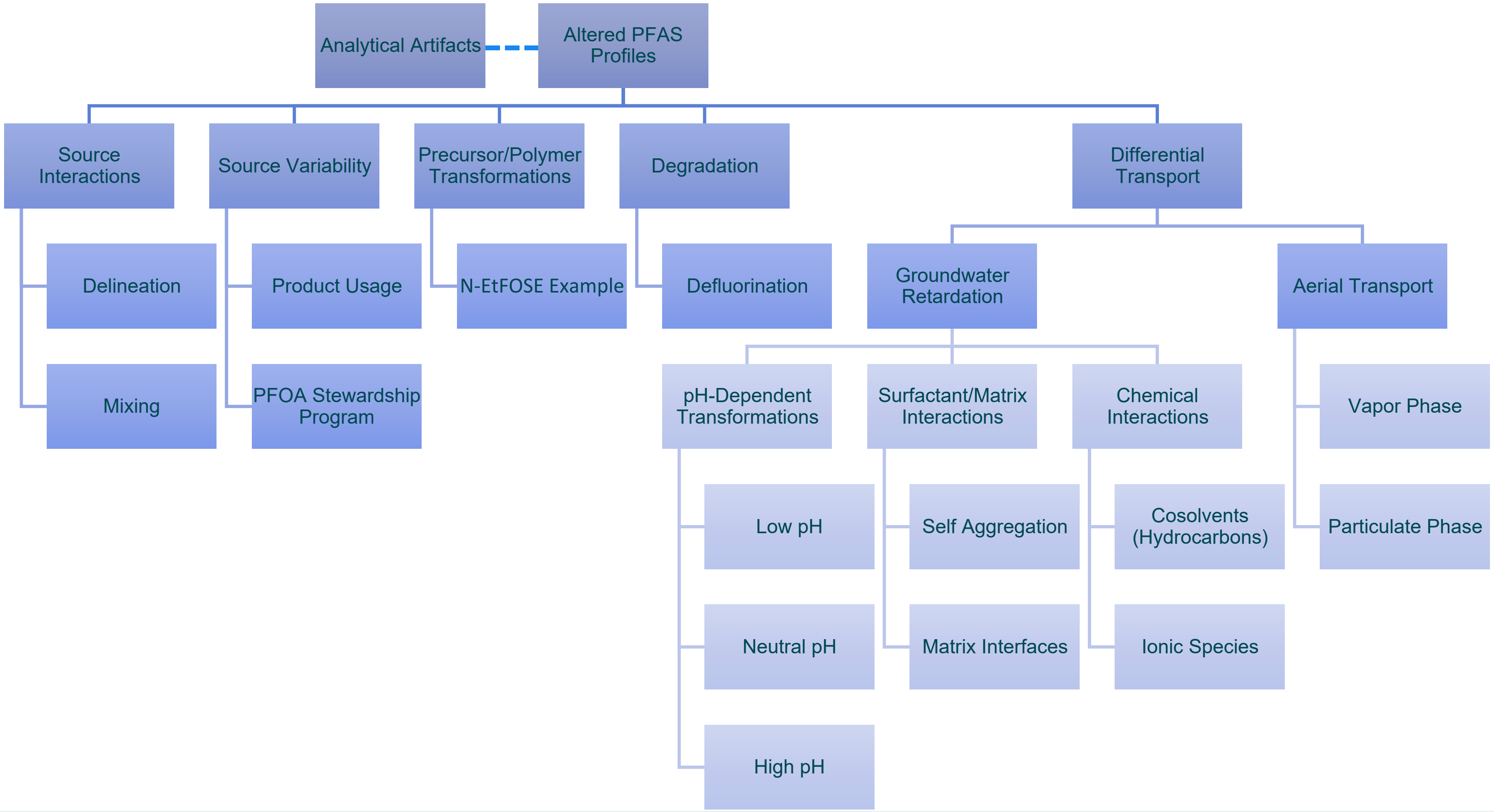
# Variability in PFAS Profiles-Multitude of Possibilities



# Changing PFAS Usage

**2000**
3M voluntarily begins phase out of PFOA and PFOS, initiates replacement with short-chained PFAS

**2002**
USEPA begins issuing rules under TSCA requiring notification before manufacture, use, and/or import of certain PFAS

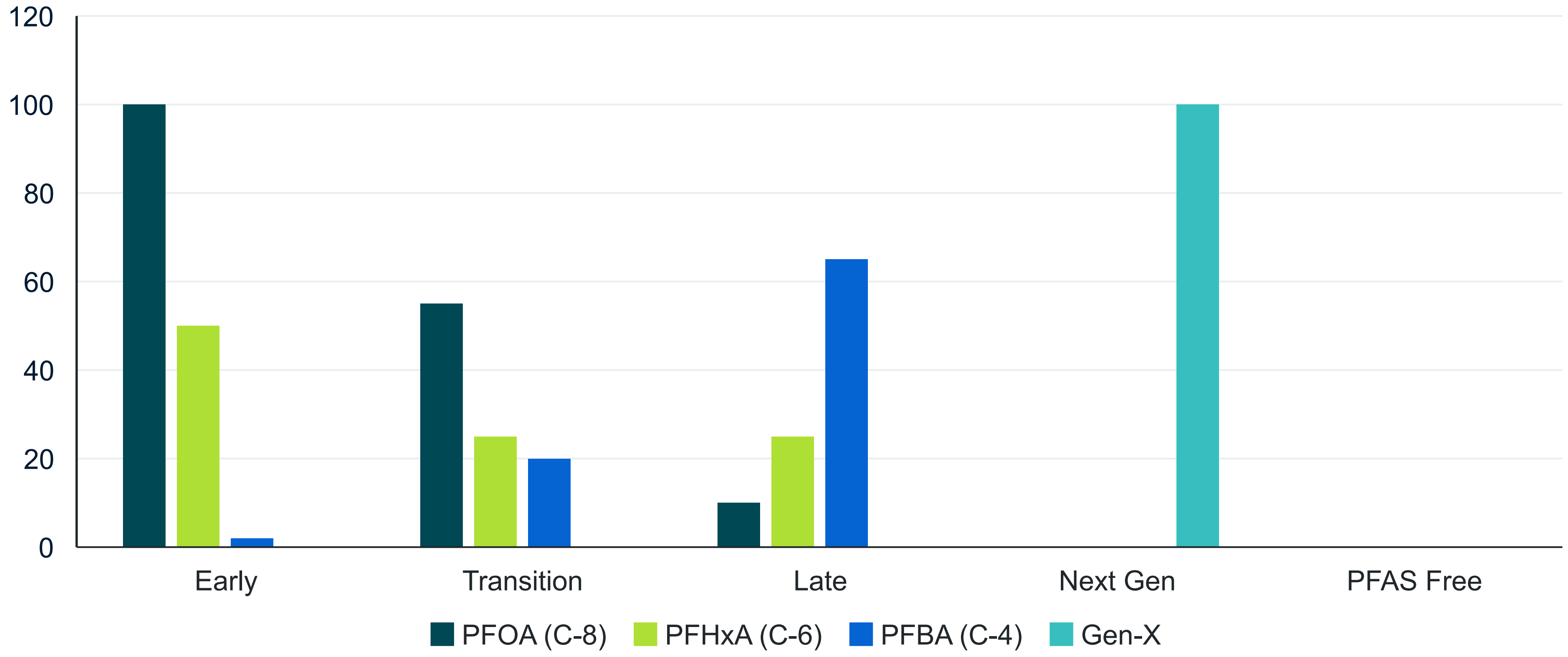
**2006**
USEPA initiates the PFOA Stewardship Program in which major manufacturers commit to reducing PFOA and long chained PFAS

**2009**
Stockholm Convention on POPs adds PFOS to Annex B (to be restricted)

**2019,2022**
Stockholm Convention on POPs adds PFOA and PFHxS to Annex A (to be eliminated)

**Current**
Increasing government and consumer pressure to phase out PFAS

# Move from long chained to short chained chemistries




Change in chemistries

- Phase out of C-8 and greater
- Replaced with C-6 and C-4
- Eventually moved to Gen-X and eventually PFAS-free for many applications

# Precursor Transformations : N-EtfOSE Example

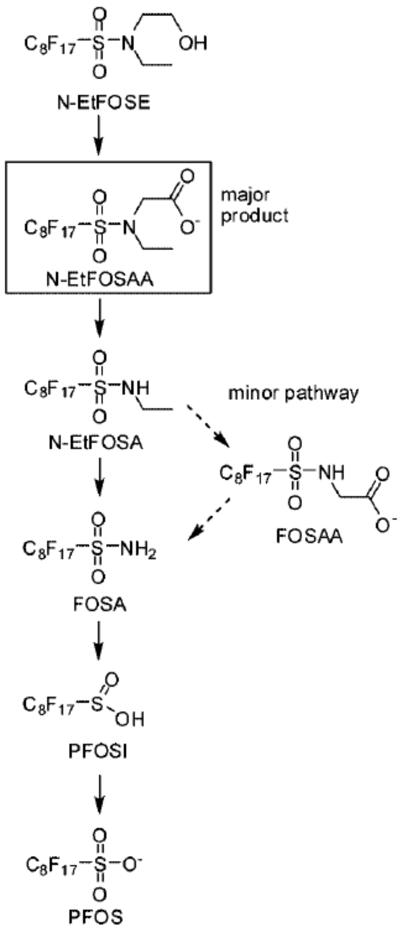


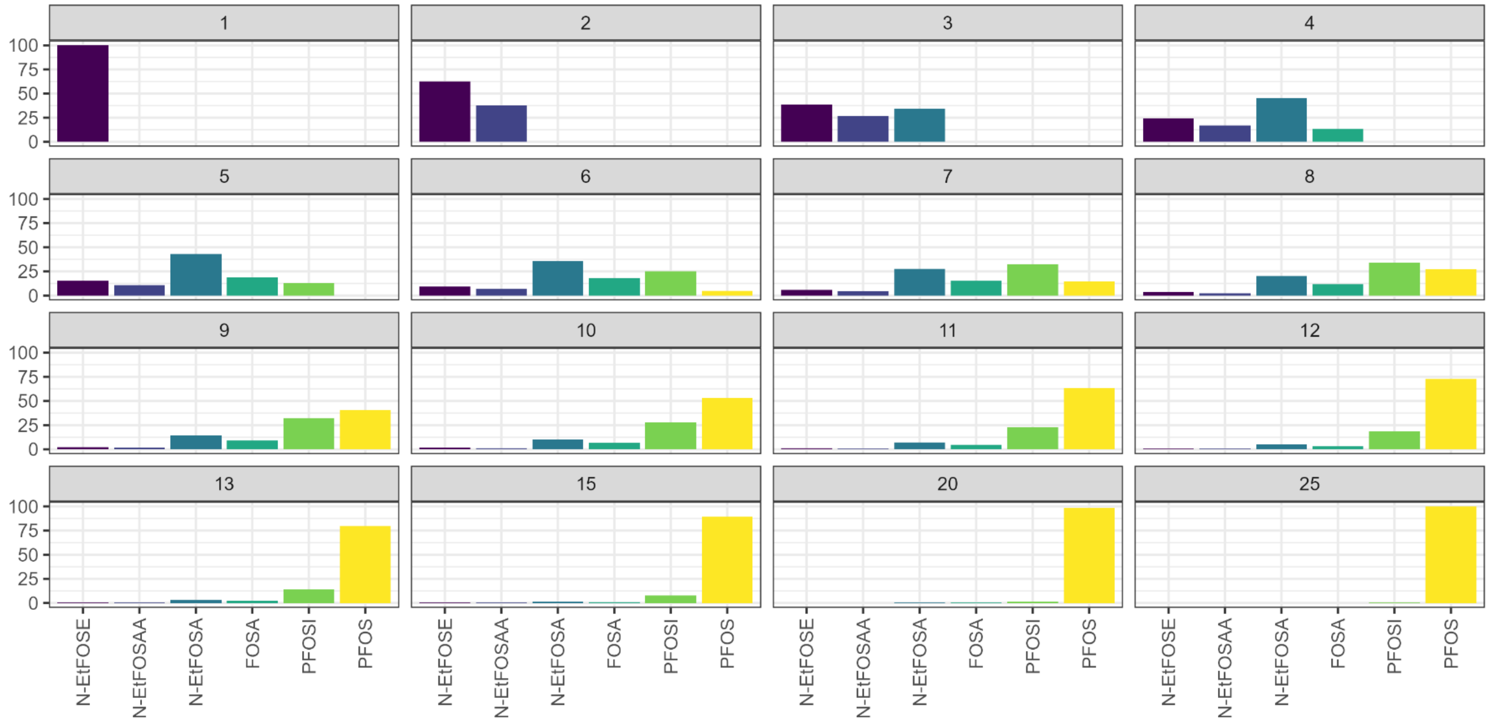

TABLE 2. Observed Rate Constants, $k_{obs}$, and Half Lives in Activated Sludge at 30 °C (mean ± standard deviation)

| test compound | first-order rate constant (day$^{-1}$) | half life (days) | pseudo-second order rate constant (L/g VSS day$^{-1}$) |
|---|---|---|---|
| *N*-EtFOSE | 0.99 ± 0.08 | 0.71 ± 0.05 | 0.26 ± 0.02 |
| *N*-EtFOSAA | 0.093 ± 0.012 | 7.5 ± 1.0 | 0.025 ± 0.003 |
| FOSAA | 0.41 ± 0.15 | 1.89 ± 0.79 | 0.11 ± 0.04 |
| FOSA | 0.075 ± 0.003 | 9.2 ± 0.3 | 0.020 ± 0.001 |
| *N*-EtFOSA | 0.92[a] | 0.75[a] | 0.24[a] |
| PFOSI | 0.95 ± 0.07 | 0.73 ± 0.054 | 0.25 ± 0.02 |


Rhoads, K.R., Janssen, E.M.L., Luthy, R.G. and Criddle, C.S., 2008. Aerobic biotransformation and fate of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) in activated sludge. *Environmental science & technology*, *42*(8), pp.2873-2878.

# Precursor Transformations N-EtfOSE Example

| | N-EtFOSE → | N-EtFOSAA → | N-EtFOSA → | FOSA → | PFOSI → | PFOS |
|---|---|---|---|---|---|---|
| Half-life (days) | 0.71 | 7.5 | 0.75 | 9.2 | 0.73 | NC |

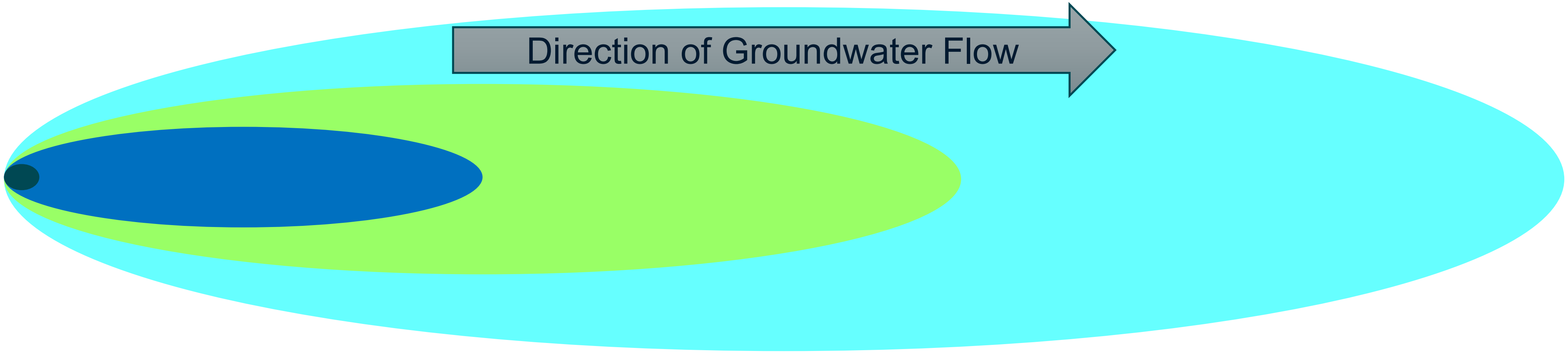



**Assumed a simple degradation series based on WWTP half-lives from day 1 to 25**

**Simple example of possible profiles associated with a degradation series**

- Gradual conversion to PFOS
- If precursors are not monitored, you see an increase in PFOS that could be erroneously attributed to a PFOS specific source

# Alteration of Profiles in Groundwater Plumes




As PFAS move through the subsurface with groundwater

- Lighter, less hydrophobic compounds move more quickly
- Heavier, more hydrophobic compounds move more slowly

- The PFAS profile could be altered as the plume propagates, alterations in chemical profiles have been noted for PCBs and other chemicals

# Groundwater Transport Rate (R–Retention Factor)

Brusseau, M.L., Yan, N., Van Glubt, S., Wang, Y., Chen, W., Lyu, Y., Dungan, B., Carroll, K.C. and Holguin, F.O., 2019. Comprehensive retention model for PFAS transport in subsurface systems. *Water research*, *148*, pp.41-50.

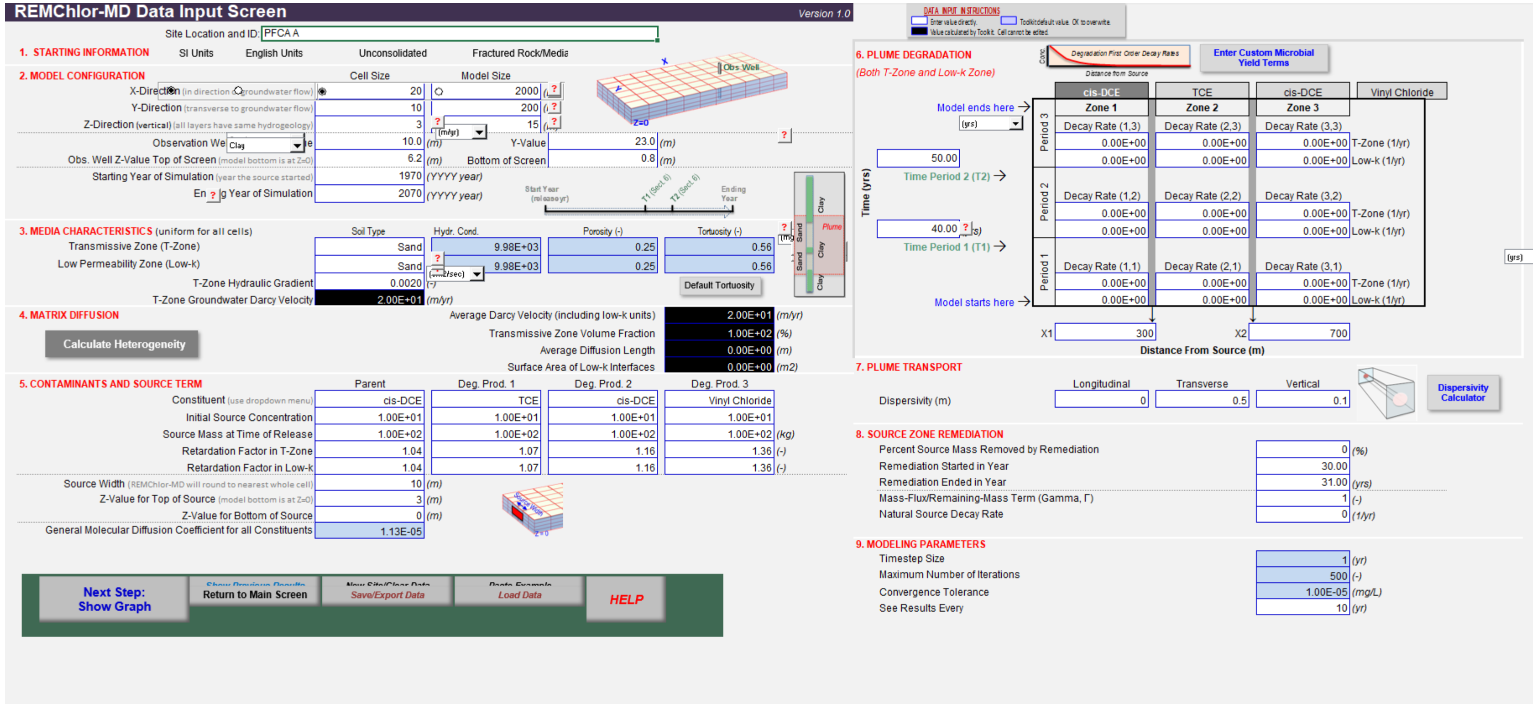
$$R=1+K_d\rho_b/\theta_w+K_a\theta_a/\theta_w+K_{aw}A_{aw}/\theta_w+K_n\theta_n/\theta_w+K_{nw}A_{nw}/\theta_w+K_{an}A_{an}/\theta_W$$

Many soil and chemical characteristics can influence the movement of PFAS through various media

- Models are being enhanced to address different processes
- Still a lot to learn

# REMChlor-MD

## Screening Model to Estimate Matrix Diffusion and Concentration Trends over Time




Two model runs

- 100 kg of source (small reservoir)
- 10,000 kg of source (large reservoir)

Modeled PFCAs (8), PFSA (5), and n:2FTOHs (3)

Simple groundwater model -> REMChlor-MD

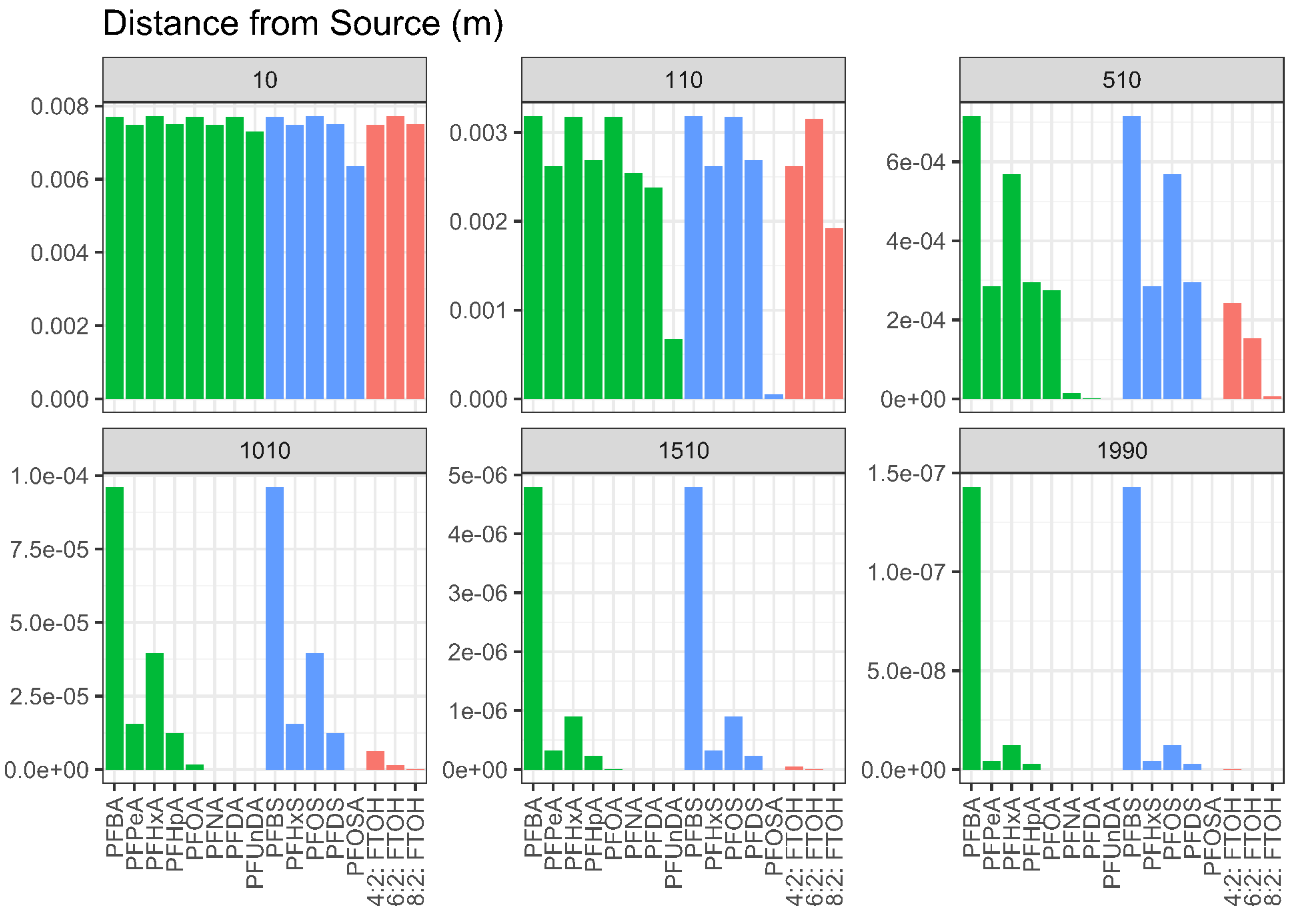
- Used $f_{oc}$ and $K_{oc}$ to estimate retardation factor
- Ignores other physico-chemical parameters (1st order estimate)
- Simple geology

REMChlor-MD does not consider properties other than $K_{oc}$, such as:

- Acidity (pH)
- Kp
- Surfactant properties and micelles
- Fractured aquifers
- etc

For a more comprehensive list of partitioning parameters see:
Brusseau, M.L., Yan, N., Van Glubt, S., Wang, Y., Chen, W., Lyu, Y., Dungan, B., Carroll, K.C. and Holguin, F.O., 2019. Comprehensive retention model for PFAS transport in subsurface systems. *Water research*, *148*, pp.41-50.

# Changing Profiles A – Large Source

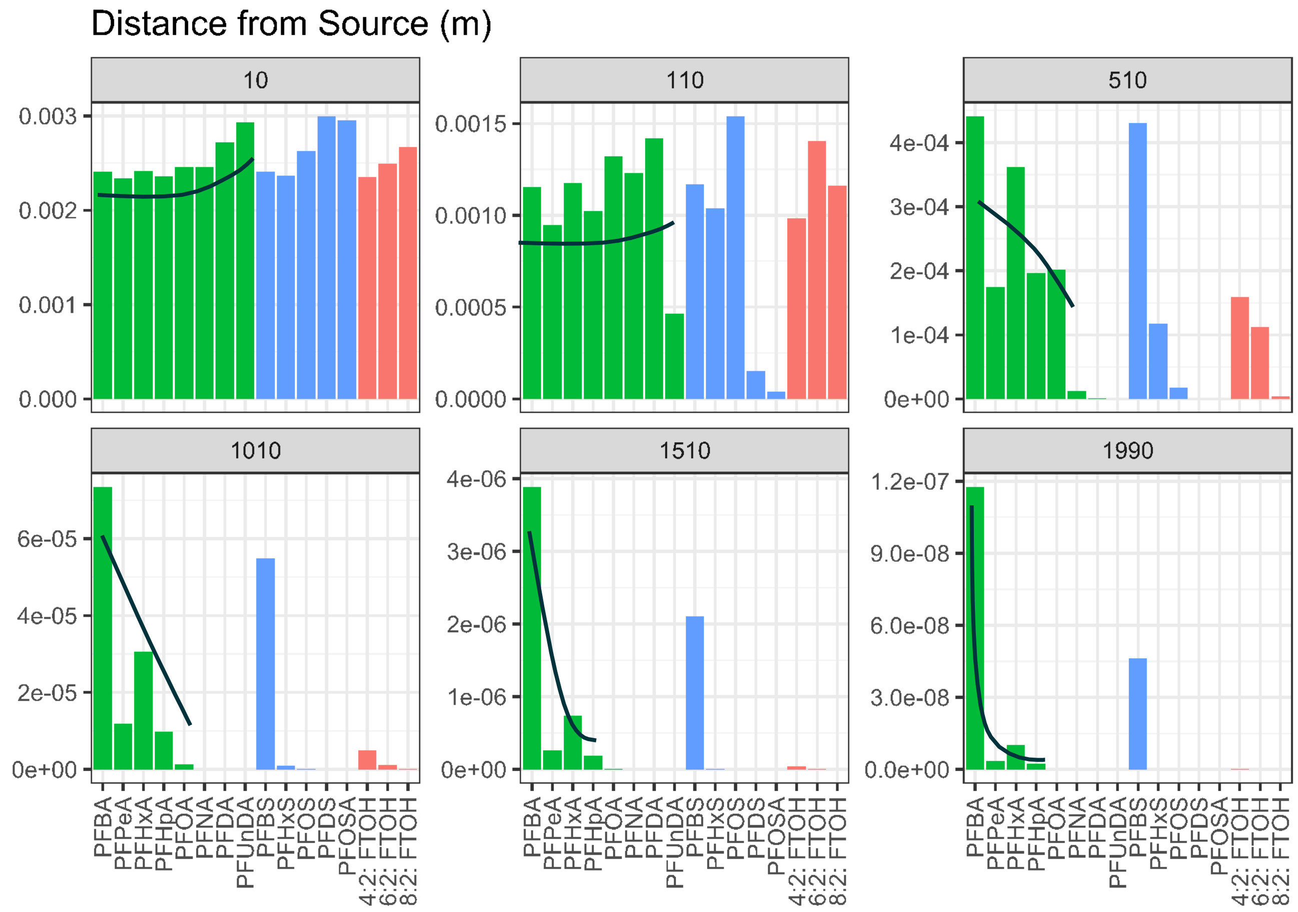



**10 years post release**
**PFAS profiles change as the plume travels**

**Compounds with lower retardation factors**

- Move more rapidly
- Are enriched relative to the original profiles as they move further downgradient
- Some PFAS groups originally present at the source may drop below the detection limit

# Changing Profiles A – Small Source



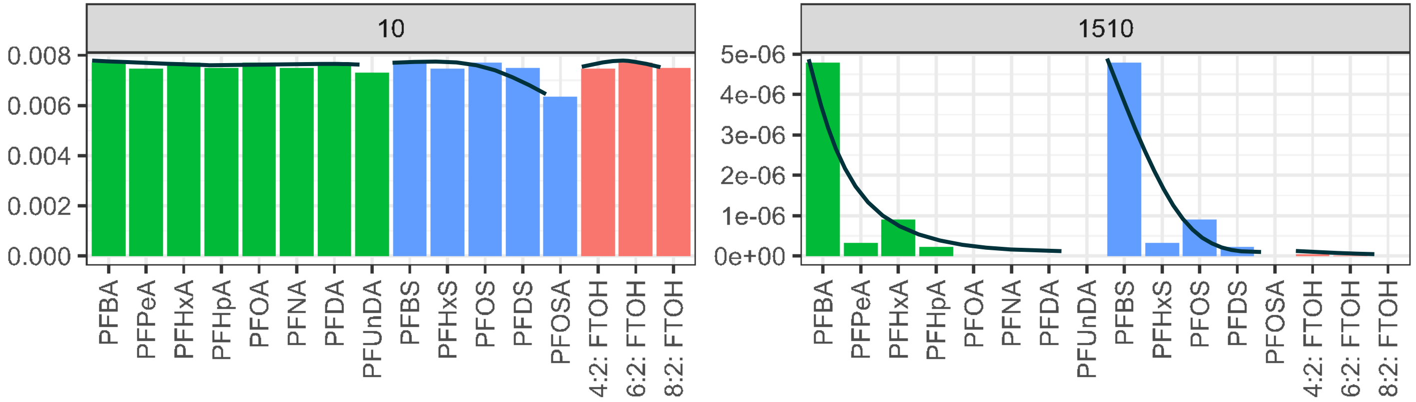

**20 years post release**
**PFAS profiles change at the source and in the plume as it plume travels**

**Compounds with lower retardation factors**

- Can be “washed” from the source area
- Can be enriched relative to the original profiles further from the source

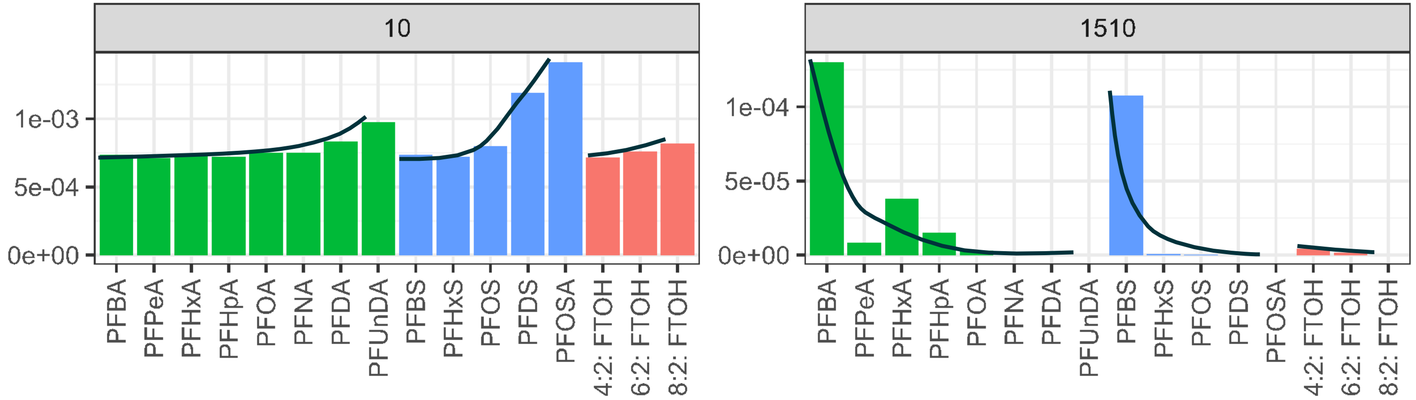
# Changing Profiles – Two Patterns

Large Source



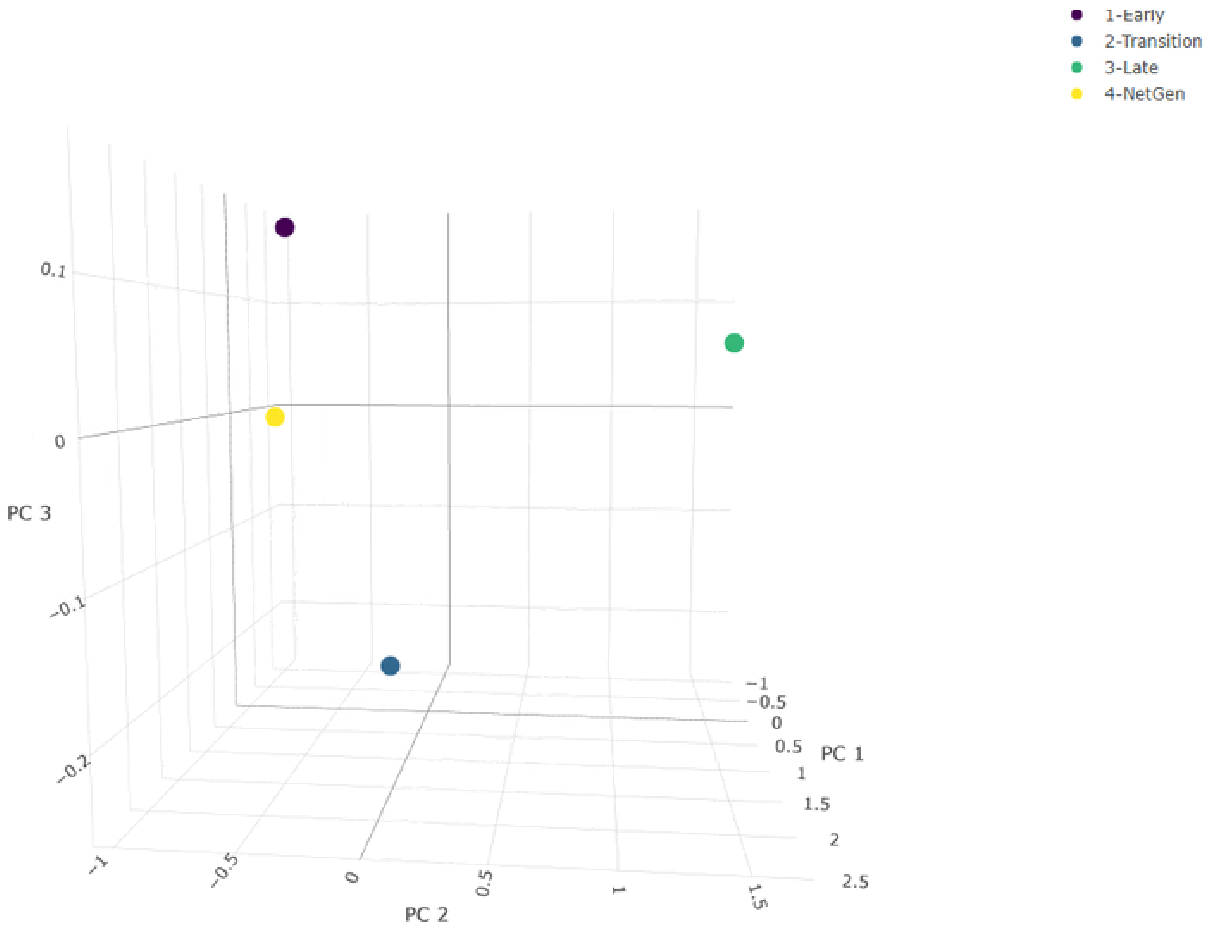

**Faster moving PFAS are enriched further from the source as the plume travels**

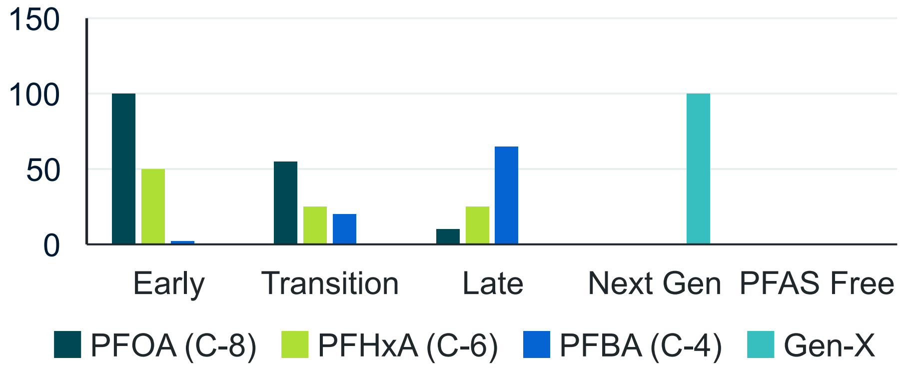
Limited Source




**Faster moving PFAS are depleted over time near the source**

# PCA Analysis of Changing Usage



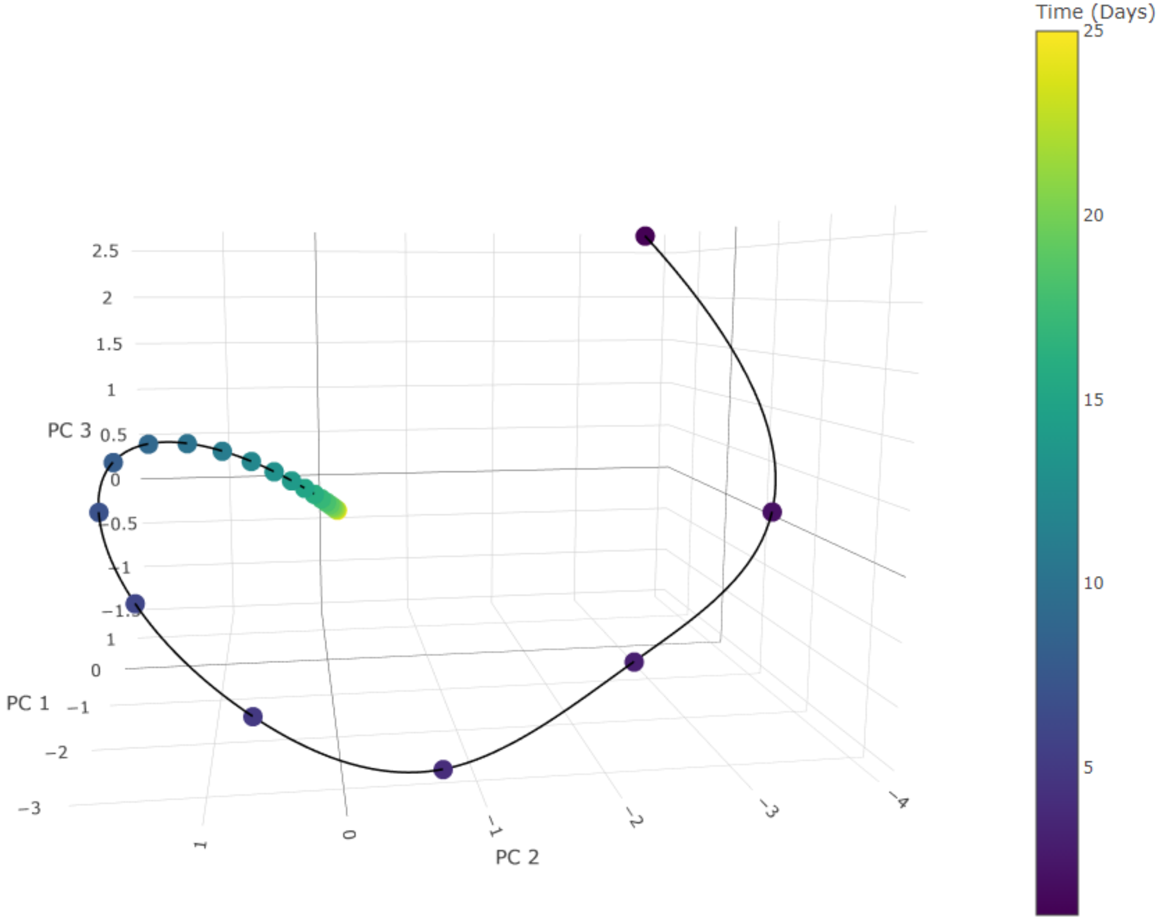



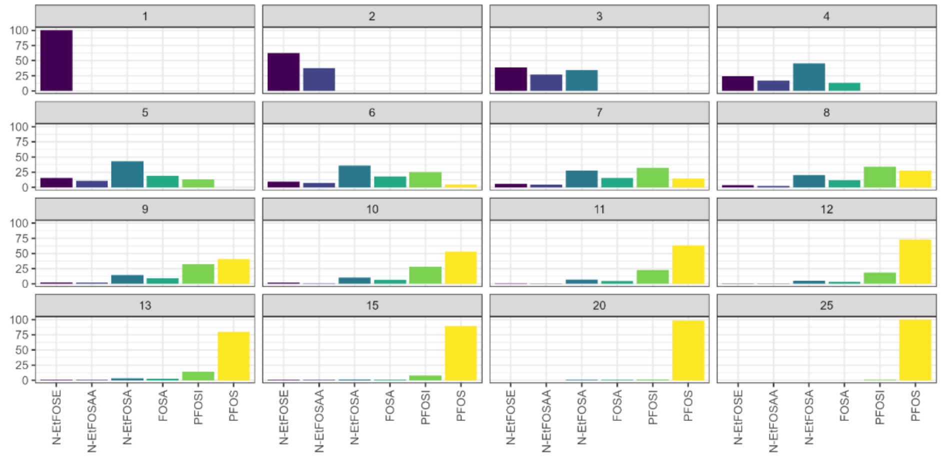

**PCA analysis performed on centered and scaled proportions**

**The changes in the profiles could be misinterpreted as different sources**

- Changes in the profiles may be gradual or quick as formulations change

# PCA Analysis of Precursor Transformations



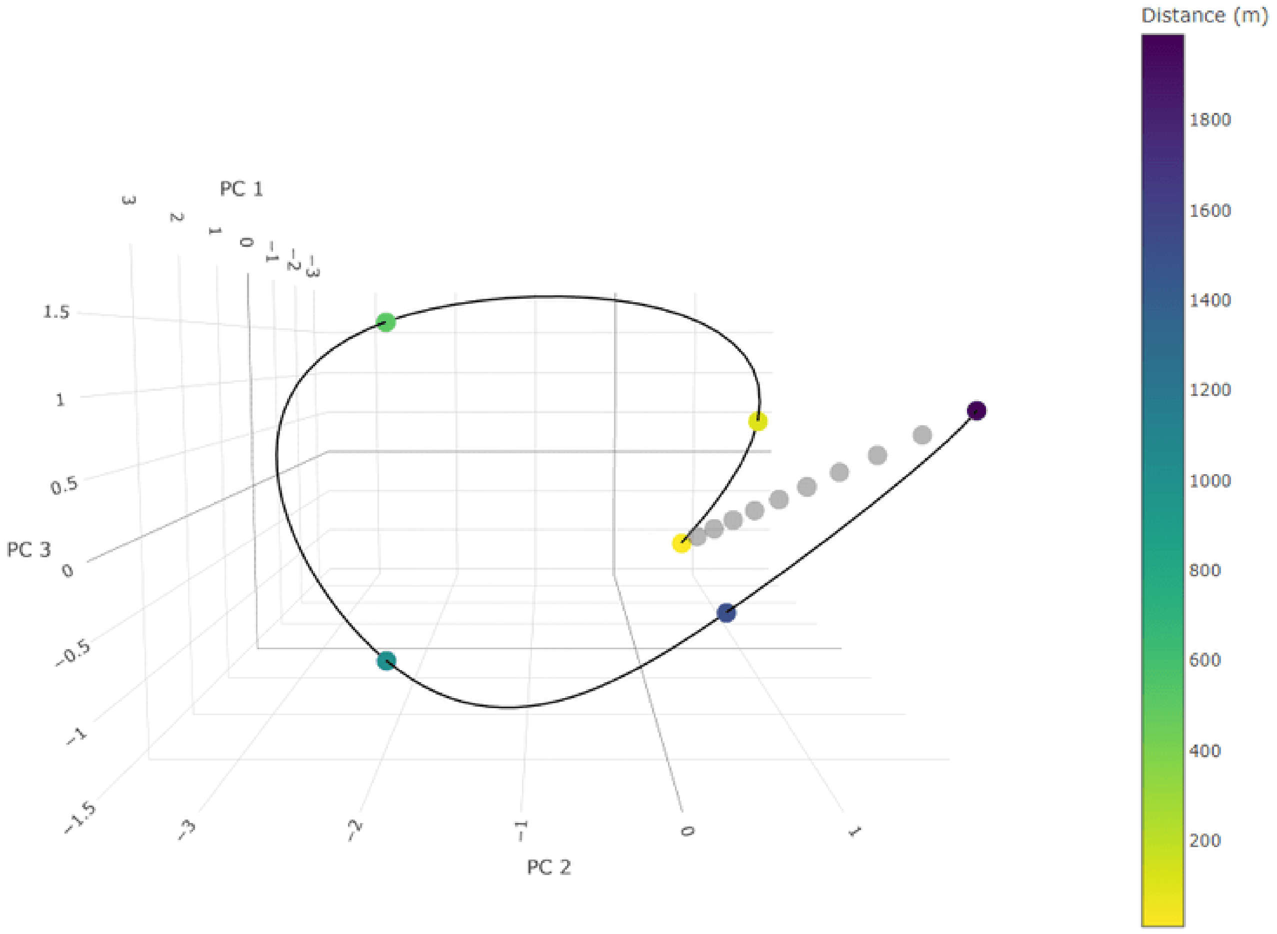




**PCA analysis performed on centered and scaled proportions**

**The changes in the profiles with time follow a curved trajectory**

- Changes in the profile follow a complex path in PCA space

# PCA Analysis of Modeled Retardation




**Modeled linear mixing of the two "pseudo end members" d=0 and d=1990**

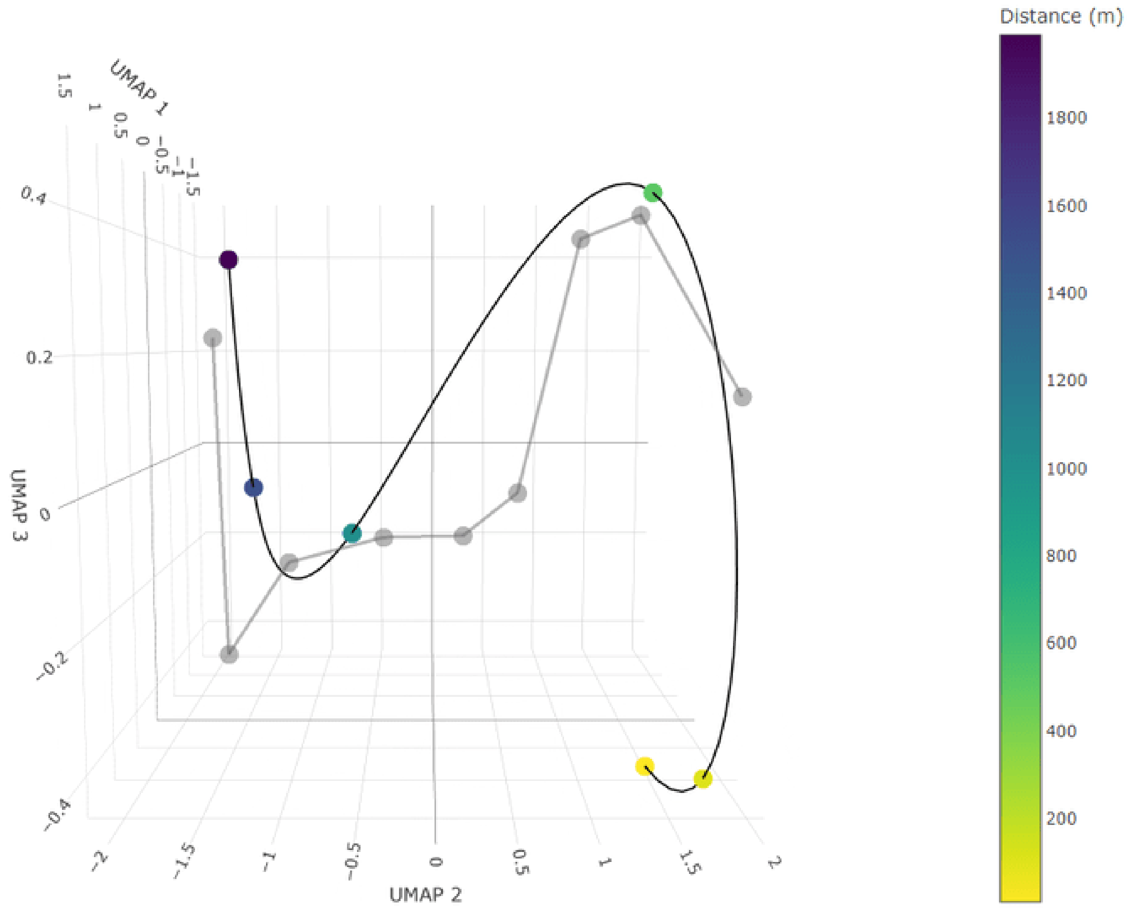
**Simple mixing in a linear process well suited to many multivariate methods that have been in use for decades**

- PCA, ratios, regression models
- Mass balance models
- Typical receptor models (PVA, PMF)

**PCA can differentiate mixing from differential retardation**

- Simple mixing manifests as a straight line between end members
- Retardation manifests as a curved trajectory
- In this case the trajectory follows a "corkscrew"
- Same trajectory found in other non-linear processes (e.g. , percussor transformations)

# UMAP Analysis of Modeled Retardation

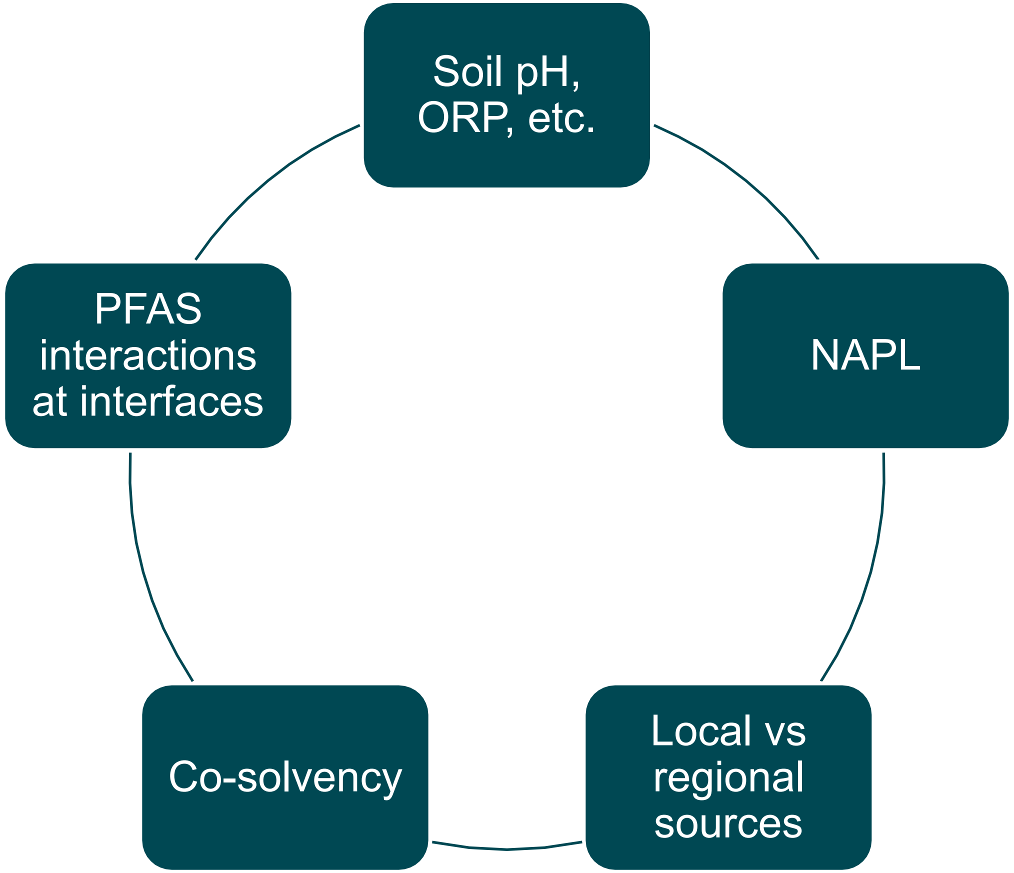



**Modeled linear mixing of the two "pseudo end members" d=0 and d=1990**
**Parameters**
- **Neighbors = 8**
- **Seed = 121**

**UMAP can show complex relationships between samples**
- Can be used to quickly identify anomalous groups of samples in a large dataset
- Can be used to explore similarities and differences but should be validated (PCA/HCA, direct inspection)

**UMAP cannot differentiate mixing from weathering**
- Simple mixing does not manifest as a straight line between end members
- Retardation manifests as a curved trajectory

# Other Possible Confounding Factors




The presence and magnitude of any differential transport is expected to be site specific

- In our work we often see little/no evidence of differential migration
- A number of other processes could lead to reduced differential migration
- PFAS profiles at interfaces could also be difficult to predict, PFAS is often concentrated at interfaces
    - Air/water
    - Water/soil
- **Still a lot to learn**

# Tools to Untangle PFAS Profiles

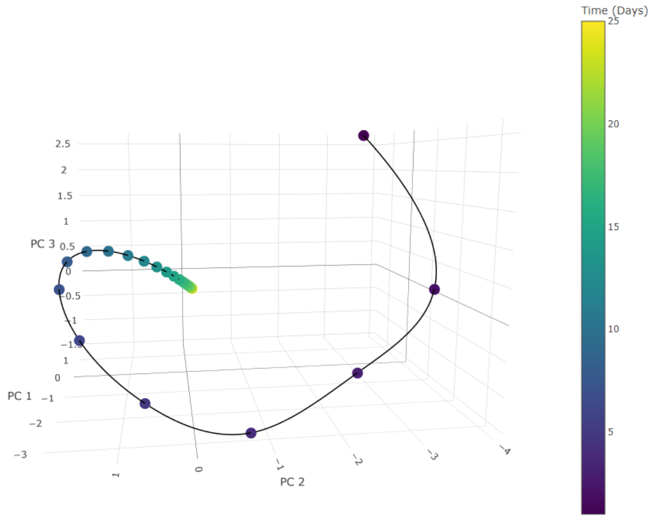
Compare profiles expected to be associated with different processes to the observed profiles

- Profile plots along transects
- HCA to classify samples into clusters and assess geospatial patterns
- PCA to compare observed to expected profiles
- PCA to differential linear processes (mixing) from non-linear processes
  - Retardation
  - Percussors
- <u>Supplement</u> PCA with nonlinear dimension reduction (e.g. UMAP)

# Conclusions

Numerous processes can alter PFAS profiles

Forensics methods can be used to rapidly and efficiently evaluate changes in profiles but these changes in profiles must be tested against a robust CSM




- Hypothesis testing provides a powerful framework for evaluating and testing the CSM
- Alternative explanations must be considered and tested
- Data gaps and uncertainties should be understood and clearly stated

# Thank You

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