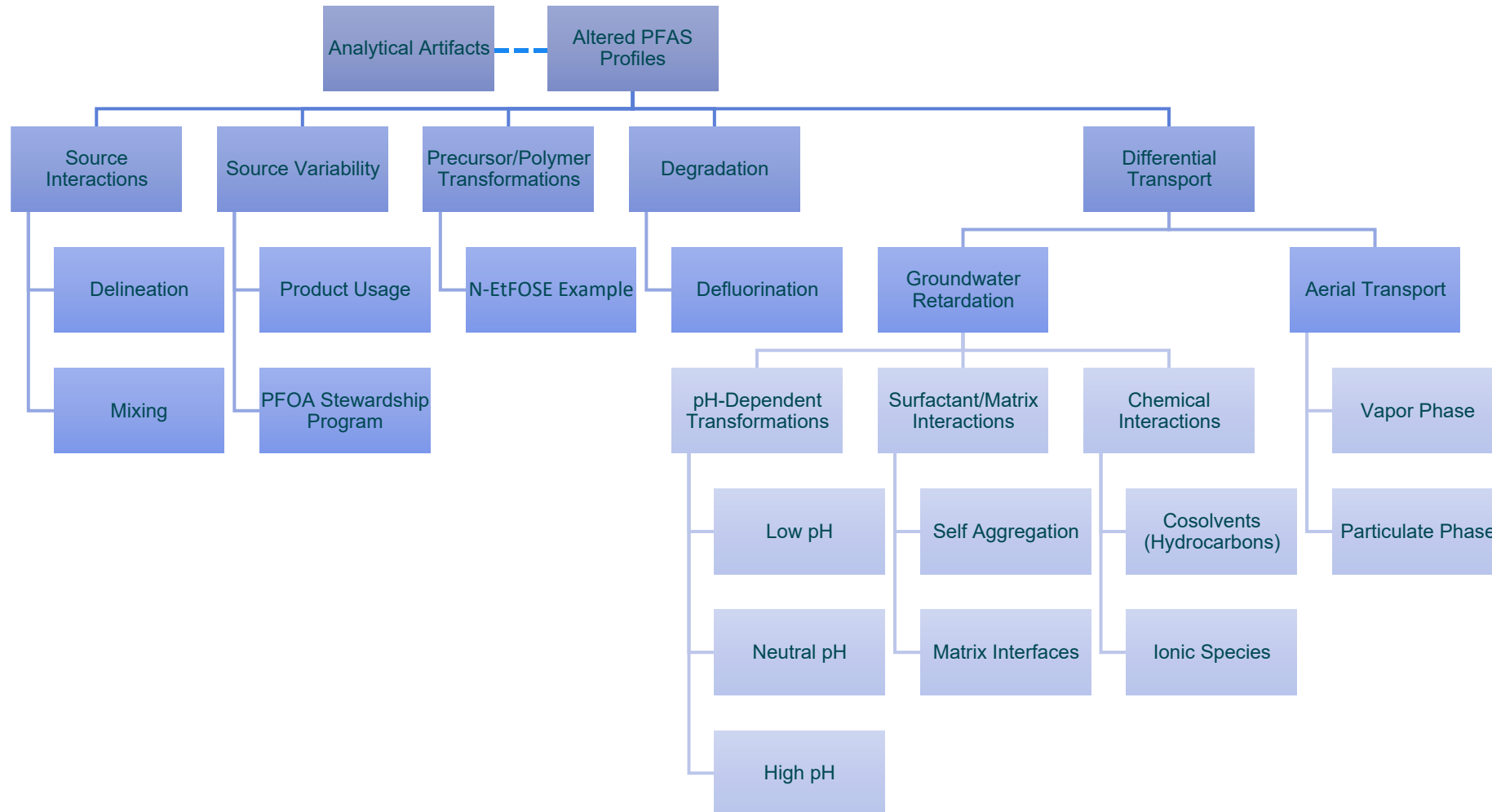


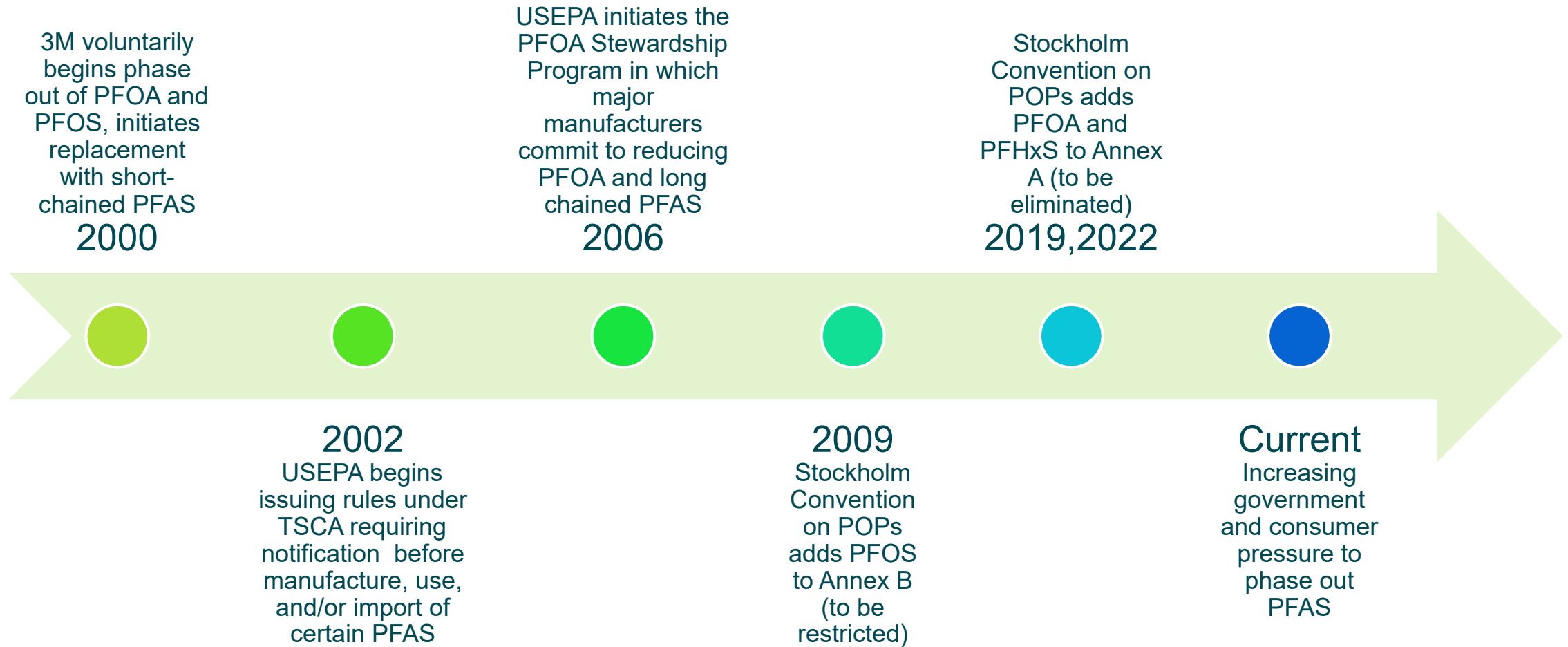
Understanding Processes That Alter PFAS Profiles

Michael Bock, Nicholas D. Rose, Jen Jones

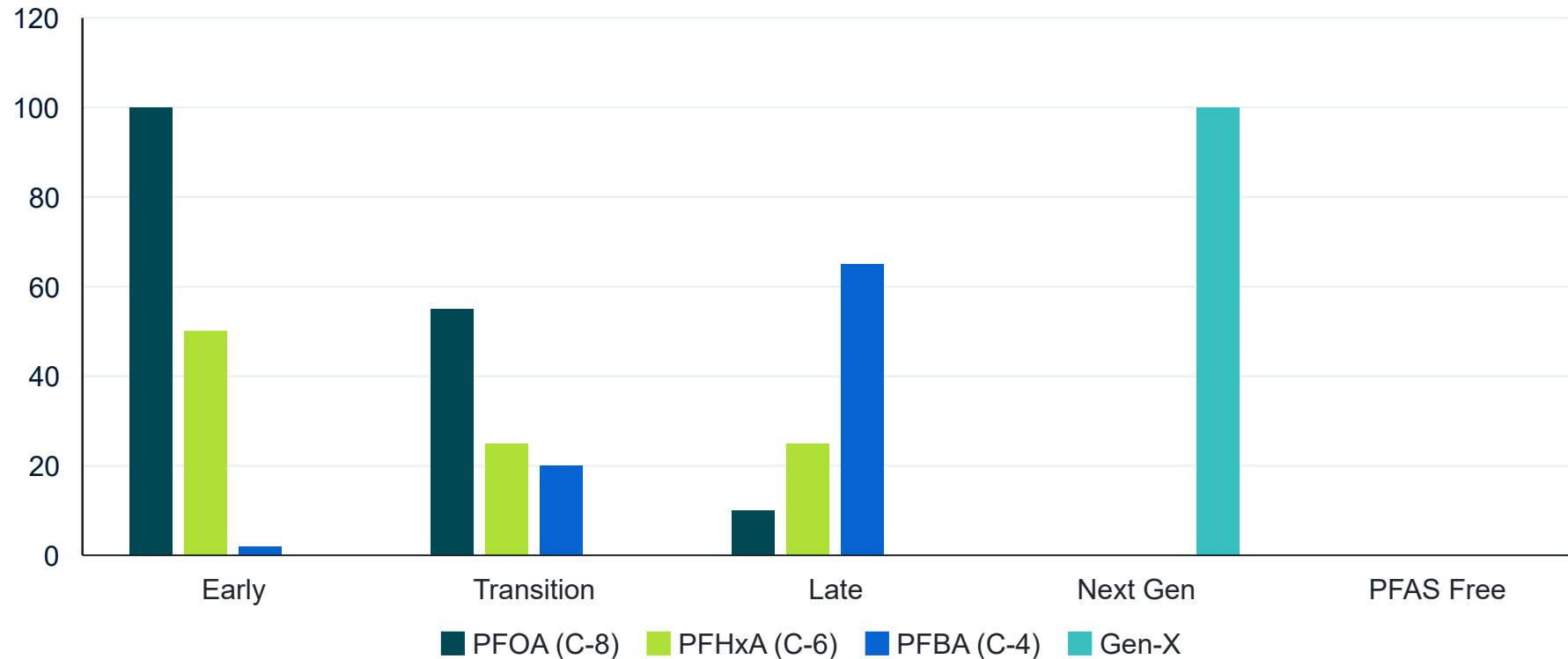
Variability in PFAS Profiles-Multitude of Possibilities



Changing PFAS Usage



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

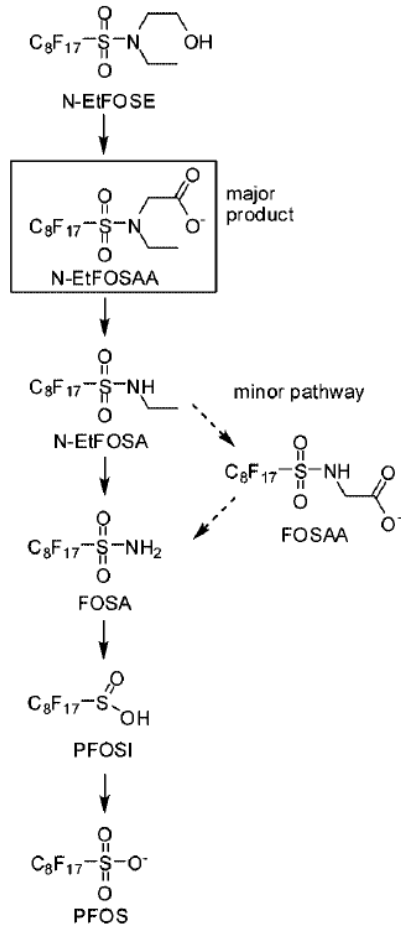


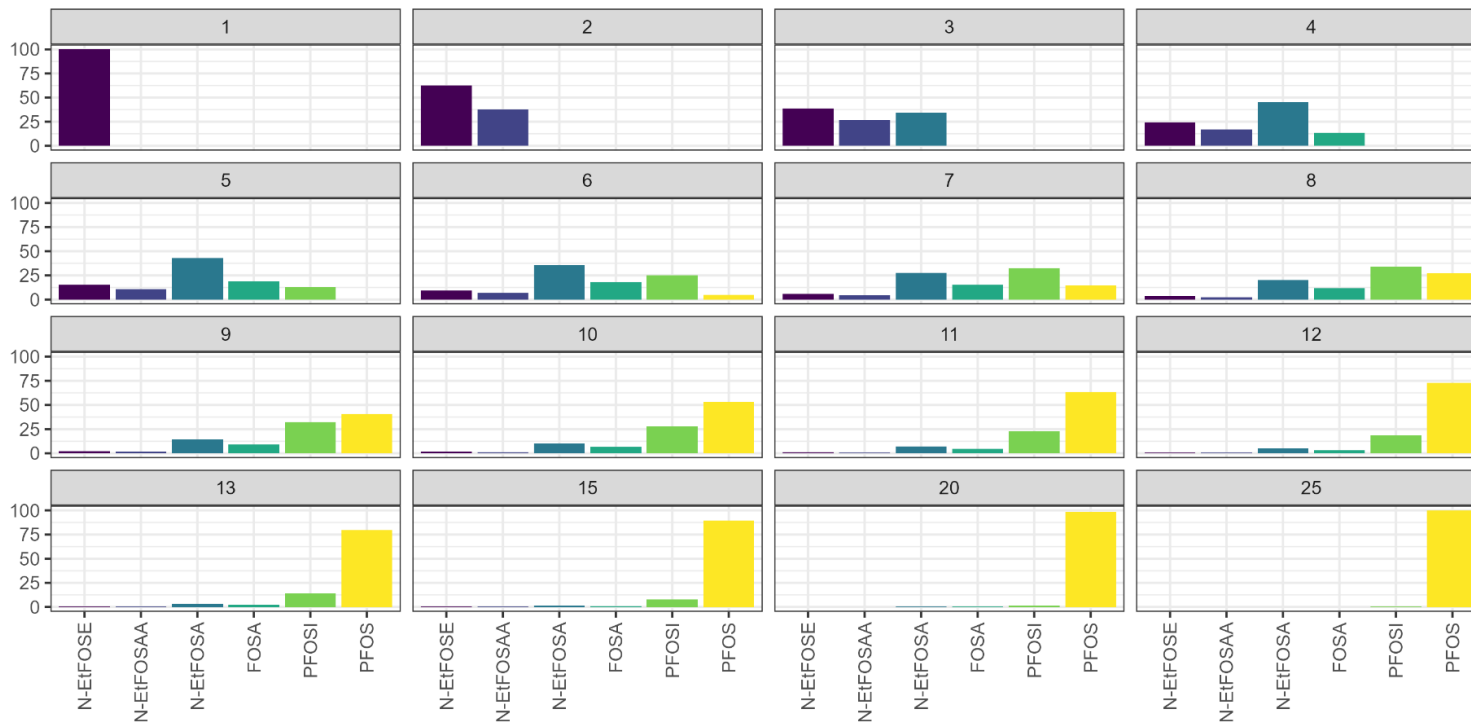
TABLE 2. Observed Rate Constants, k_{obs} , and Half Lives in Activated Sludge at 30 °C (mean $\pm$ standard deviation)

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

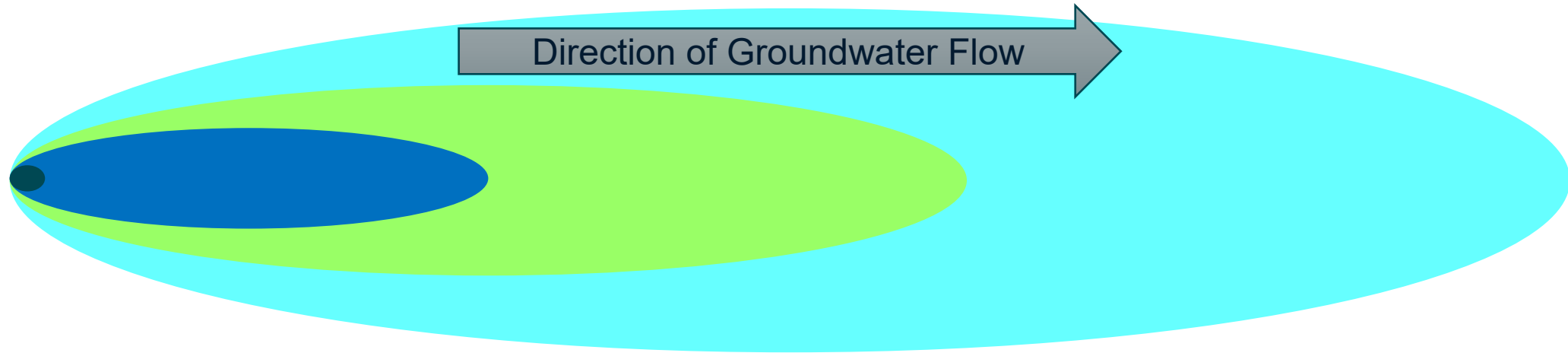


Assumed a simple degradation series based on WWTP half-lives from day 1 to 25

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.

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

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

REMChlor-MD Data Input Screen Version 1.0

Site Location and ID: PFCA A

1. STARTING INFORMATION SI Units English Units Unconsolidated Fractured Rock/Media

2. MODEL CONFIGURATION

Cell Size: 20 Model Size: 2000

X-Direction (in direction of groundwater flow): 20

Y-Direction (transverse to groundwater flow): 10

Z-Direction (vertical) (all layers have same hydrogeology): 3

Observation Well: Clay

Obs. Well Z-Value Top of Screen (model bottom is at Z=0): 10.0

Obs. Well Z-Value Bottom of Screen: 6.2

Starting Year of Simulation (year the source started): 1970

En 20 Year of Simulation: 2070

3. MEDIA CHARACTERISTICS (uniform for all cells)

Soil Type: Sand

Transmissive Zone (T-Zone): Sand

Low Permeability Zone (Low-k): Sand

T-Zone Hydraulic Gradient: 0.0020

T-Zone Groundwater Darcy Velocity: 2.00E+01

4. MATRIX DIFFUSION

Calculate Heterogeneity

Average Darcy Velocity (including low-k units): 2.00E+01

Transmissive Zone Volume Fraction: 1.00E+02

Average Diffusion Length: 0.00E+00

Surface Area of Low-k Interfaces: 0.00E+00

5. CONTAMINANTS AND SOURCE TERM

Parent	Deg. Prod. 1	Deg. Prod. 2	Deg. Prod. 3
Constituent (use dropdown menu)	dis-DCE	TCE	dis-DCE
Initial Source Concentration	1.00E+01	1.00E+01	1.00E+01
Source Mass at Time of Release	1.00E+02	1.00E+02	1.00E+02
Retardation Factor in T-Zone	1.04	1.07	1.16
Retardation Factor in Low-k	1.04	1.07	1.16
Source Width (REMChlor-MD will round to nearest whole cell)	10		
Z-Value for Top of Source (model bottom is at Z=0)	3		
Z-Value for Bottom of Source	0		
General Molecular Diffusion Coefficient for all Constituents	1.13E-05		

6. PLUME DEGRADATION (Both T-Zone and Low-k Zone)

Model ends here

Time Period 2 (T2) → 50.00

Time Period 1 (T1) → 40.00

Model starts here

Zone	dis-DCE	TCE	dis-DCE	Vinyl Chloride
Period 3	Decay Rate (1,3)	Decay Rate (2,3)	Decay Rate (3,3)	
	0.00E+00	0.00E+00	0.00E+00	T-Zone (1/yr)
	0.00E+00	0.00E+00	0.00E+00	Low-k (1/yr)
Period 2	Decay Rate (1,2)	Decay Rate (2,2)	Decay Rate (3,2)	
	0.00E+00	0.00E+00	0.00E+00	T-Zone (1/yr)
	0.00E+00	0.00E+00	0.00E+00	Low-k (1/yr)
Period 1	Decay Rate (1,1)	Decay Rate (2,1)	Decay Rate (3,1)	
	0.00E+00	0.00E+00	0.00E+00	T-Zone (1/yr)
	0.00E+00	0.00E+00	0.00E+00	Low-k (1/yr)

X1 300 X2 700

Distance From Source (m)

7. PLUME TRANSPORT

Dispersivity (m)

Longitudinal 0 Transverse 0.5 Vertical 0.1

8. SOURCE ZONE REMEDIATION

Percent Source Mass Removed by Remediation: 0

Remediation Started in Year: 30.00

Remediation Ended in Year: 31.00

Mass-Flux/Remaining-Mass Term (Gamma, Γ): 1

Natural Source Decay Rate: 0

9. MODELING PARAMETERS

Time-step Size: 1

Maximum Number of Iterations: 500

Convergence Tolerance: 1.00E-05

See Results Every: 10

Next Step: Show Graph

Return to Main Screen

Save/Export Data

Load Data

HELP

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)
- K_p
- Surfactant properties and micelles
- Fractured aquifers
- etc

Two model runs

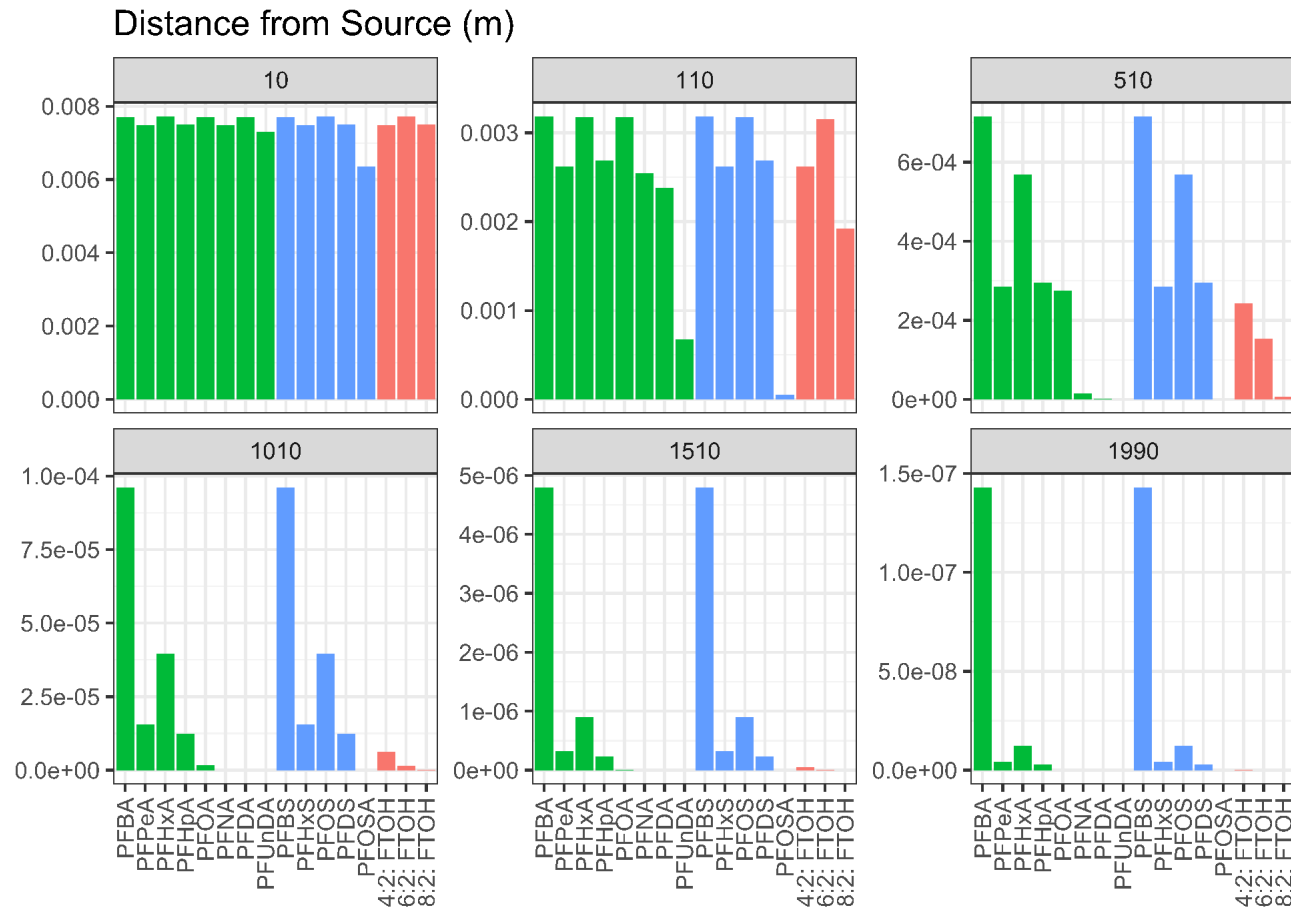
- 100 kg of source (small reservoir)
- 10,000 kg of source (large reservoir)

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

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

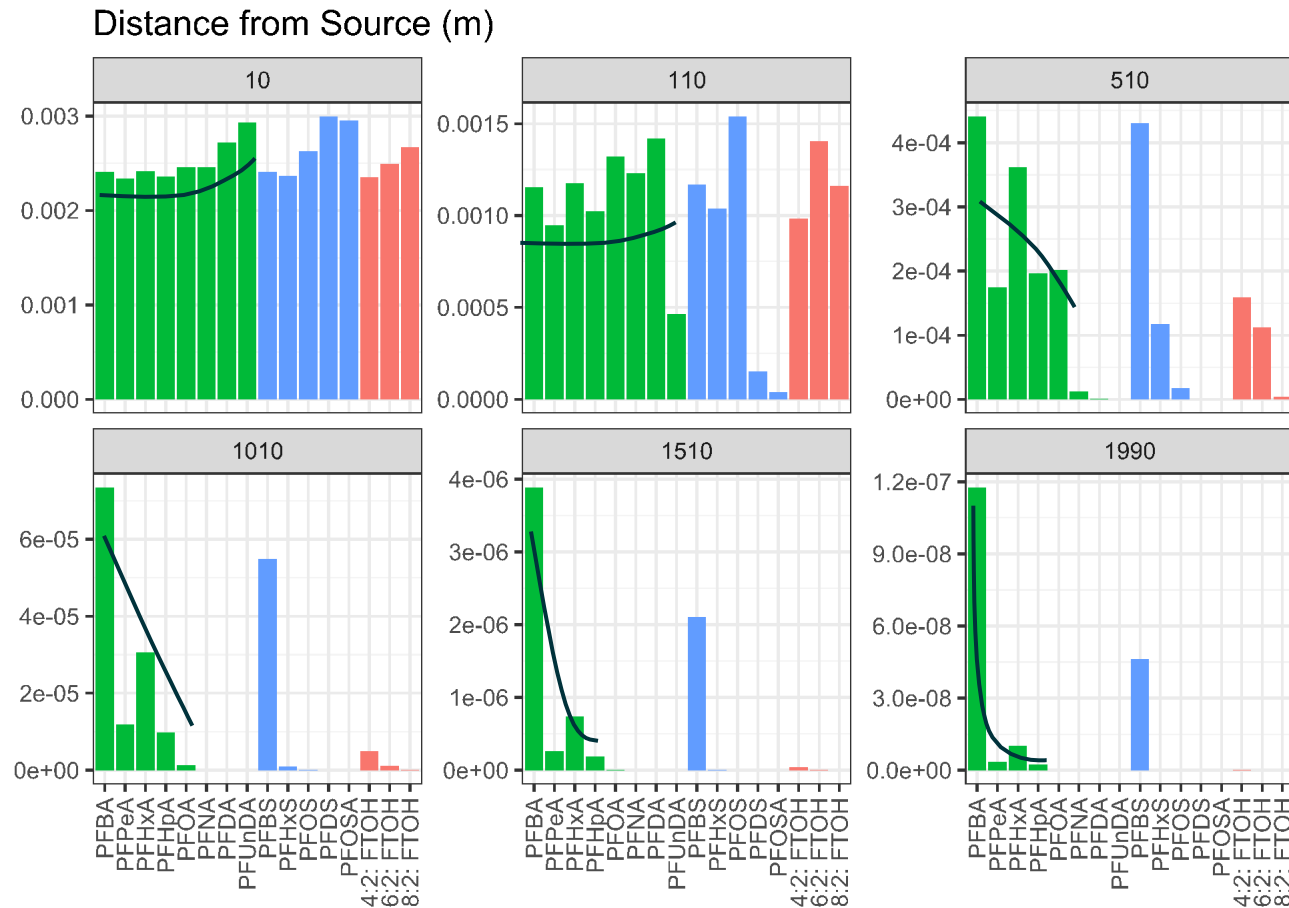


10 years post release
PFAS profiles change as the plume travels

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



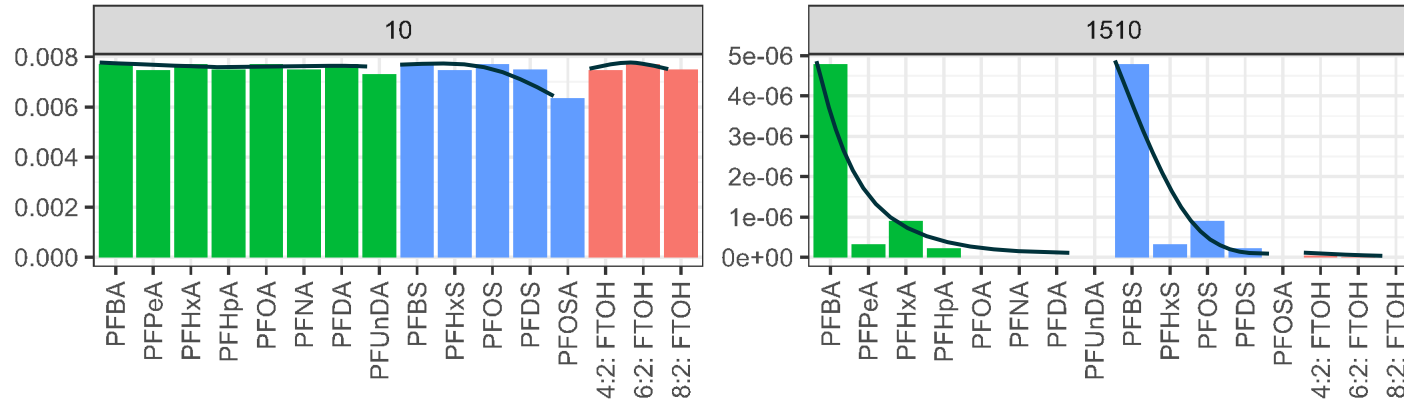
20 years post release
PFAS profiles change at the source
and in the plume as it plume travels

Compounds with lower retardation factors

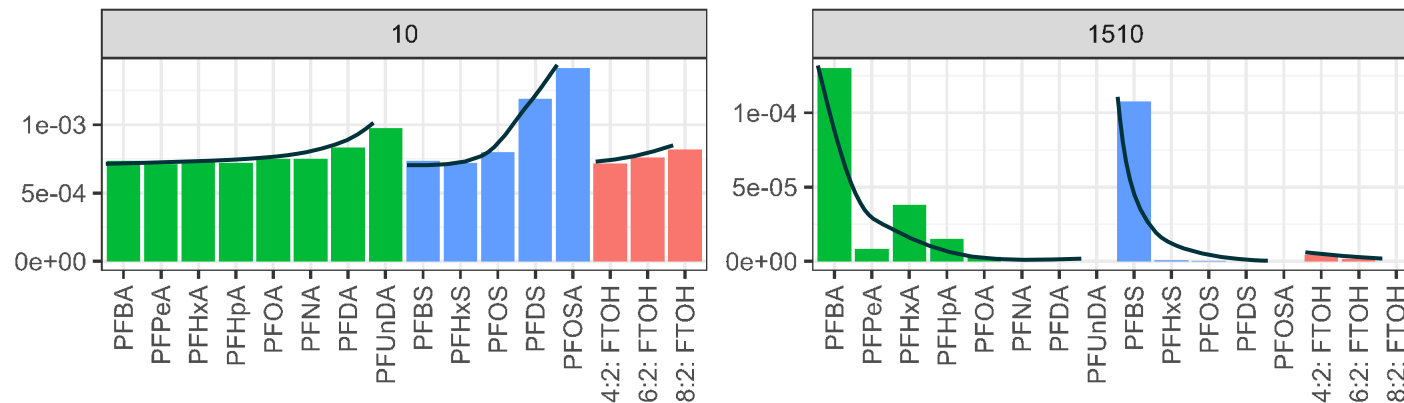
- Can be “washed” from the source area
- Can be enriched relative to the original profiles further from the source

Changing Profiles – Two Patterns

Large Source



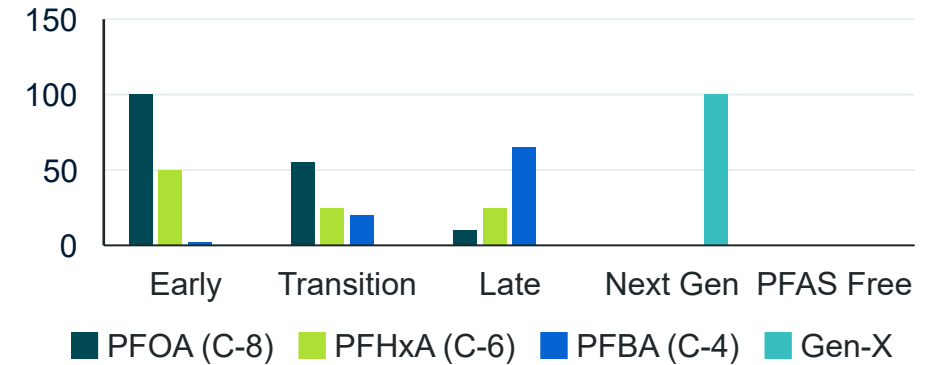
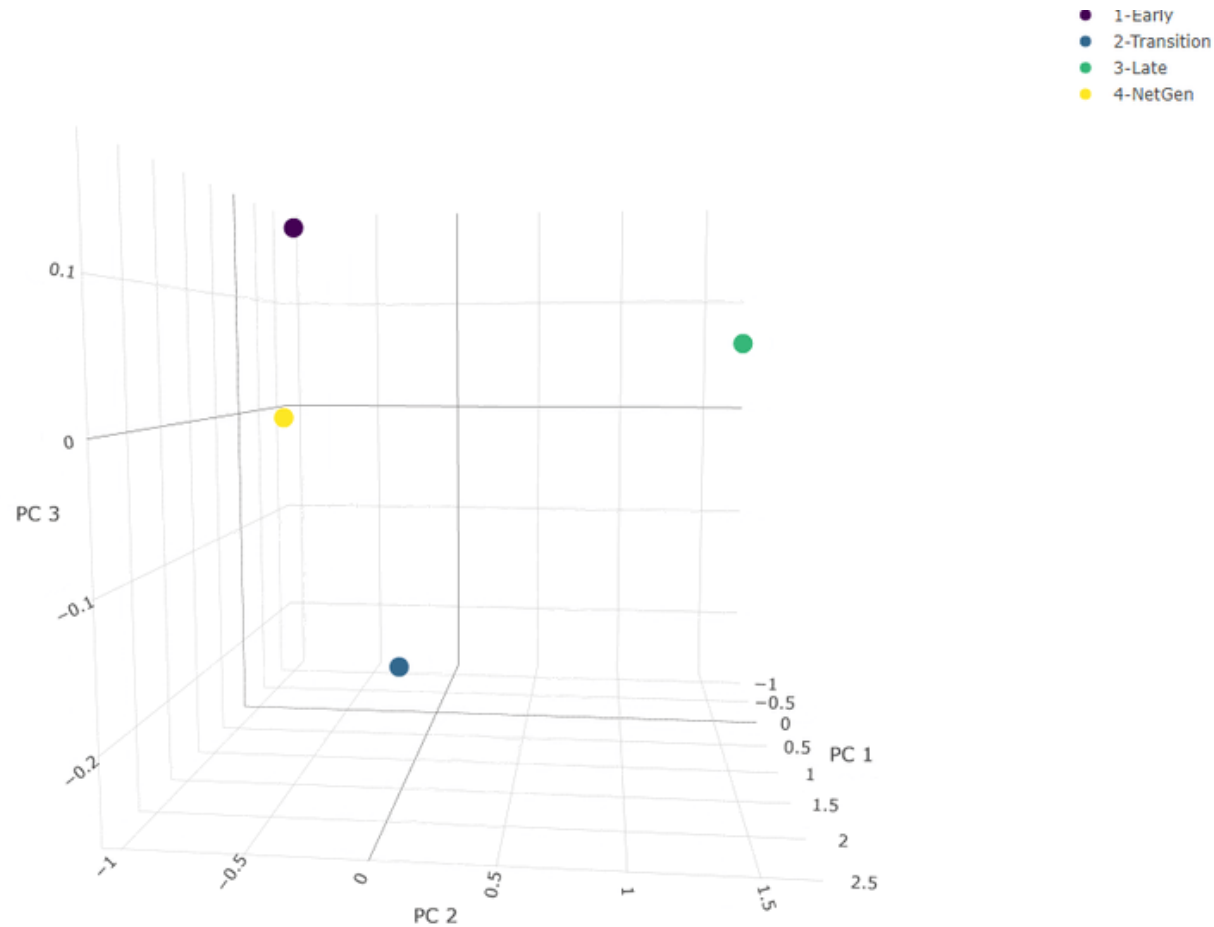
Limited Source



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

Faster moving PFAS are depleted over time near the source

PCA Analysis of Changing Usage

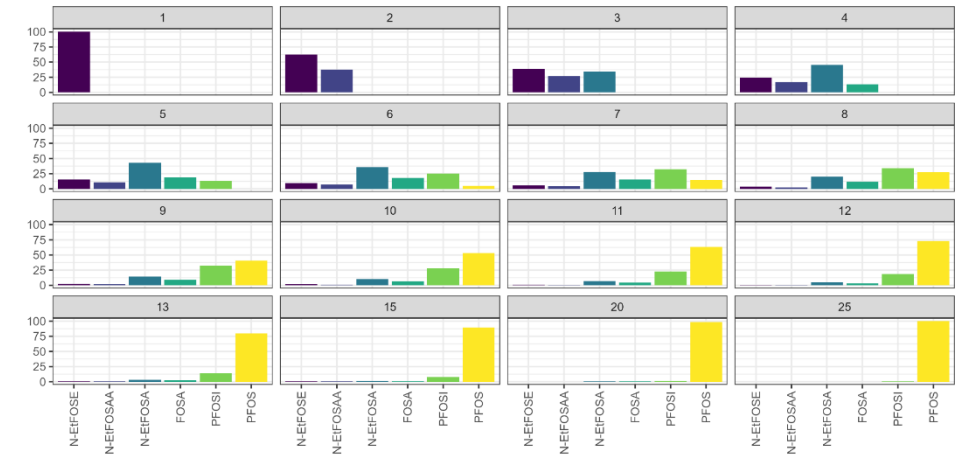
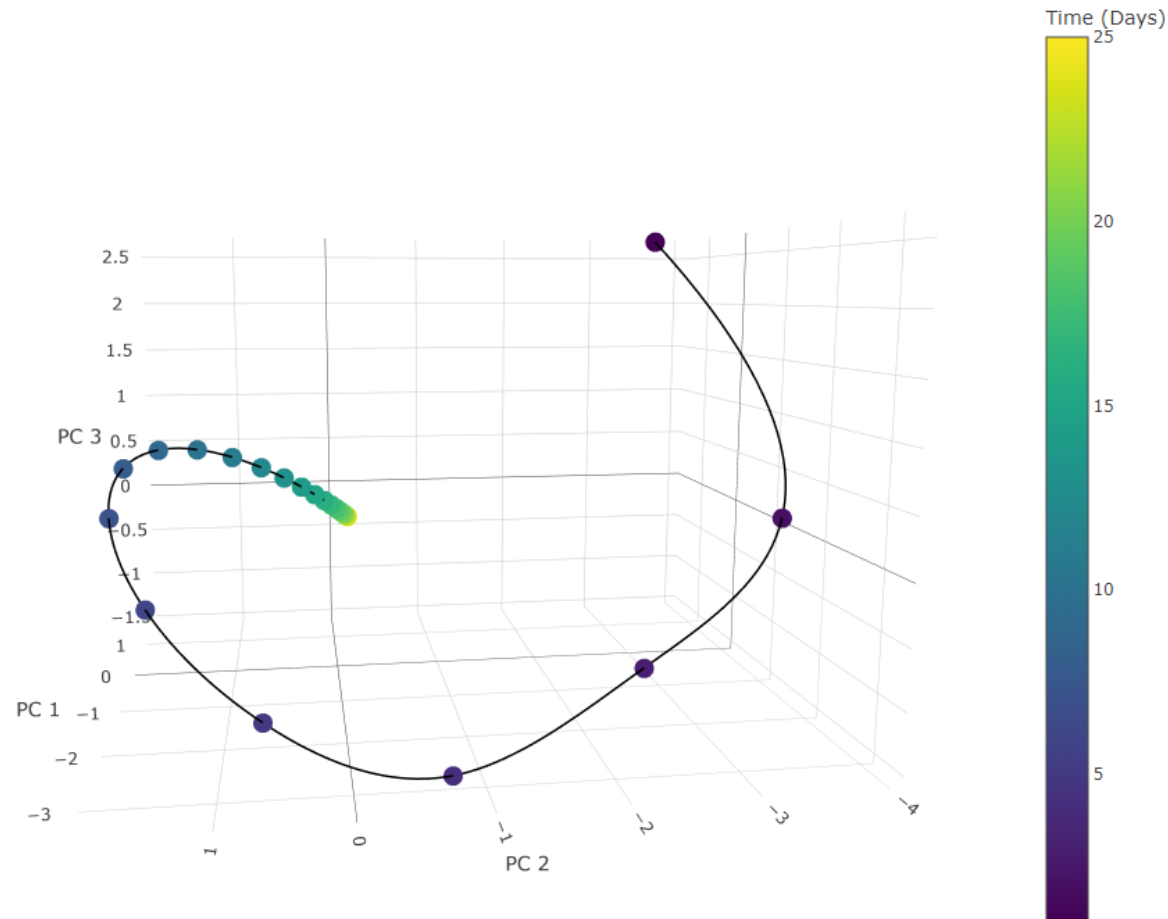


PCA analysis performed on centered and scaled proportions

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

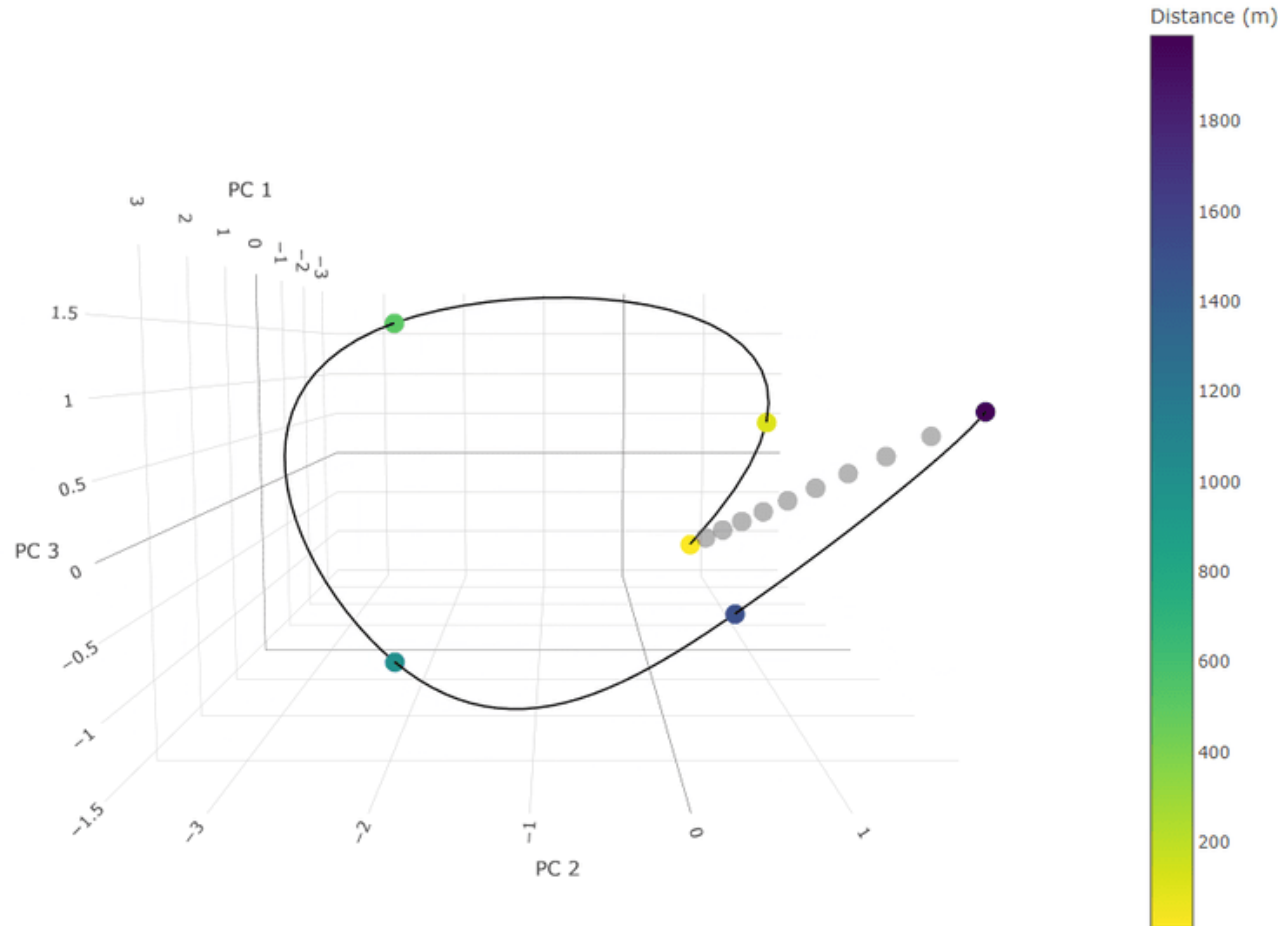


PCA analysis performed on centered and scaled proportions

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 $d=1990$

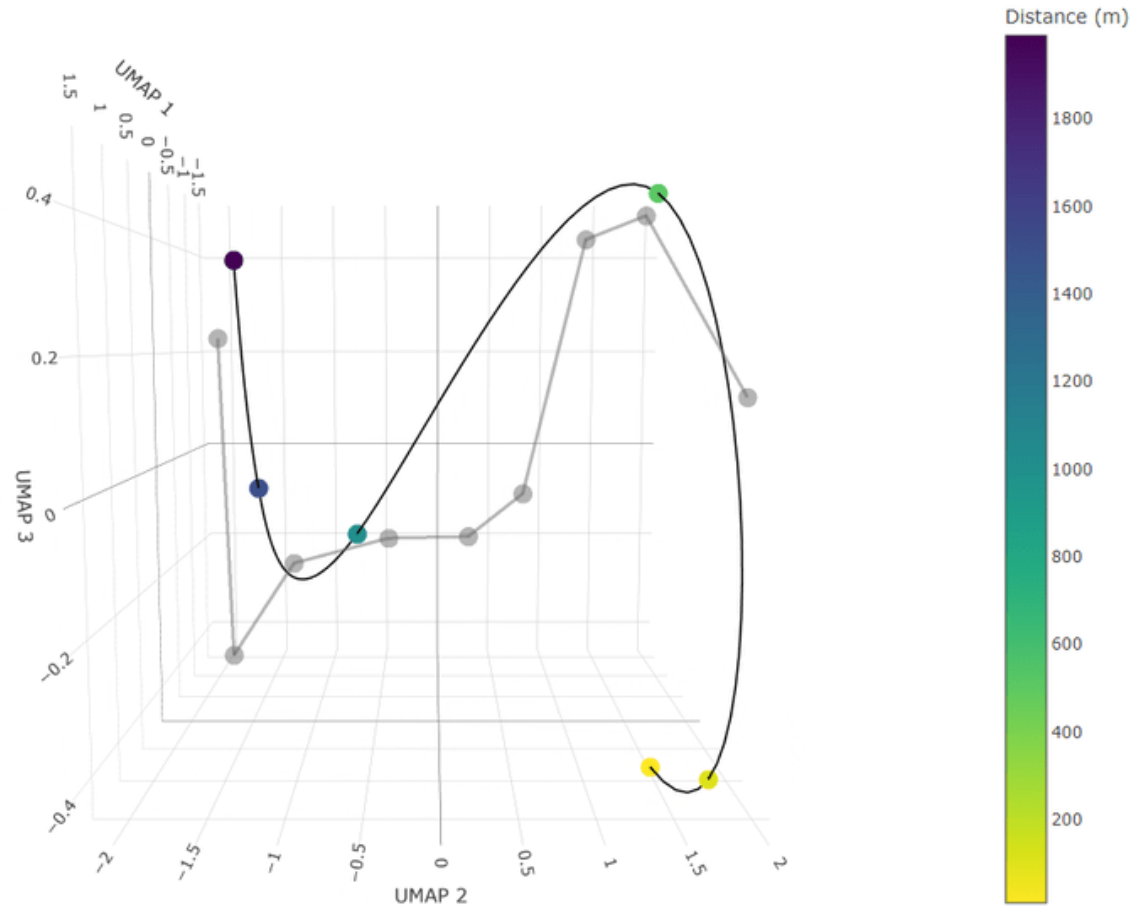
Simple mixing in a linear process well suited to many multivariate methods that have been in use for decades

- 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

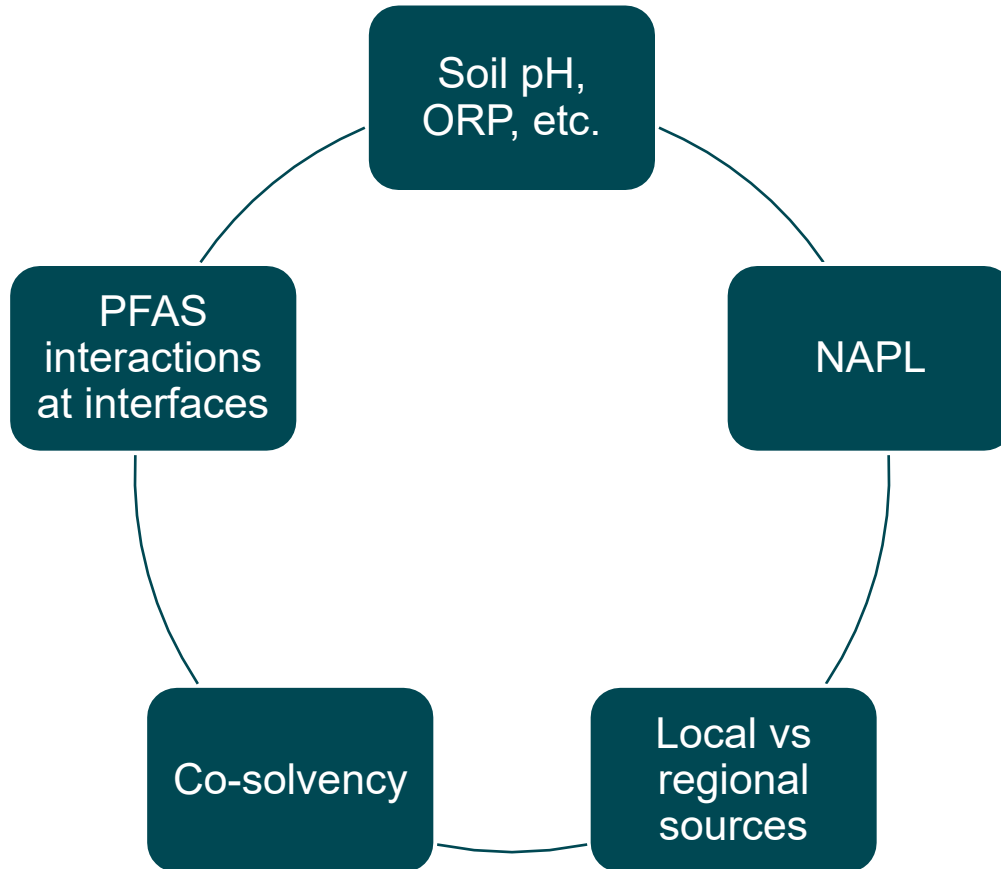
UMAP can show complex relationships between samples

- 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

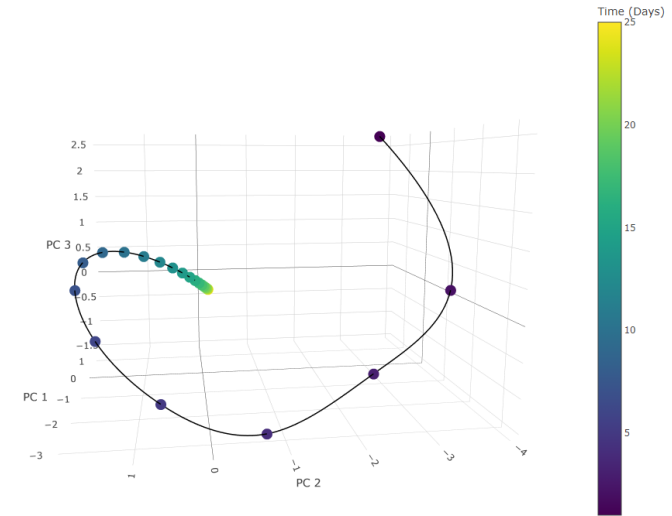
- ▶ Profile plots along transects
- ▶ HCA to classify samples into clusters and assess geospatial patterns
- ▶ PCA to compare observed to expected profiles
- ▶ PCA to differential linear processes (mixing) from non-linear processes
 - Retardation
 - Percussors
- ▶ Supplement PCA with nonlinear dimension 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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