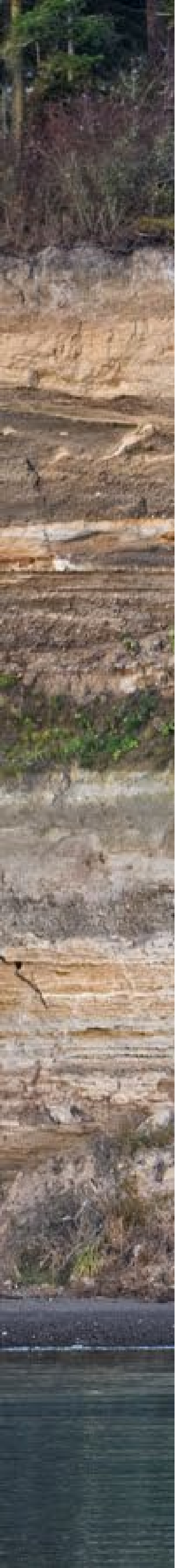

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A Scalable Reactive Transport Framework for PFAS

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U.S. DEPARTMENT OF ENERGY BATTELLE

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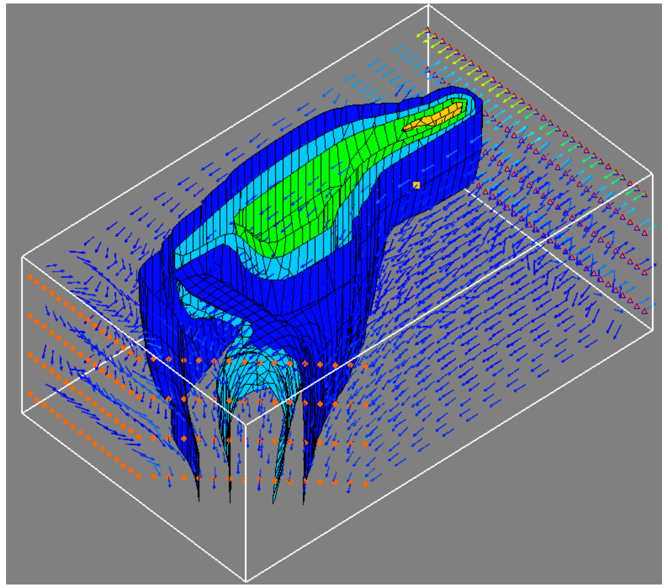
Developing a PFAS Reactive Transport Framework

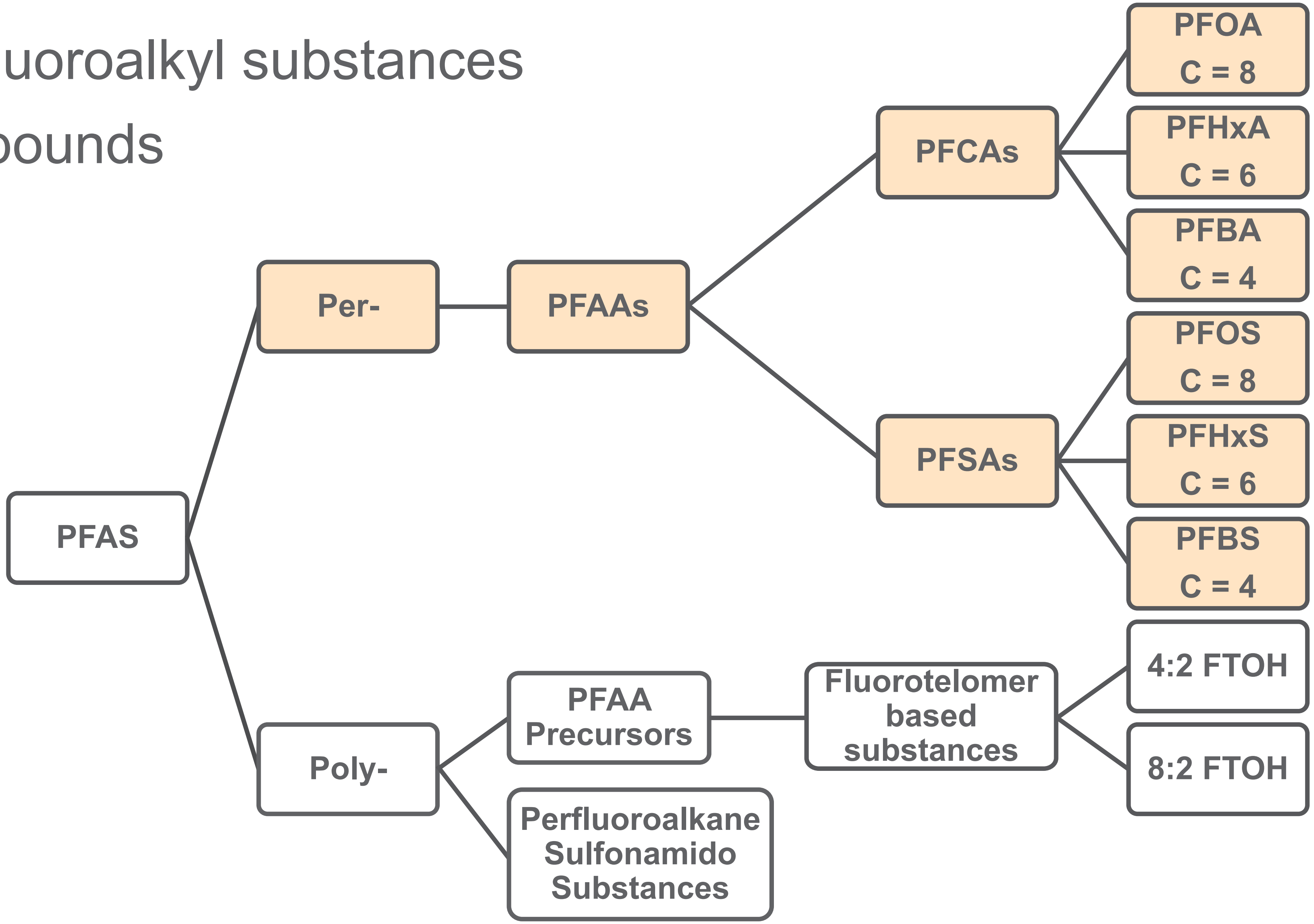
- Objective: flexible reactive transport framework
  - Predict PFAS movement in groundwater
  - Aid selection and design of effective field-scale remedies
  - Technically defensible basis for risk/remedy decision-making
- Approach: reactive transport modules for RT3D
  - Multi-species, 3-D reactive transport code for groundwater
- Targeted two reaction modules
  - PFAS kinetic adsorption/desorption
  - Biological/chemical transformation of parent PFAS compounds
- Intended as an initial starting point for reactive transport
  - As we learn more and technologies are developed, will refine the reaction framework



https://www.pnnl.gov/projects/multi-species-reactive-transport-simulation-software-groundwater-systems

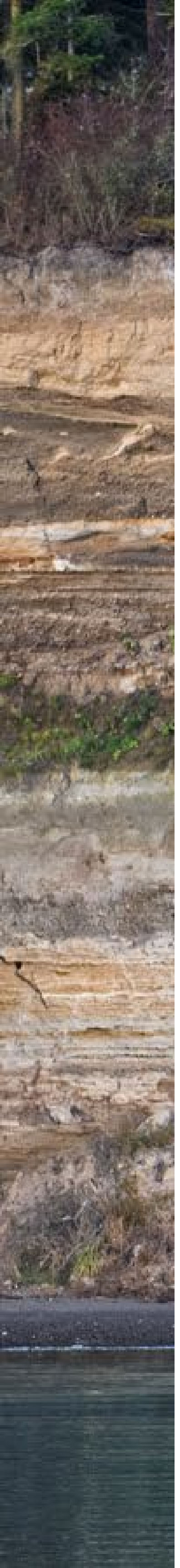
PFAS Compounds

- PFAS: per- and polyfluoroalkyl substances
- Huge number of compounds
- Simplified categorization shown here



PFAS Remediation

- Activated carbon is the only fully available in situ treatment for PFAS-impacted groundwater
  - Commercially available products include: RemBind® (AquaBlok™ in the US), FluroSorb®, PlumeStop™, Aqua ZVI™, and matCARE®
- Long-term performance of adsorptive activated carbon technologies is still an area of ongoing research
- Emerging methods
  - Bioremediation and chemical oxidation/reduction
    - ✓ Aerobic degradation of 8:2 and 6:2 FTOH
    - ✓ Huang and Jaffě (2019) "Defluorination of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) by *Acidimicrobium sp.* Strain A6a"
  - Lab or pilot scale
  - Distinguish ex situ water treatment vs. in situ groundwater remediation
- Modelling fate and transport of PFAS in the environment is necessary to develop effective remediation strategies



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Factors Important to Adsorption

- Dissolved Organic Matter (DOM)
  - Competes with PFAS for sorption sites and may promote PFAS desorption
- pH
  - Sorption coefficients tend to higher values as pH decreases
- Soil micropore volume
  - Important for anionic, longer chain PFAS compounds with respect to sorption capacity
- Chain length of compound
  - Not as important as ionic state, but longer chain compounds sorb better
- Molecular weight
  - PFSA compounds sorb better than PFCA compounds due to their increased molecular weight

Adsorption Reaction Scheme

- Spatially variable, kinetically limited adsorption

$$\frac{d(Caq)}{dt} = - eta \times (Caq - Cas)$$

$$\frac{d(Cs)}{dt} = \frac{poros}{rhob} \times eta \times (Caq - Cas)$$

```
where eta   = first-order mass transfer coefficient [1/T]
      Cs    = solid-phase concentration [M/M]
      Caq   = aqueous concentration [M/L³]
      Cas   = aqueous equilibrium sorption conc'n [M/L³]
      rhob  = bulk density [M/L³]
      poros = effective porosity [--]
      t     = time [T]
```

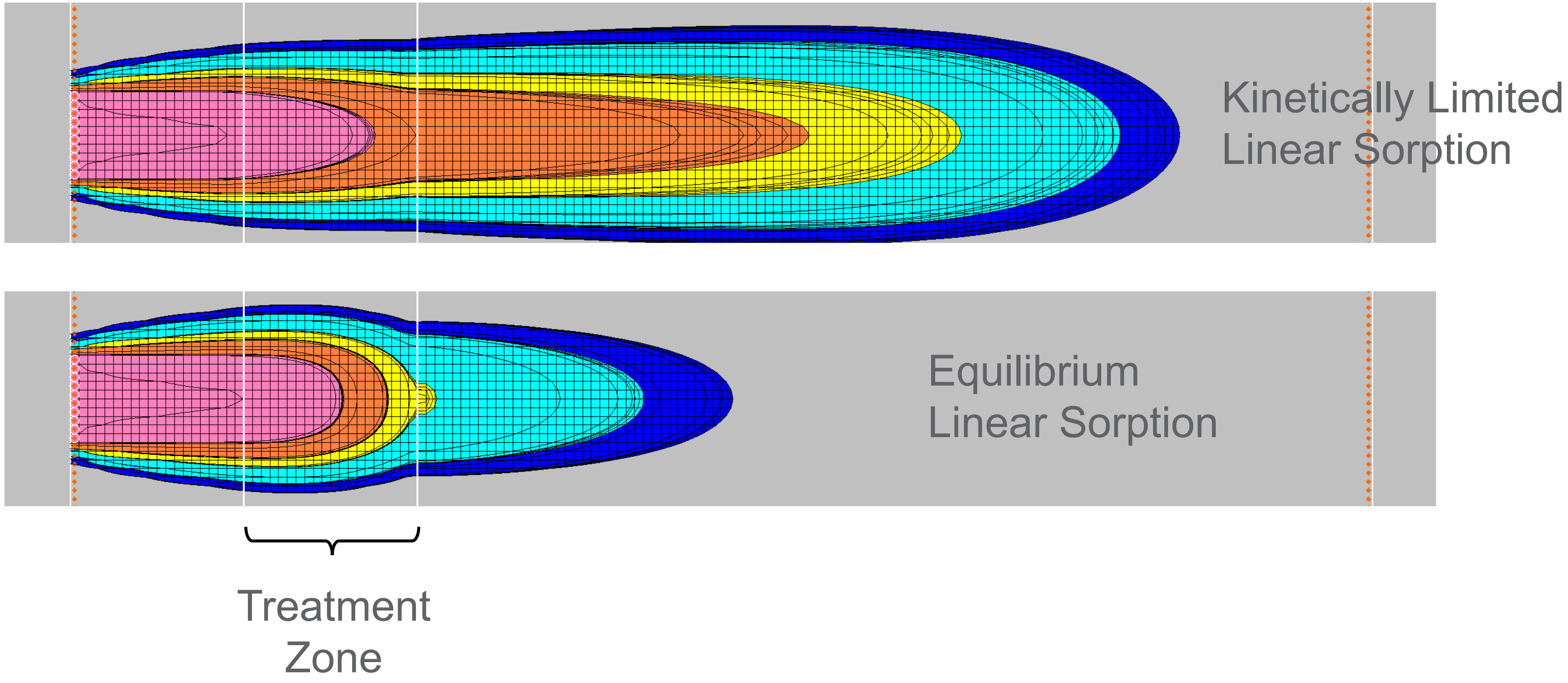
$$C_s = K \cdot C_{as}$$ Linear

$$C_s = K \cdot C_{as}^n$$ Freundlich

$$C_s = \frac{b \cdot C_{s,max} \cdot C_{as}}{1 + b \cdot C_{as}}$$ Langmuir

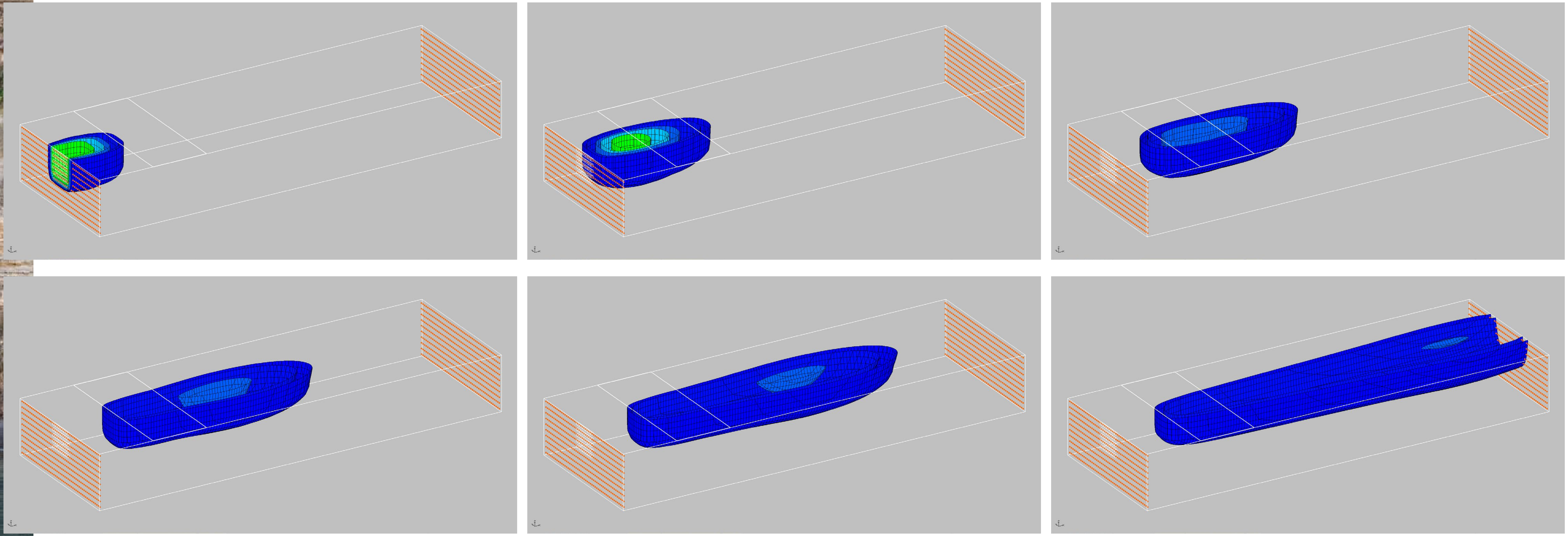
Adsorption Treatment Zone, Constant Source

- Treatment zone (i.e., treatment wall)
- Adsorption will remove PFAS contaminants
- Constant source – when loading reached, contaminants pass through treatment zone



Adsorption Treatment Zone, with Source Removal

- Kinetically limited linear adsorption
  - Aqueous-phase concentrations over time



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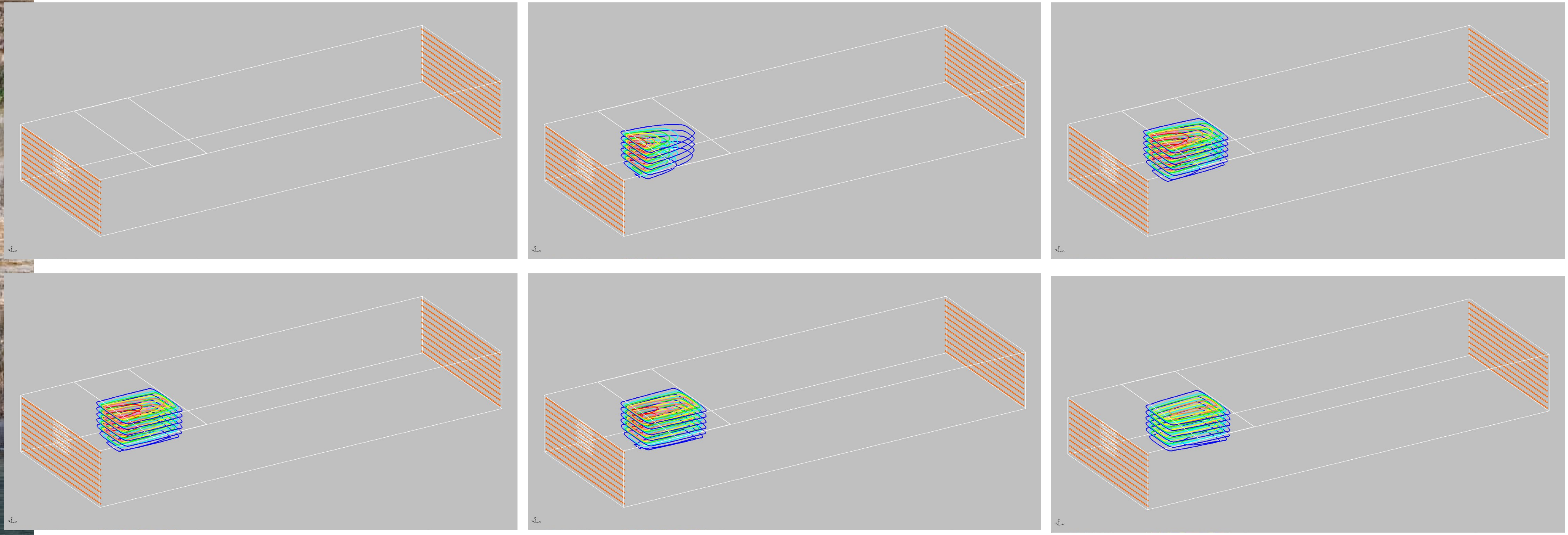
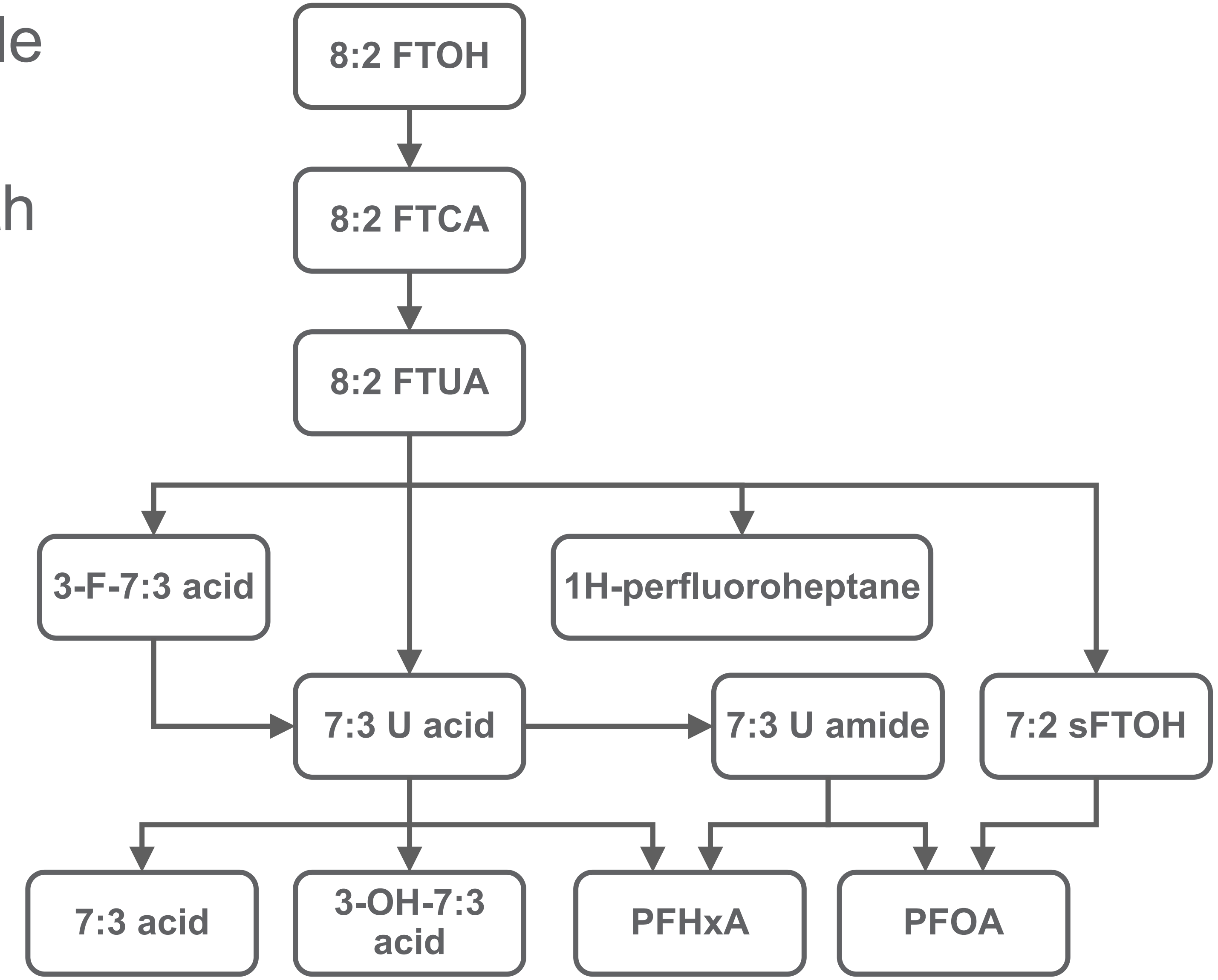


Adsorption Treatment Zone, Source Removal

PFAS Biodegradation Reaction Network

- FTOH reaction network as an example
  - Best described biotic pathways
- Can turn reaction pathways on/off with kinetic rate parameters
- Spatially variable reaction rates to reflect zones of activity
  - aerobic, nitrate-reducing, iron-reducing, or sulfate-reducing conditions



Biodegradation Reactions

- Reaction network modeled with first-order biodegradation
- For parent/daughter species:

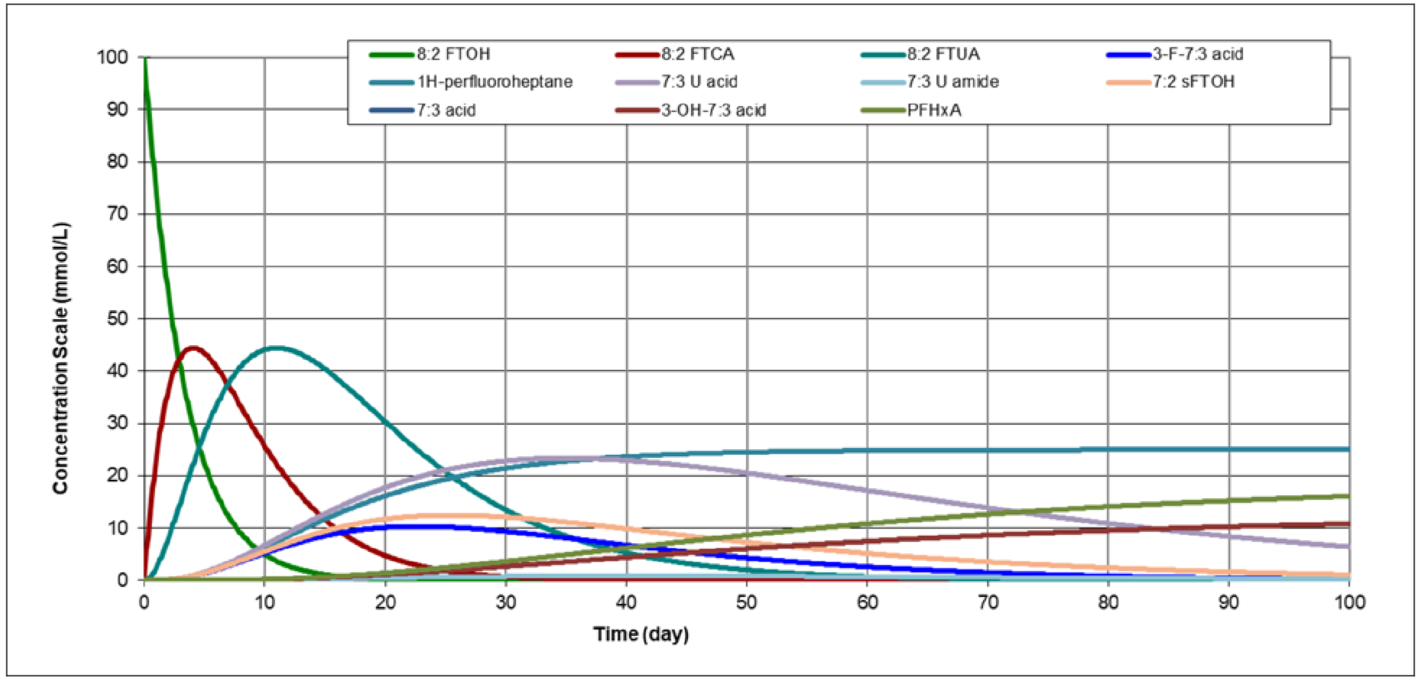
$$\frac{d(Ca_{parent})}{dt} = -k_{parent} \times Ca_{parent}$$

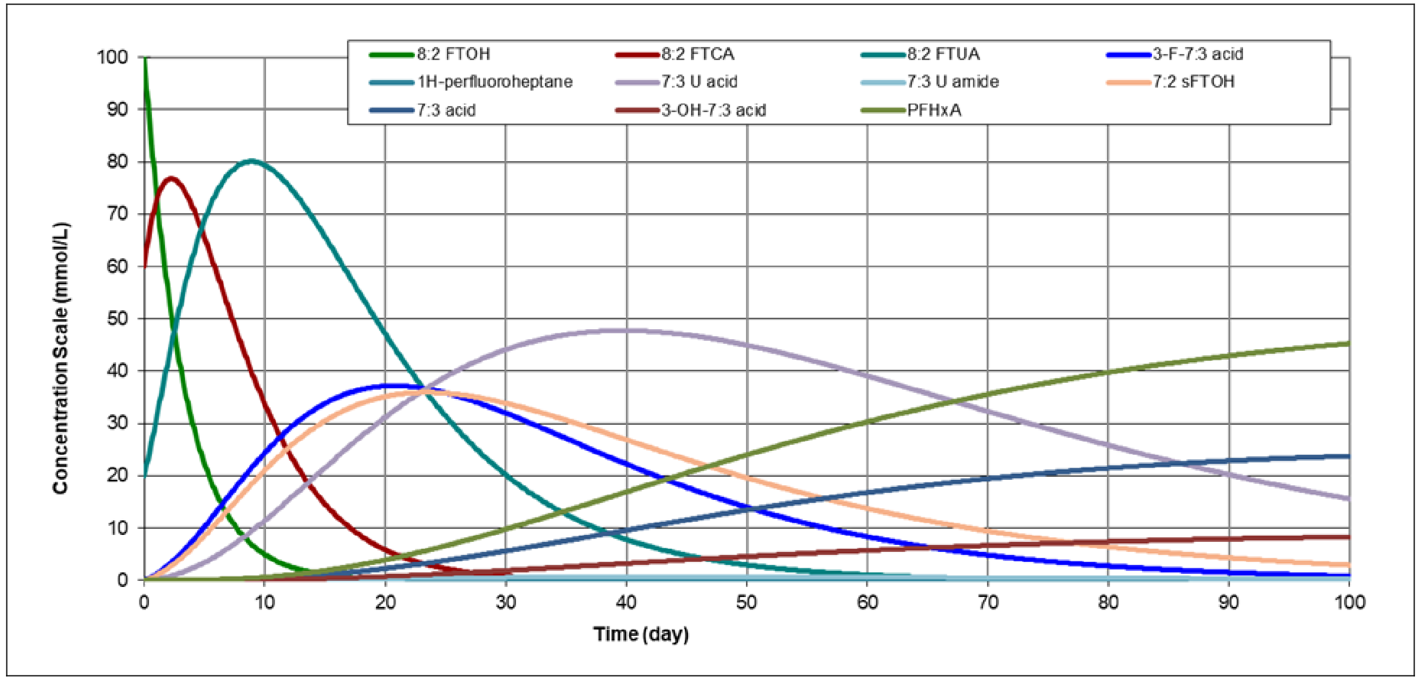
$$\frac{d(Ca_{daughter})}{dt} = -k_{daughter} \times Ca_{parent} + k_{parent} \times f_{daughter\_parent} \times Ca_{parent}$$

```
where k     = first-order reaction rate [1/T]
      f     = stoichiometric yield (split between daughters) [mol/mol]
      Cs    = solid-phase concentration [M/M]
      Ca    = aqueous concentration [M/L³]
      t     = time [T]
```

Transformation Reaction Examples

- Transformations from parents to daughters
- Dependent on
  - Initial concentrations
  - Stoichiometric split between daughters
  - Transformation rates





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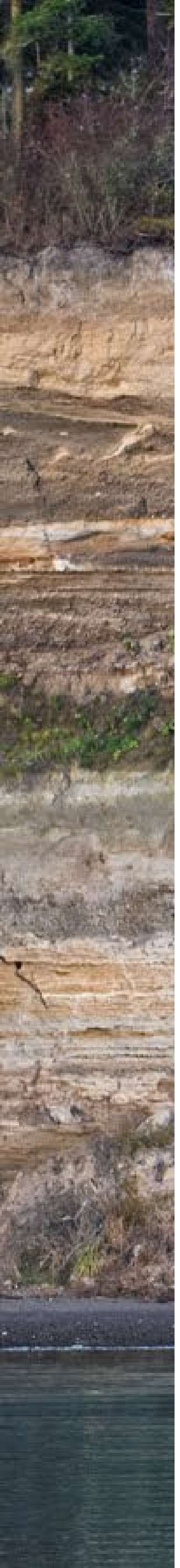
Summary

- Predicting PFAS fate and transport in groundwater is important for developing effective remediation strategies
  - Aid selection and design of effective field-scale remedies
  - Technically defensible basis for risk/remedy decision-making
- Sorption on activated carbon is the primary remedy currently for groundwater
- Multiple biological and chemical remediation approaches are on the horizon
  - With many PFAS compounds, the reaction networks can be complicated
- Developed two reaction modules for RT3D
  - Kinetic adsorption/desorption + PFOH reaction network
- These reaction modules are a starting point for reactive transport simulation
  - Reaction kinetics will need updating as more is learned and remediation technology approaches are developed
- Reaction modules available as DLLs on the RT3D web page



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Thank You

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https://www.pnnl.gov/projects/rt3d/downloads
Report: PNNL-35136