Modeling Adsorption of PFAS in Full and Pilot-Scale GAC and Ion Exchange Systems

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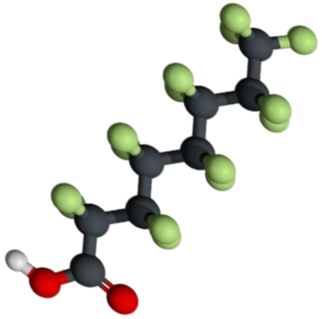
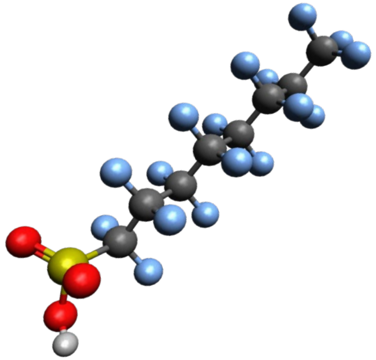


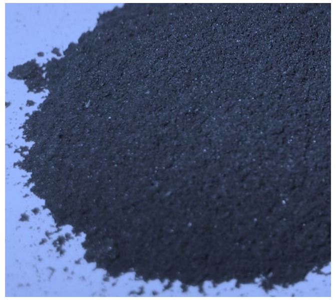
Perfluorooctanoic acid (PFOA)



Perfluorooctanesulfonic acid (PFOS)

Anion Exchange Resin (AER)

Granular Activated Carbon (GAC)



Point of Use

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  - Michael Verma
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  - John Olszewski
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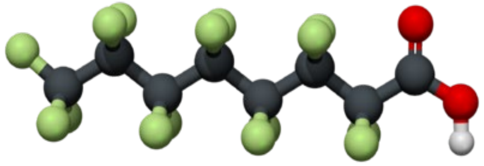
  - Tom Speth

Modeling Background

- Motivation for modeling
  - Design and interpret water treatment studies
  - Optimize treatment systems
  - Inform cost/benefit analysis
- **Subject of research**: Provide useable models to support real-world systems and help leverage laboratory and pilot-scale testing.

Preliminary Models on GitHub:
https://github.com/USEPA/Water_Treatment_Models



Perfluorooctanoic acid (PFOA)

Anion Exchange Resin

Granular Activated Carbon

Journal of Environmental Engineering / Volume 148 Issue 3 - March 2022

Technical Papers

Modeling PFAS Removal Using Granular Activated Carbon for Full-Scale System Design

Jonathan B. Burkhardt; Nick Burns; Dustin Mobley; Jonathan G. Pressman

AWWA WATER SCIENCE

REVIEW | Full Access

Avoiding pitfalls when modeling removal of per- and polyfluoroalkyl substances by anion exchange

Levi M. Haupert, Jonathan G. Pressman, Thomas F. Speth, David G. Wahman

First published: 19 April 2021 | https://doi.org/10.1002/aws2.1222 | Citations: 1

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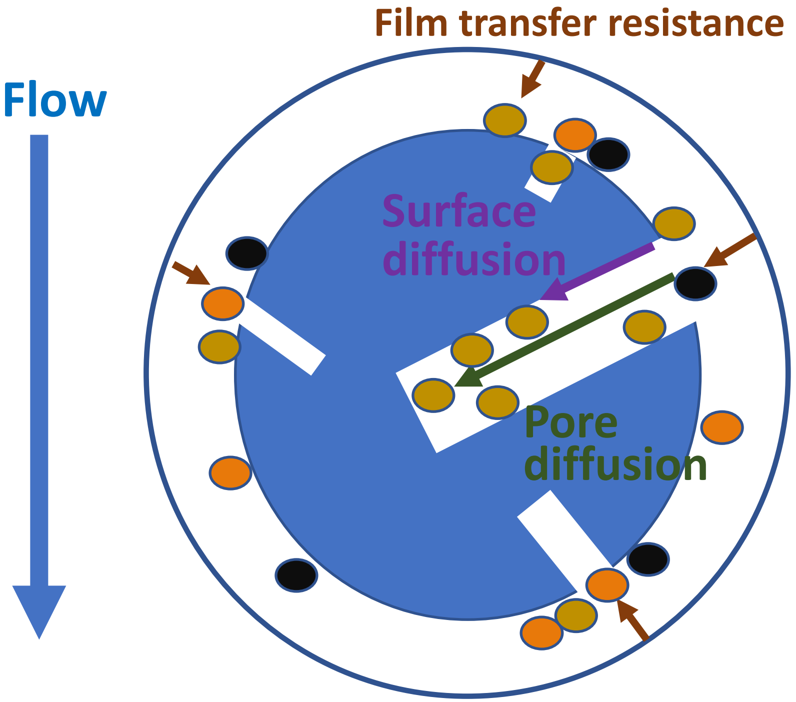
GAC Capacity Calculation

$$q = KC^{1/n}$$

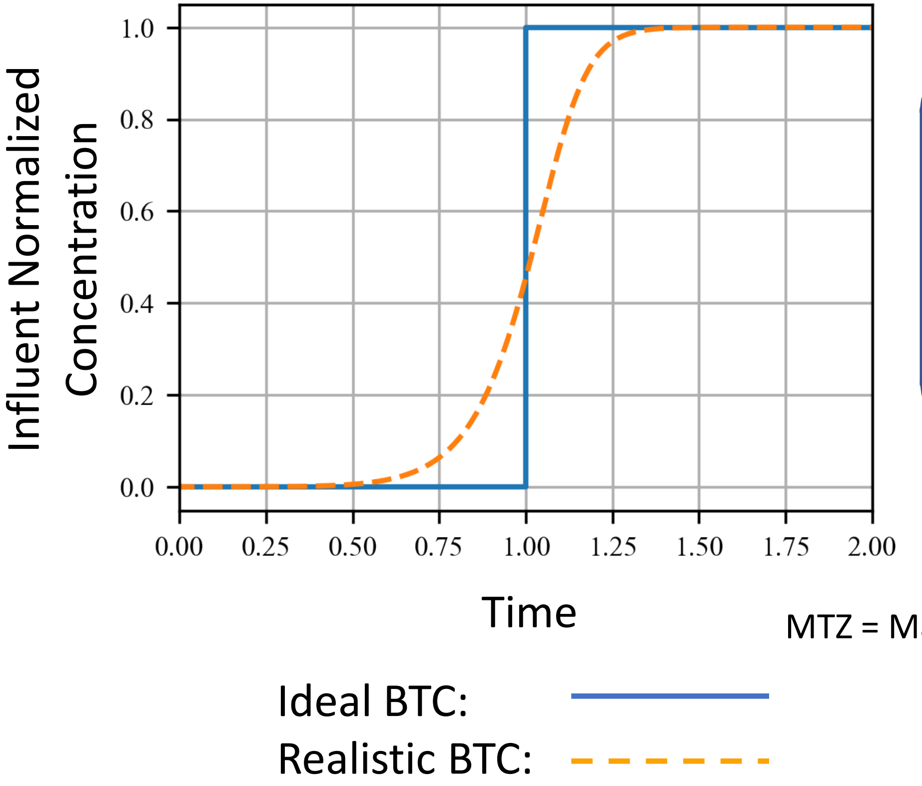
Competitive Ion Exchange (IEX) isotherm

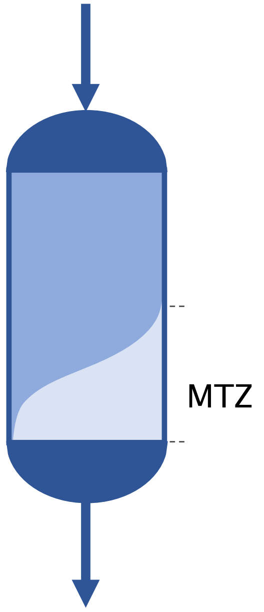
$$K_{BA} = \left(\frac{q_B}{C_B}\right)^{Z_A} \left(\frac{C_A}{q_A}\right)^{Z_B}$$



Mass Transfer and Fouling

Breakthrough Curves (BTCs)

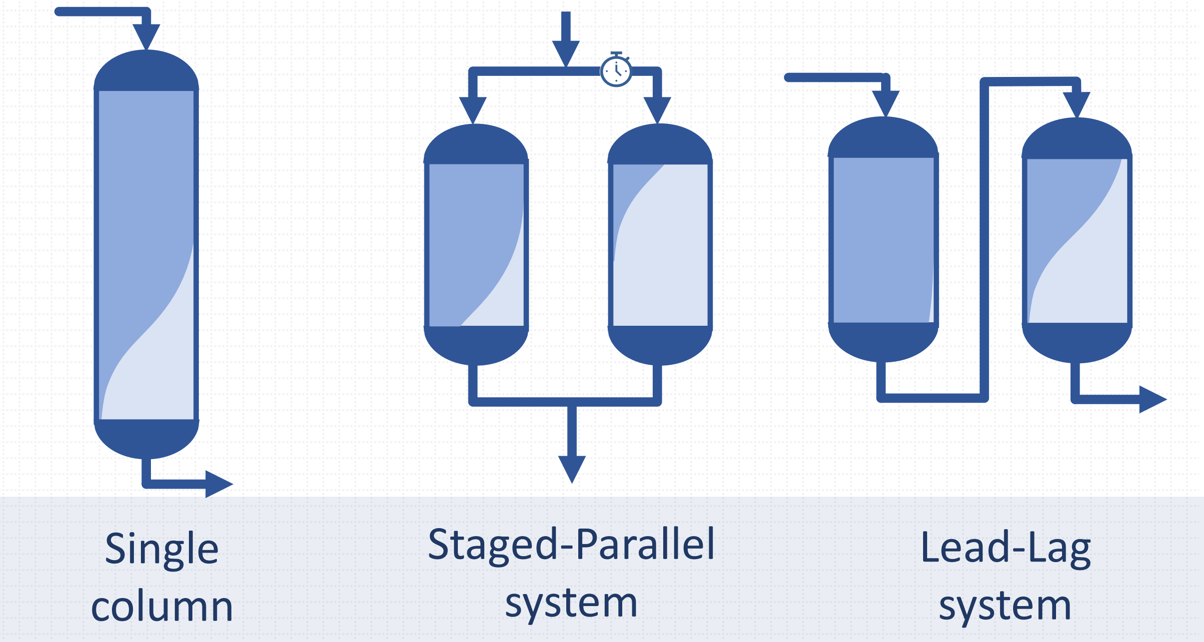




MTZ = Mass Transfer Zone

Column Configurations

- Single column system typically discards some potential sorption capacity on changeout.
- Media use efficiency can be improved at the cost of system complexity.
- When some breakthrough is acceptable, parallel systems can run media past exhaustion.
- Lead-Lag system increases media efficiency when breakthrough threshold is low and can provide increased margin of safety.

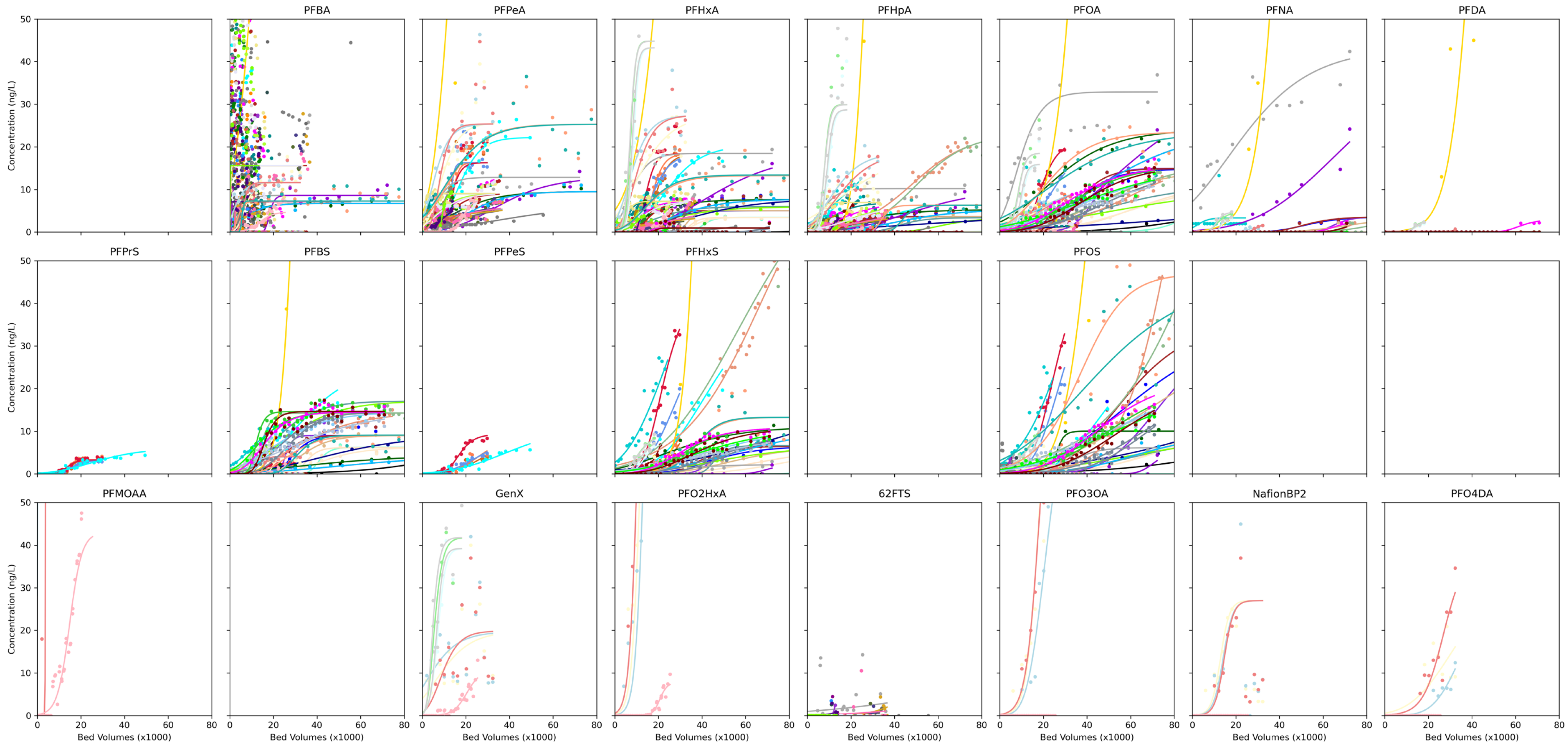


Data Collection Effort - Scott Summers

- Effort to collect PFAS effluent data from GAC or IEX systems at pilot or full scales
- Provide expanded comparison between multiple medias and conditions
- Predict media use rates
- Expand data available for modeling

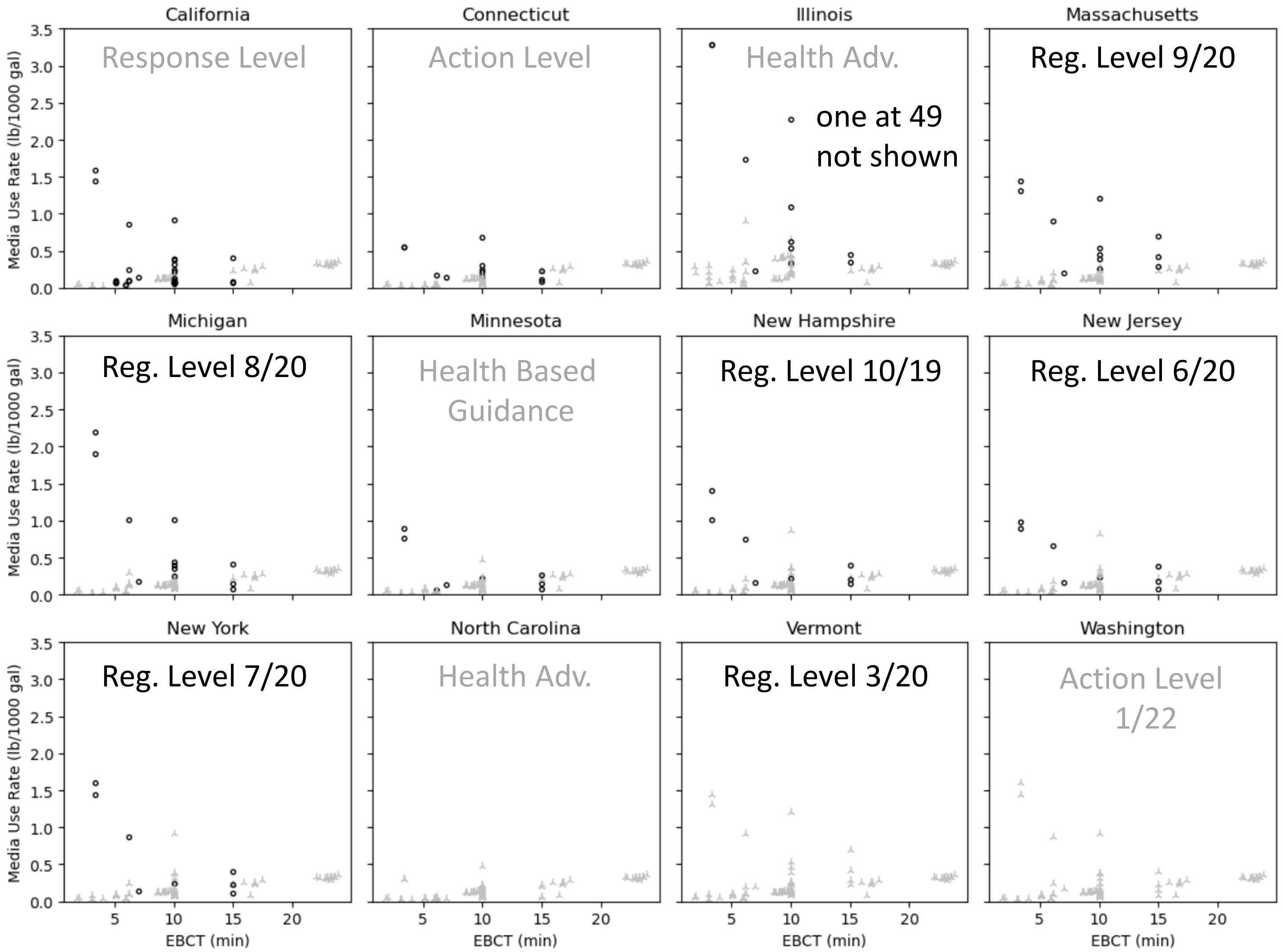
- GAC (80 datasets)
  - Surface 38, Ground 42
  - Pilots 68, Full Scale 12
  - 13 carbons
  - EBCTs: 1.85 – 24 minutes
- IEX (19 datasets)
  - Surface 10, Ground 9
  - Pilot 19
  - 7 SBA resins
  - EBCTs: 0.4 – 3 minutes

All the Data



Variability between sites/conditions → Applying pilot/full-scale results to different system would be challenging

State Levels Impact on Media Use Rate



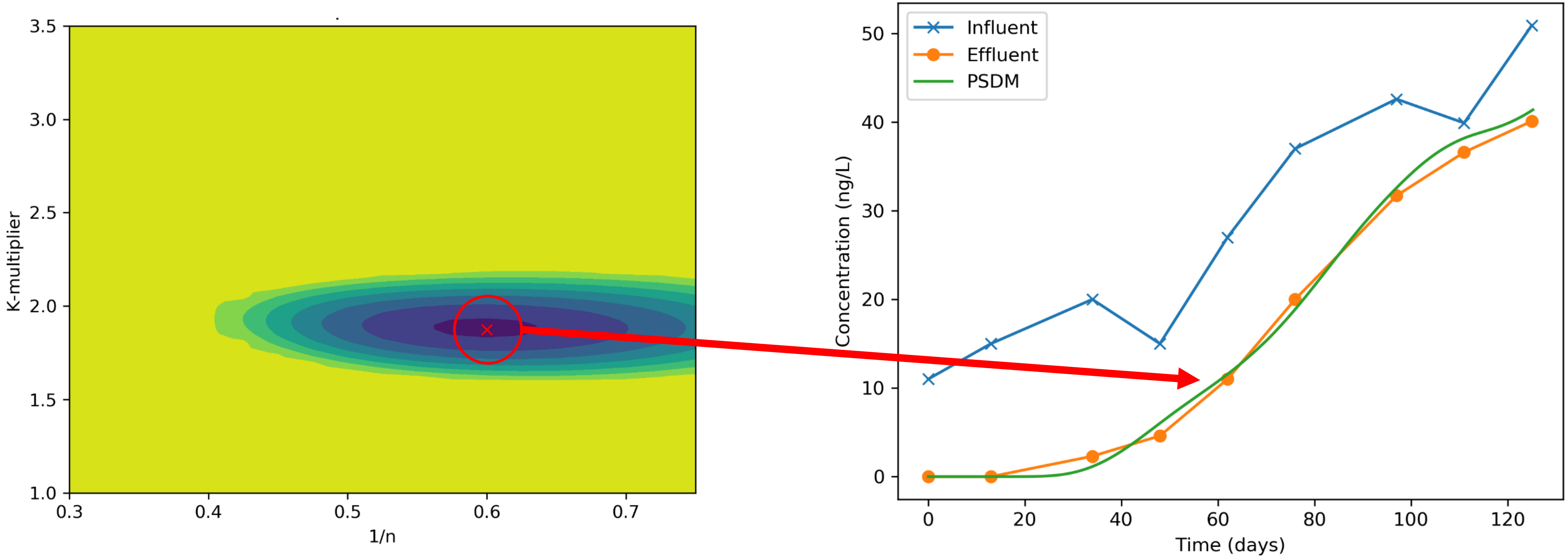
Media Use Rate from Study

Lowest Media Use Rate of Study – Trigger Level not exceeded*

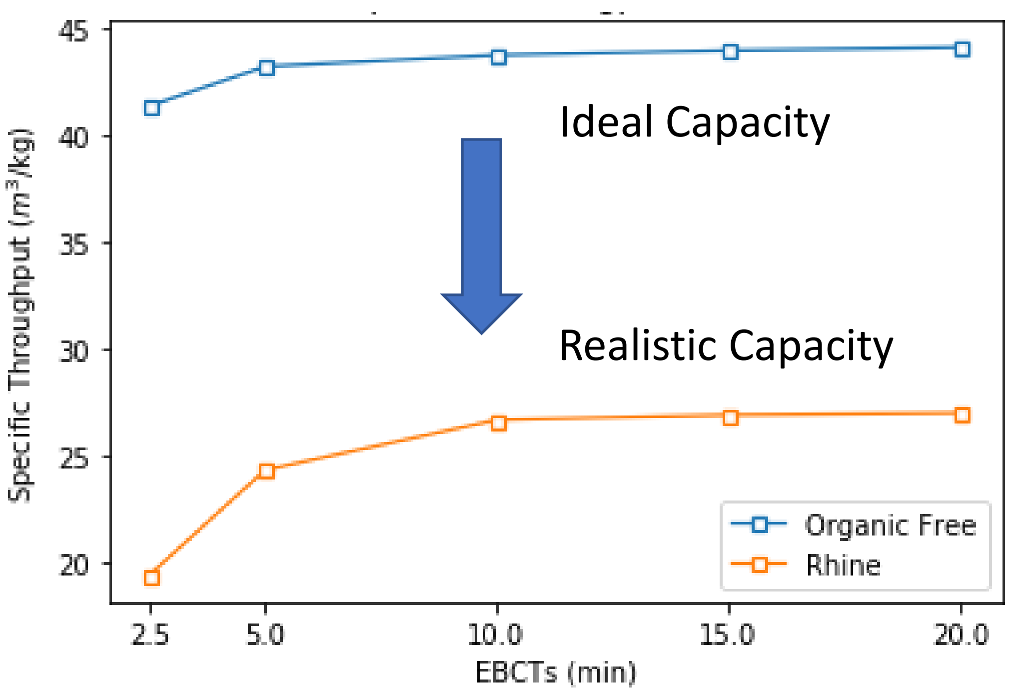
*Influent may not have exceeded trigger level
*Study may not have been run long enough for trigger level to be exceeded

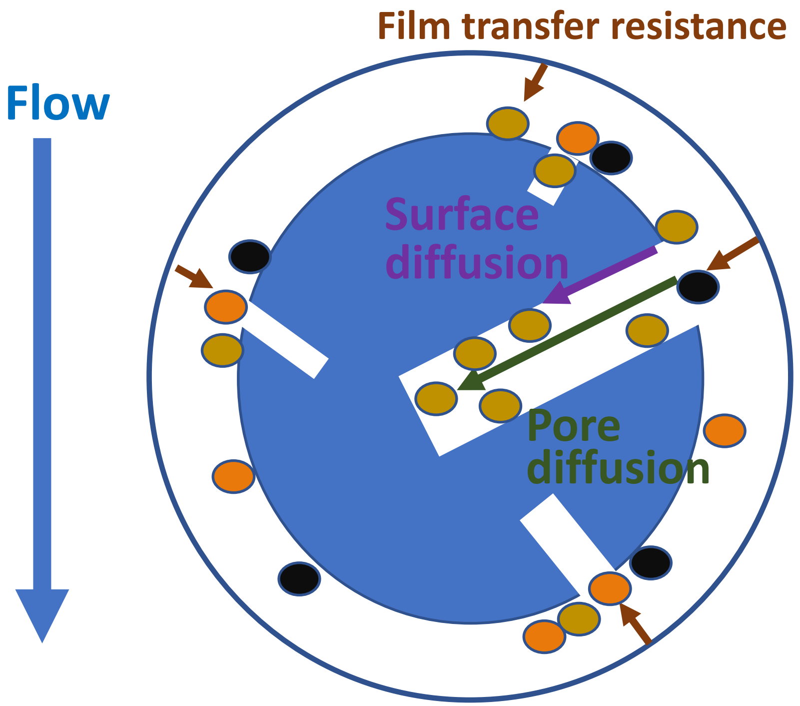
- Automated fitting of Freundlich isotherm parameters based on field data (Mar. 2022): doi.org/10.1061/(ASCE)EE.1943-7870.0001964

PSDM = Pore and Surface Diffusion Model



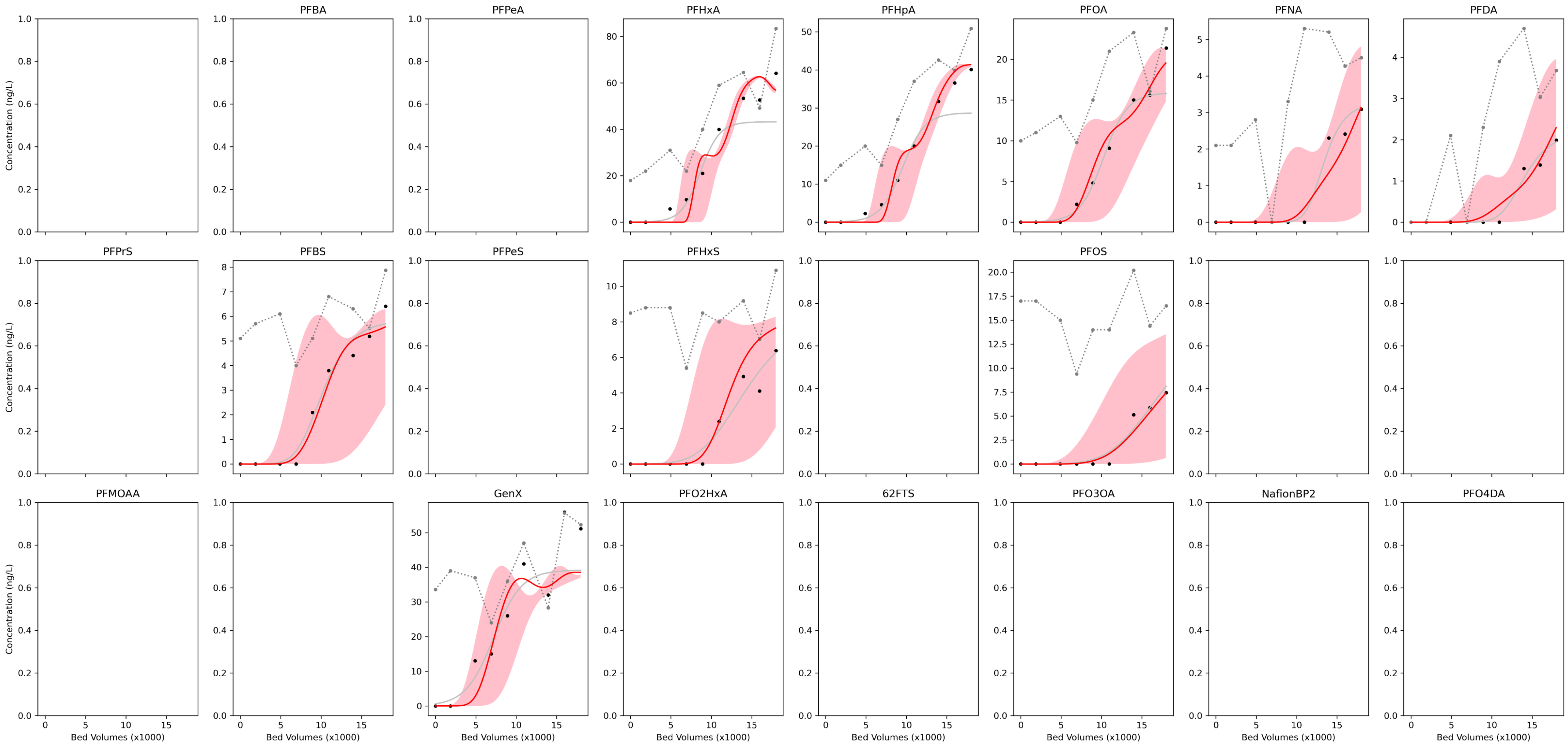
Fouling of Media





See Jarvie et al. 2005 for more details on GAC fouling

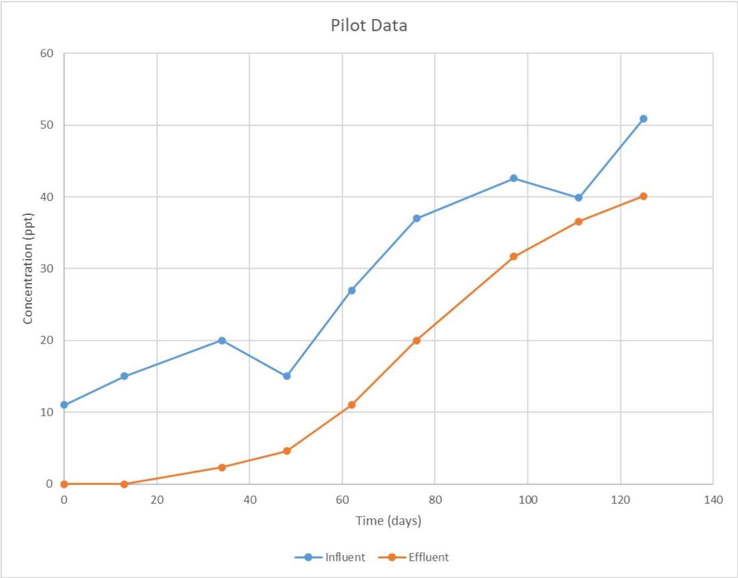
Single Site Snapshot



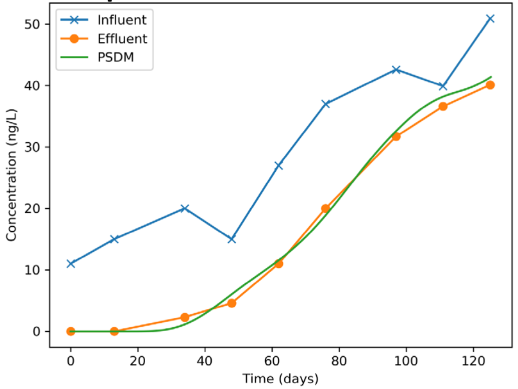
Shaded Area: ± 10% K & 1/n

Pilot to Full Scale

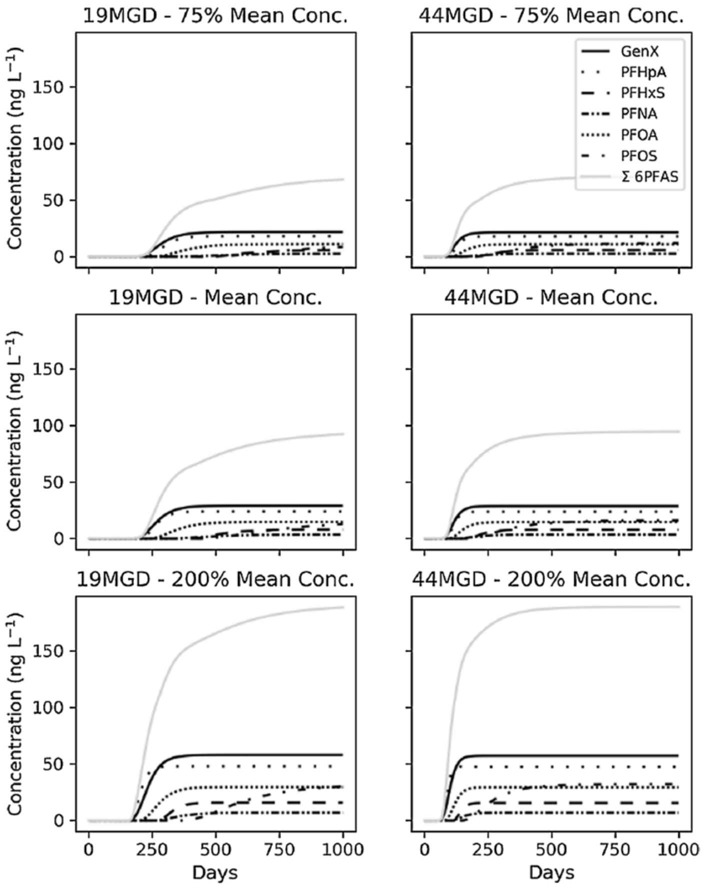
Raw Data



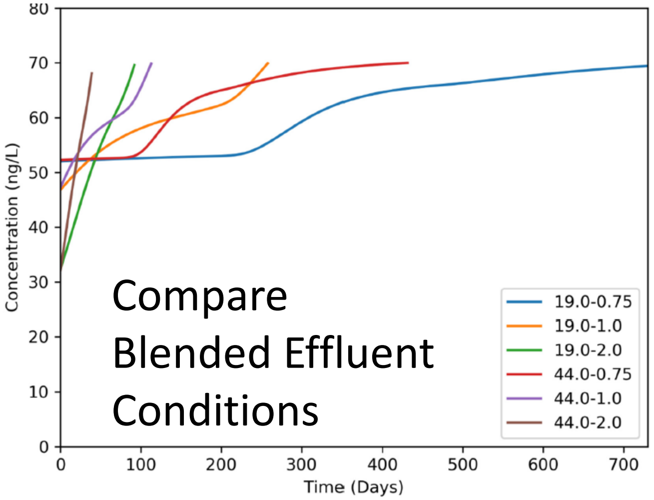
Fit parameters for model



Test Various Conditions



Burkhardt et al. 2022 JEE

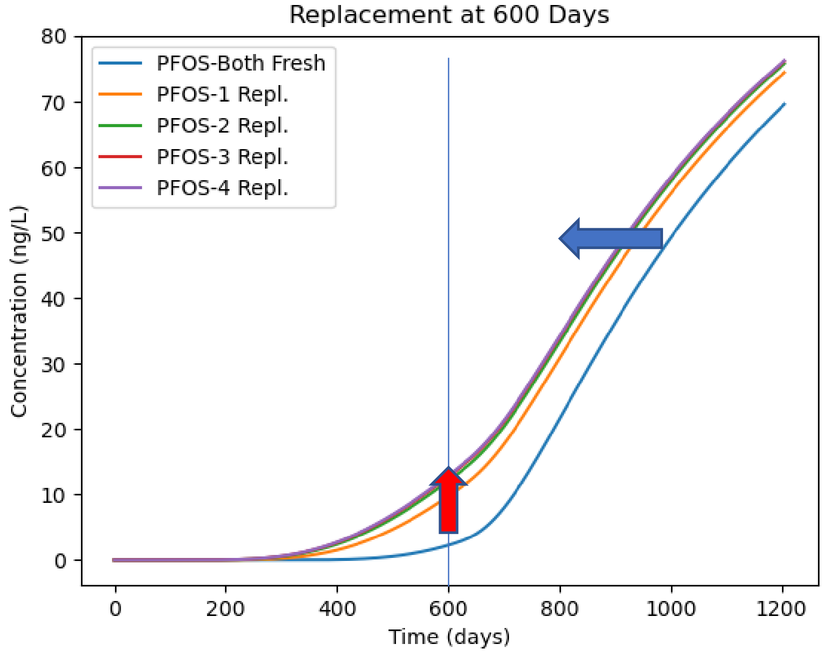


Helps predict current/future treatment for a given system

Media replacement intervals informs costs

Lead Lag Modeling

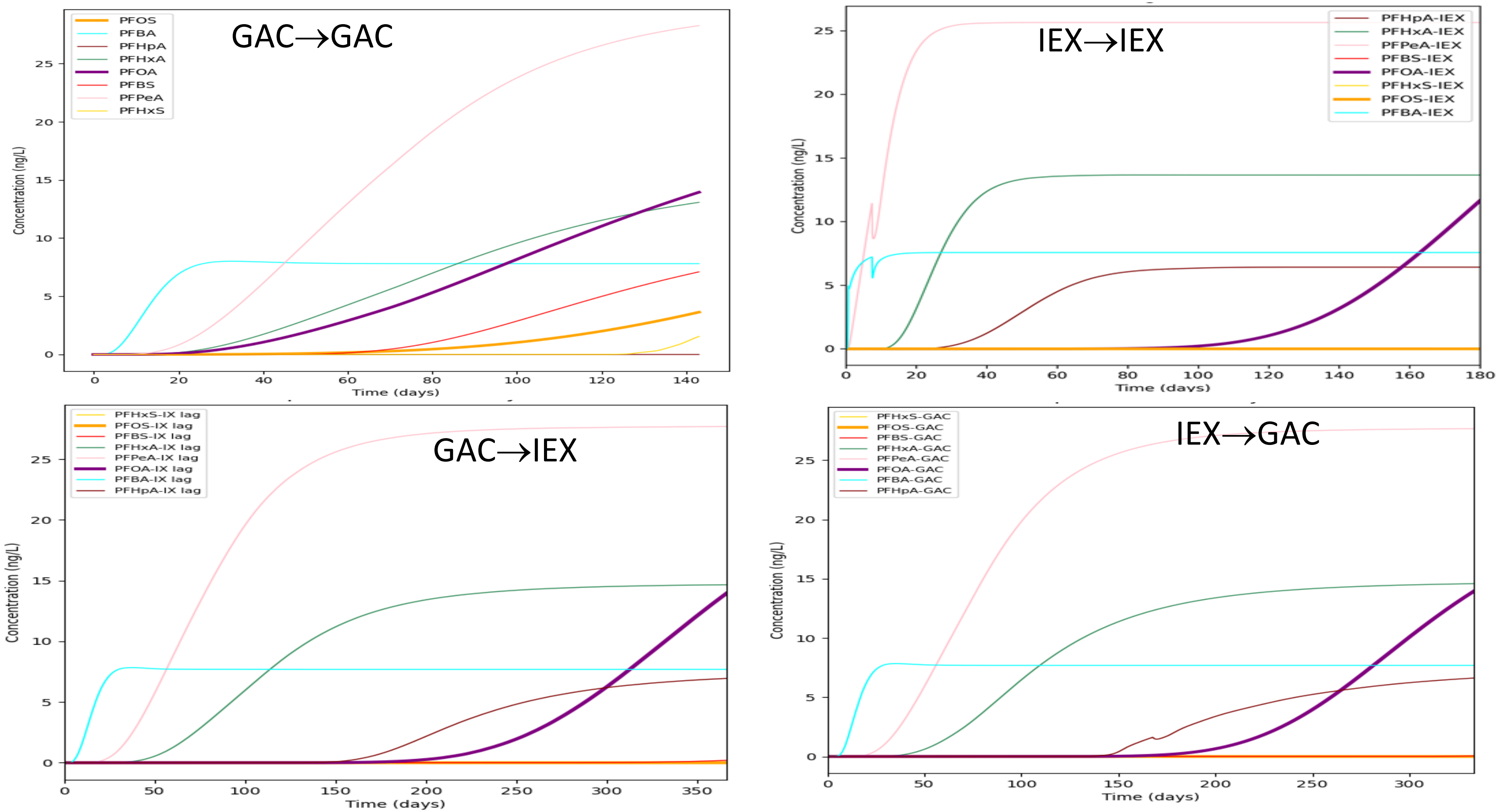
- A little more complicated
- Requires iteration
  - Must “pre-load the lag column”
  - Predict effluent from lead
  - Supply effluent concentrations to lag for initial period as influent, then raw influent (simulates its life as lead vessel).
- **Modeling tools can do this automatically!**



- Breakthrough profiles occur earlier as lead vessels are loaded more during periods as lag vessel
  - Higher effluent concentrations
- May require 4+ cycles for lead-lag vessel cycling to stabilizes for a replacement cycle
  - First replacement cycle won’t necessarily be good indicator of future performance

Variations on Lead Lag

Compare Designs

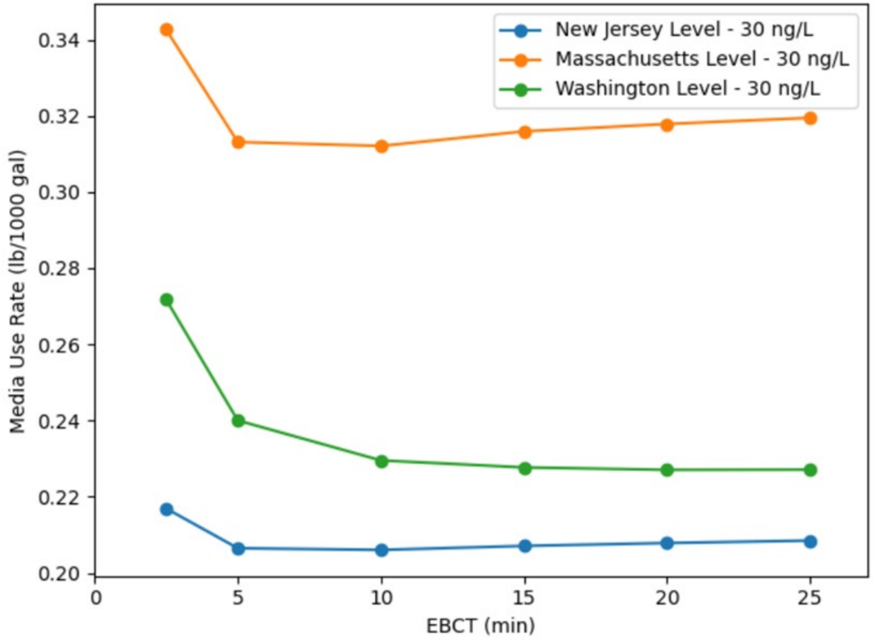


Illustrating Additional Model Uses

- **Illustrative Example**: Highlights the ability to model to a range of treatment objectives
  - Consistent cases used here, but site-specific information would be used for analysis of given system
- **Shouldn't be generalized to other case** – shows what can be done.
- Can be used to understand how different EBCTs impact treatment
- Similar Media Use Rates translate to different change out frequencies, which has practical implications

Same System – Different State Levels

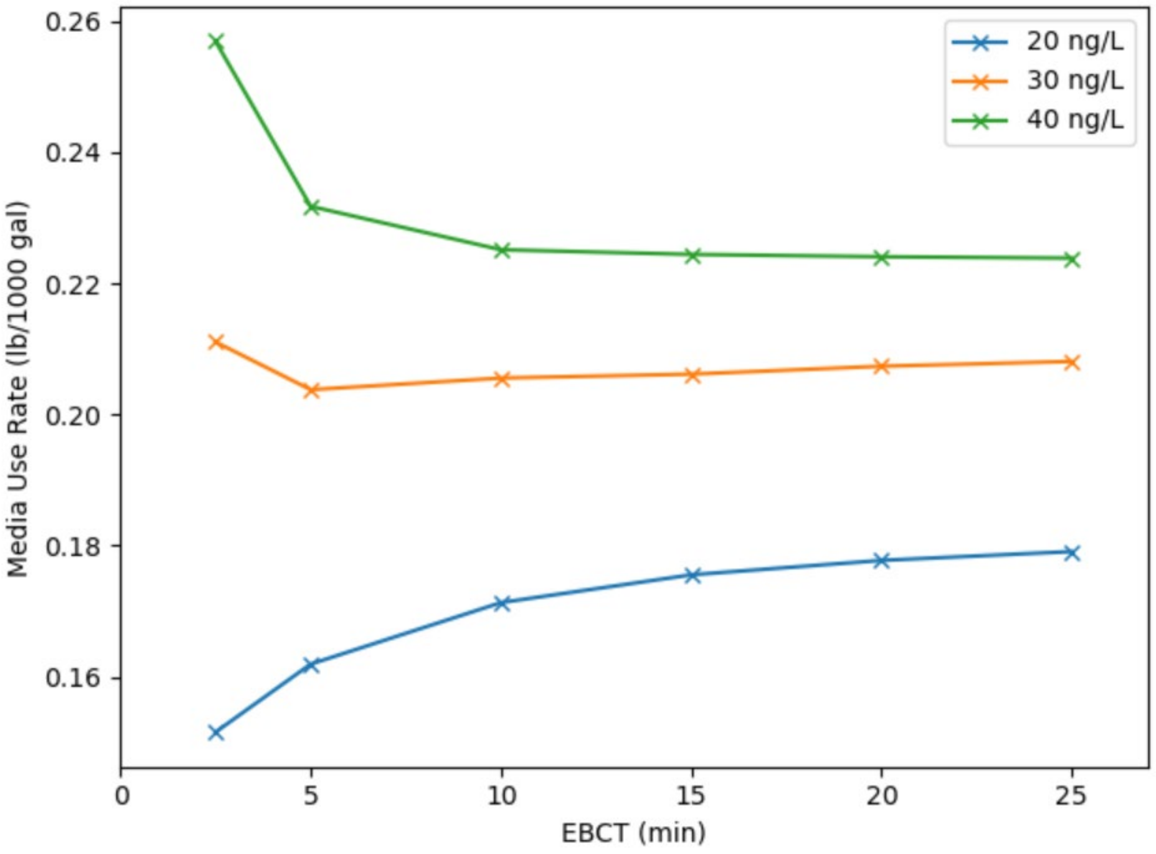
GAC



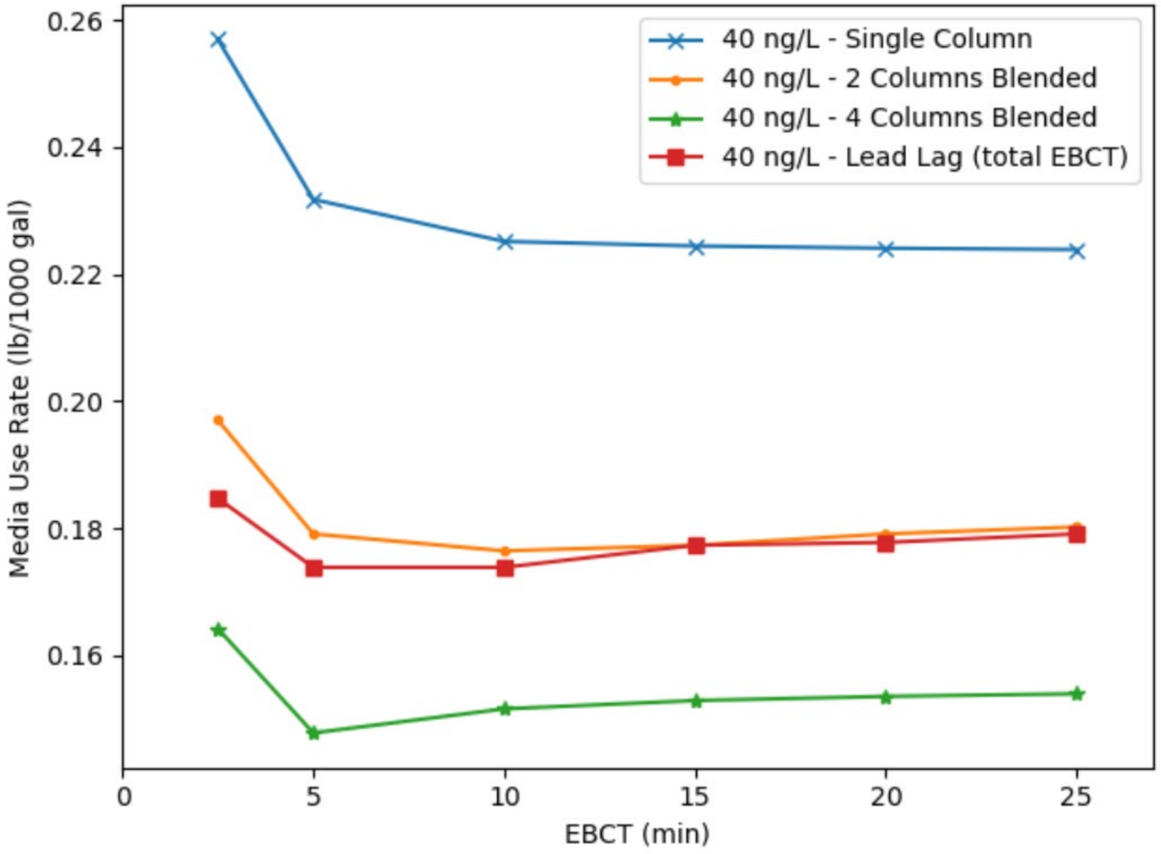
NJ: Adopted Regulation (6/20) PFNA, PFOS < 13, PFOA < 14 ppt
Mass: Adopted Regulation (9/20) Sum of PFOA, PFOS, PFNA, PFHxS, PFHpA, PFDA < 20 ppt
Wash: Action Levels (1/22) PFOA<10, PFOS<15, PFNA<9, PFHxS<65, PFBS<345 ppt

Predicting Operating Conditions

Impact of Influent Concentration on MUR

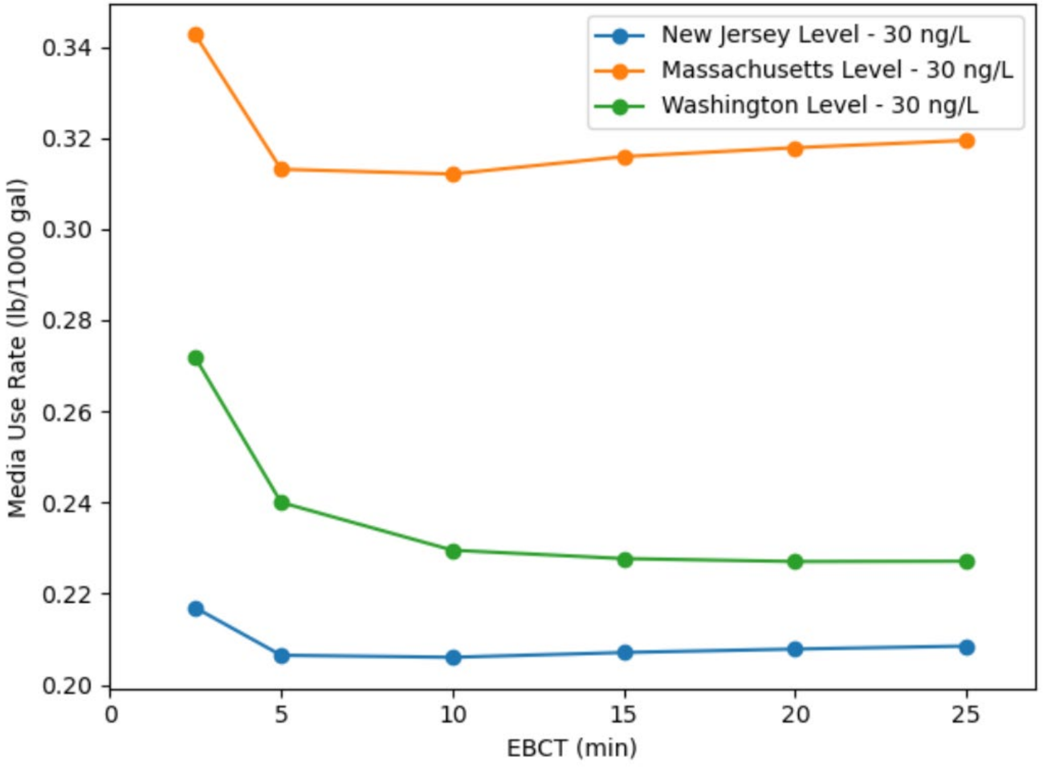


Impact of Column Configuration on MUR

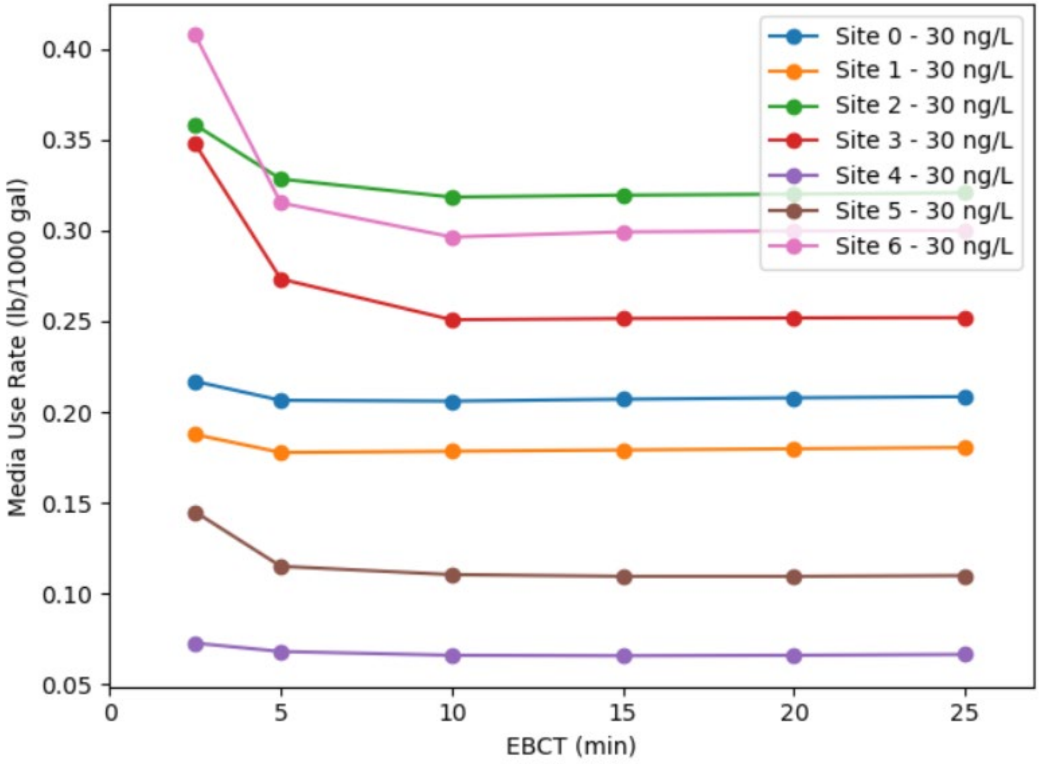


Multi-Site Considerations

Same System – Different State Levels (Reg. or AL)



Same State Level – Different Site Effective Capacities

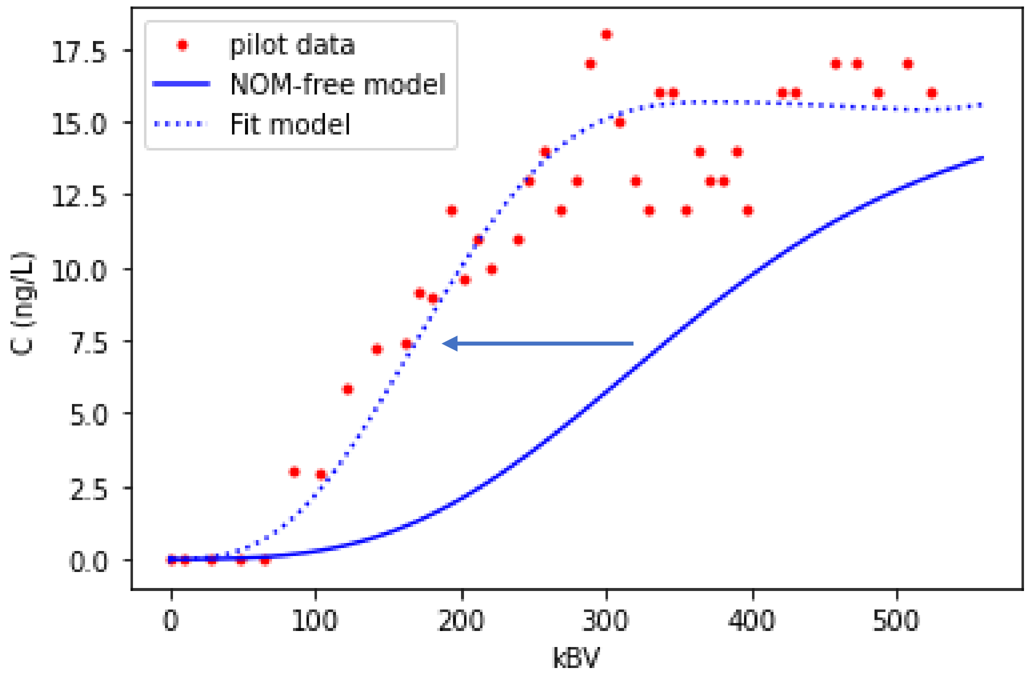


Effect of Natural Organic Matter (NOM) on Ion Exchange Pilot Performance

Jonathan Burkhardt
Levi Haupert
Boris Datsov
Tom Speth
Scott Summers
David Hand

Data/Modeling Overview

- Strategy: Use laboratory data to estimate PFAS breakthrough on NOM-free waters and compare to actual breakthrough curves.
- HSDM model with ion exchange isotherms can be used if parameter estimates are available.
  - Resin IEX capacity
  - Major counterion affinities
  - PFAS affinities
  - Kinetic parameters
- EPA has preliminary estimates of these parameters for two resins in the datasets Scott Summers compiled, covering 10 of the 19 available datasets.



Back of the Envelope Calculation

- Assumptions
  - Trace-level contaminants on large background
  - Absence of chromatographic effects
- Γ_i: Bed volumes to 50% breakthrough for the i-th trace contaminant.
- Q_f: concentration of ion exchange sites in the filter (meq/L)
- $\alpha_{i,A}$: separation factor for ion *i* against reference ion A (chloride in this case). Relative affinity.
- β : Background strength (meq/L)
- C_j : Feed concentration of the j-th major ion (meq/L)
- **Implication:** It is not possible to simultaneously determine Q_f, $\alpha_{i,A}$, and β from a single breakthrough curve.

$$\Gamma_\mathrm{i} \approx \frac{Q_f \alpha_{i,A}}{\beta}$$

$$\beta = \sum_j C_j \alpha_{j,A}$$

Example Resin/Ion Parameters

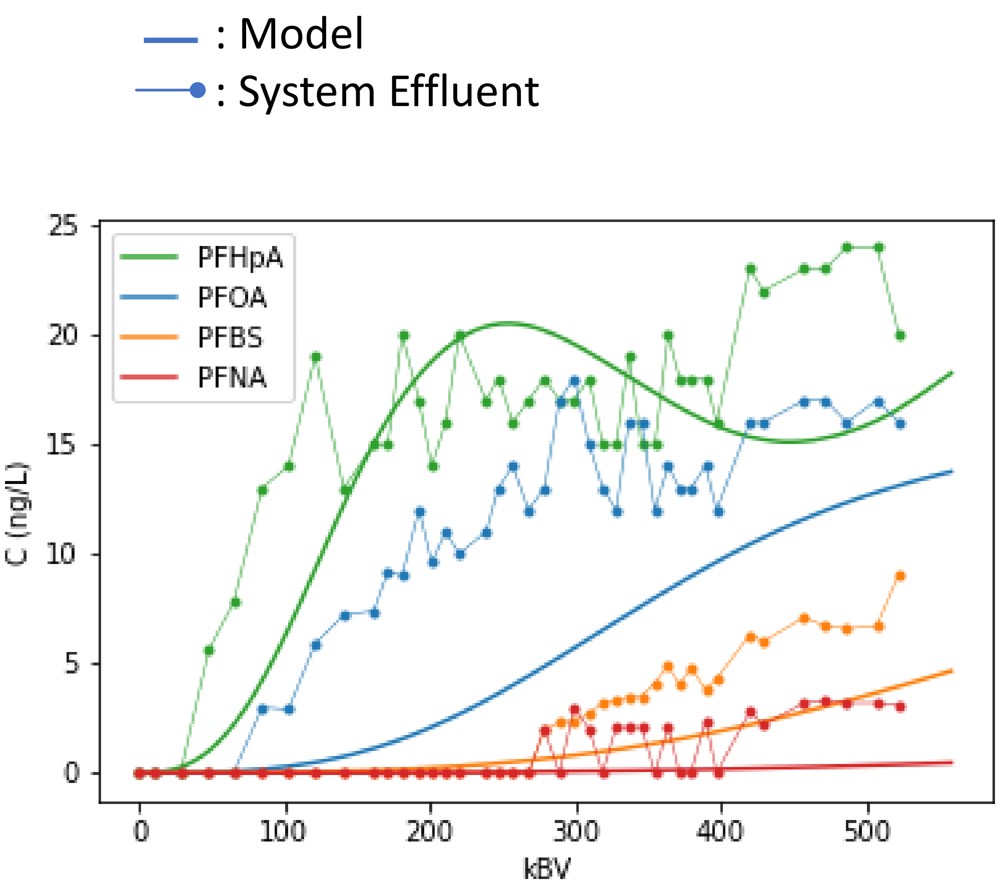
- **Filter IX capacity**: Concentration of IX sites inside the resin bed, determined by EPA† using ASTM method D2187 – 17: 845 meq/L of packed media.
- **Affinity:** Quantified by chromatographic separation factor vs. chloride.
- **Film Transfer**: 4.7 x 10^{-3} cm/s based on simplified Gnielinski correlation for PFHpA at 20 °C.
- **Intraparticle Diffusion**: 5.0 x 10^{-10} cm^2/s based on EPA column data† for PFHxA.

Name	Average Conc.	unit	Chloride Sep. Factor	Source †, ‡
Chloride	170	mg/L	1.0	definition
Nitrate	8.0	mg(N)/L	13.0	EPA
Sulfate	154	mg/L	1.54 *	EPA
Bicarbonate	64	mg(C)/L	0.39	EPA
PFHpA	6.3	ng/L	3,300	Fang et al.
PFOA	23.6	ng/L	9,100	EPA
PFBS	8.2	ng/L	17,000	EPA
PFNA	2.1	ng/L	24,000	EPA
PFHxS	13.5	ng/L	130,000	EPA
PFOS	46.1	ng/L	2,000,000	EPA

* Sulfate is a divalent ion, so its separation factor depends on solution composition.
† EPA, preliminary findings and conclusions, subject to revision following EPA's quality assurance review.
‡ Fang, et al. (2021). Removal of per-and polyfluoroalkyl substances (PFASs) in aqueous film-forming foam (AFFF) using ion-exchange and nonionic resins. Environmental Science & Technology, 55(8), 5001-5011.

Example IX Analysis: Initial Estimate

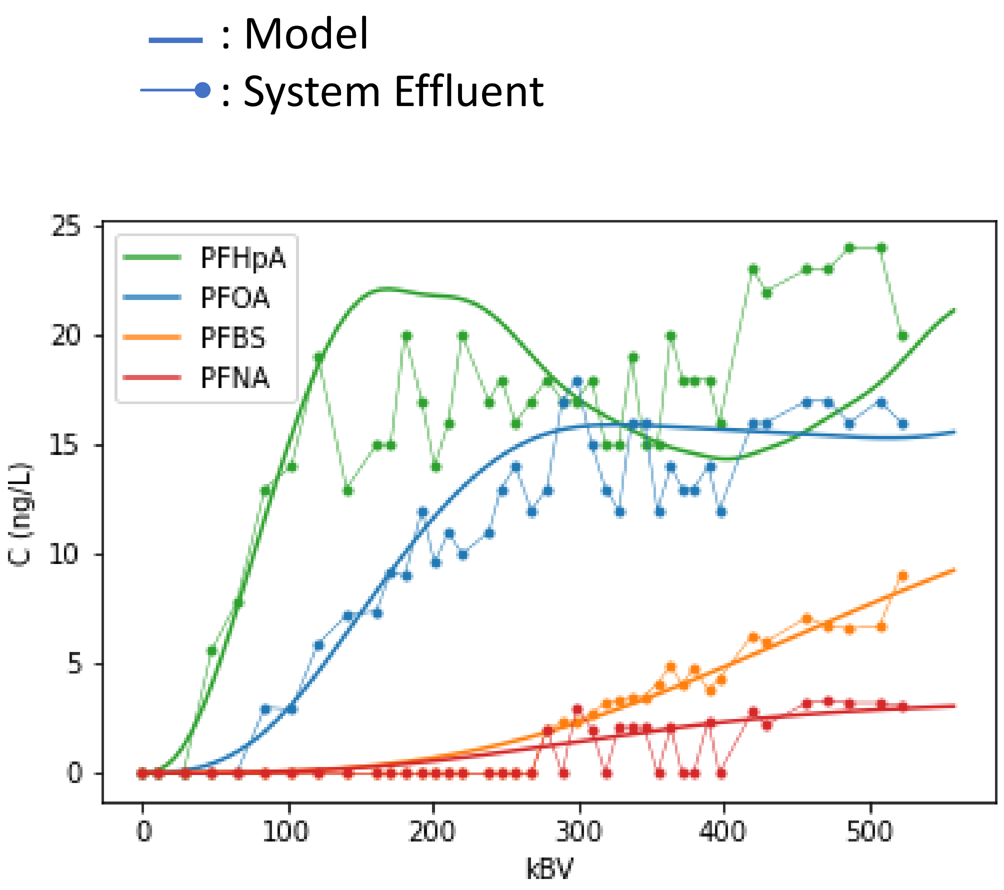
- Using all known parameters from the pilot system and the literature results in model with later breakthrough than observed.
- PFAS/PFAS competition was predicted to be negligible, so the error is not likely unaccounted for PFAS (unless concentration is very high).
- Under these conditions, it is not possible to differentiate errors in resin IX capacity from errors in background ion interference.
- However, some effect from natural organic matter is expected.



Example IX Analysis: Refinement

- It was not possible to fit all four breakthrough curves with a single parameter adjustment.
- This suggests that NOM does not affect PFAS equally.
- It is possible that later eluting NOM fractions affect higher affinity PFAS more strongly.
- An alternate hypothesis might be non-exchange fouling.
- Differences in mass transfer efficiency may also contribute with PFBS.

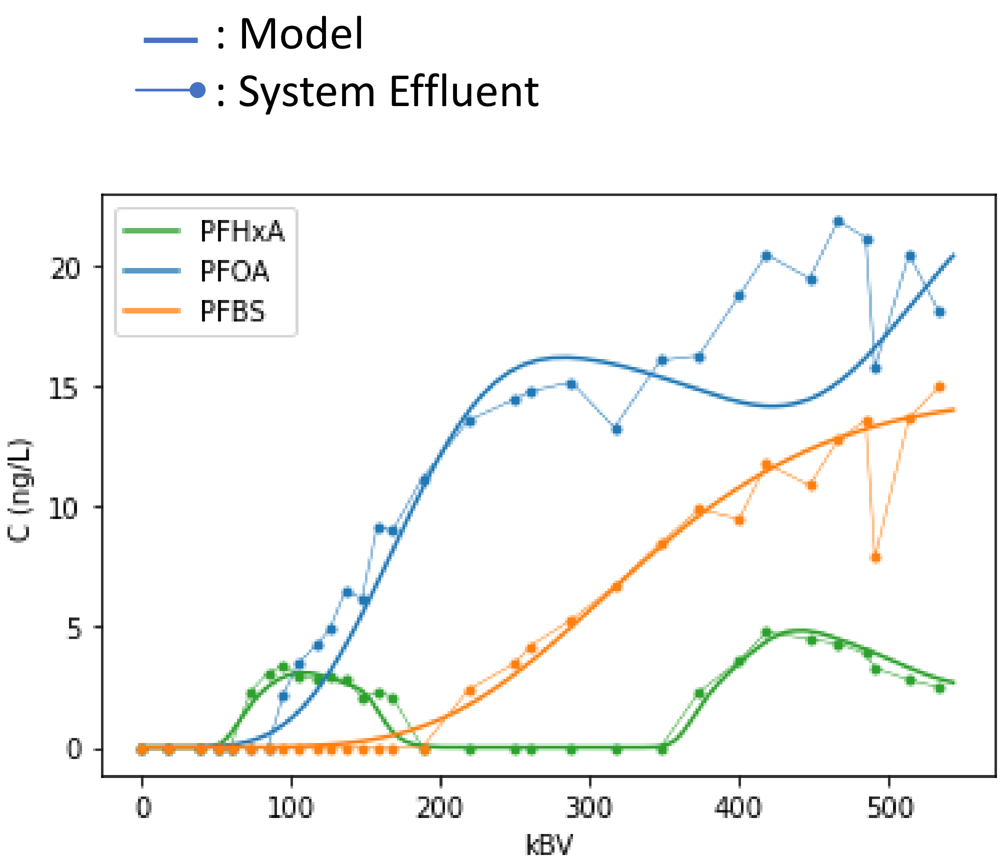
PFAS	Affinity Multiplier
PFHpA	0.60
PFOA	0.45
PFBS	0.70
PFNA	0.35



Example IX Analysis: Different Groundwater

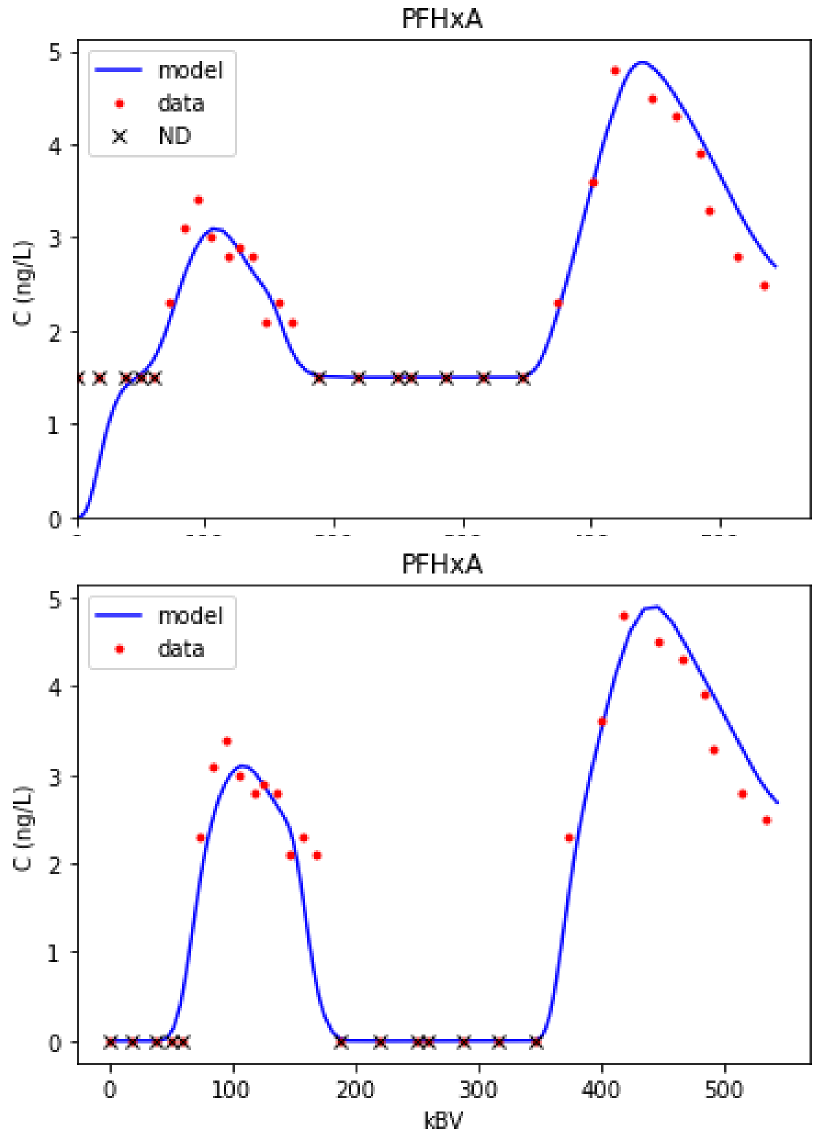
- Same resin.
- Nearly same TOC (1.3 vs 1.23 mg/L).
- But the impact of NOM on this system was much larger overall and affected PFAS more uniformly.
- NOM composition matters but is difficult to quantify.
- More work is needed in this area.

PFAS	Affinity Multiplier
PFHpA	0.30
PFOA	0.28
PFBS	0.30



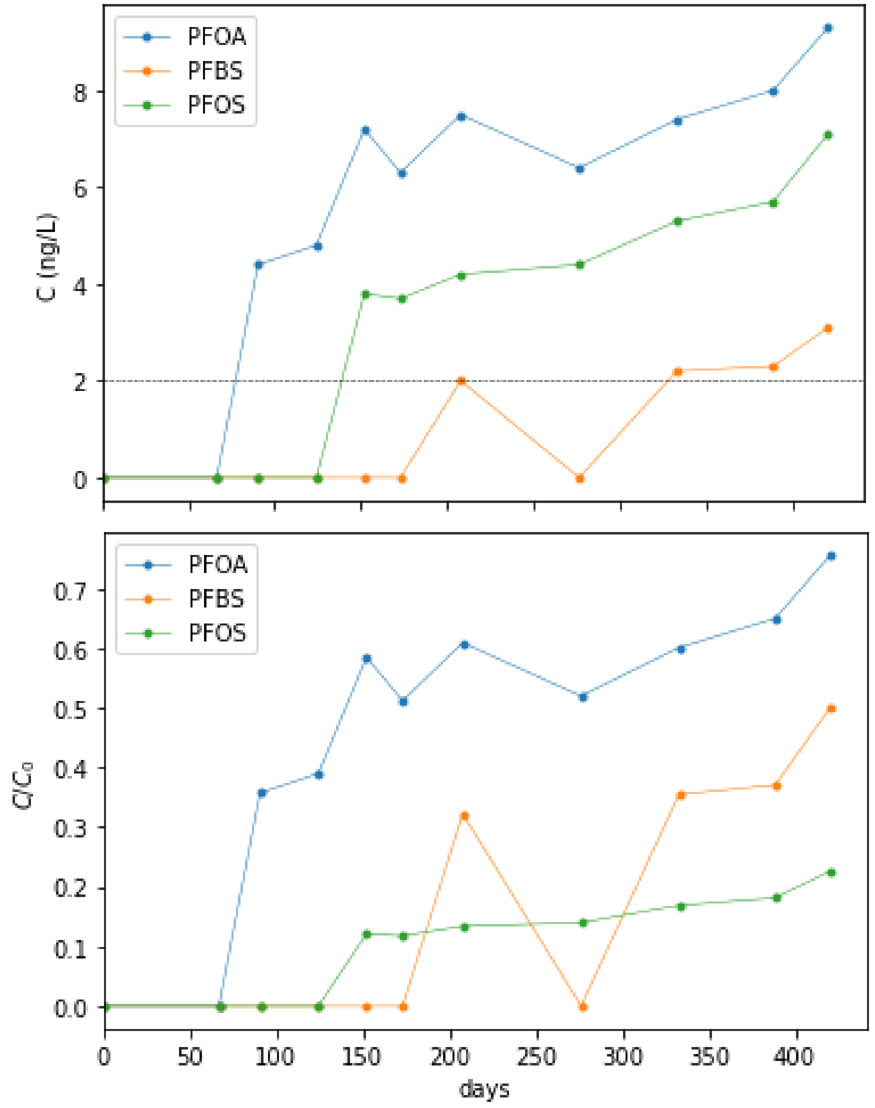
Censored Data

- Modeling can provide additional insight into datasets with censored data.
- Example: suppose reporting limit is 1/3rd of maximum concentration.
- Multiple "ND" regions in influent and effluent data.
- Example: PFOA controls single column configuration but sum controls parallel configuration.
- Model can be used to extract worst-case parameters by assuming maximum concentration at ND points in effluent and zero concentration at ND points in influent.
- PFHxA performance for this ground water is only about 30% of what is expected for NOM-free waters.



PFOS in Short Contactors

- In one of the datasets, PFOS broke through earlier than expected on a 30 s EBCT contactor.
- Breakthrough appears early compared to PFBS even when concentrations are normalized.
- Data suggest that the contactor was too short for PFOS MTZ to fully develop.
- PFOS mass transfer kinetics seem significantly slower than short PFAS (not surprising).
- Non-detect data (below dotted line) complicate interpretation in this case.
- Further data/experiments needed to estimate mass transfer, affinity, and capacity of PFOS.



IX Modeling Summary

- PFAS treatment generally ranged from about 110% to 28% of that expected from NOM-free waters.
- This knowledge can help design pilot systems and laboratory experiments.
- Several additional datasets could be analyzed once we obtain:
  - Resin IX capacities
  - Major ion affinities
  - PFAS affinities
- Obtaining this information would help in developing a better understanding of how NOM affects IX treatment efficiency.
- Would lead to more reliable design tools and cost estimates.

EPA's Drinking Water Cost Models

- Adsorptive media
- **Anion exchange***
- Biological treatment*
- Cation exchange
- **GAC***
- Greensand filtration
- Microfiltration / ultrafiltration
- Multi-stage bubble aeration*

- Non-treatment
- Packed tower aeration
- **POU/POE#**
- **Reverse Osmosis / Nanofiltration**
- UV disinfection
- UV Advanced Oxidation

***Search: EPA WBS** https://www.epa.gov/sdwa/drinking-water-treatment-technology-unit-cost-models

 # For POU/POE search: EPA small system compliance help
http://water.epa.gov/type/drink/pws/smallsystems/compliancehelp.cfm

Model Development and Availability

Updated AdDesignS (originally Michigan Tech. U.) for Windows10

https://github.com/USEPA/Environmental-Technologies-Design-Option-Tool

https://tdb.epa.gov/ - Treatability Database
https://comptox.epa.gov/dashboard/ - CompTox Database

python™

- Converted PSDM GAC model into Python.
  - Automate parameter estimation from lab and field data
  - Simulate lead-lag and parallel system operation
- Implemented Ion Exchange Models
- https://github.com/USEPA/Water_Treatment_Models

Questions?

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https://github.com/USEPA/Environmental-Technologies-Design-Option-Tool
https://github.com/USEPA/Water_Treatment_Models
https://tdb.epa.gov/
https://comptox.epa.gov/dashboard/
https://www.epa.gov/sdwa/drinking-water-treatment-technology-unit-cost-models