AWWA Water Quality Technology Conference
and Exposition
Dallas, TX
November 3-7, 2019

Modeling Pilot-Scale GAC PFAS Adsorption for the Simulation of Full-Scale Performance and Costs

Jonathan Burkhardt[a], Carel Vandermeyden[b], Nick Burns[c], Dustin Mobley[c], Craig Patterson[a], Rajiv Khera[a], Jonathan Pressman[a], Thomas Speth[a]

[a] U.S. Environmental Protection Agency

[b] Cape Fear Public Utility Authority

[c]Black & Veatch

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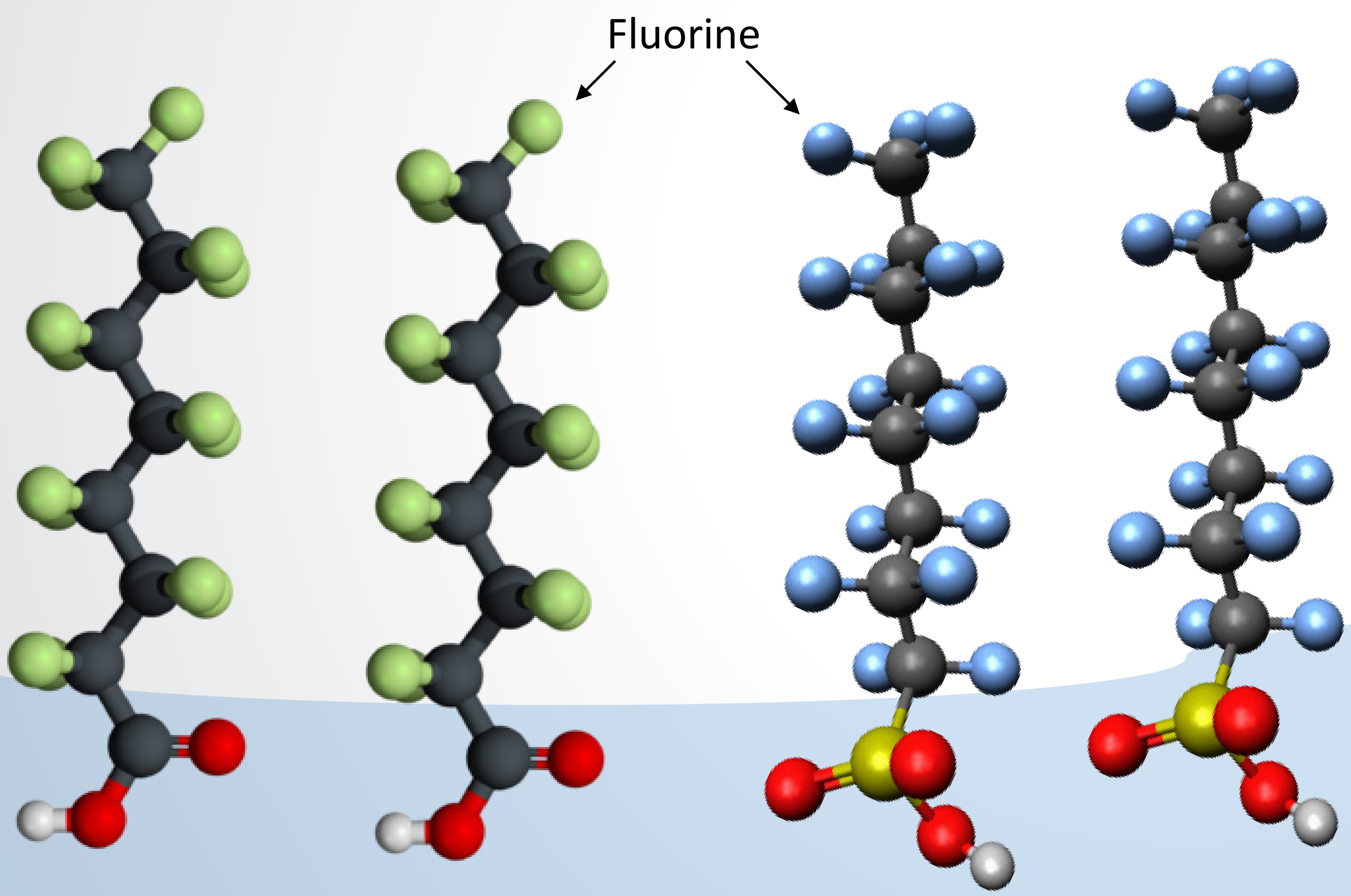
Per- and Polyfluoroalkyl Substances (PFAS)



Perfluorooctanoic acid (PFOA) *Perfluorooctanesulfonic acid (PFOS)*

A class of chemicals

- Chains of carbon (C) atoms surrounded by fluorine (F) atoms
  - ➢ Water-repellent (hydrophobic body)
  - ➢ Stable C-F bond
- Some PFAS include oxygen, hydrogen, sulfur and/or nitrogen atoms, creating a polar end.

Thousands of Chemicals: More Than Just PFOA and PFOS

PFAS

- **Non-polymers**
  - **Perfluoroalkyl acids (PFAAs)** $C_nF_{2n+1}R$
    - Perfluoroalkyl carboxylic acids (PFCAs)
    - Perfluoroalkane sulfonic acids (PFSAs)
    - Perfluoroalkyl phosphonic acids (PFPAs)
    - Perfluoroalkyl phosphinic acids (PFPIAs)
  - **Perfluoroalkane sulfonyl fluoride (PASF)** $C_nF_{2n+1}SO_2F$ → **PASF-based derivatives** $C_nF_{2n+1}SO_2$-R, R = NH, $NHCH_2CH_2OH$, etc.
  - **Perfluoroalkyl iodides (PFAIs)** $C_nF_{2n+1}I$ → **Fluorotelomer iodides (FTIs)** $C_nF_{2n+1}CH_2CH_2I$ → **FT-based derivatives** $C_nF_{2n+1}CH_2CH_2$-R, R = NH, $NHCH_2CH_2OH$, etc.
  - **Per- and polyfluoroalkyl ethers (PFPEs)-based derivatives**
    - Polyfluoroalkyl ether carboxylic acids
- **Polymers**
  - **Fluoropolymers**
    - Polytetrafluoroethylene (PTFE)
    - Polyvinylidene fluoride (PVDF)
    - Fluorinated ethylene propylene (FEP)
    - Perfluoroalkoxyl polymer (PFA)
    - Others
  - **Side-chain fluorinated polymers**
    - Fluorinated (meth)acrylate polymers
    - Fluorinated urethane polymers
    - Fluorinated oxetane polymers
  - **Perfluoropolyethers**

Overview: EPA Drinking Water Research

- **Problem**: Utilities lack treatment technology cost data for PFAS removal
- **Action**:
  - Gather performance and cost data from available sources (DOD, utilities, industry, etc.)
  - Conduct EPA research on performance of treatment technologies including home treatment systems
  - Update EPA's Treatability Database and Unit Cost Models
  - Connect EPA's Treatability Database to EPA's Unit Cost Models for ease of operation
  - Model performance and cost, and then extrapolate to other scenarios
    - Variable source waters
    - Variable PFAS concentrations in source water
    - Different reactivation/disposal options
    - Document secondary benefits
    - Address treatment impact on corrosion
  - Evaluate reactivation of granular activated carbon
- **Impact**: Enable utilities to make informed decisions about cost-effective treatment strategies for removing PFAS from drinking water

EPA Resources

Publically Available Drinking-Water Treatability Database

- Interactive literature review database that contains over 65 regulated and unregulated contaminants and covers 34 treatment processes commonly employed or known to be effective (thousands of sources assembled on one site)

Currently available:

- **Nitrate**
- **Perchlorate**
- **Microcystins**
- **PFOA, PFOS, PFTriA, PFDoA, PFUnA, PFDA, PFNA, PFHpA, PFHxA, PFPeA, PFBA, PFDS, PFHpS, PFHxS, PFBA, PFBS, PFOSA, FtS 8:2, FtS 6:2, N-EtFOSAA, N-MeFOSAA and GenX**

https://www.epa.gov/water-research/drinking-water-treatability-database-tdb

Search: EPA TDB

Treatability Database

An official website of the United States government.

We've made some changes to EPA.gov. If the information you are looking for is not here, you may be able to find it on the EPA Web Archive or the January 19, 2017 Web Snapshot. Close

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Drinking Water Treatability Database (TDB)

Provides information on the control of contaminants

EPA's Drinking Water Treatability Database (TBD) is an easy to use tool that provides referenced information on the control of contaminants in drinking water. It was designed for use by utilities, first responders to spills or emergencies, consultants and technical assistance providers, treatment process designers, and researchers.

Information in the TDB is gathered from thousands of literature sources and assembled on one site. Information is available for over 70 regulated and unregulated contaminants and more than 30 treatment processes.

Quick Start

- Find a Contaminant
- Find a Treatment Process

Navigating the TDB | Capabilities | Future Updates | Support

Find a Contaminant

The Find a Contaminant option contains several tabs of information on each contaminant. Because control strategies for disinfection byproducts (DBPs) are different from contaminants present in source waters and entering into a water treatment plant, DBPs are not included in the TDB. Contaminants include those that are regulated in drinking water on the Contaminant Candidate List (CCL), of water security and pesticide registration interest, and endocrine disruptors and pharmaceuticals. Searching by contaminant retrieves information on any treatment processes that have been tested for the contaminant, properties of the contaminant, and fate and transport information.

On the page, there are multiple search options for finding a particular contaminant:

- **Search Box**—Enter a contaminant name, CAS number, any synonyms, and the contaminant type (microbial, radiological, or chemical). If there are no results after performing a search, an error message will appear.
- **Rolodex Search**—Allows a search for all contaminants starting with a particular letter or number. After a selection is made, a second rolodex appears that allows sorting by contaminant type (chemical, microbial, or radiological).
- **Manual Search—**Scroll through the table to find a contaminant. The table displays the contaminants' name, CAS numbers, any synonyms, and types (microbial, radiological, or chemical).

Treatability Database

Per- and Polyfluoroalkyl Substances

Overview | Treatment Processes | Properties | Fate and Transport | References

CAS Number:

Synonyms: 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate (FRD-902), 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (FRD-903), GenX, Heptadecafluorononanoic acid, Heptafluorobutyric acid, Nonadecafluorocapric acid, Nonadecafluorodecanoic acid, Pefluorobutane sulfonate, Perfluorobutanoic acid (PFBA), Perfluorobutyl sulfonate (PFBS), Perfluorobutyric acid, Perfluorocapric acid, Perfluorodecanoic acid (PFDA), Perfluorohexanesulfonic acid potassium salt, Perfluorohexyl sulfonate (PFHxS), Perfluorononanoic acid (PFNA), Potassium tridecafluoro-1-hexanesulfonate, Tridecafluorohexane-1-sulfonic acid potassium salt, heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether (E1)

Contaminant Type: Chemical

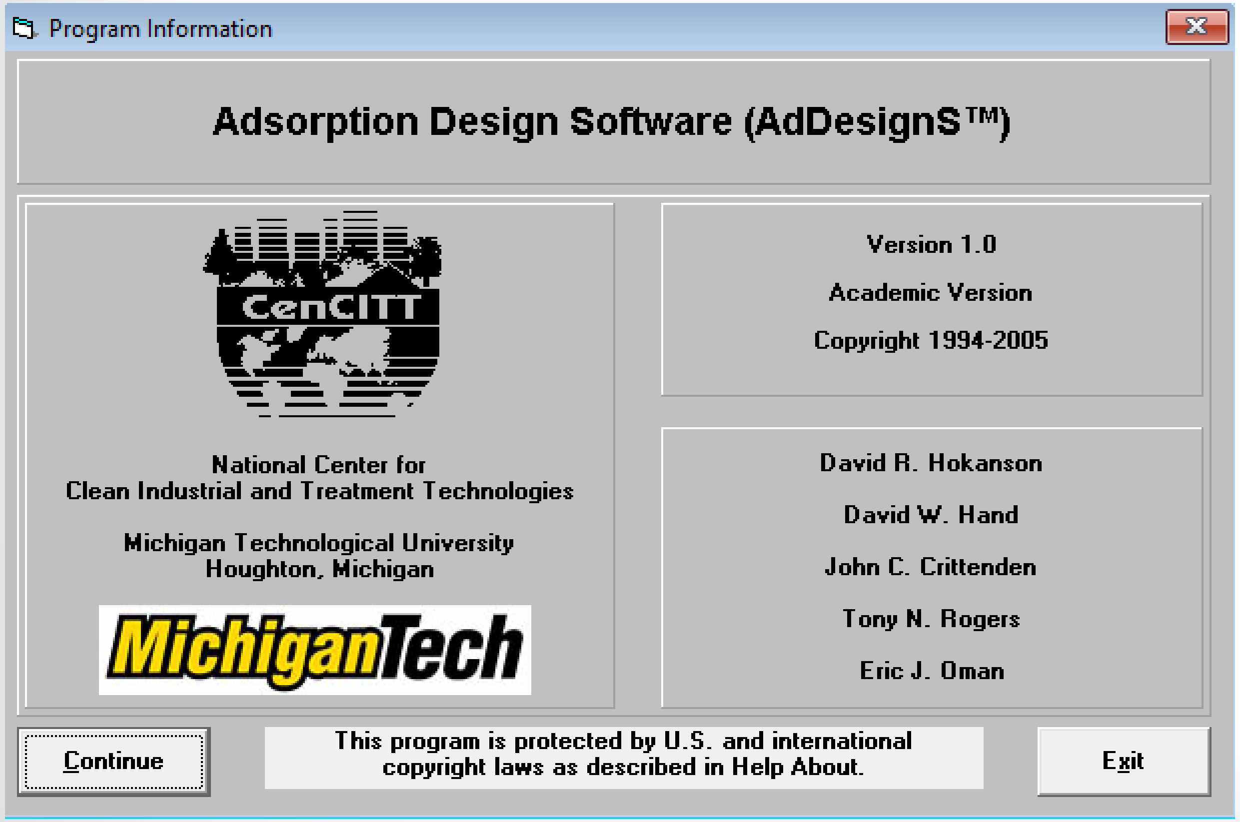
Per- and polyfluoroalkyl substances (PFASs) are fluorinated aliphatic substances with unique properties, such as being both hydrophobic, lipophobic, and extremely stable due to the strength of the C-F bond [2539]. Their properties have led to their extensive use as surface active agents in products like stain repellants and fire-fighting foams [2527, 2539]. The two most frequently studied PFASs, perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA), have their own, separate entries in this treatability database. Both PFOS and PFAS are compounds with eight carbon atoms. This group entry covers treatability data for other PFASs, including those with more or fewer carbon atoms. It currently includes data for:

- Perfluorotridecanoic acid (PFTriA): Chemical Abstract Service number (CAS No.) 72629-94-8, a 13-carbon compound
- Perfluorododecanoic acid (PFDoA): CAS No. 307-55-1, a 12-carbon compound
- Perfluoroundecanoic acid (PFUnA): CAS No. 2058-94-8, an 11-carbon compound
- Perfluorodecanoic acid (PFDA): CAS No. 335-76-2, a 10-carbon compound
- Perfluorononanoic acid (PFNA): CAS No. 375-95-1, a 9-carbon compound
- Perfluorohexanoic acid (PFHpA): CAS No. 375-85-9, a 7-carbon compound
- Perfluorohexanoic acid (PFHxA): CAS No. 307-24-4, a 6-carbon compound
- Perfluoropentanoic acid (PFPeA): CAS No. 2706-90-3, a 5-carbon compound
- Perfluorobutanoic acid (PFBA): CAS No. 375-22-4, a 4-carbon compound
- Perfluorodecyl sulfonate (PFDS): CAS No. 335-77-3, a 9-carbon compound
- Perfluoroheptyl sulfonate (PFHpS): CAS No. 375-92-8, a 7-carbon compound
- Perfluorohexyl sulfonate (PFHxS): CAS No. 3871-99-6, a 6-carbon compound
- Perfluorobutyl sulfonate (PFBS): CAS No. 29420-49-3, a 4-carbon compound
- Perfluorooctanesulfonamide (PFOSA): CAS No. 754-91-6, an 8-carbon compound
- Fluorotelomer sulfonate 8:2 (FtS 8:2): CAS No. 39108-34-4
- Fluorotelomer sulfonate 6:2 (FtS 6:2): CAS No. 27619-97-2
- N-ethyl perfluorooctane sulfonamidoacetic acid (N-EtFOSAA): CAS No. 2991-50-6
- N-methyl perfluorooctane sulfonamidoacetic acid (N-MeFOSAA): CAS No. 2355-31-9

This group also includes the 6-carbon compound GenX (CAS No. 62037-80-3 as ammonium salt; CAS No. 13252-13-6 as acid), although limited treatability data are currently available for that particular PFAS.

Modeling Effort

Convert AdDesignS™ (Michigan Tech) into Python



python™

Enables automated fitting of pilot data to model results

Pore and Surface Diffusion Model Overview

2414 M.E. Jarvie et al. / Water Research 39 (2005) 2407–2421

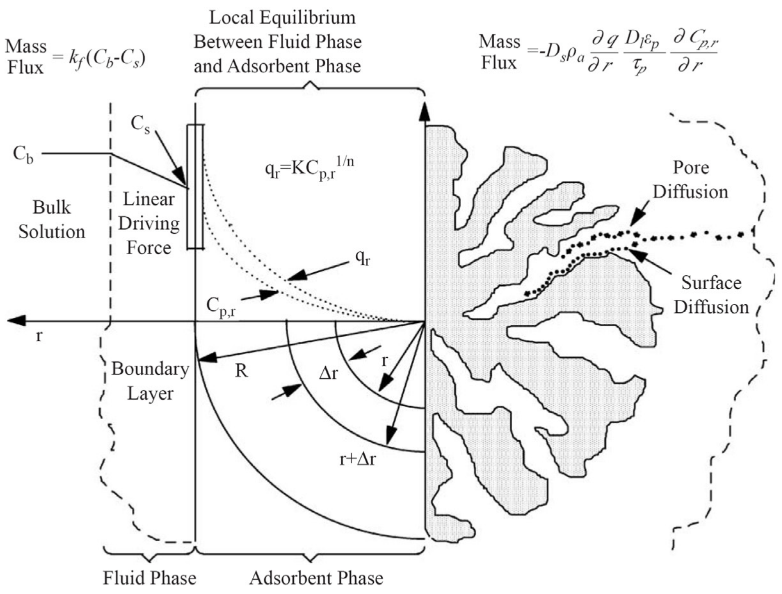


Fig. 4. Mechanisms which are included in partial differential equations that describe the pore surface diffusion model (PSDM).

Pore and Surface Diffusion Model

Uses Freundlich isotherm to model adsorptive capacity

Applies time-based fouling effect (capacity reduction) described in Jarvie et al., (Water Research, 2005)

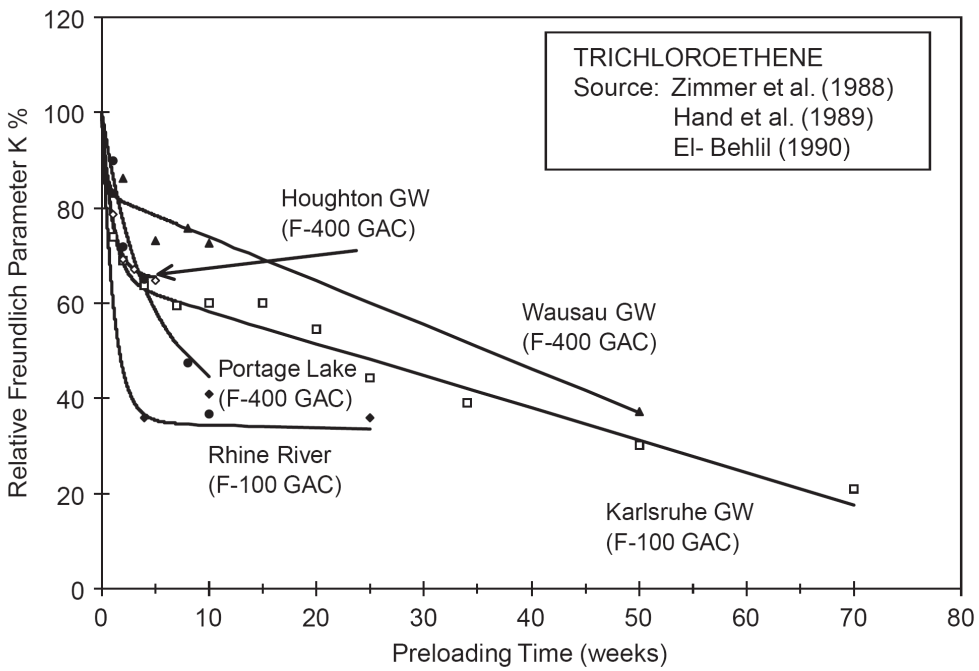
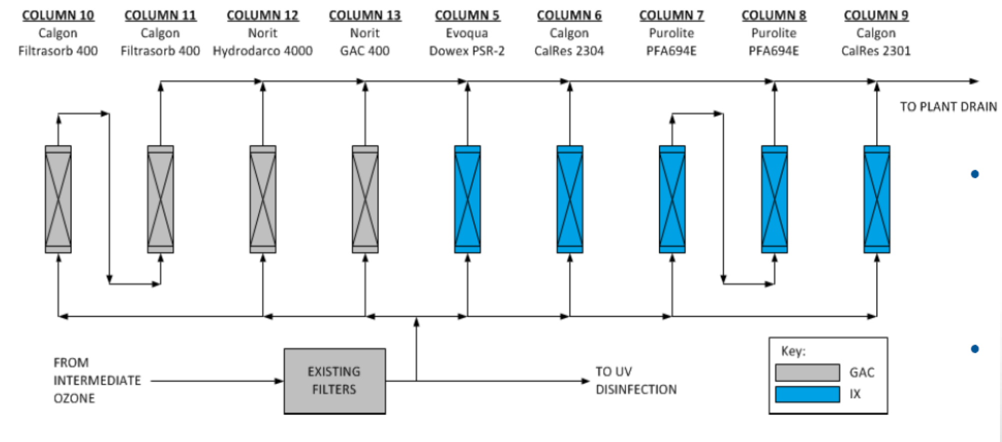


Fig. 2. Freundlich K reductions for TCE as a function of time for various background waters.

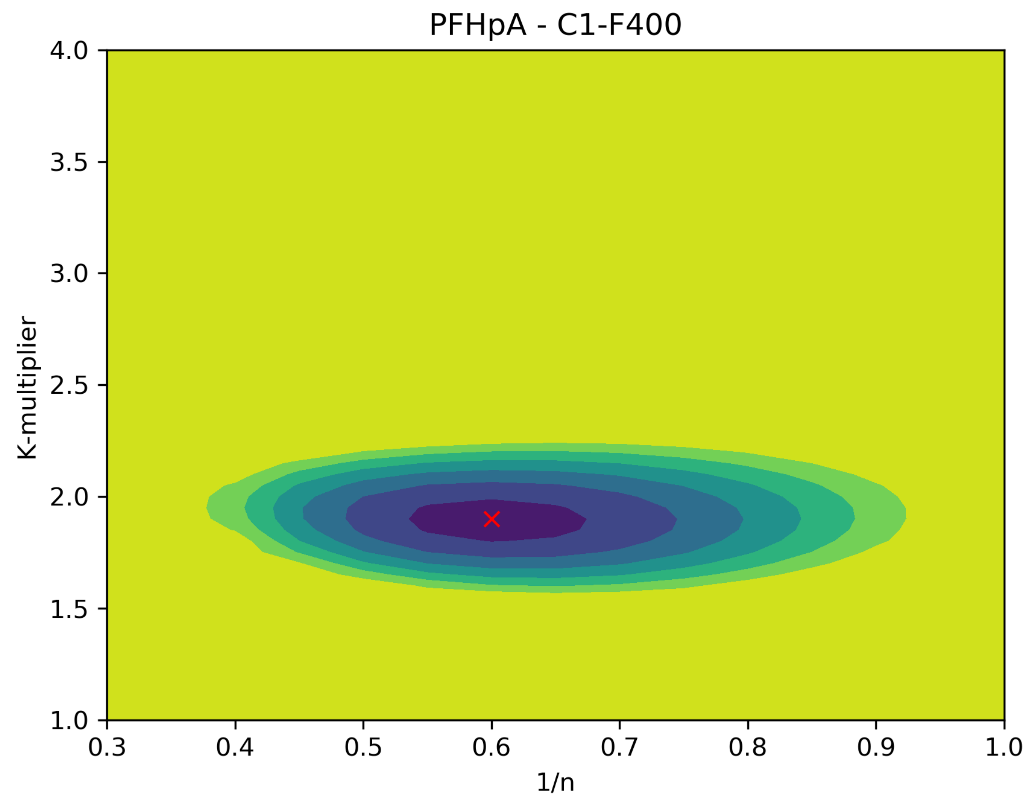
Pilot Overview

- 2 Phases (~125 days & ~225 days)
- 5 different carbons , 3 anion exchange resins
- 2 different feed waters (raw and post-treatment)
- Tested 10- and 20-min Empty Bed Contact Time (EBCT)
- Measured a range of PFAS analytes

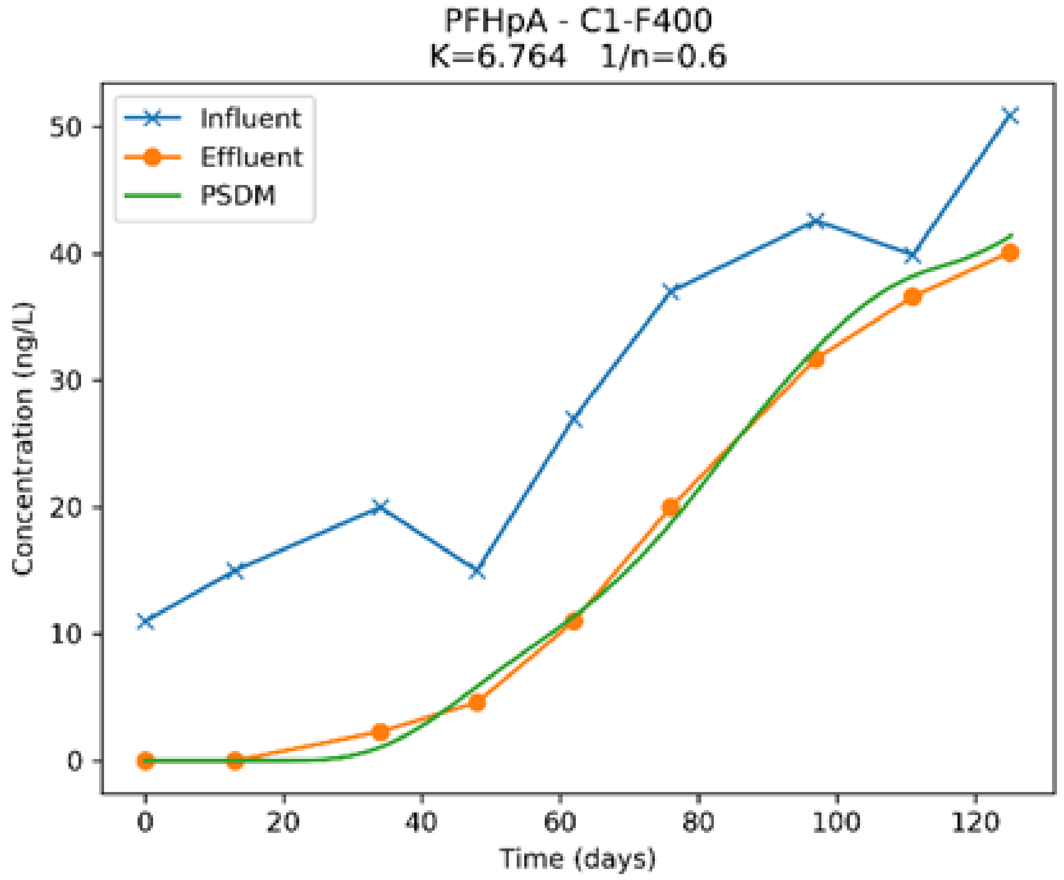


Model Fitting

Vary K and 1/n for each Carbon/PFAS combination
Select the pair that minimizes sum-of-squared difference



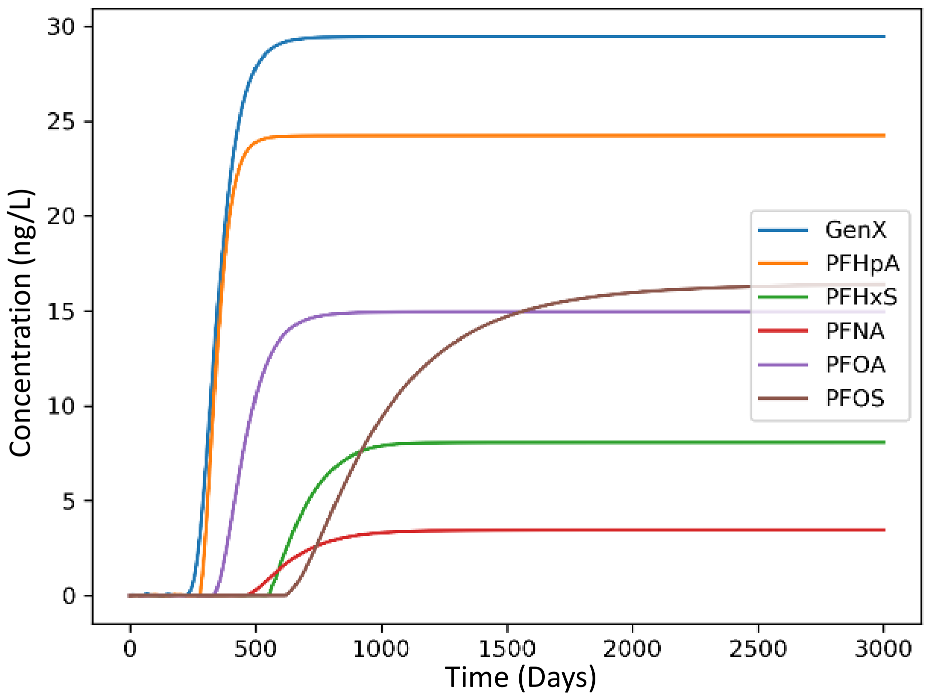
Example of best fit for PFHpA/Calgon F400



Model Application

Model Full-Scale Treatment from Pilot-Scale Fit

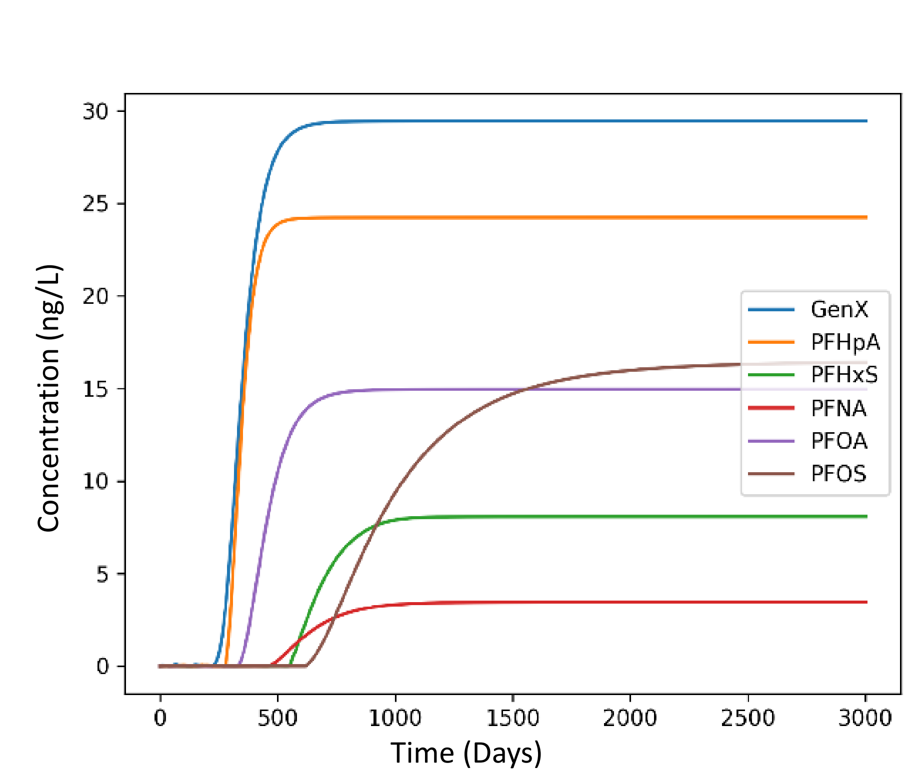
- Establish overall treatment performance
  - Example: 6 PFAS to a treatment goal
- Select influent for PFAS chemicals
  - Example: Average experienced at site for a period
  - Test other values of interest (i.e., maximum experienced)
- Input proposed design of GAC bed
  - Bed Height
  - Bed Area or Dimensions
  - Mass of Carbon
  - Type of Carbon
  - Flow Rate(s) of Interest
- Model extended operations
- Predict multi-bed operation/bed replacement frequency



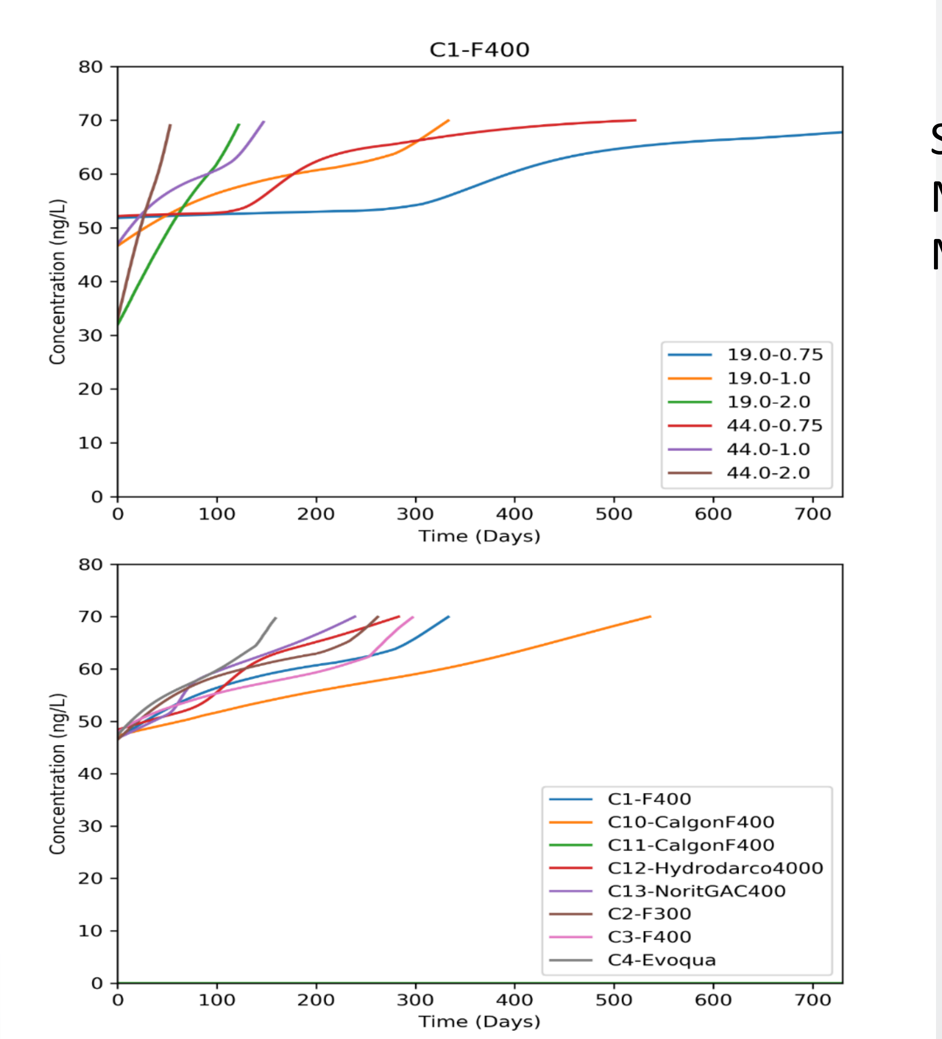
Example Output

Predictions Allow for Design Evaluation

Simulated Single Bed through Time



Simulated Multi-Bed Blended Scenario through Time



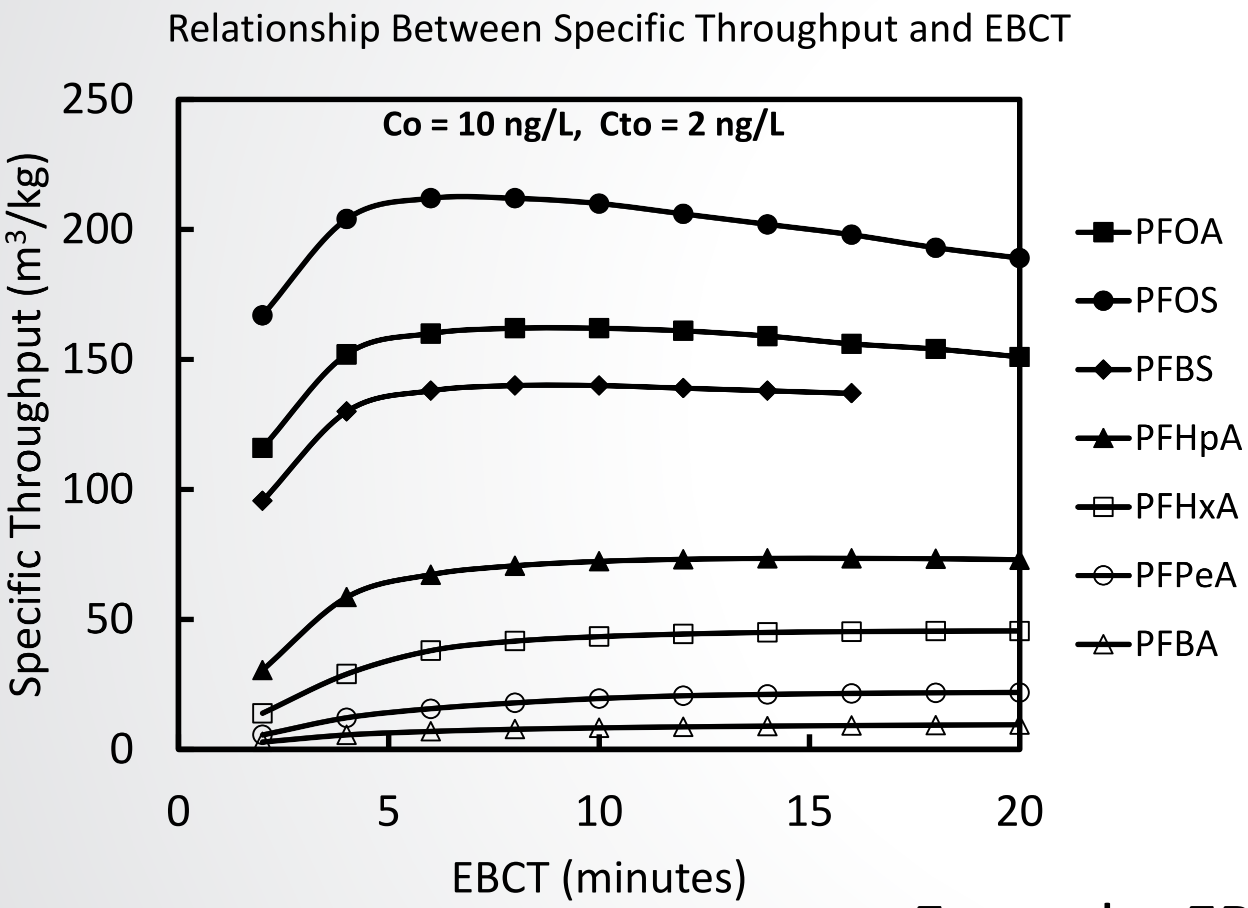
Single Carbon
Multiple Influent
Multiple Flow Rates

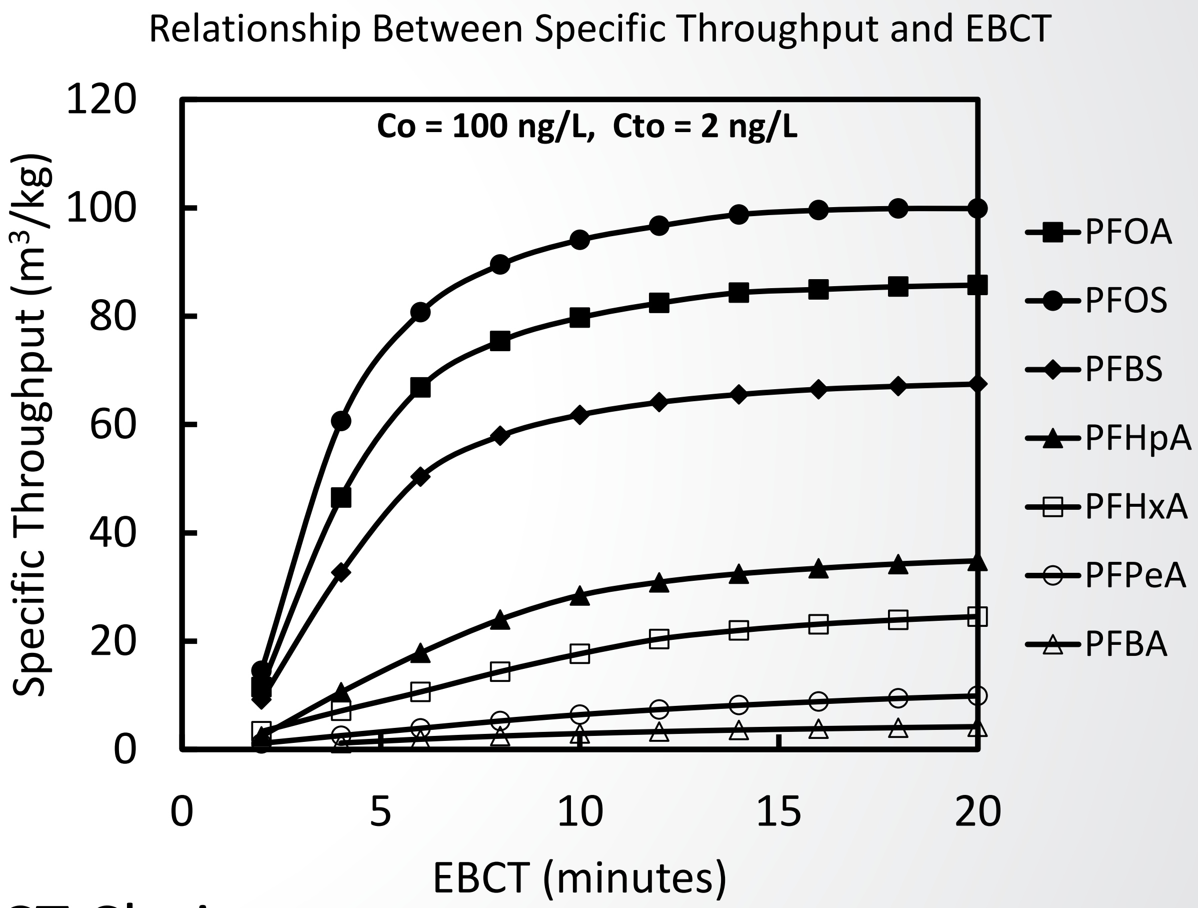
Multiple Carbon
Single Influent
Single Flow Rate

Take an effluent profile for a single GAC bed and extrapolate to multi-bed performance

Projected effluent for 8 beds with 2 beds per replacement cycle

Predictions Allow for Design Evaluation



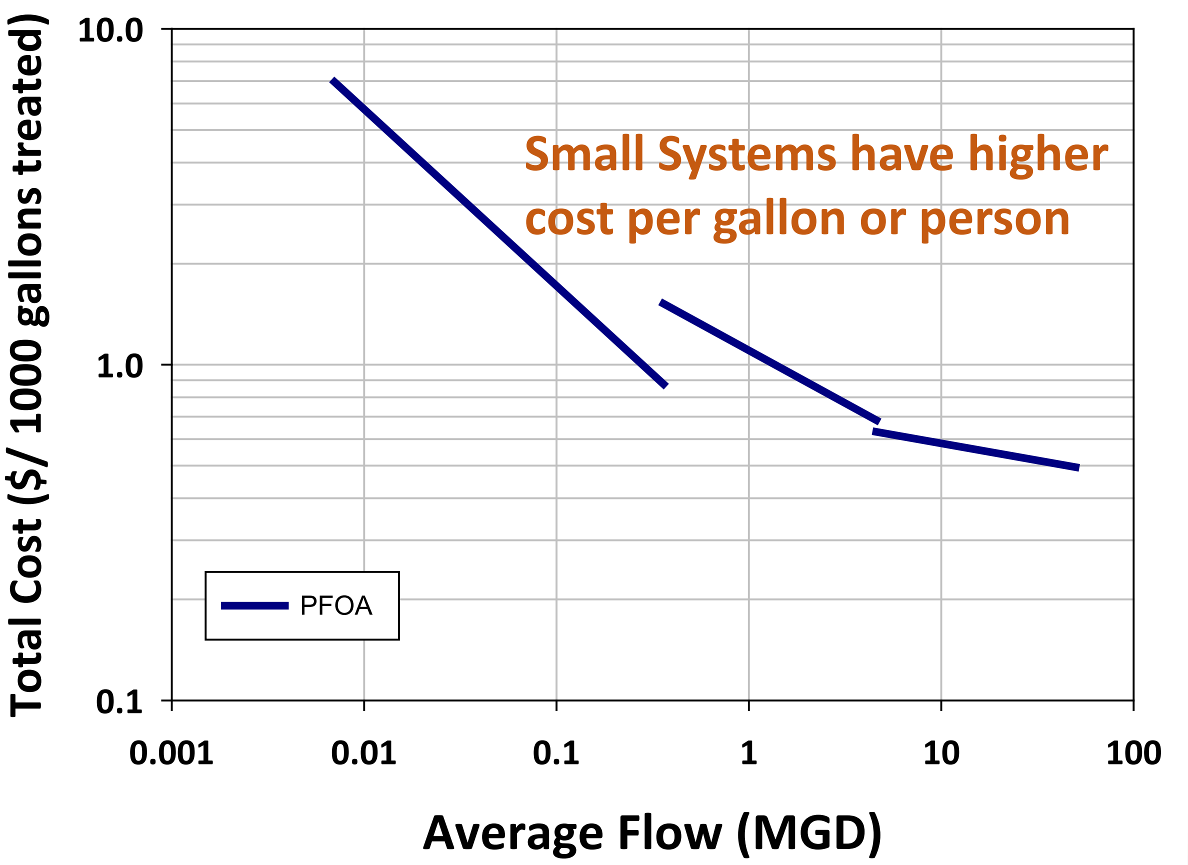


Example: EBCT Choice

- Can evaluate EBCT for various PFAS for different conditions such as influent concentration, effluent goal, etc.

GAC Treatment Cost: PFOA

Cost of treatment varies on a number



- Full Scale
- 26 min EBCT
- Lead-Lag configuration
- F600 Calgon carbon
- 1.5 m^3/min flow
- Full automation
- POTW residual discharge
- Off site regeneration
- 70,000 bed volumes to breakthrough for PFOA

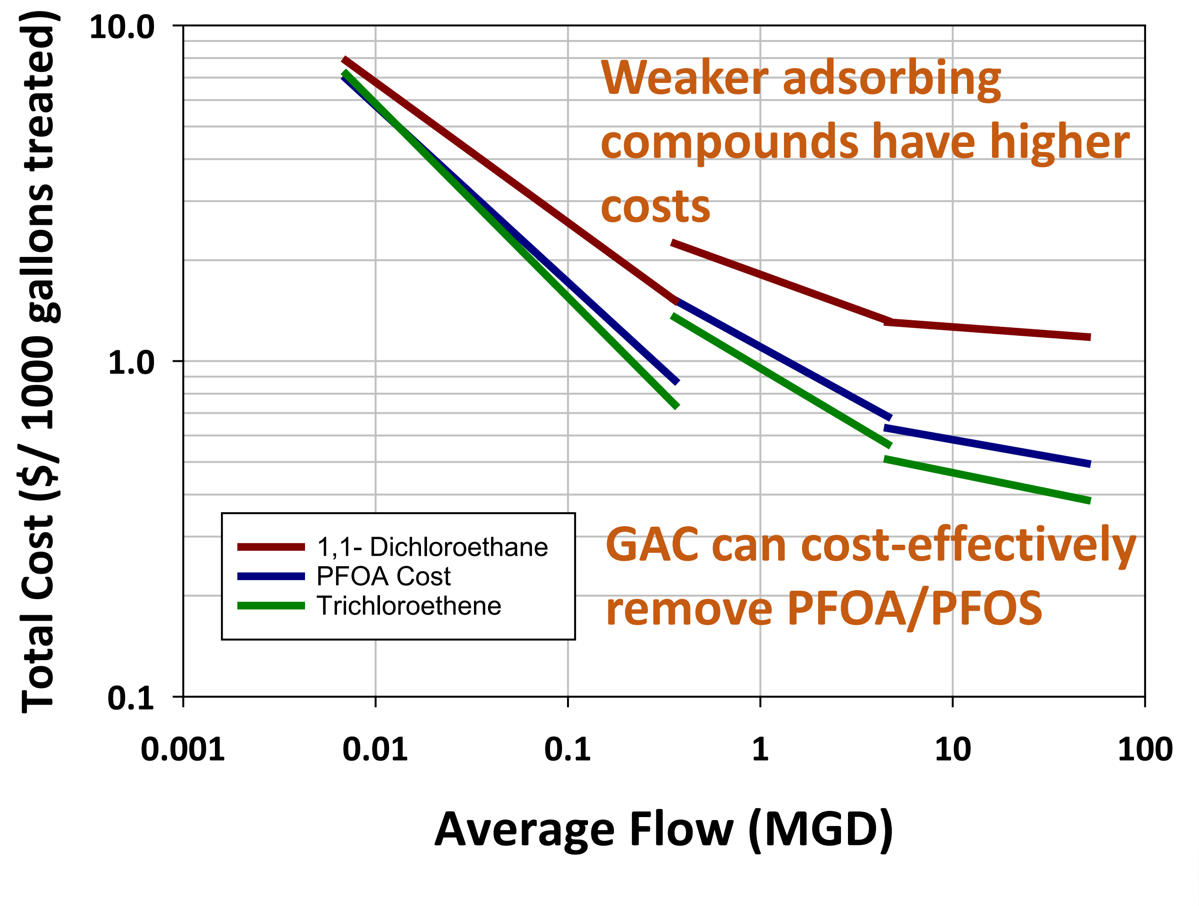
Cost Savings for Small Systems under 1 MGD

Specific Design Modifications for Smaller Systems within the Cost Model

(Considers flows under 1 MGD)

- Construction issues (building)
- Residual handling flexibility
- Reduced spacing between vessels
- Smaller and no redundant vessels
- Reduced instrumentation
- No booster pumps
- No backwash pumps
- Reduced concrete pad thickness
- Reduced indirect costs

GAC Treatment Cost: PFOA, TCE, 11 DCA



EPA will be evaluating additional water qualities and designs

- Full Scale
- 26 min EBCT
- Lead-Lag configuration
- F600 Calgon carbon
- 1.5 m^3/min flow
- Full automation
- POTW residual discharge
- Off site regeneration
- 135,000, 70,000, and 11,000 bed volumes to breakthrough for TCE, PFOA, and 11DCA, respectively.

Work Breakdown Structure Approach

- A treatment technology is broken down into discrete components that can be measured for the purpose of estimating costs. The components include specific equipment (e.g., tanks, vessels, pipes, and instruments) and other identifiable cost elements such as annual expenditures on labor, chemicals, and energy.

What is a Work Breakdown?

Pumps

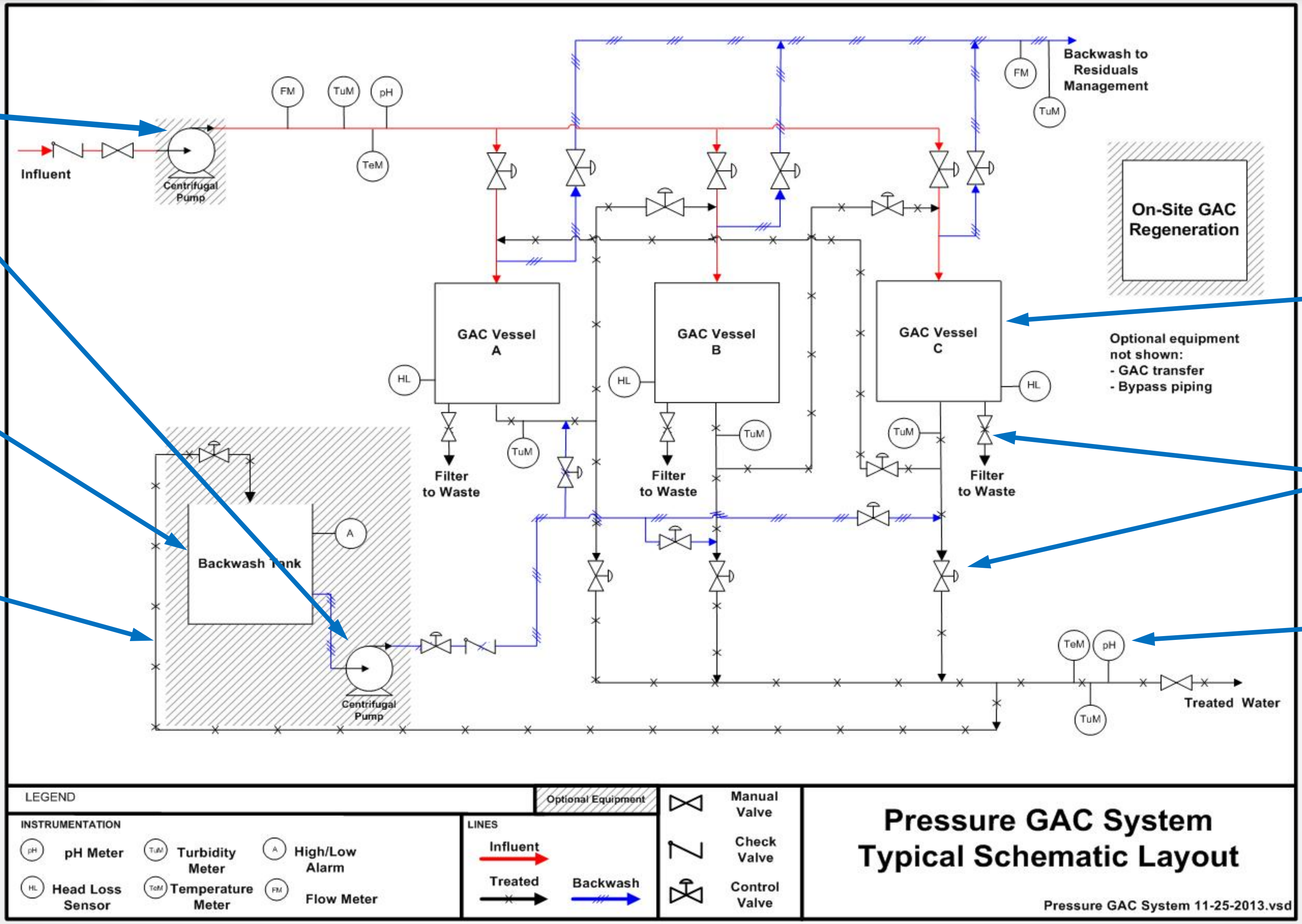
Tanks

Pipes

Pressure Vessels

Valves

Instruments



What Costs Do the WBS Models Estimate?

Capital Costs

- Equipment costs
  - pumps
  - tanks/vessels
  - pipes
  - instruments
- Buildings
- Add-on costs
  - pilot study
  - permits
  - land
- Indirect costs
  - engineering
  - construction management
  - sitework/electrical

Annual Operating Costs

- Labor
  - technical
  - managerial
  - administrative
- Materials and supplies
  - chemicals
  - equipment maintenance
- Residuals management
  - POTW
  - GAC regeneration
  - RCRA Subtitle D or C landfill
- Energy
  - operating (e.g., pumps, blowers)
  - HVAC

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** http://www2.epa.gov/dwregdev/drinking-water-treatment-technology-unit-cost-models-and-overview-technologies

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

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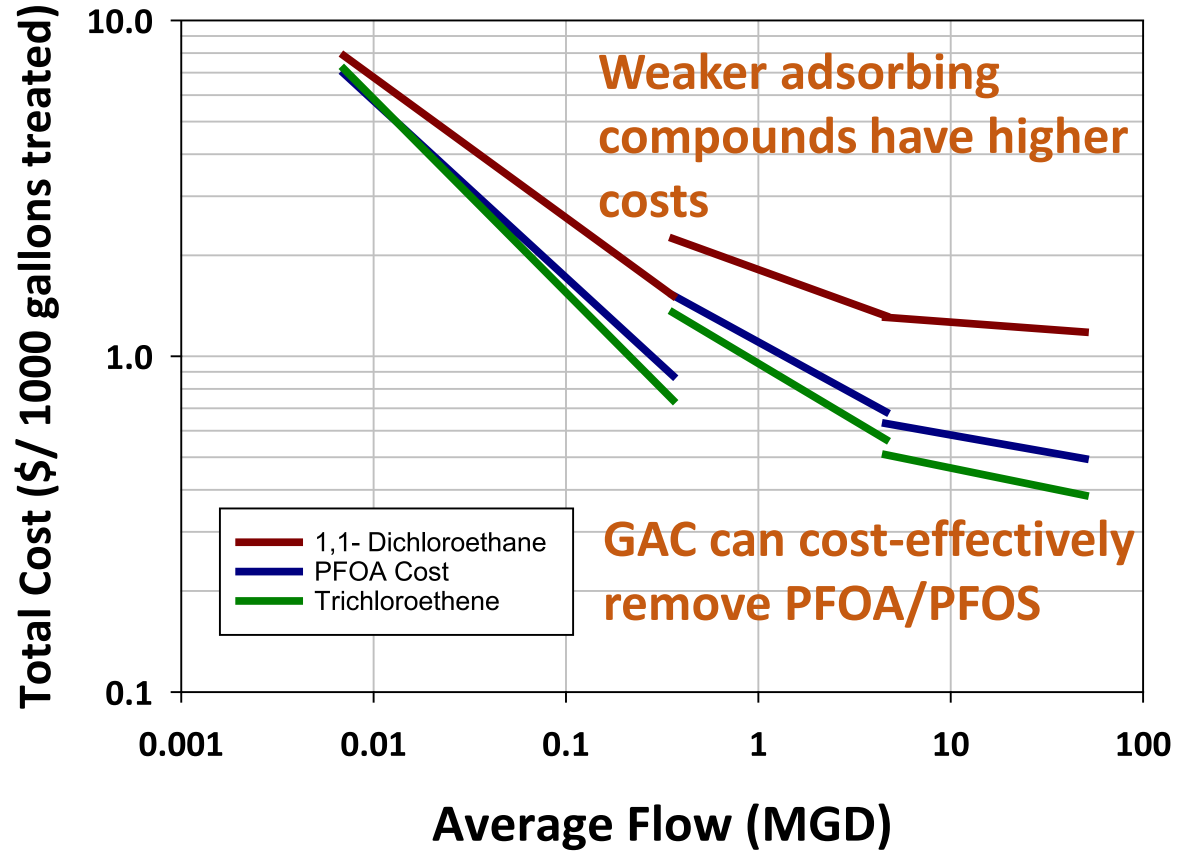
GAC Treatment Cost: PFOA, TCE, 11 DCA



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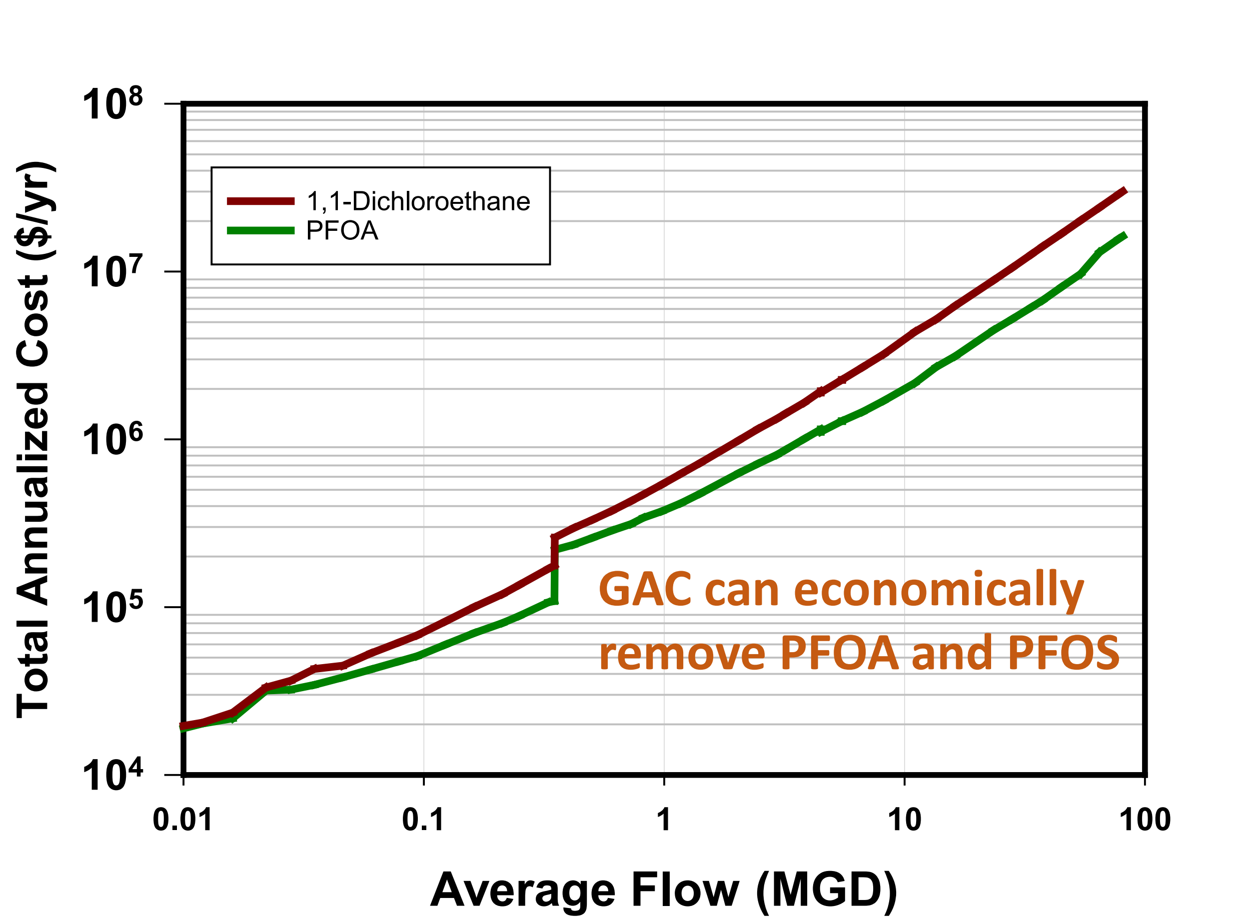
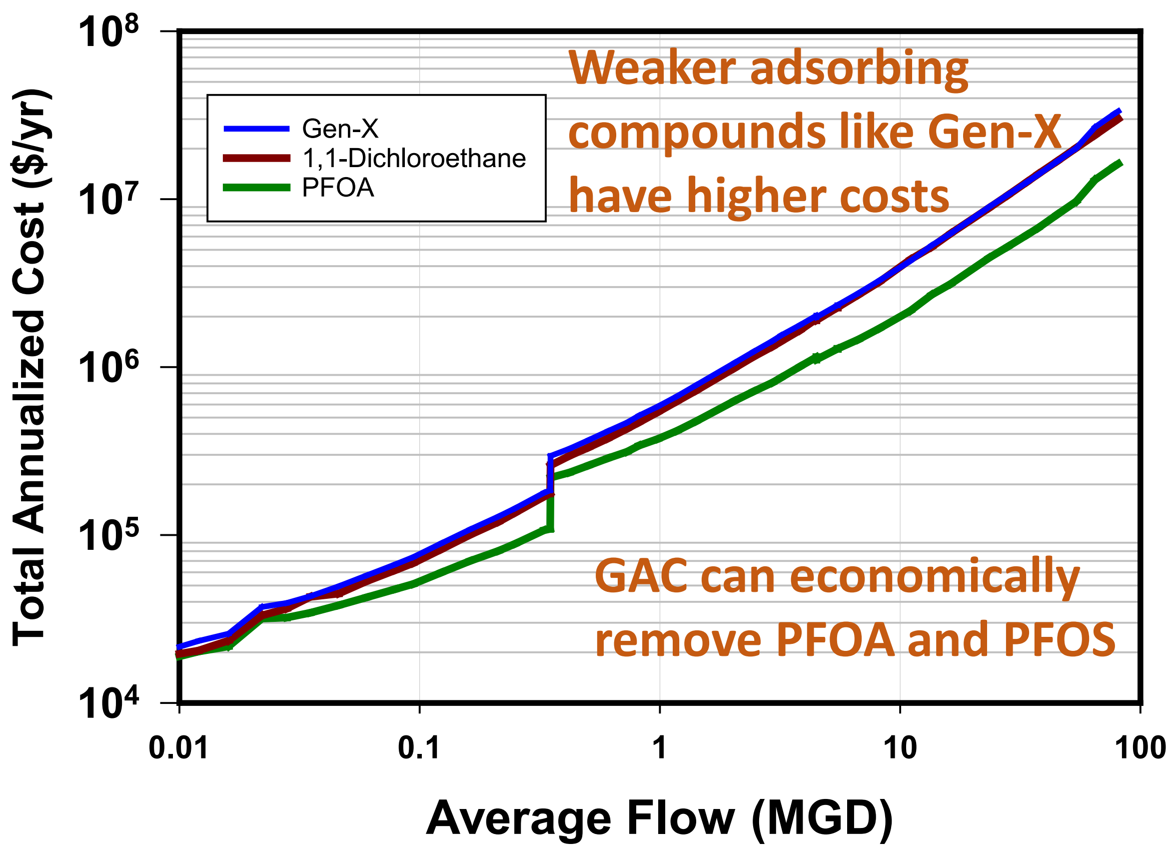
Costs for Additional PFAS



- Pilot Scale Performance Data
- 20 min EBCT
- F400 Calgon carbon
- Full automation
- POTW residual discharge
- Off site regeneration
- 31,000, 7,100, and 5,560 bed volumes to breakthrough for PFOA, Gen-X, and 11-DCA, respectively.

Cost for Additional PFAS



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- F400 Calgon carbon
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- POTW residual discharge
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- 31,000, 7,100, and 5,560 bed volumes to breakthrough for PFOA, Gen-X, and 11-DCA, respectively.

Compounds will have a range of costs depending on water quality and other factors

Comparison of Treatment Technologies

Granular Activated Carbon (GAC)	**Most studied technology** **Will remove 100% of the contaminants, for a time** **Good capacity for some PFAS** Will remove a significant number of disinfection byproduct precursors Will help with maintaining disinfectant residuals Will remove many co-contaminants Likely positive impact on corrosion (lead, copper, iron)
Anion Exchange Resin (PFAS selective)	**Will remove 100% of the contaminants, for a time** **High capacity for some PFAS** **Smaller beds compared to GAC** Can remove select co-contaminants
High Pressure Membranes	**High PFAS rejection** Will remove many co-contaminants Will remove a significant number of disinfection byproduct precursors Will help with maintaining disinfectant residuals

Issues to Consider

EPA is evaluating these issues to document where and when they will be an issue

Granular Activated Carbon (GAC)	GAC run time for short-chained PFAS (shorter run time) Potential overshoot of poor adsorbing PFAS if not designed correctly Reactivation/removal frequency Disposal or reactivation of spent carbon
Anion Exchange Resin (PFAS selective)	Run time for select PFAS (shorter run time) Overshoot of poor adsorbing PFAS if not designed correctly Unclear secondary benefits Disposal of resin
High Pressure Membranes	Capital and operations costs Membrane fouling Corrosion control Lack of options for concentrate stream treatment or disposal

Drinking Water Goals

For utilities that have PFAS in their source water at concentrations of health concern

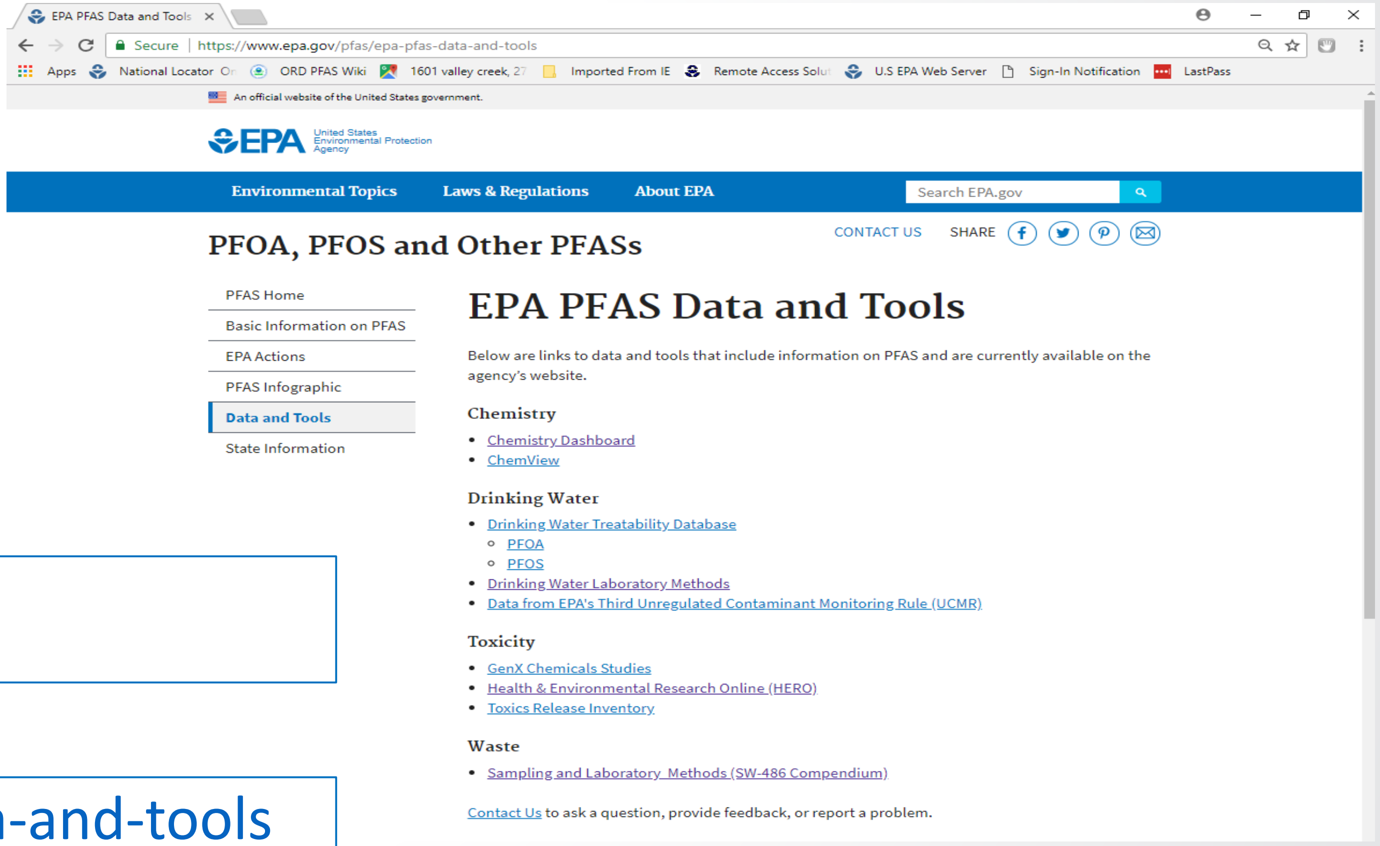
1) Eliminate source of PFAS to the source water
2) Either choose a new source of water or choose a **technology, design, and operational scheme** that will reduce PFAS to safe levels at the lowest possible cost in a **robust, reliable, and sustainable manner** that avoids unintended consequences

Issues to address (not inclusive)

1) Capital and operating costs are affordable
2) Staff can handle operational scheme over the long term
3) Technology can operate long term under a reasonable maintenance program
4) Technology and treatment train can handle source water quality changes
5) Any waste stream generated can be treated or disposed in a sustainable and cost-effective manner over the long term

EPA PFAS Data and Tools

- Links to data and tools that include information related to PFAS are available on EPA's website:



https://www.epa.gov/pfas

https://www.epa.gov/pfas/epa-pfas-data-and-tools

Conclusions

- Pilots are a valuable resource in predicting treatment performance of PFAS chemicals
- Models can extend pilot results to full-scale treatment
  - They help to address complexities associated with different treatment goals, carbons, influent waters, bed designs and operations
- GAC can be a cost effective approach to PFAS removal with proper bed design

Contact

Burkhardt.Jonathan@epa.gov
Speth.Thomas@epa.gov

https://www.epa.gov/pfas

https://www.epa.gov/pfas/epa-pfas-data-and-tools