EPA United States Environmental Protection Agency

Session 3: PFAS Treatment in Drinking Water and Wastewater – State of the Science

Thomas Speth, PhD, PE
US EPA Office of Research and Development

PFAS Science Webinars for EPA Region 1 and State & Tribal Partners

September 16, 2020

Overview

Drinking Water

- Overview
- Treatment
- Cost
- Residual streams

Wastewater

- Overview
- Treatment *(Residual streams and other materials to be covered on Sept. 23)*

EPA's PFAS Drinking Water Research

Problem: Utilities lack treatment technology cost data for PFAS removal

Actions:

- 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, Treatment Models 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
- Address treatment impact on corrosion
- Evaluate reactivation and incineration of spent granular activated carbon and incineration of spent ion exchange resins

Impact: *Enable utilities to make informed decisions about cost-effective treatment strategies for removing PFAS from drinking water*

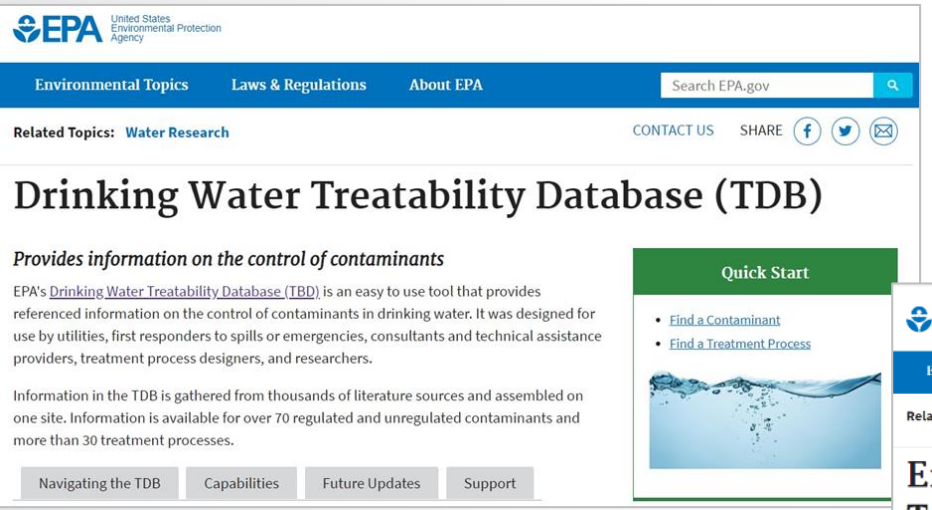
Model Scenarios

- Variable source waters
- Variable PFAS concentrations in source water
- Alternate treatment goals
- Changing production rates
- Document secondary benefits
- Different reactivation/disposal options

Suite of Tools

To provide tools to accurately predict the performance and cost of treating PFAS in drinking waters

Treatability Database



Performance Models

Cost Models

Suite of Tools

To provide tools to accurately predict the performance and cost of treating PFAS in drinking waters

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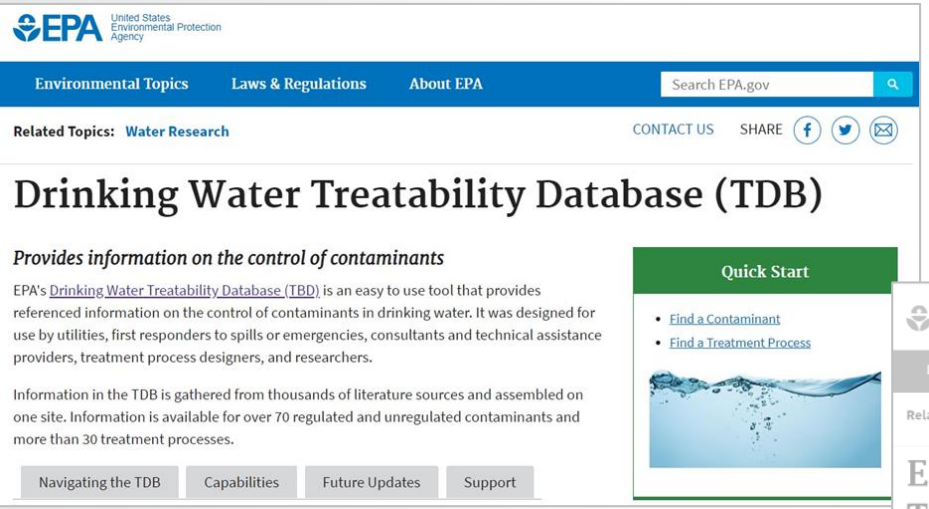
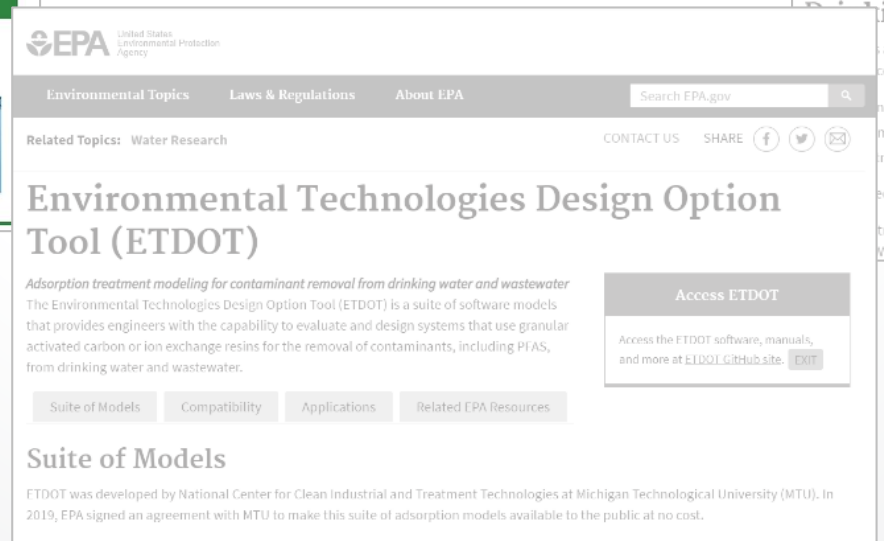
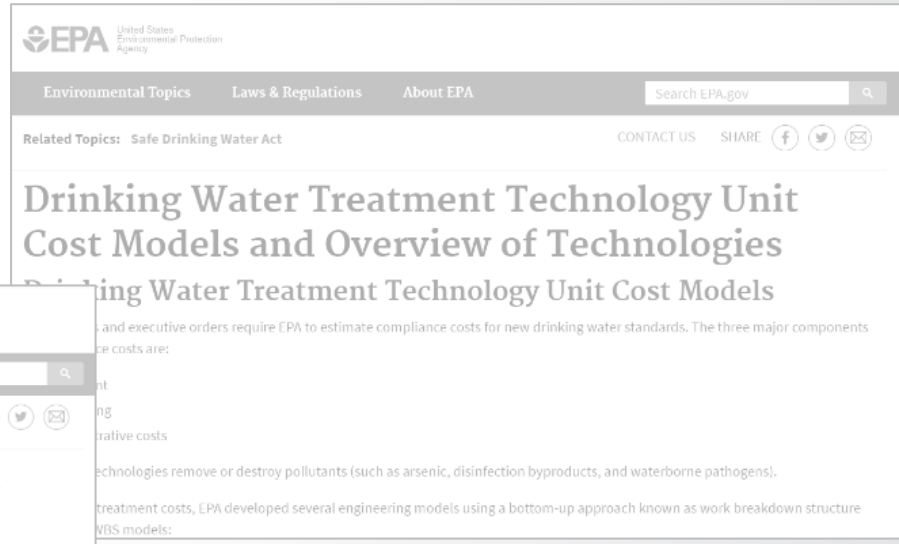


Performance Models



Cost Models



Treatment Information

Publicly Available Drinking Water Treatability Database

Recently updated!

Interactive literature review database that contains 123 regulated and unregulated contaminants and covers 35 treatment processes commonly employed or known to be effective (thousands of sources assembled on one site)

Contains treatment information to be used in performance or cost models

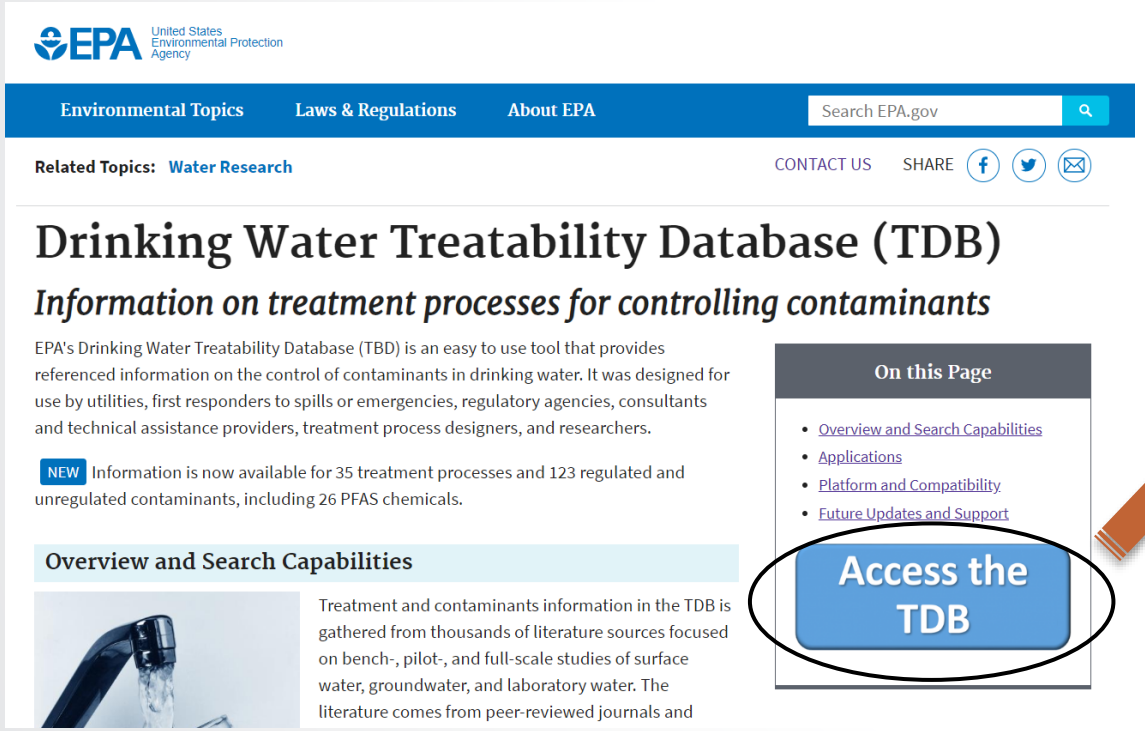
Currently available:

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

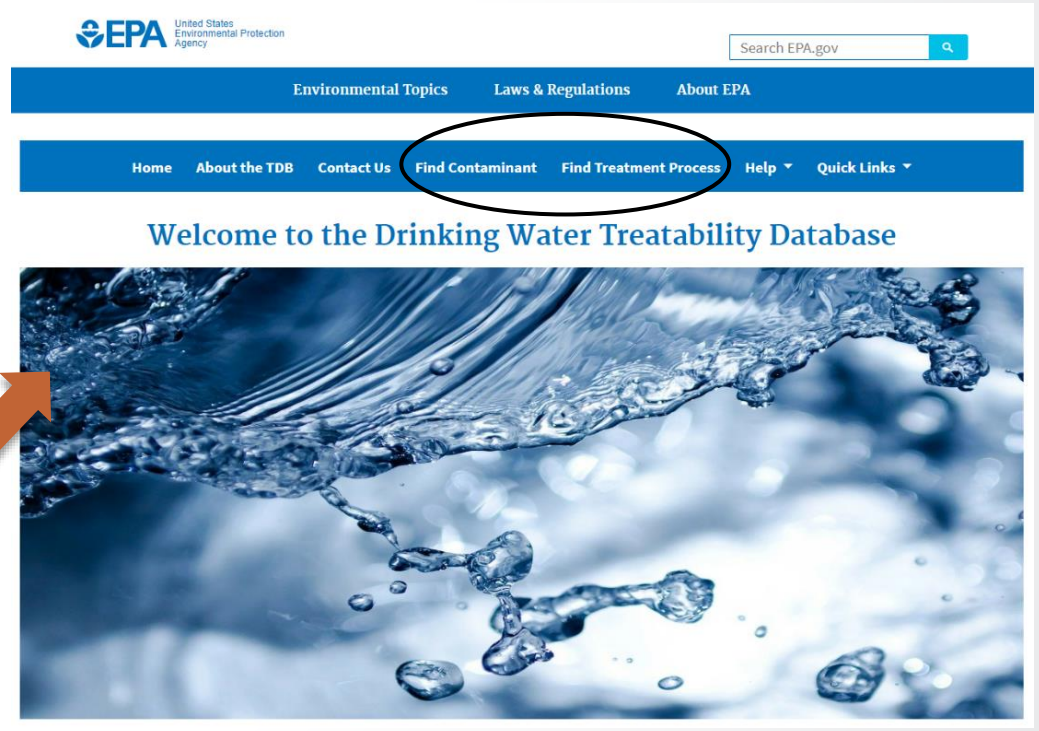
Access EPA's Drinking Water Treatability Database.

Treatability Database

Agency Landing Page



Database Homepage



[Access EPA's Drinking Water Treatability Database.]

PFAS Treatment

Per- and Polyfluoroalkyl Substances

Informational Links

Contaminant Navigation

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

Overview

CAS Number:

Synonyms:
Heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether (E1),2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate (FRD-902),2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (FRD-903),Ammonium perfluoro-2-methyl-3-oxahexanoate (GenX),Heptadecafluorononanoic acid,Heptafluorobutyric acid,Nonadecafluorocapric acid,Nonadecafluorodecanoic acid,Pefluorobutane sulfonate,Perfluorobutyric acid,Perfluorocapric acid,Perfluorohexanesulfonic acid potassium salt,Potassium tridecafluoro-1-hexanesulfonate,Tridecafluorohexane-1-sulfonic acid potassium salt

Contaminant Type: Chemical

Description:
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 PFOA are compounds with eight carbon atoms. This group entry covers

Per- and Polyfluoroalkyl Substances

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Treatment Processes

The following processes were found to be effective for the removal of PFASs: granular activated carbon (GAC) (up to > 98 percent), membrane separation (up to > 99 percent), and ion exchange (up to > 99 percent). These results cover the removal of specific PFASs including PFTriA, PFDoA, PFUnA, PFDA, PFNA, PFHpA, PFHxA, PFPeA, PFPeS, PFDS, PFHpS, PFHxS, PFBA, PFBS, PFPrS, PFOSA, PFMOAA, PFO3OA, PFO2HxA, FtS 8:2, FtS 6:2, N-EtFOSAA, N-MeFOSAA, and GenX. For results on the removal of PFOS and PFOA, see the separate treatability database entries for those specific contaminants.

Studies were identified evaluating the following treatment technologies for the removal of PFASs:

Adsorptive Media
A bench-scale study conducted batch tests of adsorption using magnetic nanoparticles with different polymer coatings. In ultrapure water, the best performing of these achieved high removals of long chain and sulfonated PFASs (e.g., >90 percent ...

See more

Aeration and Air Stripping
At a full-scale site, packed tower aeration was not effective for removing PFASs [2441].

PFAS Treatment: Activated Carbon

Matrix of conditions and results from treatment references that can be downloaded into a spreadsheet

Ref #	Author	Year	Log or Percent Removal	Removal Type	Contaminant Influent	Contaminant Effluent	Contaminant Units	Contaminant	Scale	Design Flow	Water	Location Studied	GAC Type	Manufacturer	Product Name
2441	Dickenson,	2016	-10.5 to 13.7#	Percent	4.4 to 5.1#	5.7 to 6.3#	ng/L	PFHpA	F	5	SW	New Jersey	B	Calgon	F300
2441	Dickenson,	2016	-11 to 5#	Percent	3.6 to 5.8#	4.0 to 5.5#	ng/L	PFHxS	F	5	SW	New Jersey	B	Calgon	F300
2441	Dickenson,	2016	-13 to 6#	Percent	1.8 to 2.4#	1.7 to 2.7#	ng/L	PFNA	F	5	SW	New Jersey	B	Calgon	F300
2441	Dickenson,	2016	-19 to 10#	Percent	6.8 to 7.3#	6.1 to 8.7#	ng/L	PFHxA	F	5	SW	New Jersey	B	Calgon	F300
2441	Dickenson,	2016	-26#	Percent	<5.0#	6.3#	ng/L	PFBA	F	5	SW	New Jersey	B	Calgon	F300
2441	Dickenson,	2016	-34 to 8#	Percent	0.59 to 0.97#	0.54 to 1.3#	ng/L	PFDA	F	5	SW	New Jersey	B	Calgon	F300
2441	Dickenson,	2016	-66 to 70#	Percent	1.23 to 1.81#	0.537 to 2.48#	ng/L	PFBA	F	0.5472 to	GW	Minnesota	B	Calgon	F600
2441	Dickenson,	2016	0 to 19#	Percent	<0.05 to 0.085	<0.05 to 0.069#	ng/L	PFPeA	F	0.5472 to	GW	Minnesota	B	Calgon	F600
2441	Dickenson,	2016	0 to 76#	Percent	<0.05 to 0.210	<0.05#	ng/L	PFHxS	F	0.5472 to	GW	Minnesota	B	Calgon	F600
2441	Dickenson,	2016	33#	Percent	15#	10#	ng/L	PFBA	F	5#	SW	Colorado	B	Norit	GAC 300
2441	Dickenson,	2016	46 to 60#	Percent	0.127 to 0.192	<0.05 to 0.1023	ng/L	PFHxA	F	0.5472 to	GW	Minnesota	B	Calgon	F600
2441	Dickenson,	2016	5 to 6#	Percent	2.1 to 3.6#	2.0 to 3.4#	ng/L	PFBS	F	5	SW	New Jersey	B	Calgon	F300
2441	Dickenson,	2016	7.2 to 12.7#	Percent	4.8 to 5.5#	6.4 to 6.9#	ng/L	PFPeA	F	5	SW	New Jersey	B	Calgon	F300
2441	Dickenson,	2016	74#	Percent	17#	4.4#	ng/L	PFPeA	F	5#	SW	Colorado	B	Norit	GAC 300
2441	Dickenson,	2016	91#	Percent	11#	0.97#	ng/L	PFNA	F	5#	SW	Colorado	B	Norit	GAC 300
2441	Dickenson,	2016	>89#	Percent	4.5#	<0.50#	ng/L	PFHpA	F	5#	SW	Colorado	B	Norit	GAC 300
2441	Dickenson,	2016	>96#	Percent	5.8#	<0.25#	ng/L	PFHxS	F	5#	SW	Colorado	B	Norit	GAC 300
2441	Dickenson,	2016	>96#	Percent	6.4#	<0.25#	ng/L	PFBS	F	5#	SW	Colorado	B	Norit	GAC 300
2505	Cummings,	2015	>72 to >93#	Percent	18 to 72	<5	ng/L	PFNA	F		SW	Logan System Birch	B	Calgon	F-400

Drinking Water Treatment for PFOS

Ineffective Treatments

- Conventional Treatment
- Low Pressure Membranes
- Biological Treatment (including slow sand filtration)
- Disinfection
- Oxidation
- Advanced Oxidation

PAC Dose to Achieve

50% Removal	16 mg/l
90% Removal	>50 mg/L

Dudley et al., 2015

Effective Treatments

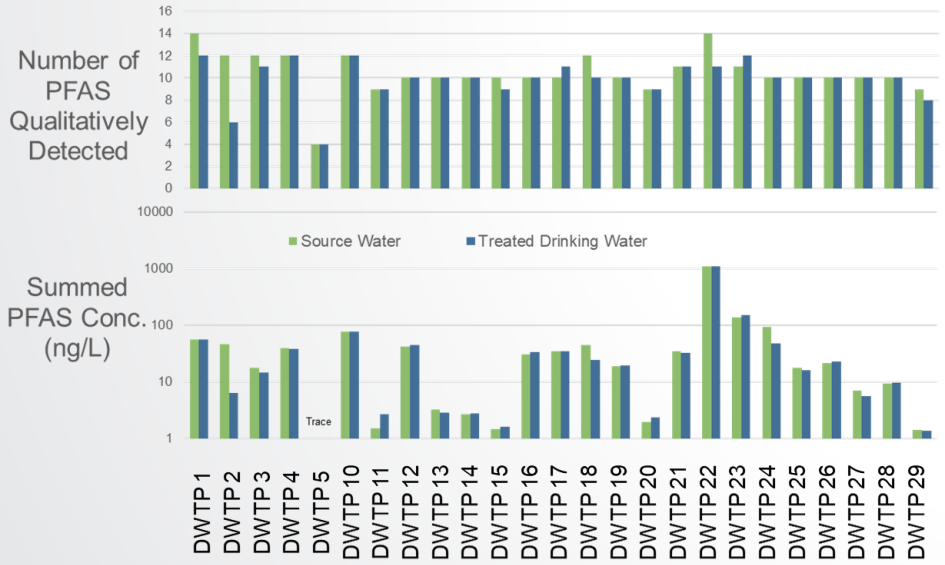
	Percent Removal	
Anion Exchange Resin (IEX)	90 to 99	- **Effective**
High Pressure Membranes	93 to 99	- **Effective**
Powdered Activated Carbon (PAC)	10 to 97	- **Effective for only select applications**
Granular Activated Carbon (GAC)		
- Extended Run Time	0 to 26	- **Ineffective**
- Designed for PFAS Removal	> 89 to > 98	- **Effective**

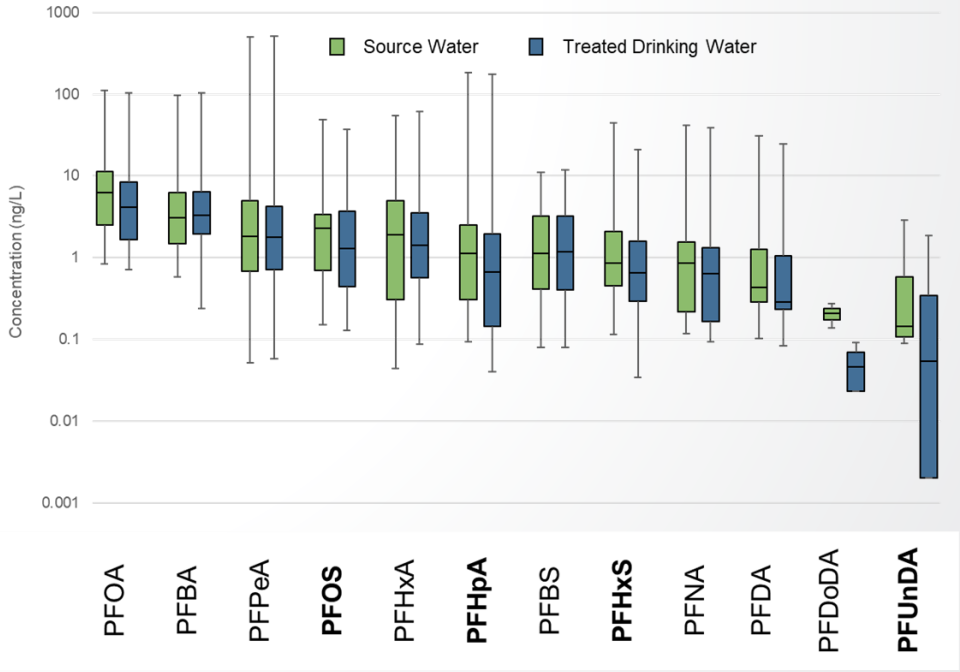
Facility Evaluations

Project: Evaluation of chemicals of emerging concern including PFAS

Actions: Numerous sources evaluated including drinking water facilities

Results: Results confirm previous conclusions that advance technologies are needed, and they must be adequately designed





Drinking Water Cost Models

United States Environmental Protection Agency

Environmental Topics | Laws & Regulations | About EPA | Search EPA.gov

Related Topics: Safe Drinking Water Act | CONTACT US | SHARE

Drinking Water Treatment Technology Unit Cost Models and Overview of Technologies

Drinking Water Treatment Technology Unit Cost Models

Federal laws and executive orders require EPA to estimate compliance costs for new drinking water standards. The three major components of compliance costs are:

- Treatment
- Monitoring
- Administrative costs

Treatment technologies remove or destroy pollutants (such as arsenic, disinfection byproducts, and waterborne pathogens).

To estimate treatment costs, EPA developed several engineering models using a bottom-up approach known as work breakdown structure (WBS). The WBS models:

Access the Drinking Water Treatment Unit Cost Models and Overview of Technology webpage or search EPA WBS.

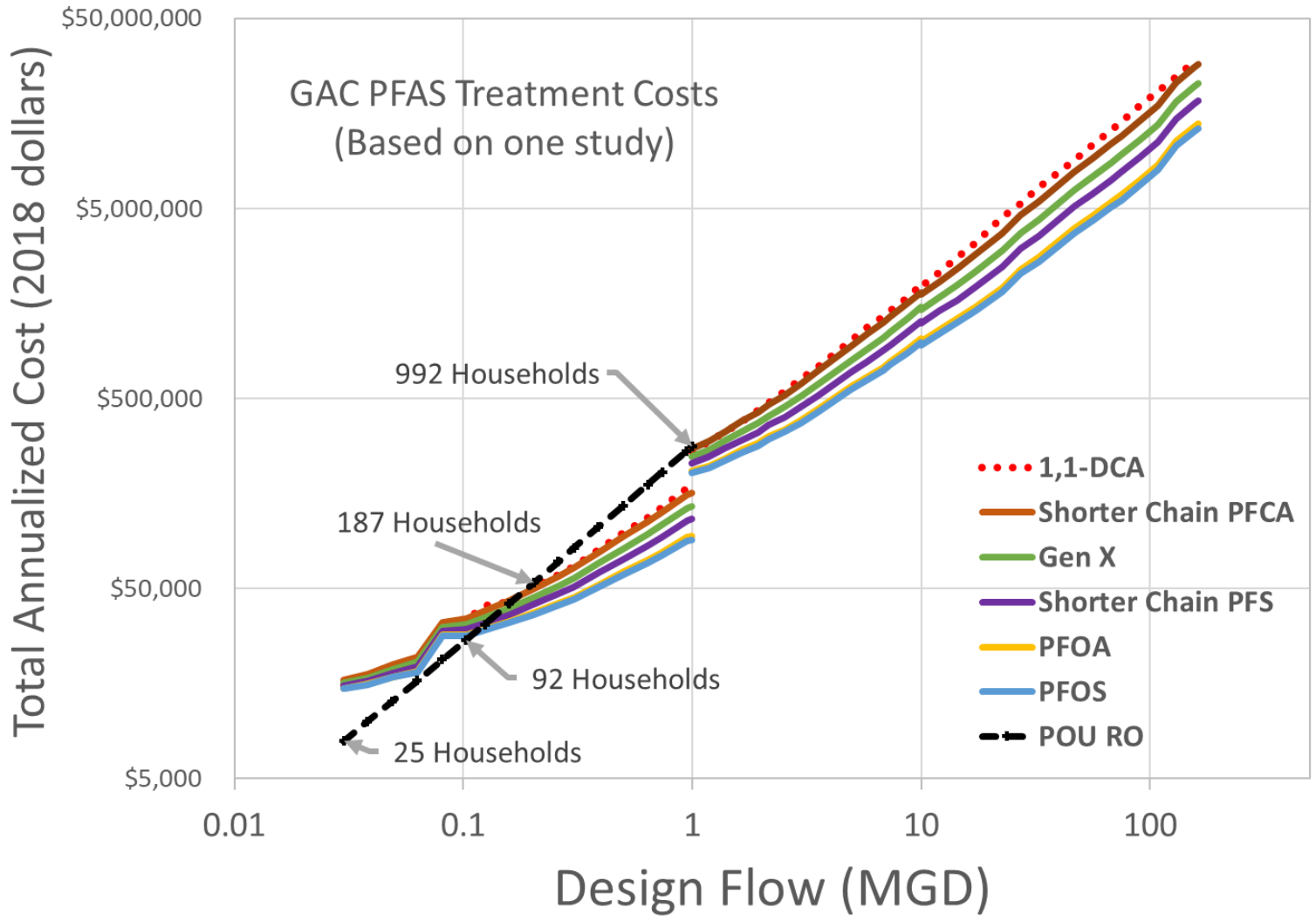
Various Models are Available

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

- Non-treatment
- Packed tower aeration
- Point of Use (POU)/
- Point of Entry (POE)*
- Reverse Osmosis / Nanofiltration
- UV disinfection
- UV advanced oxidation

*POU/POE temporarily taken off web. Please contact Rajiv Khera

Costs for PFAS Treatment: One GAC Example

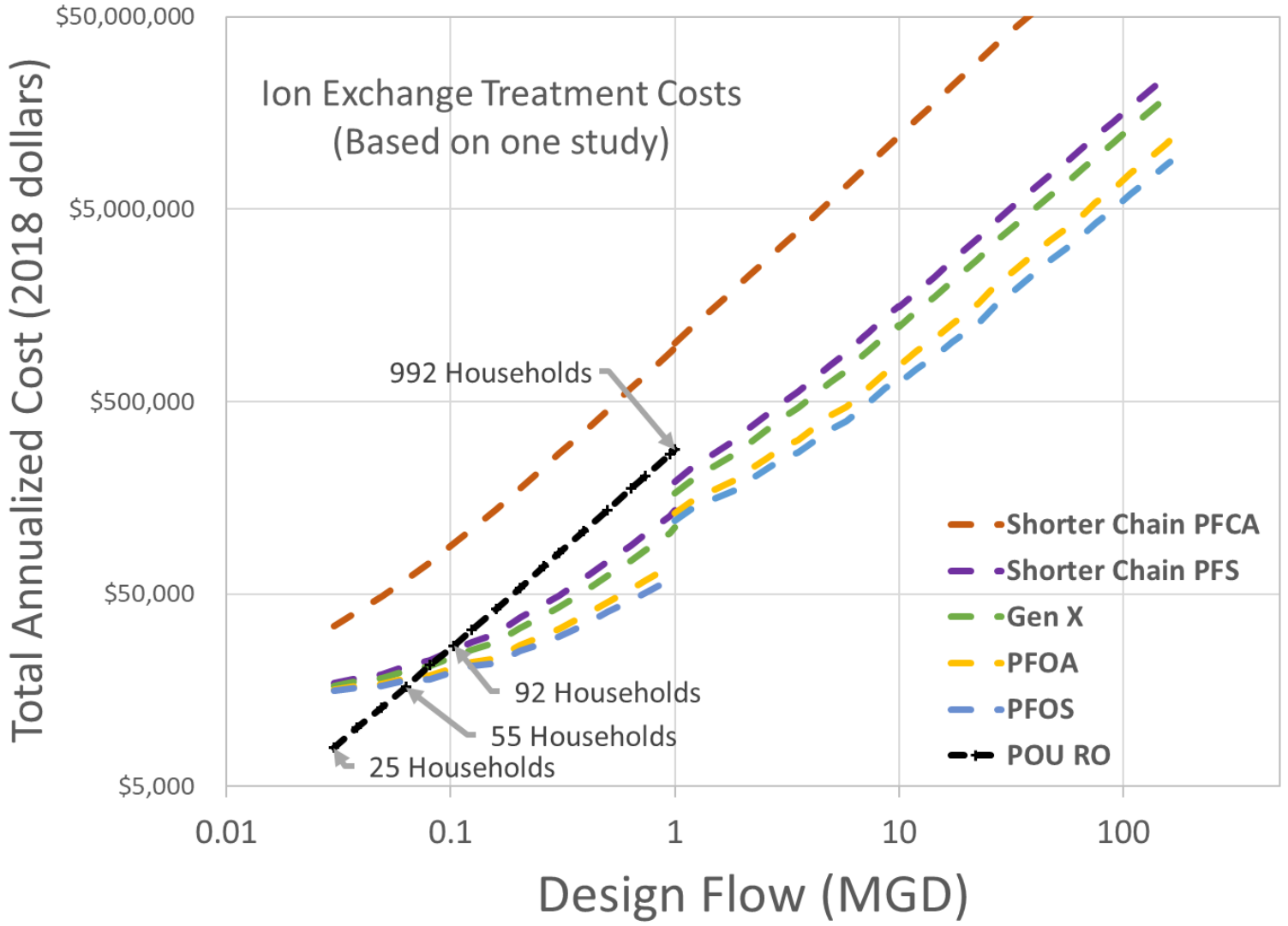


Costs can be generated for various sizes, contaminants, and even POU scenarios

Primary Assumptions:

- Two vessels in series
- 20 min Empty Bed Contact Time (EBCT) Total
- Bed Volumes Fed
  - 1,1-DCA = 5,560 (7.5 min EBCT)
  - Shorter Chain PFCA = 4,700
  - Gen-X = 7,100
  - Shorter Chain PFS = 11,400
  - PFOA = 31,000
  - PFOS = 45,000
- 7% Discount rate
- Mid-level cost

Costs for PFAS Treatment: One IEX Example



Costs can be generated for various sizes, contaminants, and even POU scenarios

Primary Assumptions:

- Two vessels in series
- 3 min EBCT Total
- Bed Volumes Fed:
  - Shorter Chain PFCA = 3,300
  - Gen-X = 47,600
  - Shorter Chain PFS = 34,125
  - PFOA = 112,500
  - PFOS = 191,100
- 7% Discount rate
- Mid-level cost

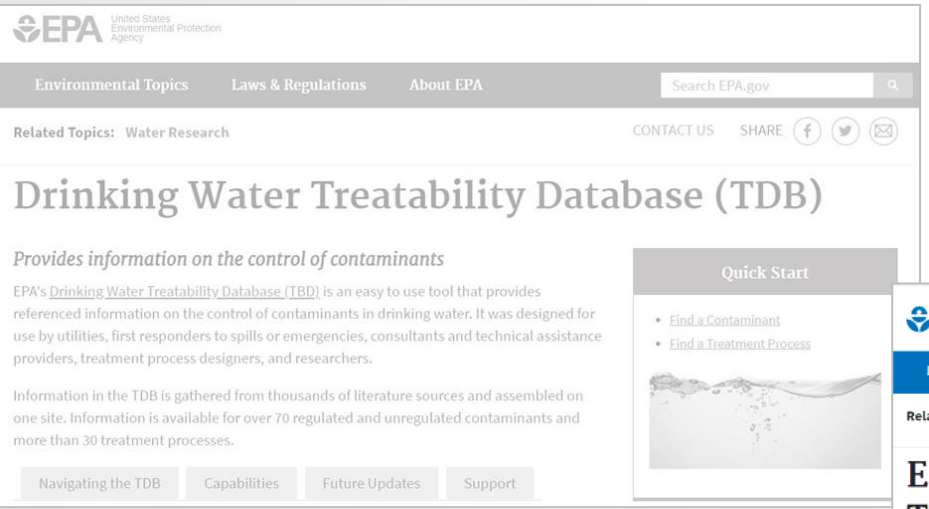
Cost Modeling: Additional Data Needs

- As-built costs:
  - Installed equipment cost
  - System engineering and other indirect cost
  - Annual operating cost
- The more detail, the better:
  - Detailed breakdown of cost by line item
  - Total cost with list of categories included, for example:
    - "Equipment includes vessels, piping, valves, instrumentation, concrete pad, buildings"
    - "Indirect includes engineering, permitting, pilot testing, site work, mobilization"
    - "Operating cost includes media replacement, labor, electricity"
  - Total only
- Associated flow rates, vessel sizes, materials of construction for major components (e.g., stainless steel, fiberglass)

Performance Model Demonstration

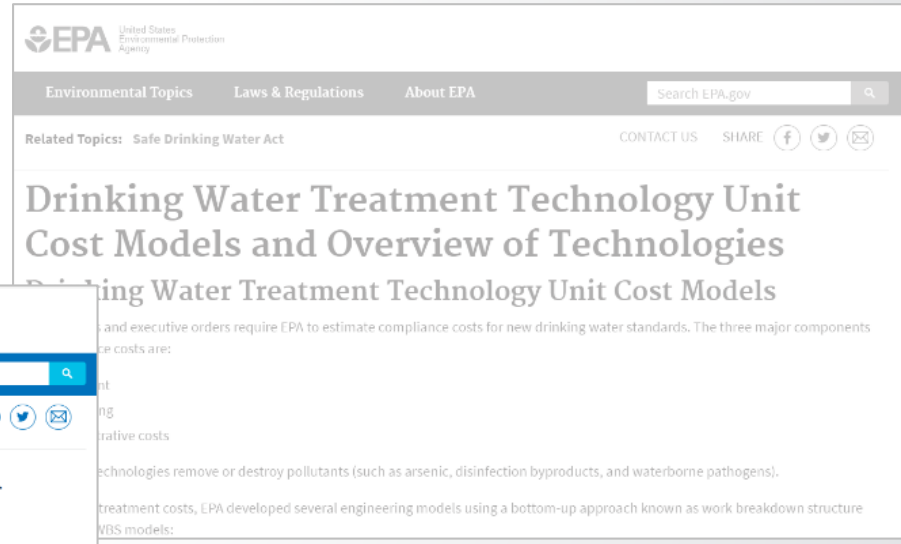
To provide tools to accurately predict the performance and cost of treating PFAS in drinking waters

Treatability Database



Performance Models

Cost Models



Environmental Technologies Design Option Tool (ETDOT)

ETDOT is a series of treatment models, data sets, and parameter estimation tools developed by National Center for Clean Industrial and Treatment Technologies at Michigan Technological University (MTU)

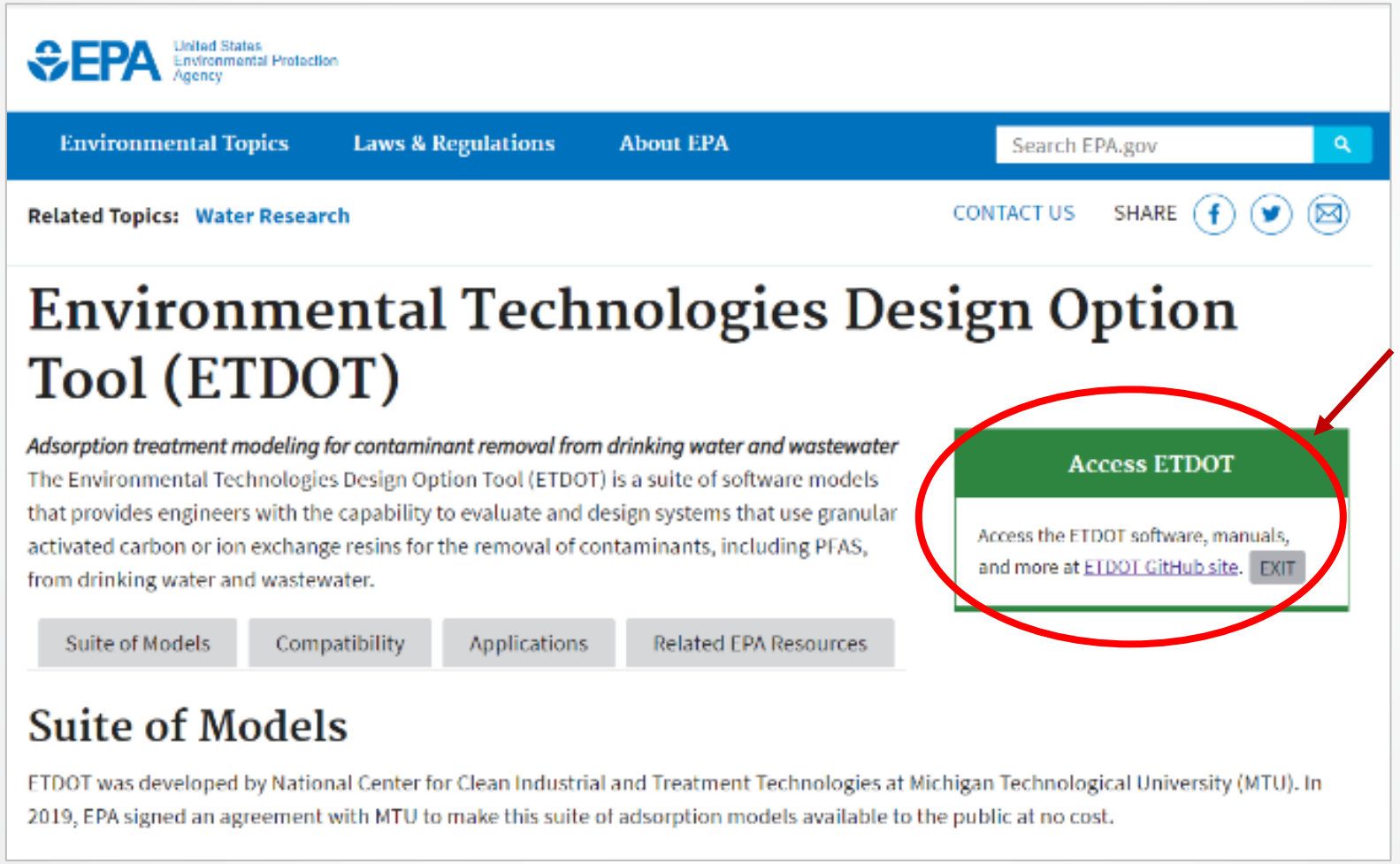
- The models were sold as a package for many years
- In 2019, EPA signed an agreement with MTU to make this suite of water and air treatment models available to the public at no cost

Expected interested users:

- State primacy personnel interested in evaluating data sets
- Water utilities with experience in running models
- Consulting engineers
- University academicians

Access the ETDOT software, manuals and more at the ETDOT GitHub site.

Available Modeling Tools



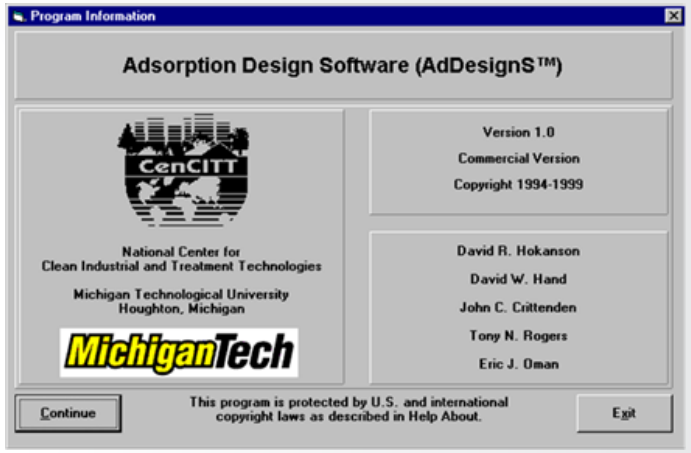
GitHub Site

[Access the Environmental Technologies Design Option Tool](#) **(ETDOT)** or search EPA ETDOT.

Available Modeling Tools

Models available at the GitHub site:

- Adsorption Design Software for Windows (AdDesignS) *Version 1.0*
- Advanced Oxidation Process Software (AdOx) *Version 1.0.2*
- Aeration System Analysis Program (ASAP) *Version 1.0*
- Biofilter Design Software *Version 1.0.27*
- Continuous Flow Pore Surface Diffusion Model for Modeling Powdered Activated Carbon Adsorption *Version 1.0*
- Dye Study Program (DyeStudy) *Version 1.0.0*
- Predictive Software for the Fate of Volatile Organics in Municipal Wastewater Treatment Plants (FaVOr) *Version 1.0.11*
- Ion Exchange Design Software (IonExDesign) *Version 1.0.0*
- Software to Estimate Physical Properties (StEPP) *Version 1.0*

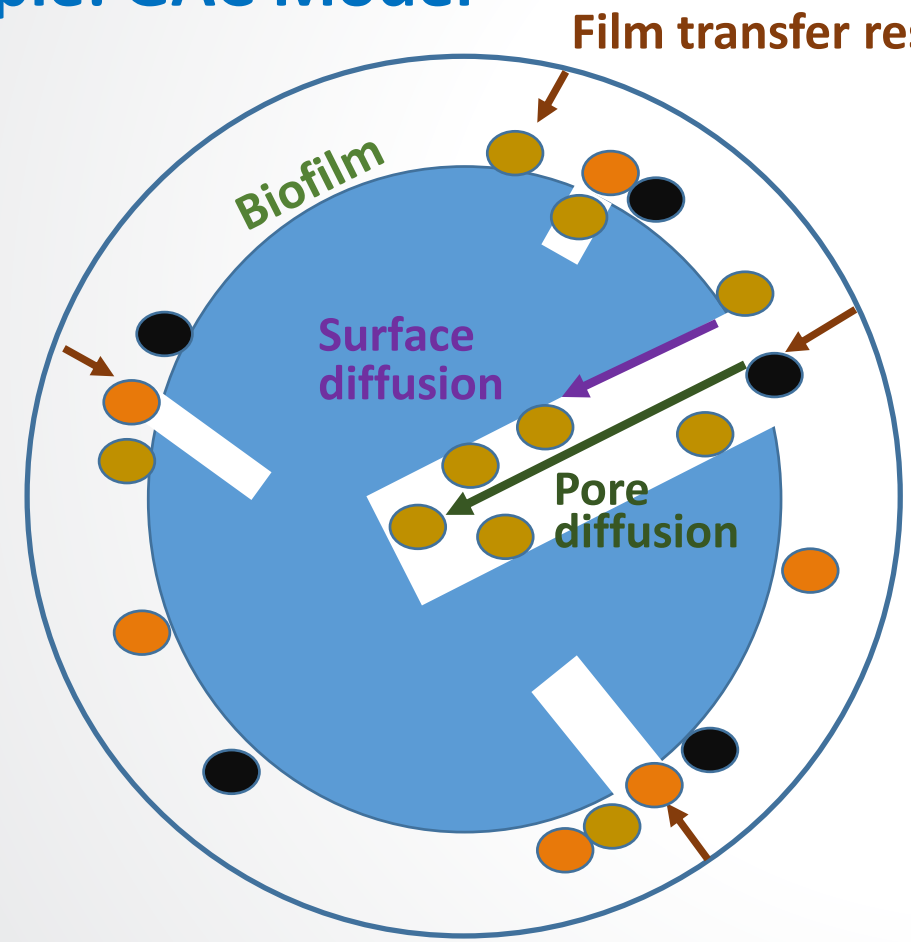


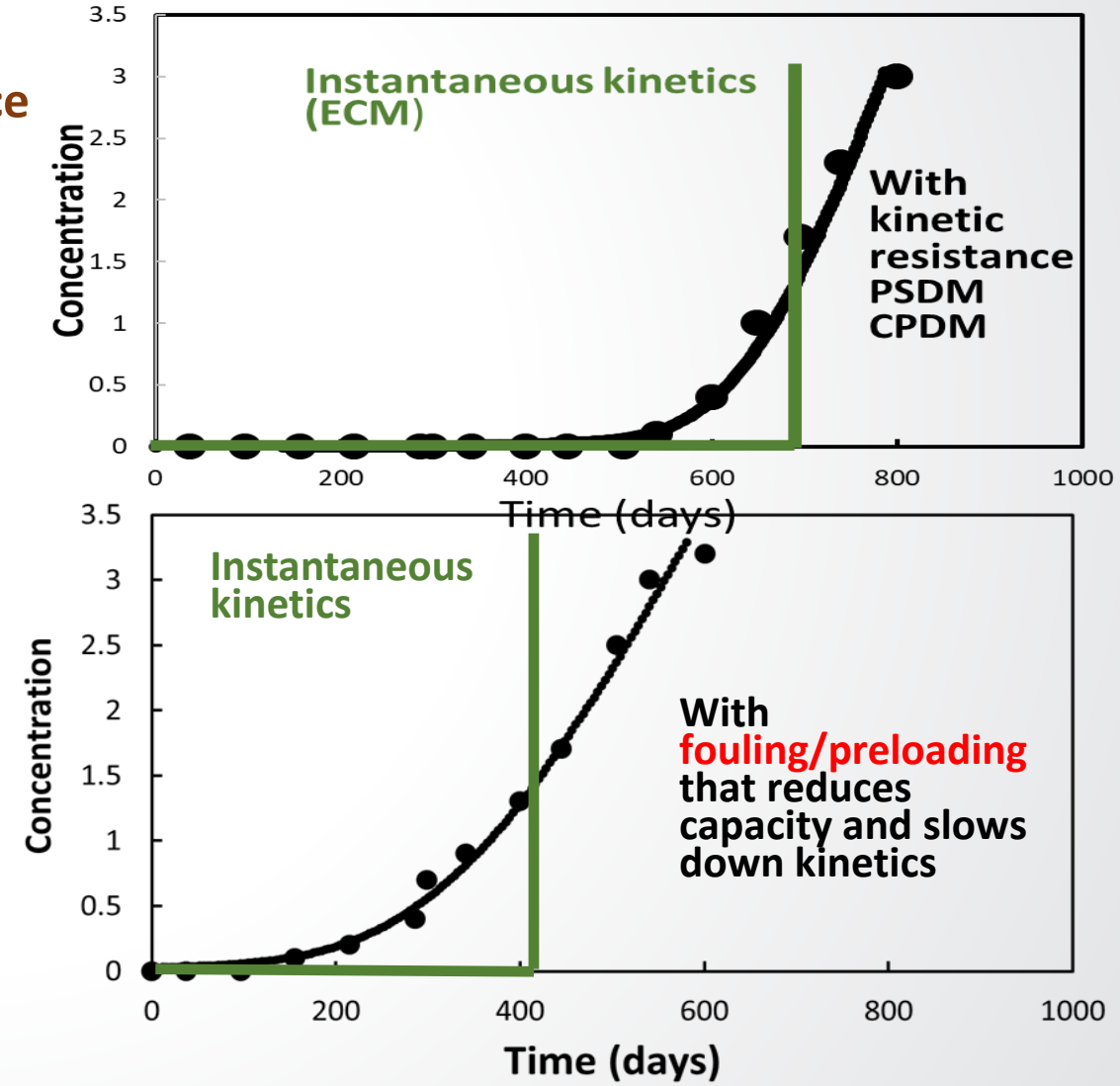
The engines are written in FORTRAN with a Visual Basic front end

[Access the Environmental Technologies Design Option Tool](#) or search EPA ETDOT.

Incorporation of Complex Mechanisms

Example: GAC Model

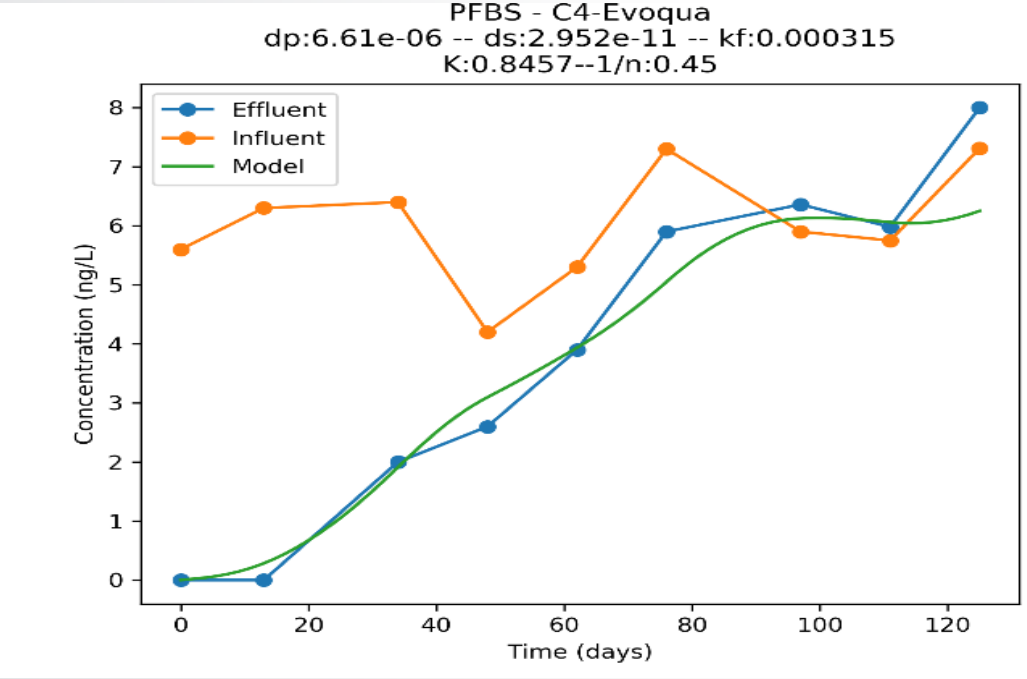




The models range from simple to complex

Modeling to Consistent Design Parameters

Modeling Pilot-/Full-scale Data



Allows for predicting performance for other scenarios

- Other designs: number of contactors, contactor Empty Bed Contact Time (EBCT), different treatment goals, changing concentrations of PFAS or background constituents, changing demand, lead/lag operation, etc.

Working with EPA's Office of Ground Water and Drinking Water and the US Air Force on drinking water and remediation cost models

- Allows for comparison within and across technologies by cost

Treatment and cost models will soon be made available to the public at no charge on EPA's website.

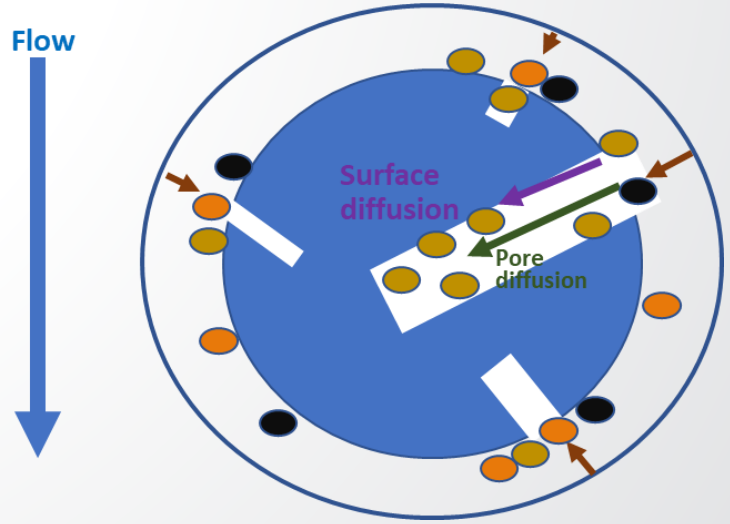
Future Plans

Treatability Database

- Further update treatability database with new references

Performance Models

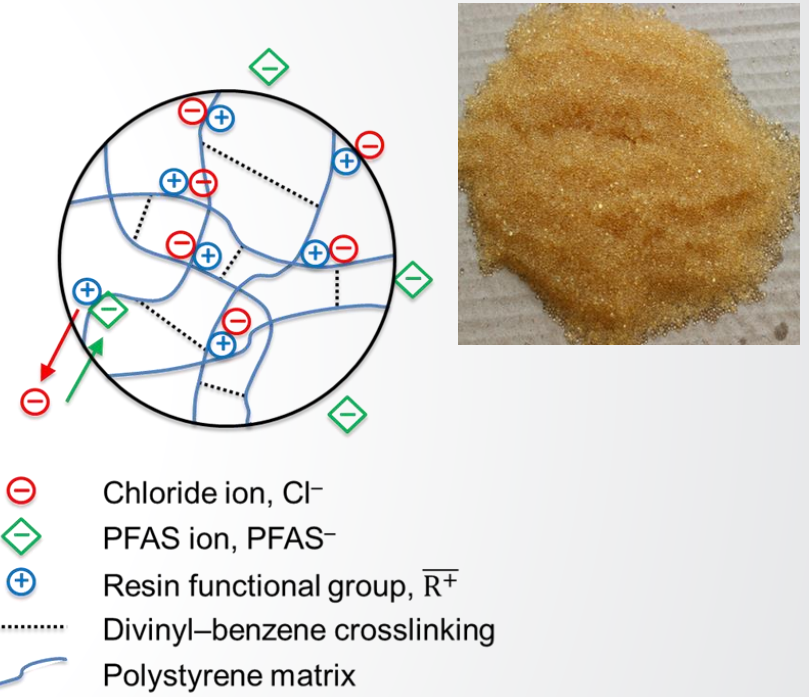
- Update Graphical User Interface to work with Windows 10
- Provide Python code for pore surface diffusion model (PSDM GAC) to automate the optimization routines for:
  - Specific throughput and carbon use rate calculations for multiple scenarios
  - Automated fitting of parameters
  - Automated optimal bed configuration
  - Automated optimal Empty Bed Contact Time (EBCT) selection
  - Automated evaluation of bed replacement frequency
  - Evaluation of multiple feed conditions
  - Evaluation of multiple flow conditions
  - Automated fitting and predicting lead/lag operations



Future Plans (continued)

Performance Models *(continued)*

- Provide code for ion exchange models for
  - Include competition (e.g., inorganic ions and PFAS)
  - Continuous flow (columns) and batch (isotherm and kinetics)
  - Gel (HSDM) and macro porous (PSDM) resins
  - with automation features



Cost Models

- Further updates to the cost models

Combined Models

- Further merge Treatability Database, performance models and cost models
- Further merge the Treatability Database with EPA's CompTox Chemicals Dashboard

Ultimate Goal

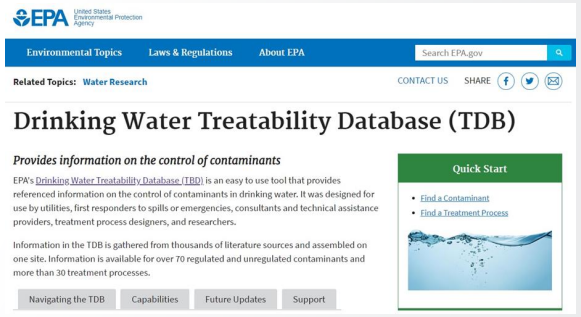
For the treatment/cost models housed at EPA…

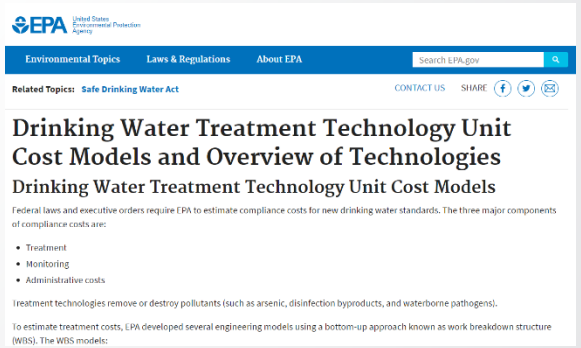
- Provide tools and approaches to accurately predict the performance and cost of treating PFAS in waters

- Environmental Technologies Design Option Tool Models or search EPA ETDOT

- Drinking Water Treatability Database or search EPA TDB

- Drinking Water Treatment Cost Models or search EPA WBS





Thermal Treatment Research

Problem: There are many sources of materials that may need to be thermally treated:

- Manufacturing wastes
- Wastewater sludges
- Municipal waste
- Obsolete flame retardants
- ***Spent water treatment sorbents – in conjunction with reactivation***

What minimum conditions (temperature, time) are needed to adequately destroy PFAS and what are the products of incomplete combustion?

Action: Conduct bench- pilot- and full-scale incineration studies and modeling to evaluate:

- Impact of source material
- Impact of temperature on degree of destruction
- Impact of calcium
- PFAS releases from incineration systems

Research Needs: Spent Media

Needs

- Destruction and removal efficiency? Can the ash be landfilled? Can the GAC be reused?
- Release of off gas (incineration, pollution control devices)?
- Mass balance closure to determine the fate of the contaminants?

Chemistry

- What PFAS to analyze for? What sampling protocols?
- Analytical protocols for air, solid and liquid samples
- Effectiveness of conservative tracers?

Source Material

- Do spent GAC and IX have different considerations?
- Co-treated materials, calcium and other additives?
- Size and chemical makeup

Design and Operating Conditions

- Reactor type (temperature, residence time)
- Reaction zone (flow, movement of materials and gases)

Extramural Project (Univ. of North Dakota)

Thermal Stability and Decomposition of Perfluoroalkyl Substances on Spent Granular Activated Carbon

Feng Xiao,* Pavankumar Challa Sasi, Bin Yao, Alena Kubátová, Svetlana A. Golovko, Mikhail Y. Golovko, and Dana Soli
Environ. Sci. Technol. Lett. 2020, 7, 343−350 - USEPA ORD Science to Achieve Results (STAR) Program (RD83966; F.X.)

Objectives

- Improve our understanding of the thermal stability of PFAS
- Investigate their decomposition mechanisms on spent GAC during thermal reactivation

Design

- 7 perfluoroalkyl carboxylic acids (PFCAs), 3 perfluoroalkyl sulfonic acids (PFSAs), and 1 perfluoroalkyl ether carboxylic acid (PFECA) in different atmospheres (N_2, O_2, CO_2 and air)

Bench Scale Results

- Decomposition of PFCAs such as PFOA on GAC was initiated at temperatures as low as 200 °C
- PFSAs such as PFOS, on the other hand, required a much higher temperature (≥450 °C) to decompose
- Volatile organofluorine species were the main thermal decomposition product of PFOA and PFOS at ≤600 °C
- Efficient decomposition (>99.9%) of PFOA and PFOS on GAC occurred at 700 °C or higher, accompanied by high mineralization of fluoride ions (>80%)

Extramural Project (North Carolina State Univ.)

Thermal Reactivation of Spent GAC from PFAS Remediation Sites

Detlef Knappe, S. James Ellen: North Carolina State University, SERDP Proposal (with EPA cooperation)

Objective: To identify conditions that effectively mineralize PFAS during the thermal reactivation of PFAS-laden GAC

Design: To identify the roles of 1) reactivation temperature, 2) reactivation time, 3) calcium, and 4) pretreatment with base on PFAS fate during thermal reactivation of GAC

Questions to Resolve:

- What is the difference in behavior between the acid and salt forms of PFAS during thermal reactivation of GAC?
- What are the roles of calcium and base on the fate of PFAS during thermal reactivation of GAC?
- What are products of incomplete combustion (PICs) in air emissions and on the reactivated GAC?

Emission Stack Testing of PFAS Residuals from Full-Scale GAC Reactivation Facilities

When DW treatment plant GAC is reactivated, the PFAS may be thermally destroyed or transformed into residual byproducts

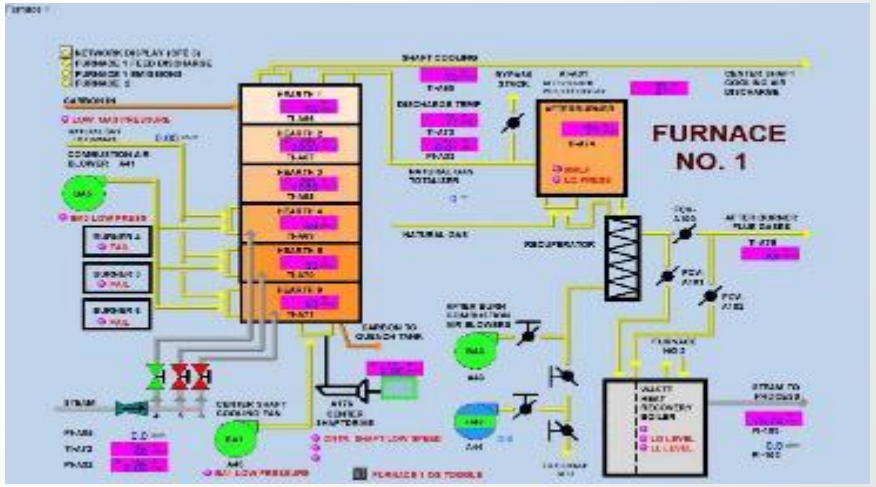
- Spent GAC, reactivated GAC and scrubber water will be analyzed for PFAS
- Summa Canister, Modified Method 5 for Semi-Volatile Organics and PAHs and Modified Method 18 air samples will be collected and analyzed as follows:

Test Parameter	EPA Method
Carbon dioxide/Oxygen	U.S. EPA 3A
Volumetric flow rate, moisture	U.S. EPA 1, 2, 4
Hydrogen fluoride	U.S. EPA 26A
Speciated semivolatile organics	U.S. EPA 0010/8270D
Polar, volatile PFAS compounds	Modified U.S. EPA 18
Volatile organic compounds	U.S. EPA TO-15

Multiple Hearth Furnace for GAC Reactivation

Multiple Hearth Furnace Access Doors

Afterburner



EPA is actively looking for partners for sampling of GAC reactivation facilities

Cement Kiln Incinerators

Cement kilns are operated under different operating conditions

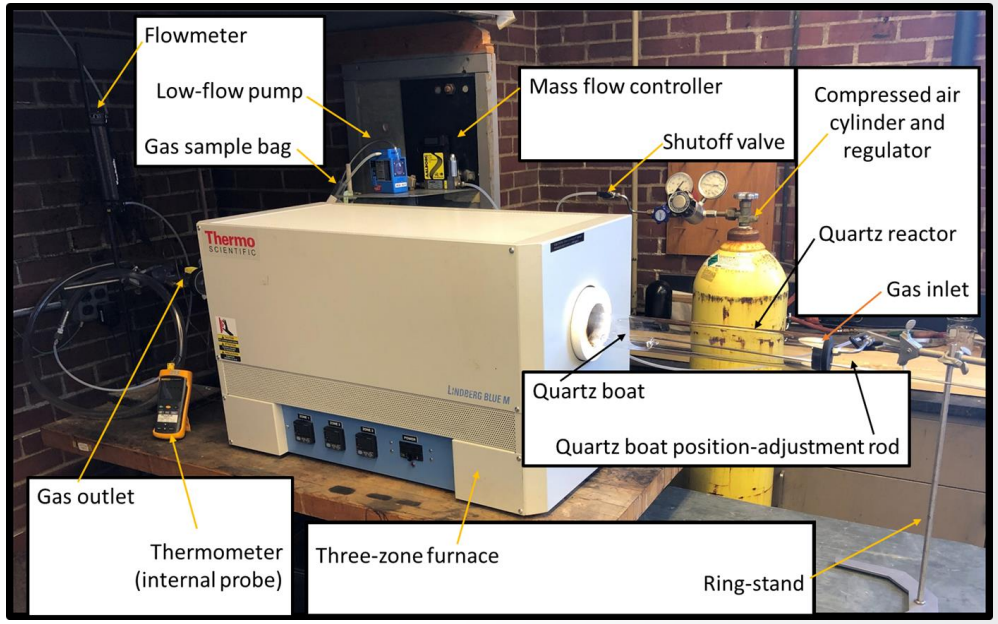
- Gas temperatures of up to ~2,000 °C
- Gas residence times of up to 10 seconds
- Solid residence time of up to 30 minutes

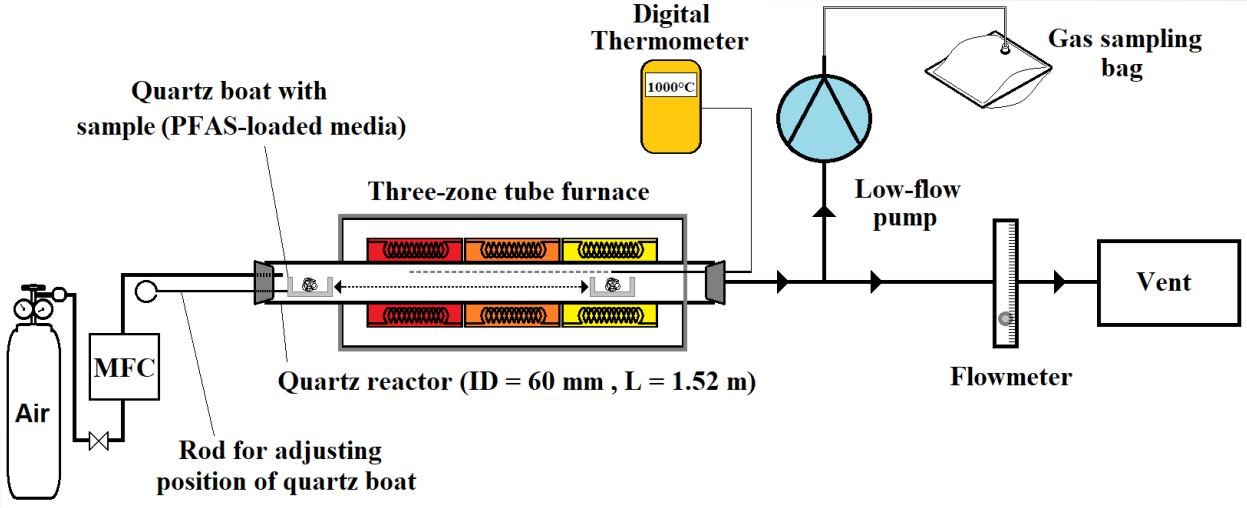
EMERGING CONTAMINANTS SUMMIT

Source: Purolite presentation and case study. F. Boodoo et al.

Incineration of Spent Ion Exchange Resin

- Anion exchange resins loaded with different PFAS compounds with or without calcium additives are placed in quartz crucibles and inserted into a preheated furnace
- Samples are incinerated (simulating a cement kiln) under constant air flow
- Samples are being collected and analyzed for calcium fluoride (CaF_2) in incinerated ash and hydrogen fluoride (HF), tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6) in air emissions



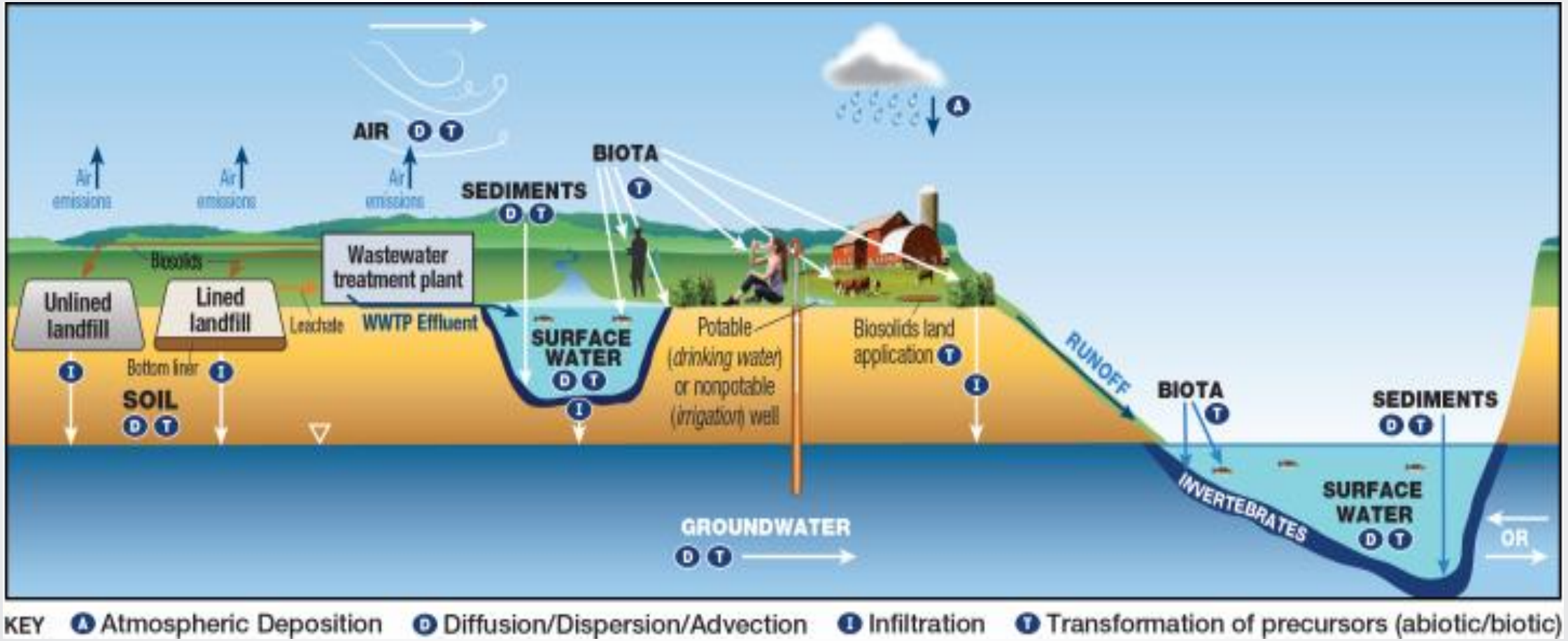


Lab-Scale Thermal Treatment and Incineration System

PFAS Fate and Transport for WWTPs & Biosolids

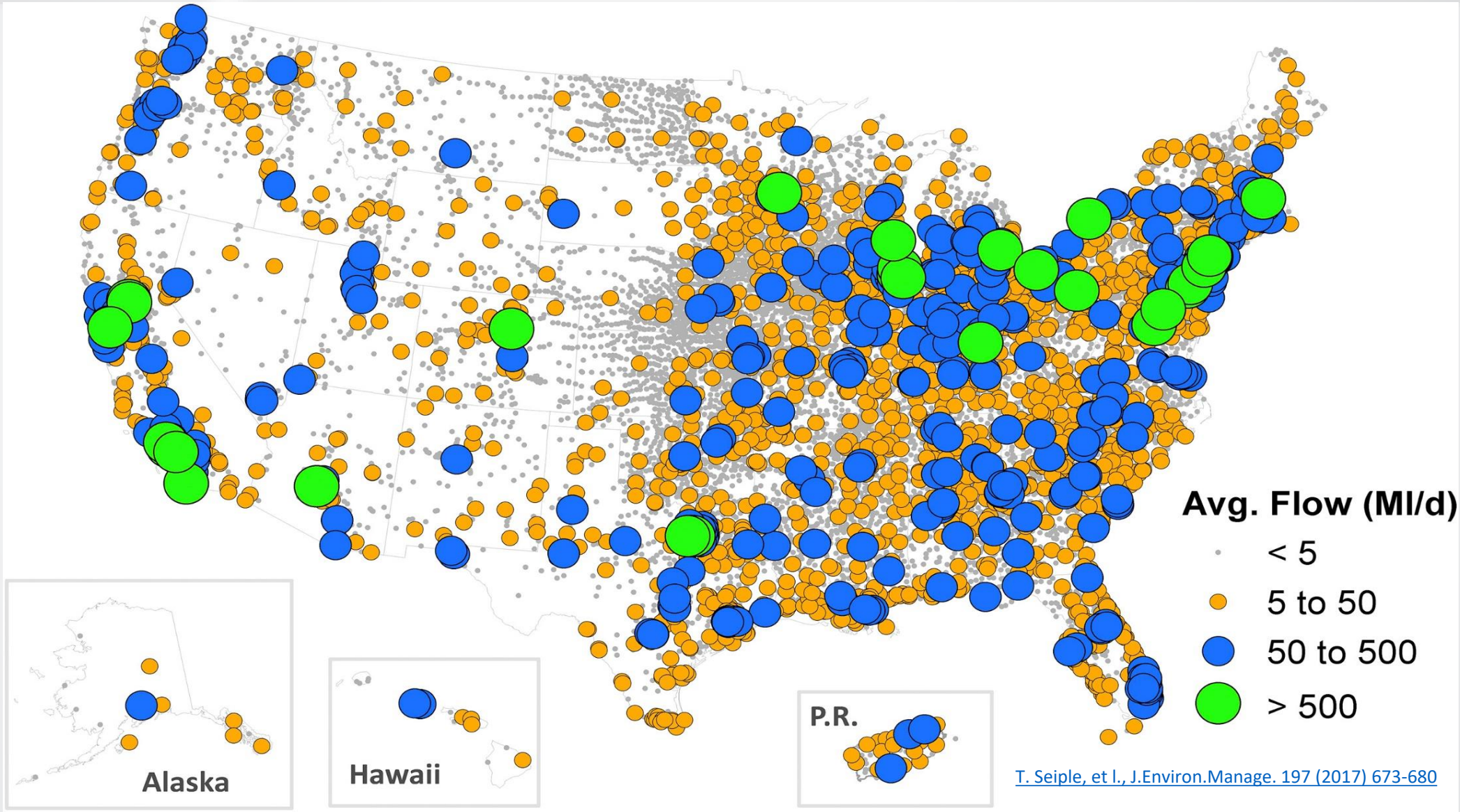
Wastewater Treatment Plants (WWTPs) may introduce PFAS into the environment through:

- Effluent discharge to surface water
- Land application of biosolids and disposal of residuals
- Air emissions



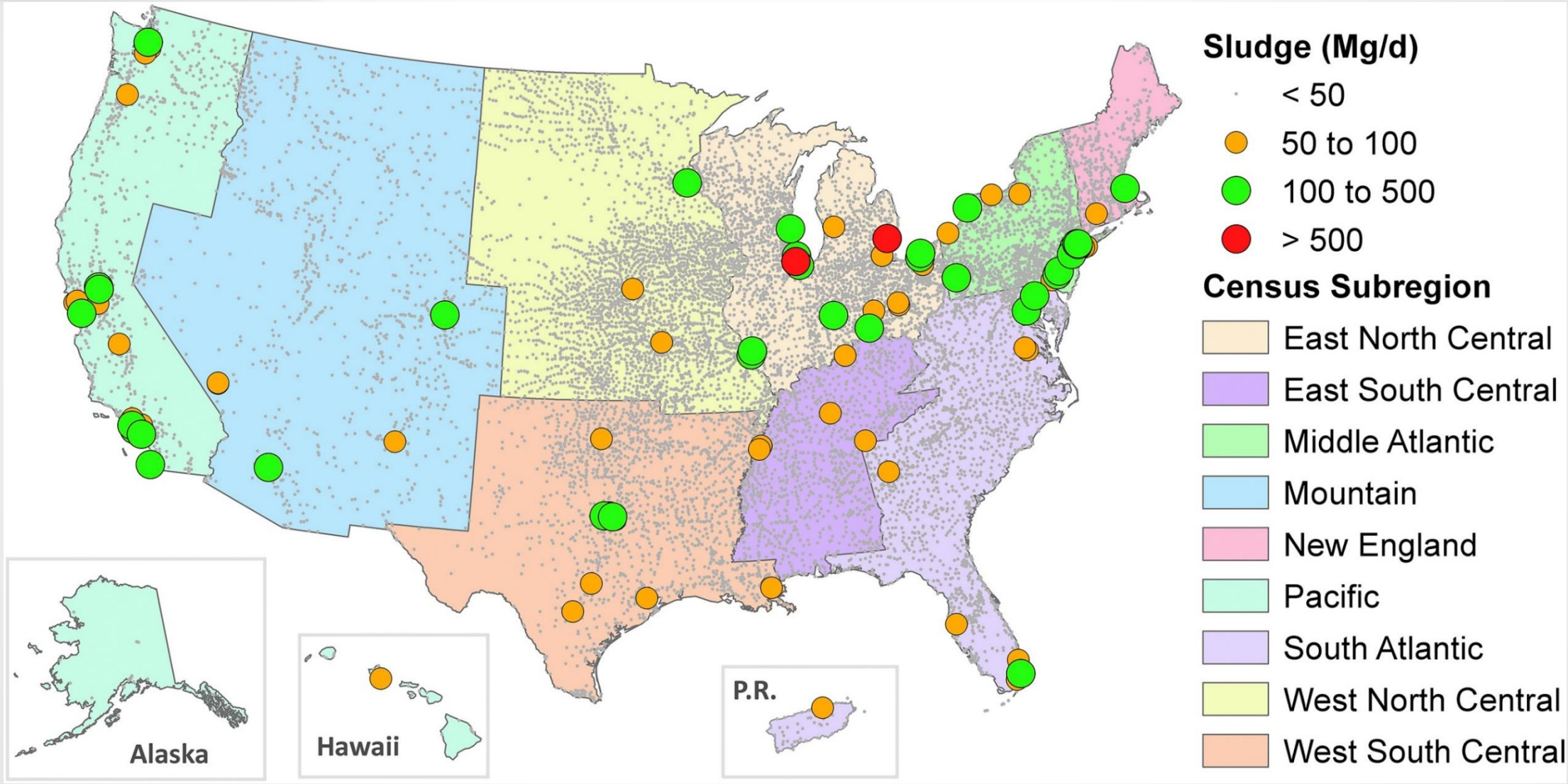
ITRC Factsheet, 2018.

US Publicly Owned Treatment Works (POTW) by daily average flow



T. Seiple, et l., J.Environ.Manage. 197 (2017) 673-680

Wastewater Sludge Production in the US



T. Seiple, et al., J.Environ.Manage. 197 (2017) 673-680

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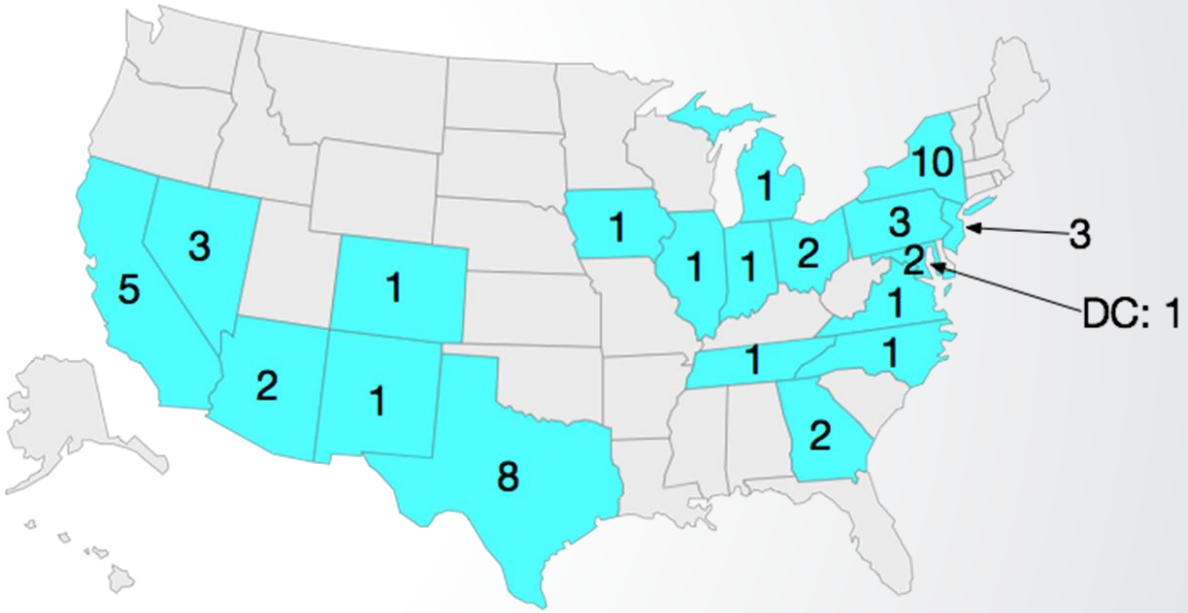
PFAS in the ORD National Effluent Survey

Problem: Survey of 50 wastewater treatment plant effluents show the presence of PFAS

- Greater than 80% WWTPS had measurable C4-10 PF carboxylates, PFBS, PFHS, PFOS
- PFHxA, PFOA and PFOS were predominant
- Median levels ~ 10–30 ng/L, although some plants were much higher
- Results shows temporal and spatial variability



50 Largest Plants (20% pop, 17% discharge)

EPA's PFAS Wastewater Treatment Research

Problem: PFAS removal in wastewater plants is largely unknown

Actions:

- Analytical methods for the targeted compounds
- Bioassays to better understand if treatments are effective and to identify risks
- Evaluate air emissions from activated sludge and sludge treatment processes
- Evaluate conventional and advanced treatment processes for various size facilities
- Chemical and microbial transformation processes will also be evaluated in wastewater residuals/biosolids operations

Impact: *Enable entities to make informed decisions about wastewater treatment choices and residual handling*

Residual Streams
(to be covered Sept. 23)

- Wastewater residuals incineration
  - Multi hearth furnaces
  - Rotary kilns
  - Fluidized beds
- Biosolids formation
- Advanced technologies
- Landfill disposal
- Land application
- Plant uptake

Wastewater Treatment: Conventional and Advanced

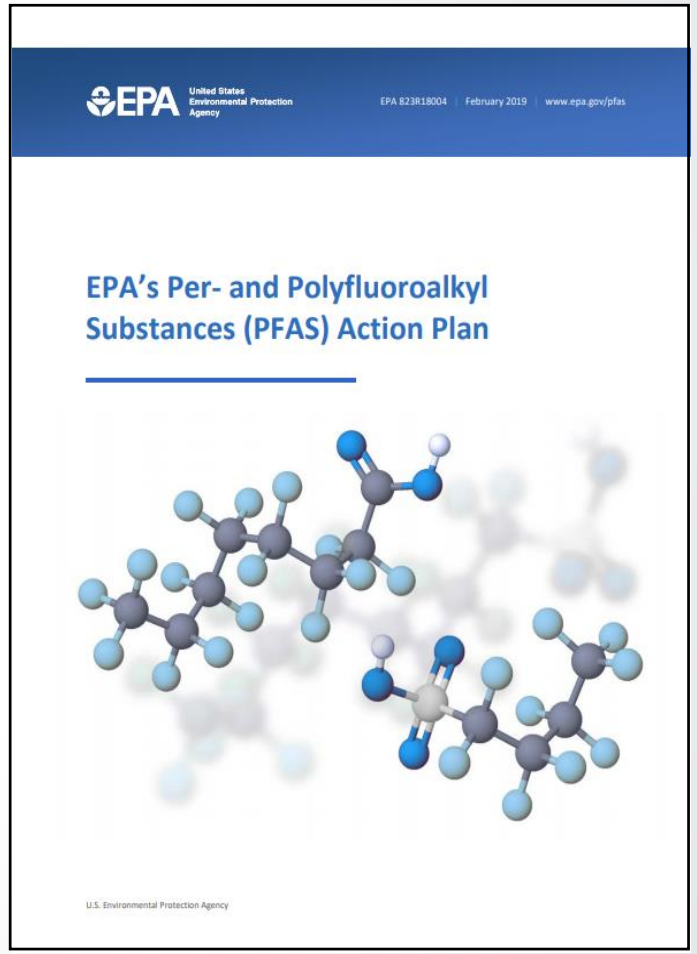
Problem: Data are needed for PFAS removal for conventional and advanced wastewater treatment processes

Action: Develop research to support:

- Treatment in conventional & advanced wastewater and biosolids treatment. Consider factors such as facility size, waste sources, treatment technologies, retention time, etc.
- Combinations of technologies
- Determination of where PFAS is coming from (e.g., industrial, landfills) and potential pretreatment technologies to address “sources” to wastewater plants
- Determination of fate & transport of PFAS in wastewater treatment: Chemical and biological transformations, and do shorter chain PFAS tend to end up in effluents than in biosolids?

Contacts

Thomas Speth, PhD, PE
Associate Director
Center for Environmental Solutions and Emergency Response
US EPA Office of Research and Development
Speth.Thomas@epa.gov
513-569-7208

EPA Team:
Carolyn Acheson (Acheson.Carolyn@epa.gov)
Marc Mills (Mills.Marc@epa.gov)
Craig Patterson (Patterson.Craig@epa.gov)
Jonathan Pressman (Pressman.Jonathan@epa.gov)

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