Practical Guide to PFAS Treatment for both Potable and Polluted Water with Single-Use Ion Exchange Resin

Guide Pratique du Traitement des PFAS dans l'eau Potable et Polluée avec une Résine Echangeuse d'ions à Usage Unique

Cathy Swanson

June 14, 2023

Purolite®
An Ecolab Company

Purolite Contacts

Cathy Swanson

- Global Business Development
- Based in Fullerton, CA
- 5 years with Purolite and > 15 years in ion exchange
- +011 714-292-2531
- cathy.swanson@purolite.com

Rodrigo Salvatierra Galaz

- General Director Purolite
- France, Belux, Spain, Nordics
- Based in Paris
- Over 20 years with Purolite
- +33 679475378
- rodrigo.salvatierra@purolite.com

Agenda

European Regulations vs United States

Choosing the Right Treatment

Ion Exchange Performance Modeling

Cost Analysis

Other Important Criteria

European Union's Drinking Water Directive

- The maximum concentration of **all PFAS** compounds combined is going to be 0.5 µg per liter of water → 500 ppt
- Alternatively, member states can monitor the **sum of 20 PFAS** compounds, for which the maximum is 0.1 µg/l → 100 ppt

20 PFAS

— Perfluorobutanoic acid (PFBA)
— Perfluoropentanoic acid (PFPA)
— Perfluorohexanoic acid (PFHxA)
— Perfluoroheptanoic acid (PFHpA)
— Perfluorooctanoic acid (PFOA)
— Perfluorononanoic acid (PFNA)
— Perfluorodecanoic acid (PFDA)
— Perfluoroundecanoic acid (PFUnDA)
— Perfluorododecanoic acid (PFDoDA)
— Perfluorotridecanoic acid (PFTrDA)
— Perfluorobutane sulfonic acid (PFBS)
— Perfluoropentane sulfonic acid (PFPS)
— Perfluorohexane sulfonic acid (PFHxS)
— Perfluoroheptane sulfonic acid (PFHpS)
— Perfluorooctane sulfonic acid (PFOS)
— Perfluorononane sulfonic acid (PFNS)
— Perfluorodecane sulfonic acid (PFDS)
— Perfluoroundecane sulfonic acid
— Perfluorododecane sulfonic acid
— Perfluorotridecane sulfonic acid

US EPA Proposed Maximum Contaminant Limits

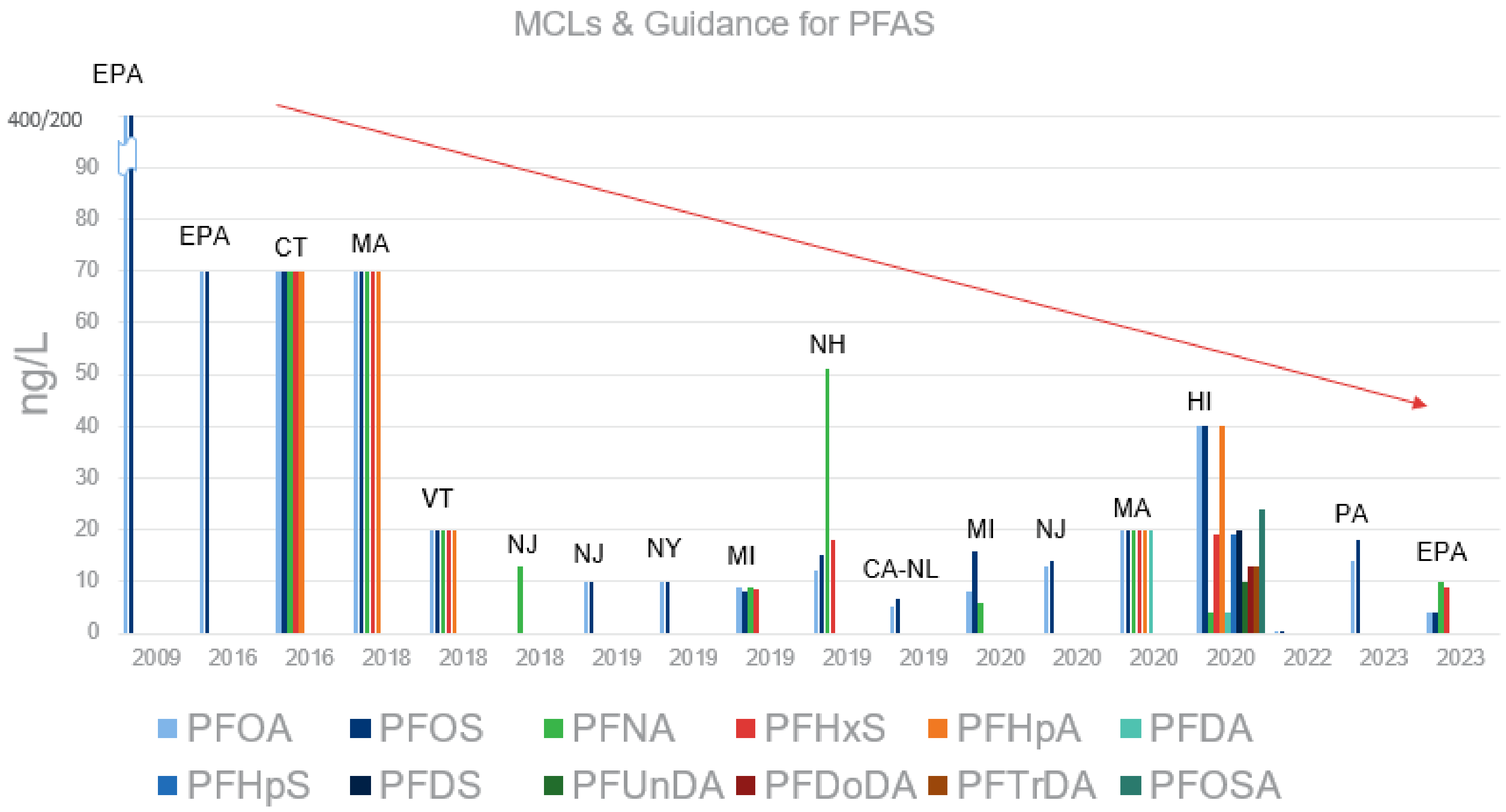
March 14, 2023

PFAS	Effective Limit
PFOA	4.0 ppt absolute
PFOS	4.0 ppt absolute
PFNA	9 ppt per Hazard Index
PFHxS	10 ppt per Hazard Index
PFBS	2000 ppt per Hazard Index
HFPO-DA (GenX)	10 ppt per Hazard Index

Equation

$$\text{Hazard Index} = \left(\frac{[\text{GenX}_{\text{water}}]}{[10\ \text{ppt}]}\right) + \left(\frac{[\text{PFBS}_{\text{water}}]}{[2000\ \text{ppt}]}\right) + \left(\frac{[\text{PFNA}_{\text{water}}]}{[10\ \text{ppt}]}\right) + \left(\frac{[\text{PFHxS}_{\text{water}}]}{[9.0\ \text{ppt}]}\right)$$

MCLs and Health Advisories over Time in USA



Trend: If you can detect it, you need to treat it.

Accurate as of 4/26/23

EPA Region 9 and Hawaii Dept of Health: PFAS Toxicity vs Mobility

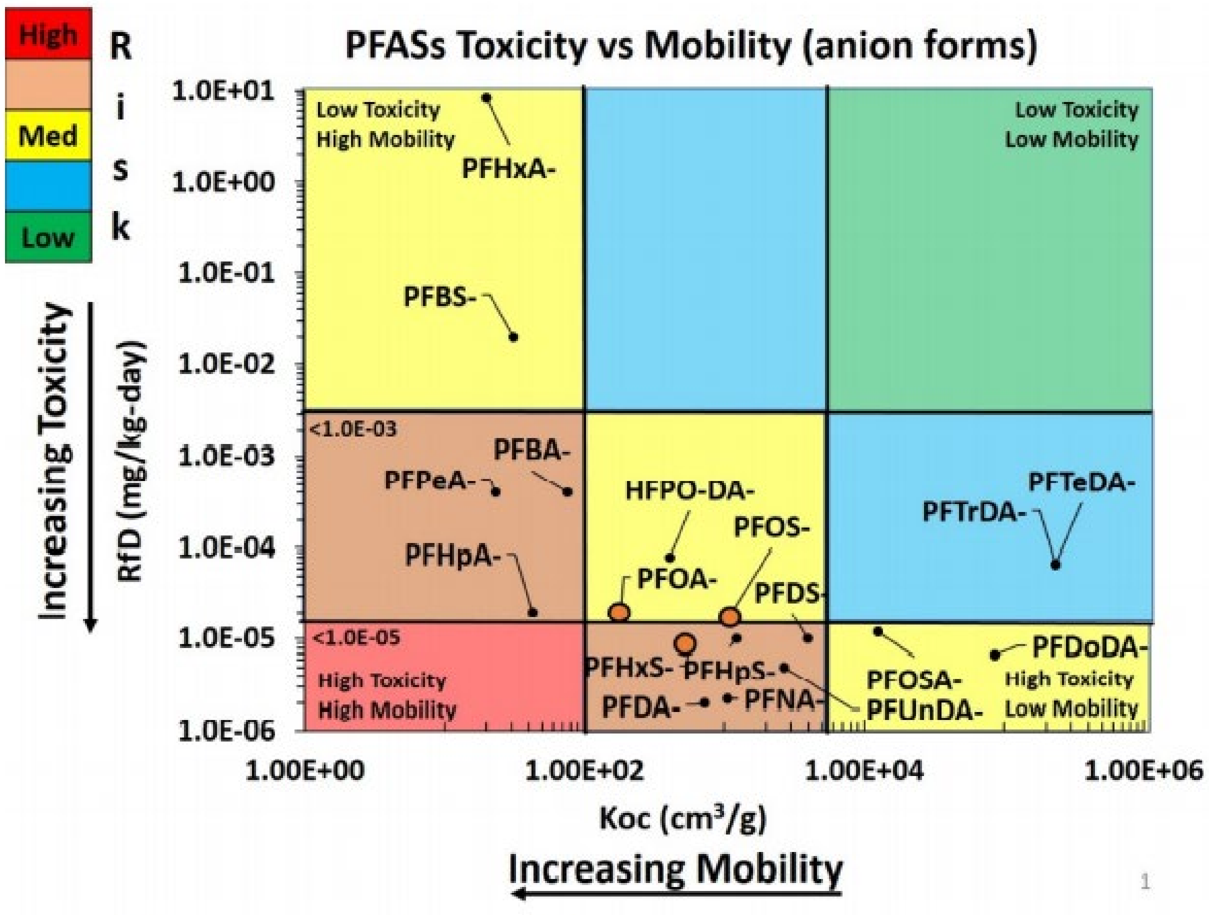


Figure 5. Comparison of PFASs mobility versus toxicity.

25 (HIDOH December 2020)

Pollutant Discharge

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF WATER

Recommendations from the PFAS NPDES Regional Coordinators Committee

Interim Strategy for Per- and Polyfluoroalkyl Substances in Federally Issued National Pollutant Discharge Elimination System Permits

Workgroup Recommendations:

1) **Include permit requirements for phased-in monitoring and best management practices, as appropriate, taking into consideration when PFAS are expected to be present in point source wastewater discharges.**

2) **Include permit requirements for phased-in monitoring and stormwater pollutant control, as appropriate, taking into consideration when PFAS are expected to be present in stormwater discharges.**

PFAS Treatment Options

Capture

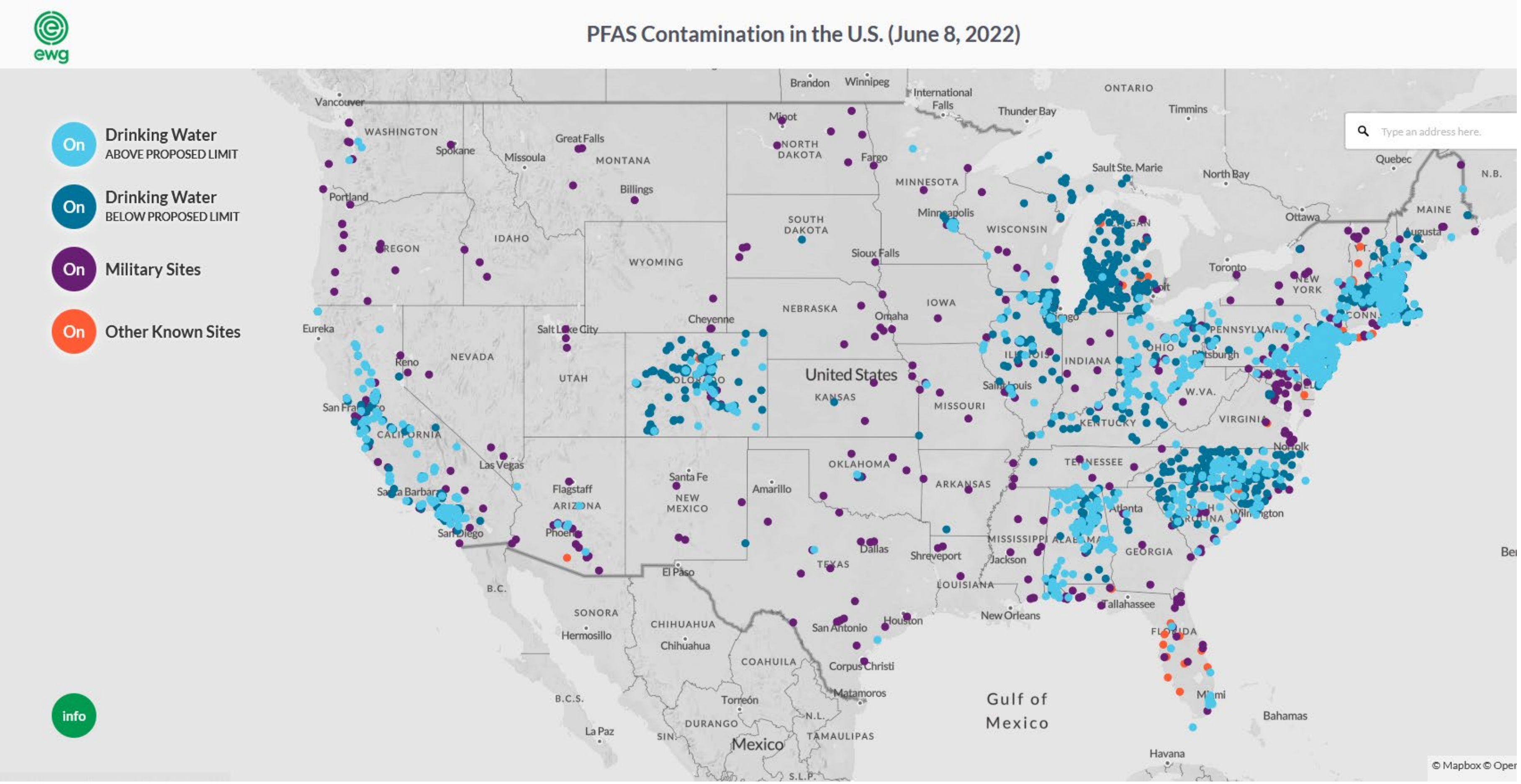
- Bulk removal of high concentrations
  - Part per million levels
  - Military bases, airports
- Trace removal – most drinking water
  - Part per trillion, part per billion levels

Destroy

- Incineration
- Other high energy technologies

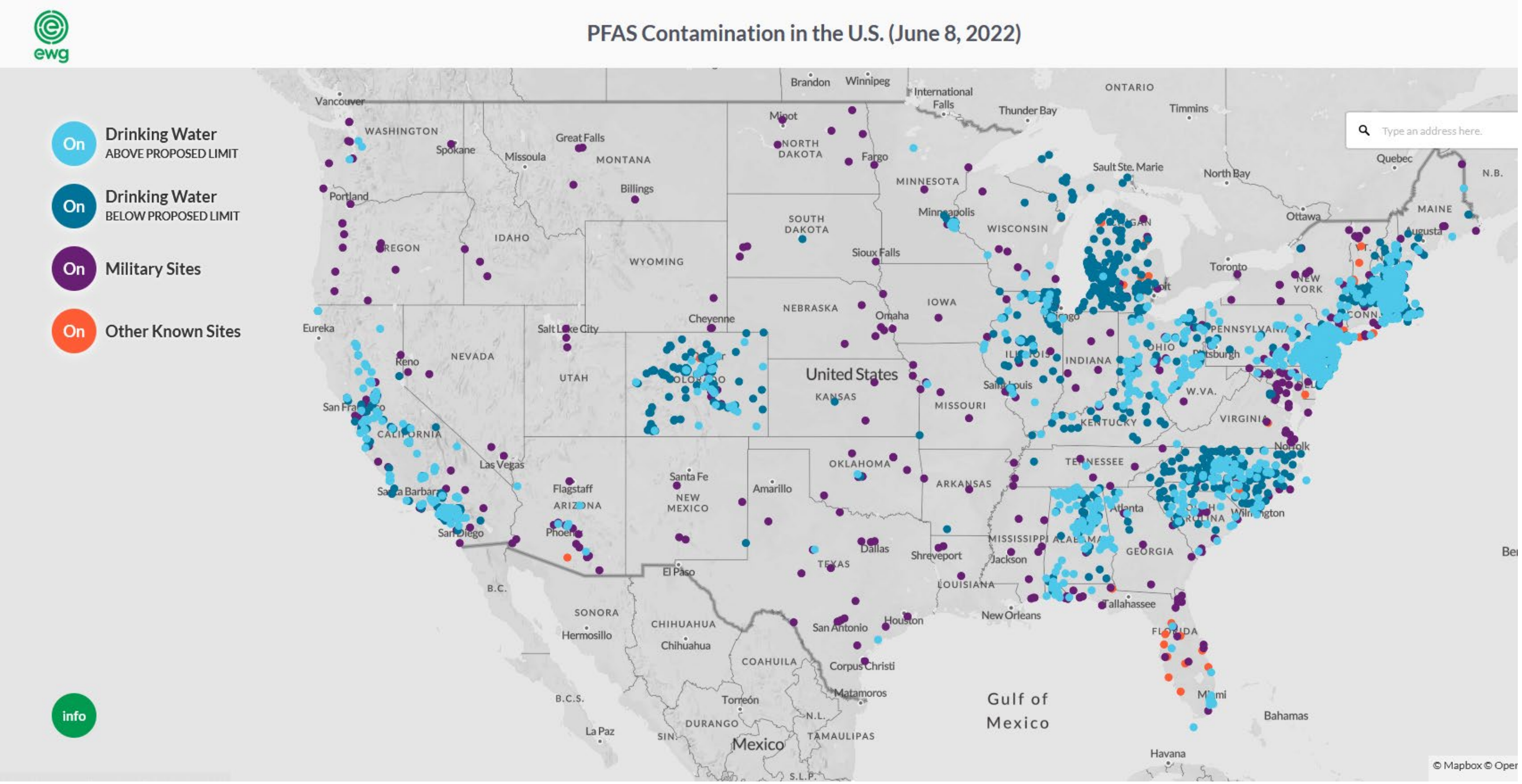
Often used in combination

Where are PFAS Found in US?



Source: https://www.ewg.org/interactive-maps/pfas_contamination/map/

Where are PFAS Found in US?
Where they have tested!



Source: https://www.ewg.org/interactive-maps/pfas_contamination/map/

PFAS Treatment Options

Capture

- Bulk removal of high concentrations
  - Part per million levels
  - Military bases, airports
- Trace removal – most drinking water
  - Part per trillion, part per billion levels

In the US, 80 to 90% of PFAS treatment applications are drinking water

Destroy

- Incineration
- Other high energy technologies

Often used in combination

US EPA "Best Available Technologies" for PFAS Treatment


Carbon Adsorption


Single-Use Resin

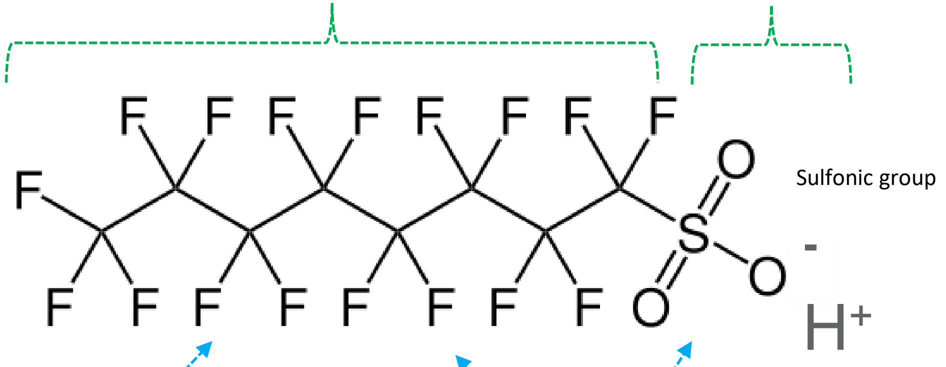

Membrane Filtration

Source: https://www.epa.gov/research-states/pfas-treatment-drinking-water-and-wastewater-state-science

PFOS: Perfluorooctane Sulfonic Acid

PFOS – Perfluoro octane Sulfonic Acid

Hydrophobic "Tail" Ionized "Head"



GAC
removes by adsorption
using hydrophobic "Tail"

PFAS - Selective IX Resins
removes by both ion exchange
and adsorption using both
"Head" & "Tail"

GAC Mechanism

- Van Der Waals forces
- Takes contact time
- One of the weakest chemical reactions

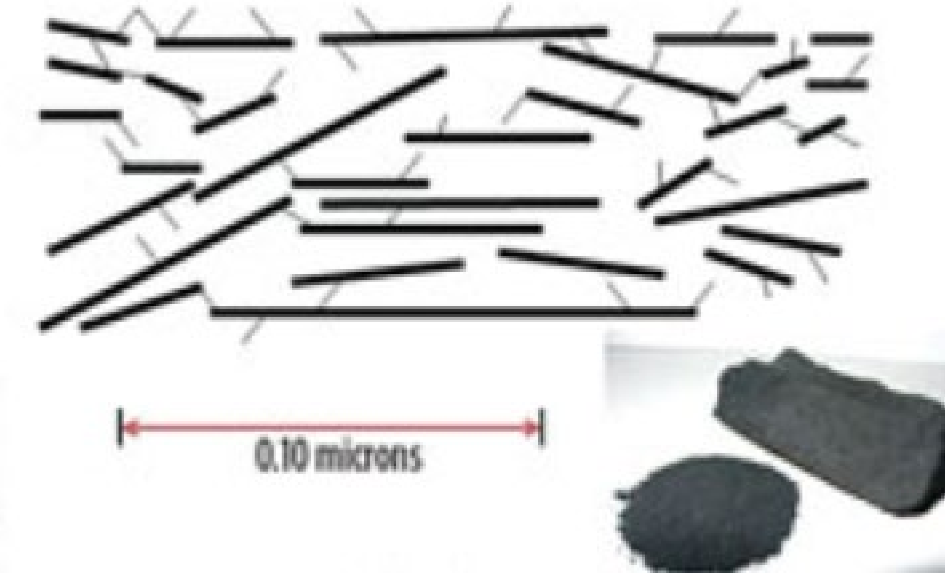
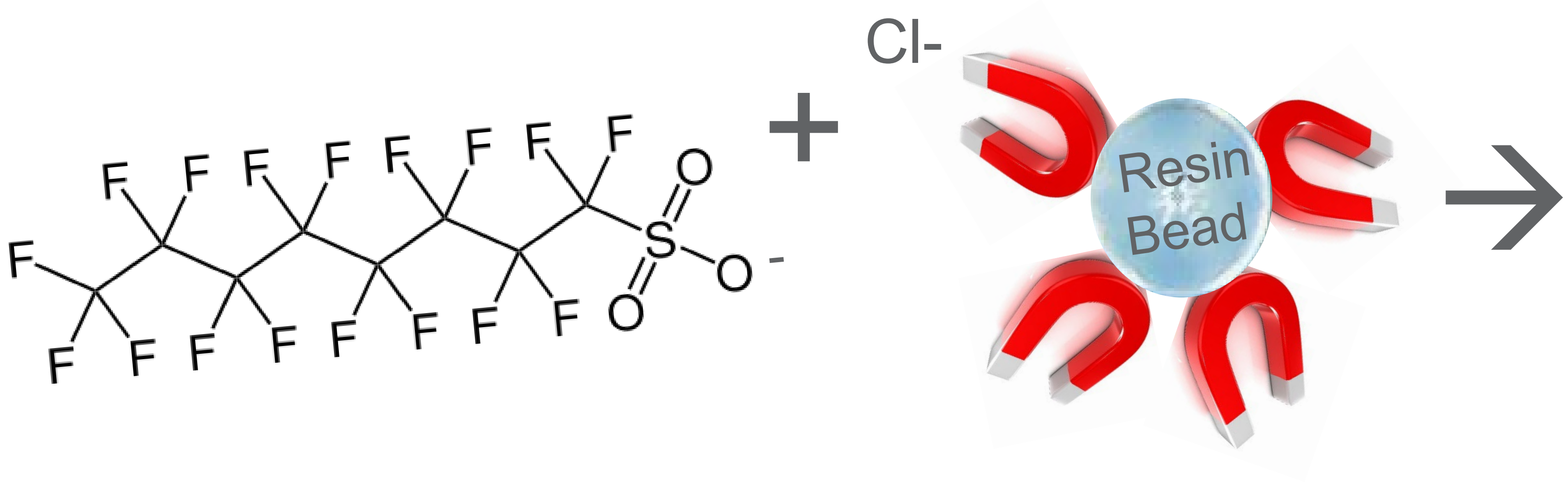


Photo Source: http://www.gasprocessingnews.com/features/201608/manage-activated-carbon-effects-on-mdea-solution-foaming.aspx

Ion Exchange – Fast Attraction Reaction



Harmless salt

Ion exchange reaction is very fast and strong

PFAS Treatment Single Use Resin

- Breakthrough is dependent on water quality, and can achieve more than 99.99% removal to non-detect (< 2 ppt)
- Effective on short *and* long chain PFAS
- Long treatment life
- PFAS capacity depends heavily on competing anions in the water
  - SO_4, NO_3, HCO_3, Cl, TOC
- Offer potable, industrial, and buffered resin grades

Purofine® PFA694E

Polystyrenic Gel, Potable Water Grade

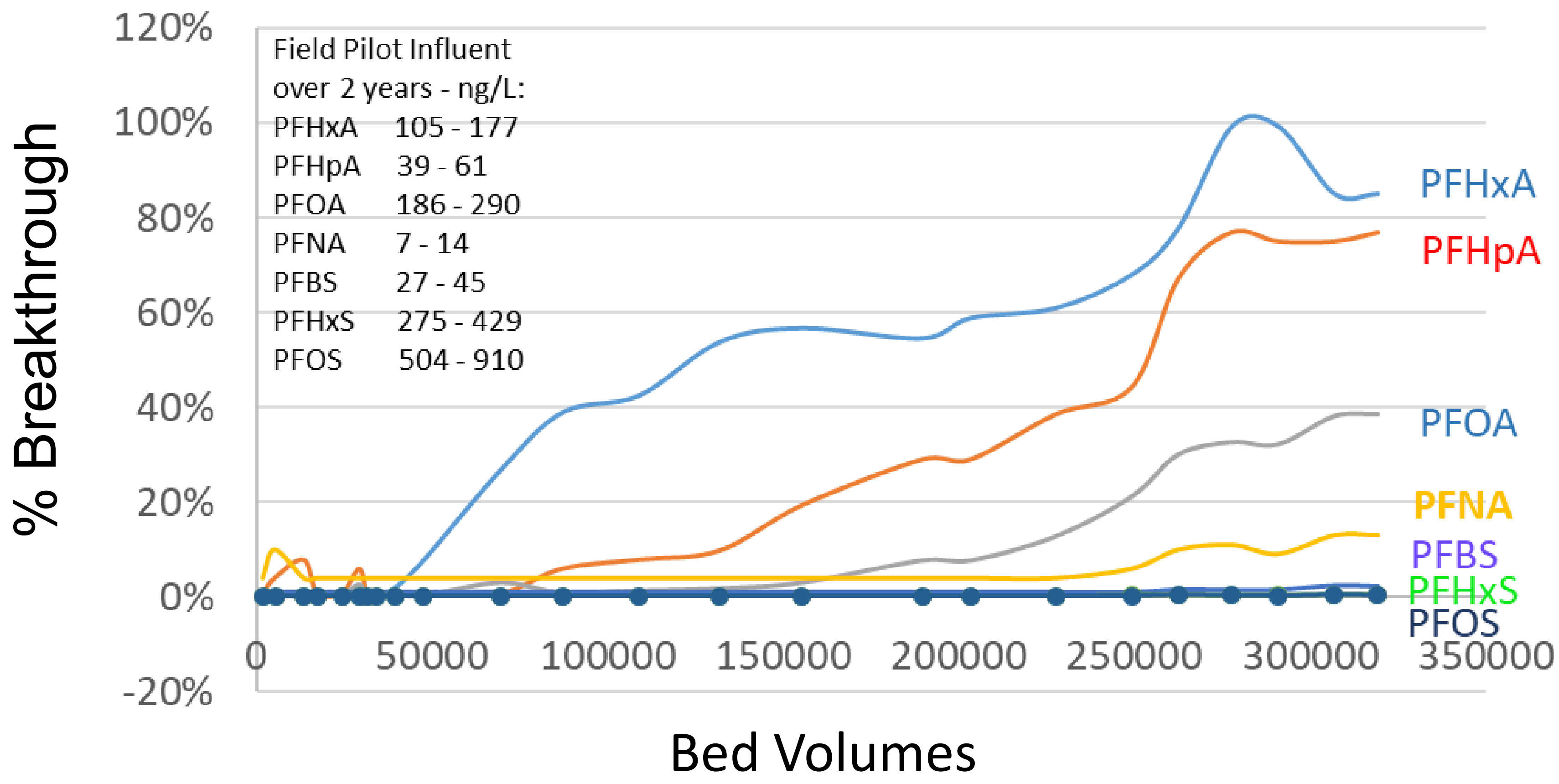
PFAS Selective Resin Performance

- Sulfonic acids are removed more easily than carboxylic acids
- Longer chains are removed more easily than shorter chains
- On the right is an approximation of selectivity

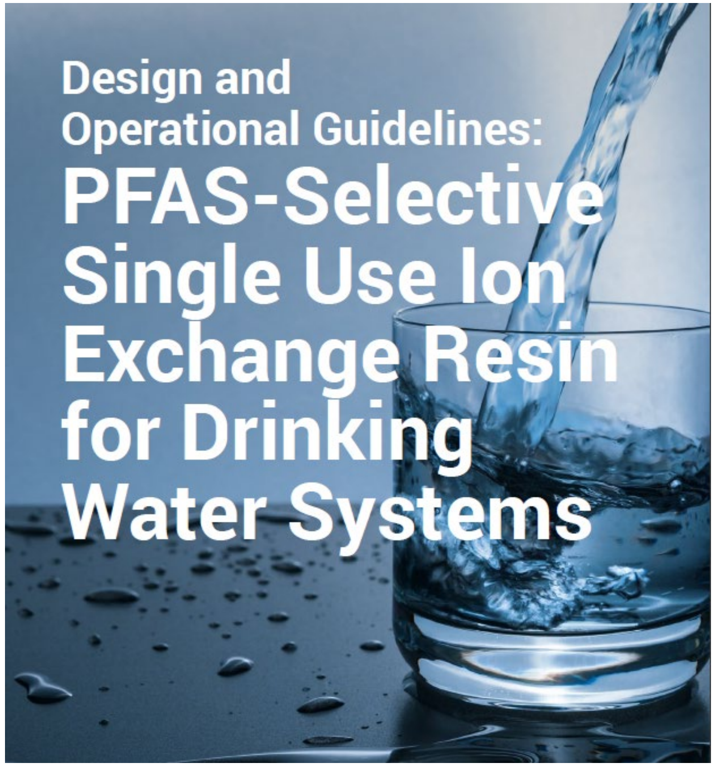
PFTrDS
PFDoDS
PFUnDS
PFDS
PFNS
PFOS
PFHpS
PFHxS
PFPS
PFBS
PFTrDA
PFDoDA
PFUnDA
PFDA
PFNA
PFOA
ADONA
GenX
PFHpA
ClO4
PFHxA
PFPA
PFBA
NO3
SO4
Cl
HCO3
F

Order of PFAS Breakthrough

PFHxA < PFHpA < PFOA < PFNA < PFBS < PFHxS < PFOS

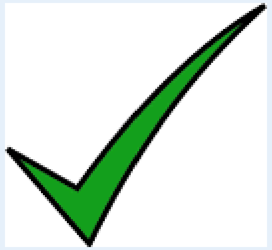


Design and Operational Guidelines



Vessel Parameter	Design Goal
Linear Velocity (LV)	15 to 45 m/h
Bed Depth for LV <= 30 m/h	0.91m minimum
Bed Depth for LV > 30 m/h	3.7 ft (1.1 m) minimum
Specific Flowrate	8 to 40 BV/h
Empty Bed Contact Time (EBCT)	2 min for drinking water 3 min for higher concentrations

Pretreatment

Harmful Parameters:	**Pretreatment may be needed for RO / NF or GAC or IX**
Suspended Solids	
TOC	
Oxidants	
Oil & Grease	
Iron/manganese	
Scaling compounds	
Microbes	

Start with Water Quality

- Critical parameters in blue
- If not provided, assumed ND in green
- Endpoint criteria key

Parameter	Units
Operational Flow Rate	gpm
Operational Schedule	hour/day
Daily Volume (average)	Gallons
Sulfate	mg/L
Nitrate	mg/L
Alkalinity (as $CaCO_3$)	mg/L
Chloride	mg/L
Fluoride	mg/L
Perchlorate	ppb
Arsenic	ppb
Hexavalent chromium	ppb
Uranium	ppb
Calcium	mg/L
Magnesium	mg/L
Sodium	mg/L
Potassium	mg/L
Iron	ug/L
Manganese	ug/L
pH	
TDS	mg/L

Parameter	Abrv.	Units
Suspended Solids		mg/L
Oil & Grease		mg/L
Total Organic Carbon		mg/L
Perfluorobutanoic acid	PFBA	ppt
Perfluoropentanoic acid	PFPeA	ppt
Perfluorohexanoic acid	PFHxA	ppt
Perfluoroheptanoic acid	PFHpA	ppt
Perfluorooctanoic acid	PFOA	ppt
Perfluorononanoic acid	PFNA	ppt
Perfluorododecanoic acid	PFDoDA	ppt
Perfluorotetradecanoic acid	PFTeA	ppt
Perfluorobutanesulfonic acid	PFBS	ppt
Perfluorohexanesulfonic acid	PFHxS	ppt
Perfluoroheptanesulfonic acid	PFHpS	ppt
Perfluorooctanesulfonic acid	PFOS	ppt
4:2 FTS (fluorotelomer sulfonate)	4:2 FTS	ppt
6:2 FTS (fluorotelomer sulfonate)	6:2 FTS	ppt
8:2 FTS (fluorotelomer sulfonate)	8:2 FTS	ppt
GenX	GenX	ppt
VOC	VOC	ppb

How do you pick your technology?

Life Cycle Costs

- Capital/ Footprint

- Operational
  - Water Quality
  - Removal Efficiency
  - Bed Life
  - Waste Generation

Treatment Options – Reverse Osmosis

- High capital for pretreatment and electrical connections
- 97 to 98% removal rate of everything
  - Advantage – reduces all contamination
  - Disadvantage – all minerals are also removed. Water is corrosive (~12 µS) and needs to be re-mineralized.
- RO requires significant pretreatment – typically anti-scalent, pH adjust, TSS filtration
- If a membrane fails, no easy way to tell. Lose "belt and suspenders." No online PFAS instrumentation.
- Bacteria can blind, so may need to chlorinate, dechlorinate, treat, and re-chlorinate
- Only captures – does not destroy PFAS
- 15-25% reject stream that needs to be discharged or treated.
- Can be complex to operate

OPEX can be $800 to $1500 per acre foot – not including disposal of waste.

High recovery dependent on TDS levels

Purolite
An Ecolab Company

Treatment Options – Reverse Osmosis

- High capital for pretreatment and electrical con ctions
- 97 to 98% removal rate of everything
  - Advantage – reduces all contamina
  - Disadvantage – all minerals are als mo d. Water is corrosive (~12 µS) and needs to be alized.
- RO requires significant pretreatment – typic lent, pH adjust, TSS filtration
- If a membrane fails, no easy way to tell. se " lt a suspenders." No online PFAS instrume n.
- Bacteria can blind, so may need to chlori ate, treat, and re-chlorinate
- Only captures – does not destroy PFAS
- 15-25% reject stream that needs to be discharged or treated.
- Can be complex to operate

OPEX can be $800 to $1500 per acre foot – not including disposal of waste.

High recovery dependent on TDS levels

PFAS Selective Single-Use Ion Exchange Resin or GAC System: 3500mm Diameter, Lead / Lag Configuration

PFAS in water →  → PFAS – free water

PFAS loaded media

Disposal

IX: EBCT ~ 2 minutes, max flow ~ 475m^3/h
GAC: EBCT ~ 10 minutes, max flow ~ 95m^3/h

Drinking Water Design Example: IX vs GAC

	Units	PFA694E Resin	GAC
Flow Rate	m^3/h	475	475
Vessel Diameter	mm	3500	3500
Number of Trains		1	5
Flow per Train	m^3/h	475	95
Total number of vessels onsite (lead+lag)		2	10
Media Volume per vessel	m^3	15.5	17.0
BV /hour		31	6
EBCT	min	2.0	10.7
Estimated throughput for lead vessel change out trigger	BV	280.000	35.000
Days between exchanges	days	381	261
Water treated per run	m^3	4.340.000	2.975.000
Change outs per year		1.0	1.4
Volume of Media consumed per year	m^3	14.9	118.9

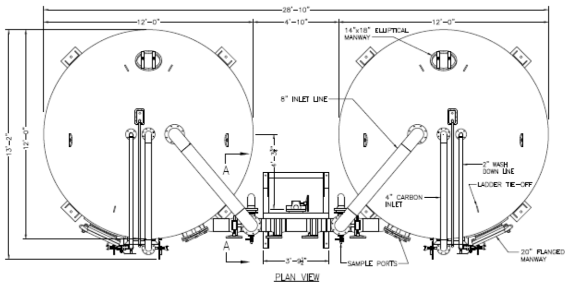
Drinking Water Design Example

	Units	PFA694E Resin	GAC	
Flow Rate	m^3/h	475	475	
Vessel Diameter	mm	3500	3500	
Number of Trains		1	5	5 x more equipment
Flow per Train	m^3/h	475	95	
Total number of vessels onsite (lead+lag)		2	10	
Media Volume per vessel	m^3	15.5	17.0	
BV /hour		31	6	
EBCT	min	2.0	10.7	
Estimated throughput for lead vessel change out trigger	BV	280.000	35.000	
Days between exchanges	days	381	261	
Water treated per run	m^3	4.340.000	2.975.000	
Change outs per year		1.0	1.4	
Volume of Media consumed per year	m^3	14.9	118.9	

Drinking Water Design Example

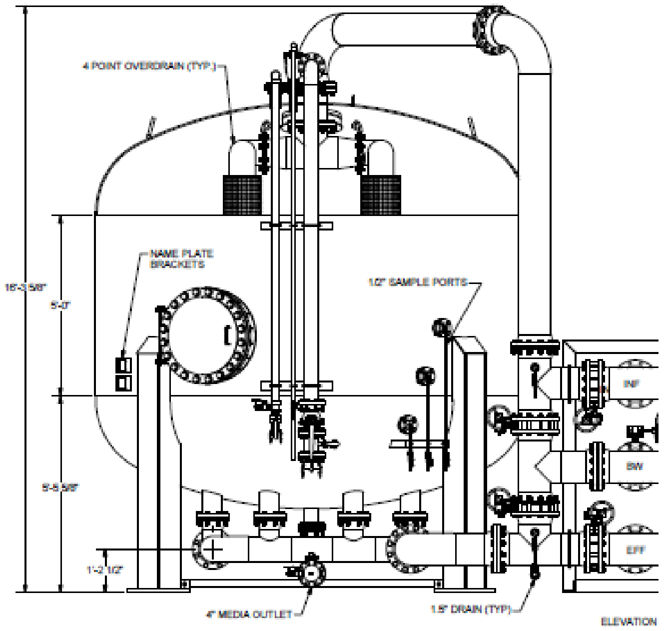
	Units	PFA694E Resin	GAC	
Flow Rate	m^3/h	475	475	
Vessel Diameter	mm	3500	3500	
Number of Trains		1	5	
Flow per Train	m^3/h	475	95	
Total number of vessels onsite (lead+lag)		2	10	
Media Volume per vessel	m^3	15.5	17.0	
BV /hour		31	6	
EBCT	min	2.0	10.7	
Estimated throughput for lead vessel change out trigger	BV	280.000	35.000	
Days between exchanges	days	381	261	
Water treated per run	m^3	4.340.000	2.975.000	
Change outs per year		1.0	1.4	
Volume of Media consumed per year	m^3	14.9	118.9	8 x more media consumed

475 m^3/h Footprint: IX Resin with High Flow Vessels



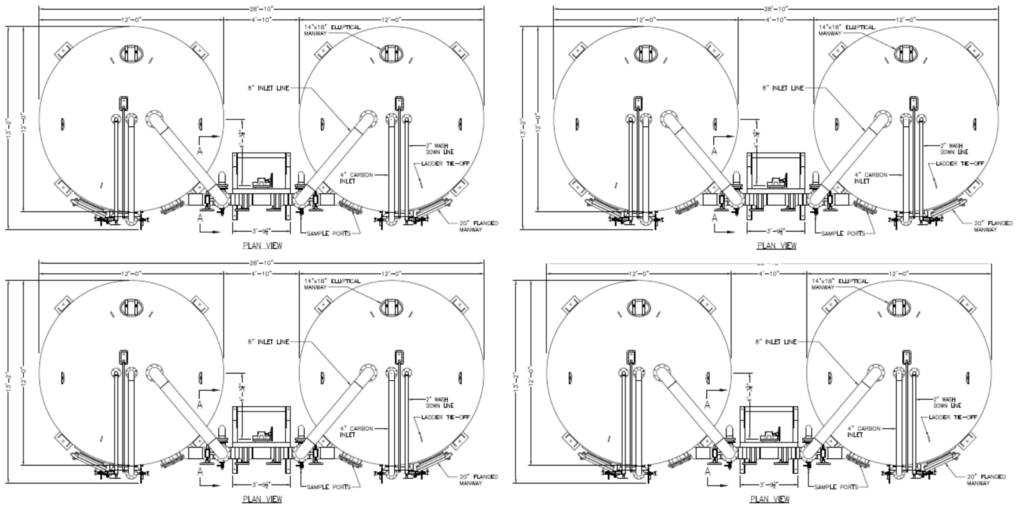
1 Systems

- 3500 mm Diameter
- Height 4950 mm
- 15.5 m^3 per vessel
- 2 min EBCT

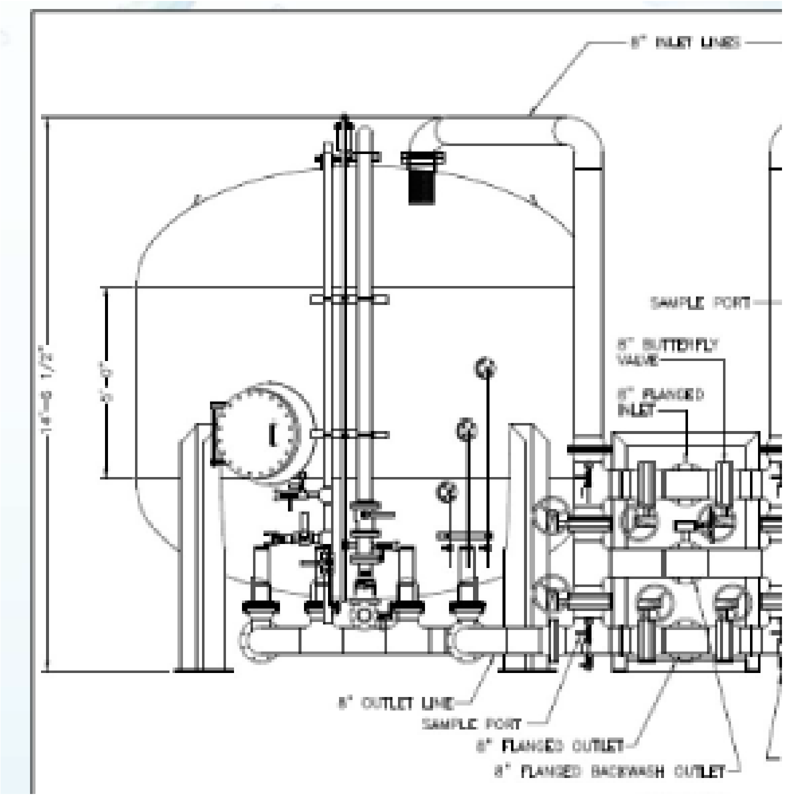


Drawings complements of Aqueous Vets

Option 1) 475 m^3/hr Footprint: GAC “20,000 pounders”

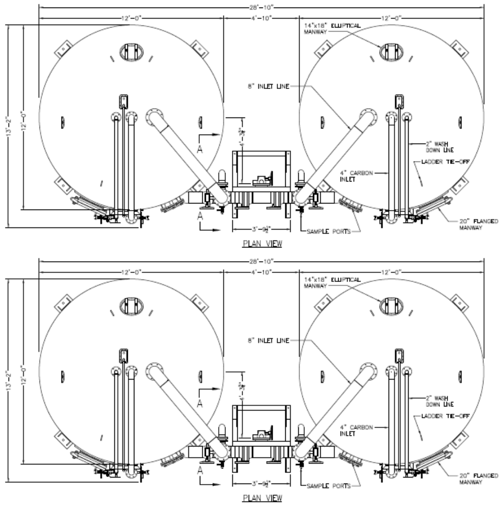


4 Systems
- 3500 mm Diameter
- Height 4450 mm
- 17 m^3 per vessel
- 10.7 min EBCT



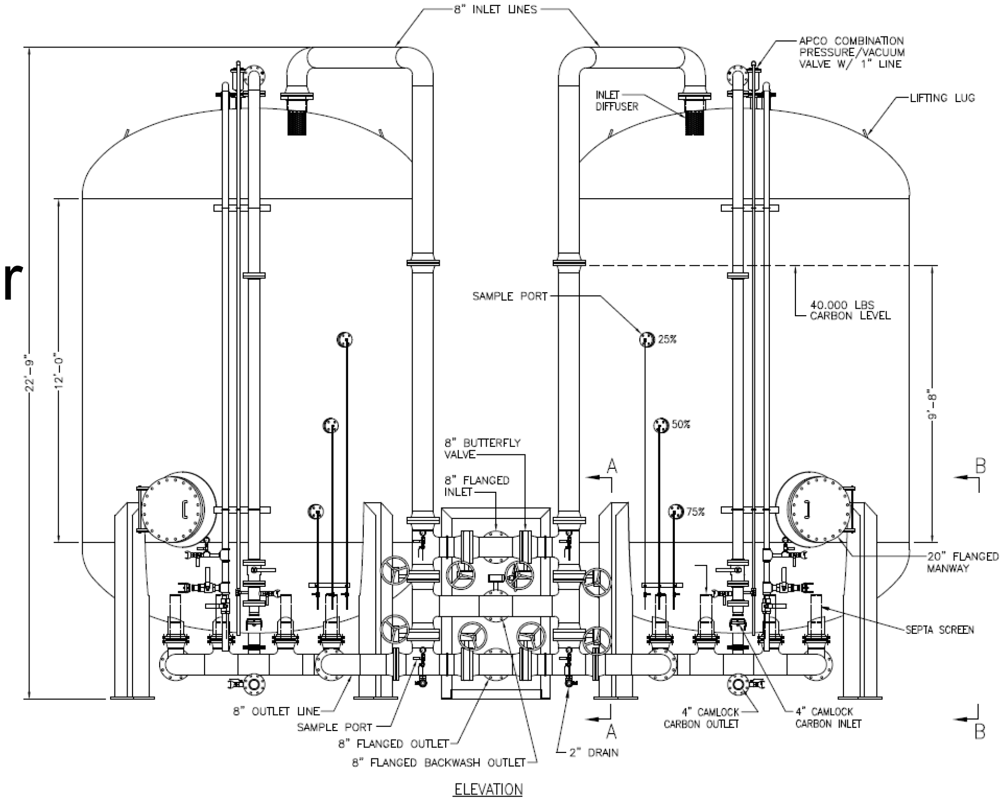
GAC capital cost is ~ four times IX

Option 2) 475 m^3/h Footprint: GAC “40,000 pounders”



2 Systems

- 3500 mm Diameter
- Height 6900 mm
- 34m^3 per vessel
- 8.9 min EBCT



GAC capital is > 2 times IX

Drinking Water Design Example

	Units	PFA694E Resin	GAC	
Flow Rate	m^3/h	475	475	
Vessel Diameter	mm	3500	3500	
Number of Trains		1	5	
Flow per Train	m^3/h	475	95	
Total number of vessels onsite (lead+lag)		2	10	
Media Volume per vessel	m^3	15.5	34	
BV /hour		31	3	
EBCT	min	2.0	21.5	
Estimated throughput for lead vessel change out trigger	BV	280.000	35.000	
Days between exchanges	days	381	522	
Water treated per run	m^3	4.340.000	5.950.000	
Change outs per year		1.0	0.7	
Volume of Media consumed per year	m^3	14.9	118.9	8 x more media consumed

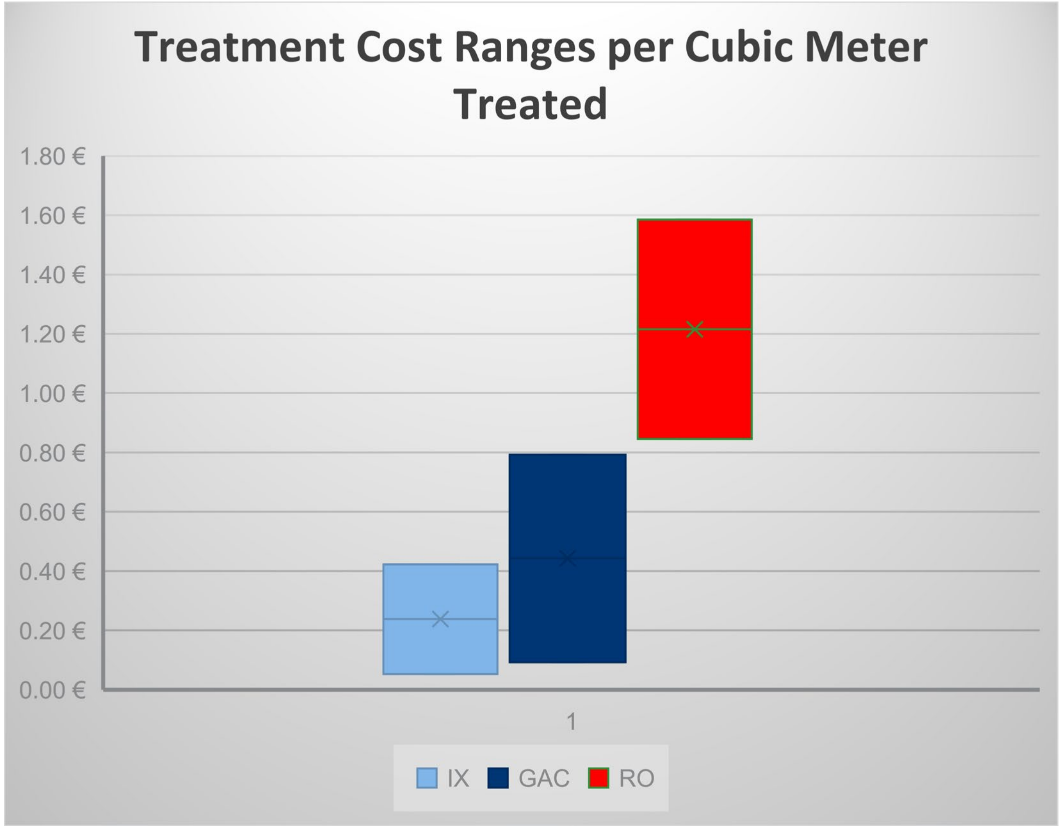
Operational Costs: Budgetary Estimation

Parameter	Resin	GAC
Volume of media consumed per year, m3	14.9	118.9
Media price per liter	€ 14	€ 4.75
Cost of treatment, euro per 1000 x m3	€ 201.15	€ 564.78
Ion Exchange Savings	>50%	

How do you pick your technology: Operational Cost

Relative Treatment Costs

- IX: 0.05€ to 0.42€ per m3
- GAC: 0.09€ to 1.06€ per m3
- RO: 0.85€ to 1.59€ per m3



How do you pick your technology: Water Quality

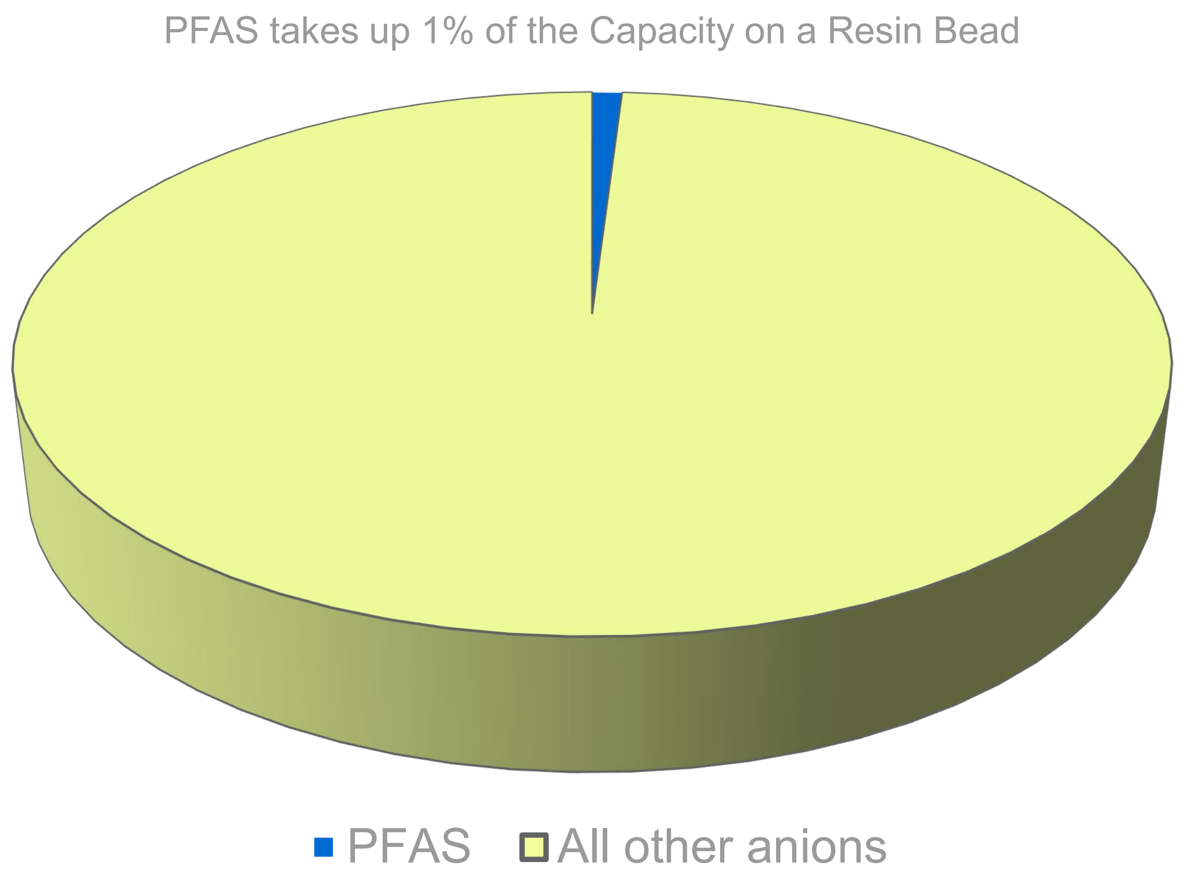
Background WQ will help determine operational treatment costs

Modeling, piloting will confirm

Description	Units
Operational Flow Rate	gpm
Operational Schedule	hour/day
Daily Volume (average)	Gallons
Sulfate	mg/L
Nitrate (as N)	mg/L as N
Nitrate (as NO3)	mg/L as NO3
Alkalinity (as $CaCO_3$)	mg/L
Chloride	mg/L
Fluoride	mg/L
Perchlorate	ppb
Arsenic	ppb
Hexavalent chromium	ppb
Uranium	ppb
Calcium (as $CaCO_3$)	mg/L
Magnesium (as $CaCO_3$)	mg/L
Sodium	mg/L
Potassium	mg/L
Iron	mg/L
Manganese	mg/L

pH		
ORP		
TDS		mg/L
Suspended Solids		mg/L
Oil & Grease		mg/L
Total Organic Carbon	TOC	mg/L
Perfluorobutanoic acid	PFBA	ng/L (ppt)
Perfluoropentanoic acid	PFPeA	ng/L (ppt)
Perfluorohexanoic acid	PFHxA	ng/L (ppt)
Perfluoroheptanoic acid	PFHpA	ng/L (ppt)
Perfluorooctanoic acid	PFOA	ng/L (ppt)
Perfluorononanoic acid	PFNA	ng/L (ppt)
Perfluorododecanoic acid	PFDoDA	ng/L (ppt)
Perfluorotetradecanoic acid	PFTeA	ng/L (ppt)
Perfluorobutanesulfonic acid	PFBS	ng/L (ppt)
Perfluorohexanesulfonic acid	PFHxS	ng/L (ppt)
Perfluoroheptanesulfonic acid	PFHpS	ng/L (ppt)
Perfluorooctanesulfonic acid	PFOS	ng/L (ppt)
4:2 FTS (fluorotelomer sulfonate)	4:2 FTS	ng/L (ppt)
6:2 FTS (fluorotelomer sulfonate)	6:2 FTS	ng/L (ppt)
8:2 FTS (fluorotelomer sulfonate)	8:2 FTS	ng/L (ppt)
GenX	GenX	ng/L (ppt)
VOC	VOC	ppb

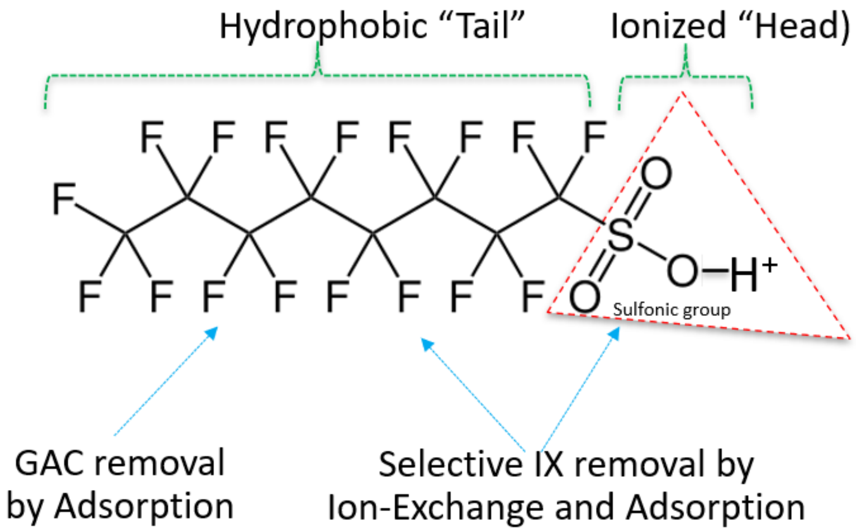
How Selective is Resin for PFAS?



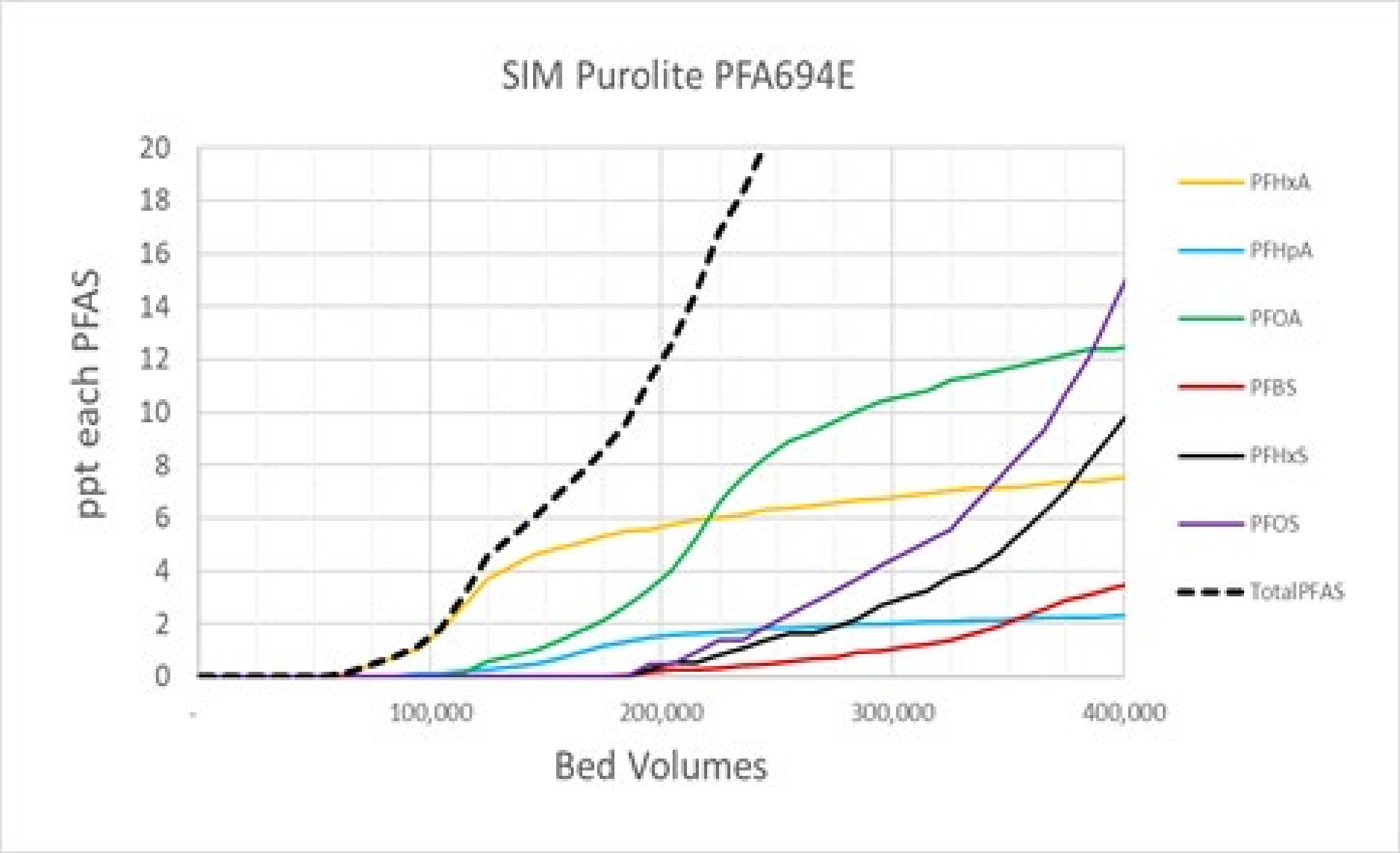
Process of Modeling - Chemistry

- Background anions drive throughput
- Resin selectivity coefficients for contaminants - highly confidential
- We use these factors → effluent breakthrough curves
- We cannot model every one of the thousands of PFAS that exist, but we can model the most studies ones

PFOS



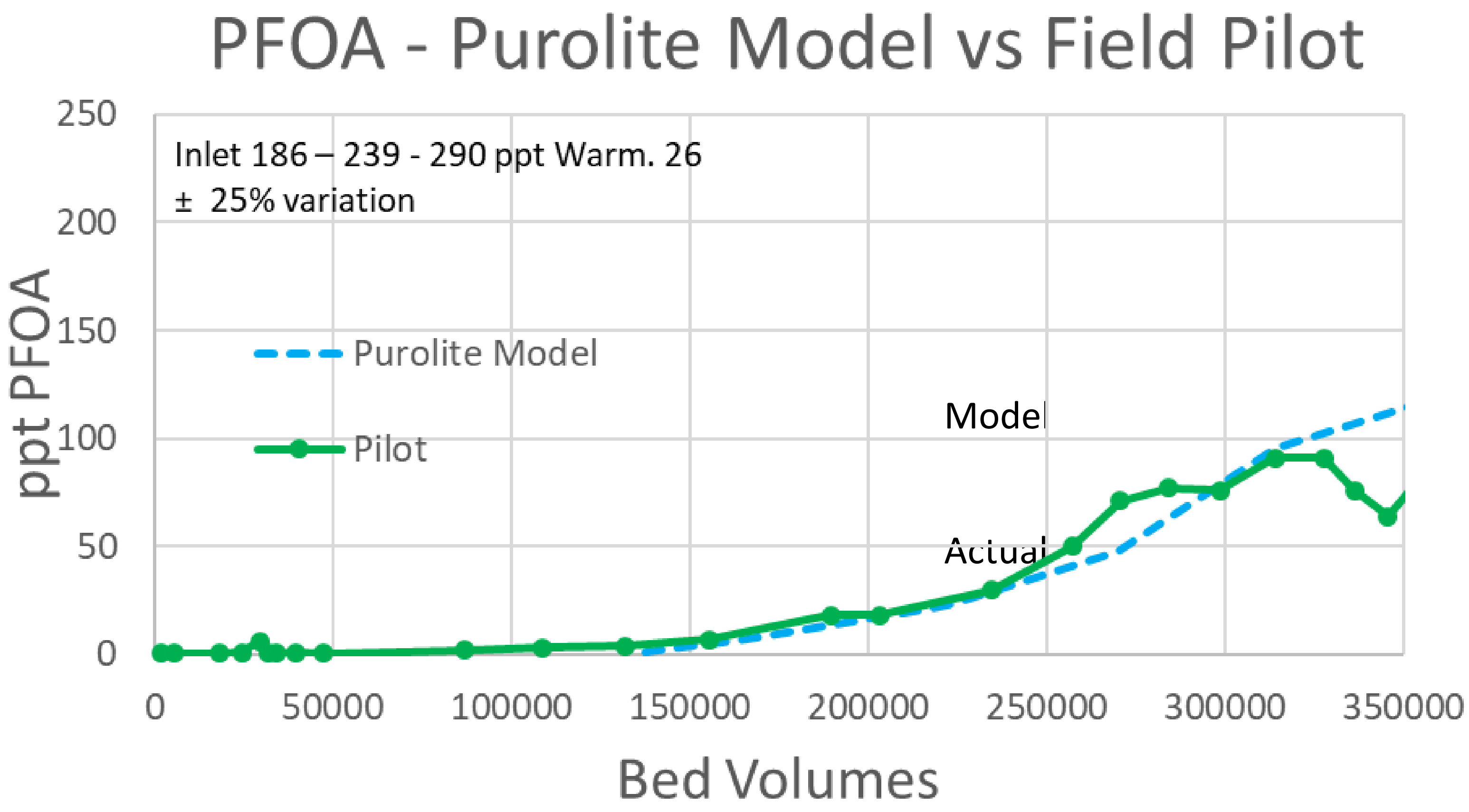
Example of Modeled Throughput Graph



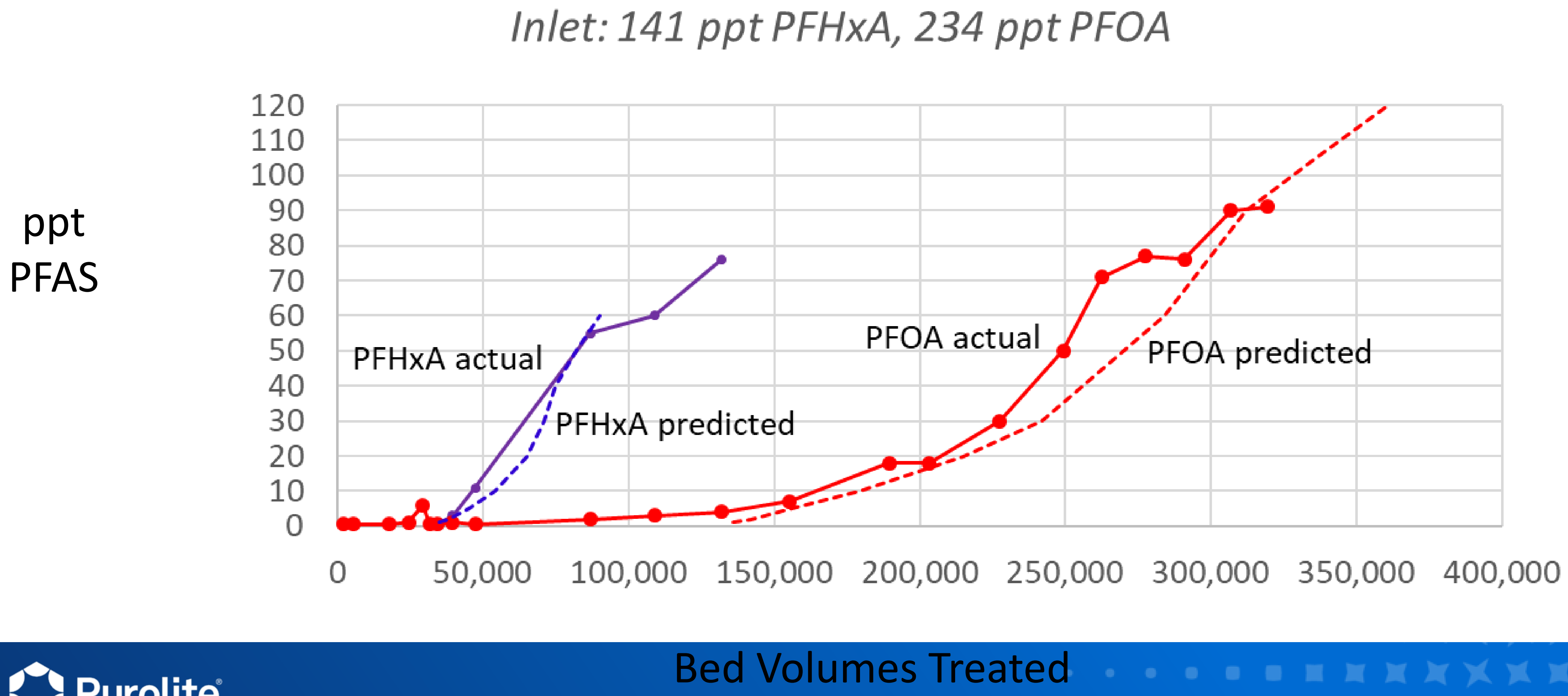
Purolite
An Ecolab Company

Warminster, PA Well 26: Full scale Modeling vs Field IX Pilot for PFOA

Close Tracking of Actual and Modeled Results at Full Scale EBCT

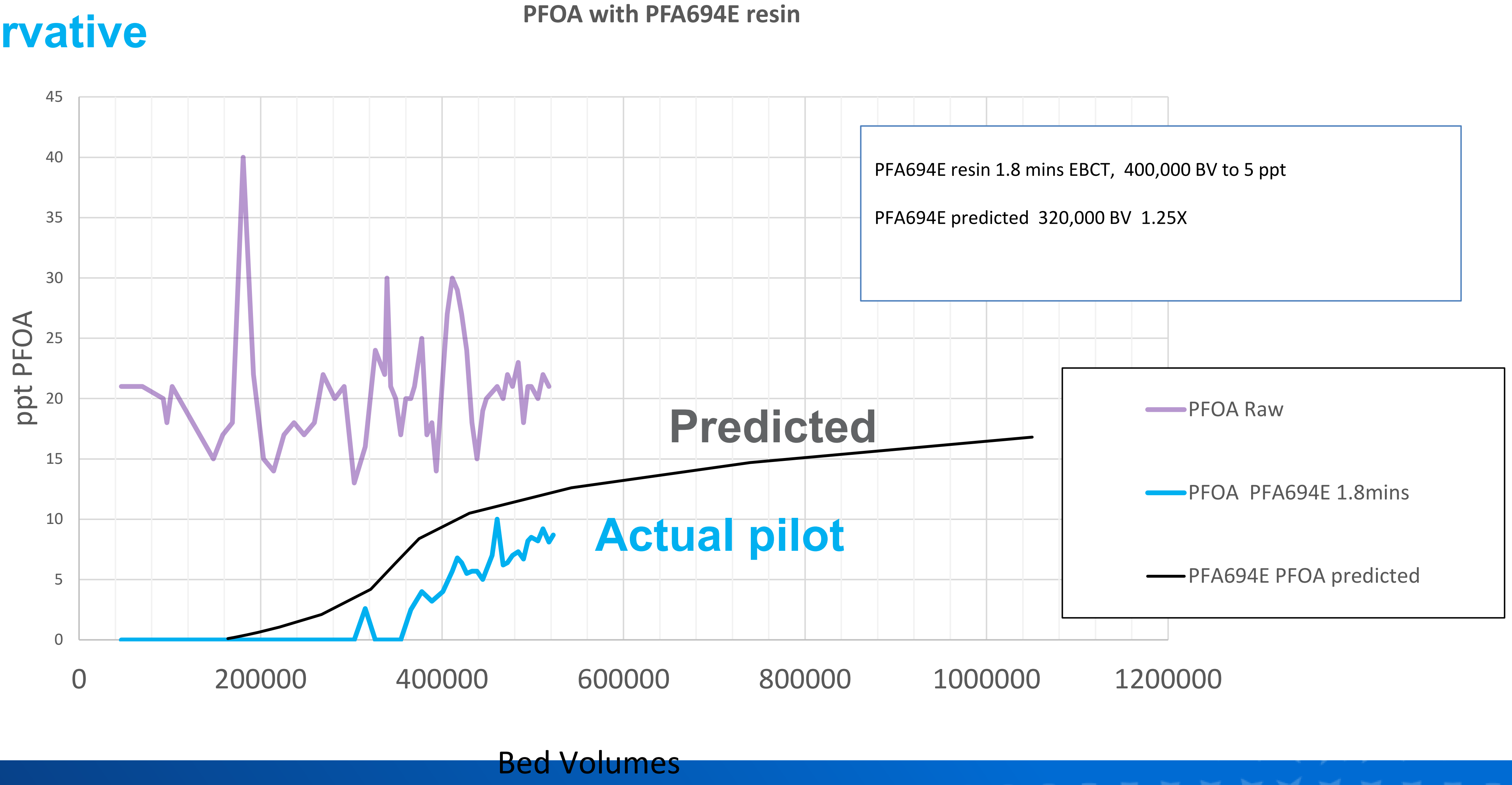


Warminster, PA Well 26: Full Scale Predicted & Actual Result Match Closely

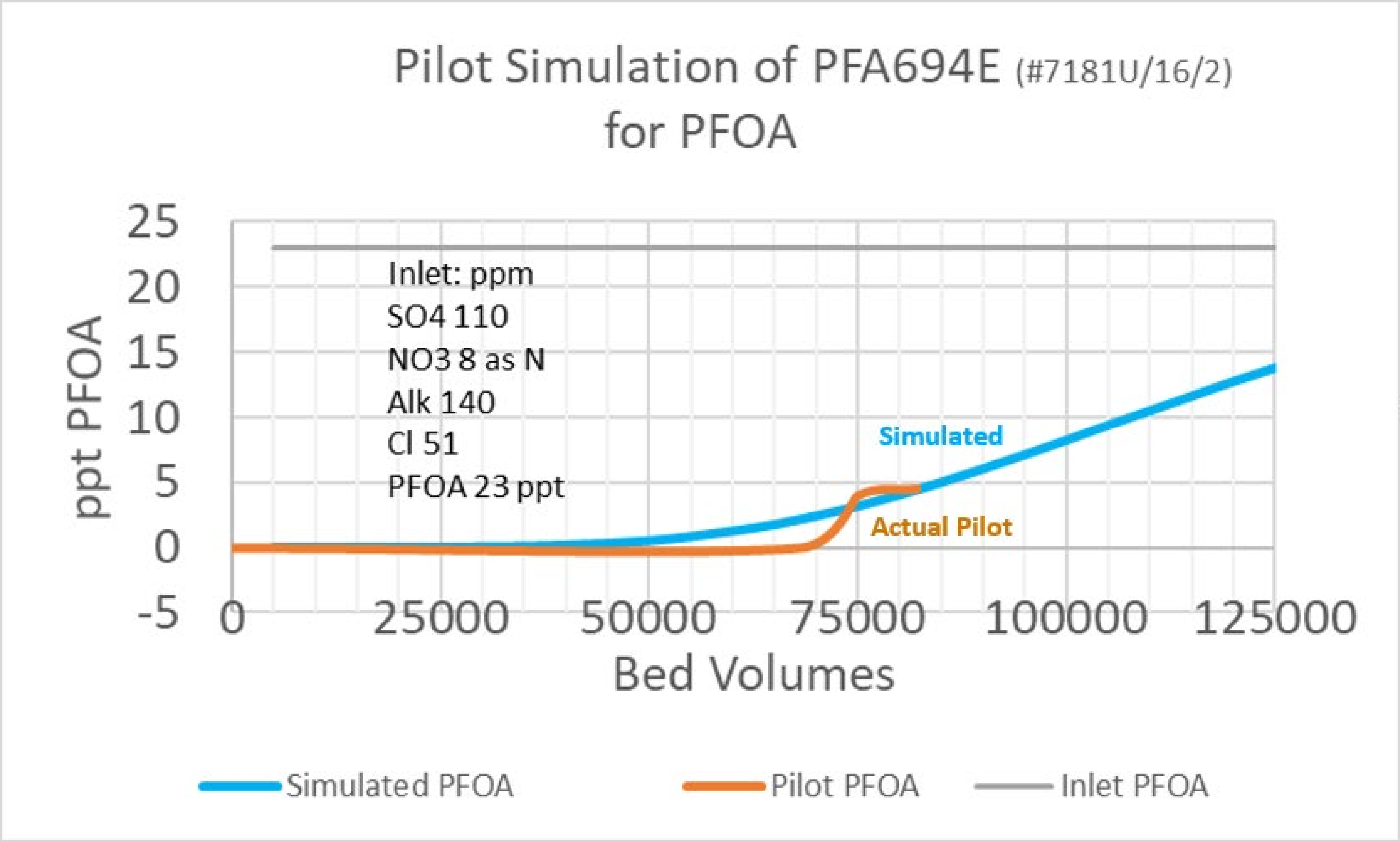


Horsham, PA: Well 10: Full Scale Modeling vs Actual

Conservative



Colorado Pilot PFOA for PFA694E Actual vs Simulated



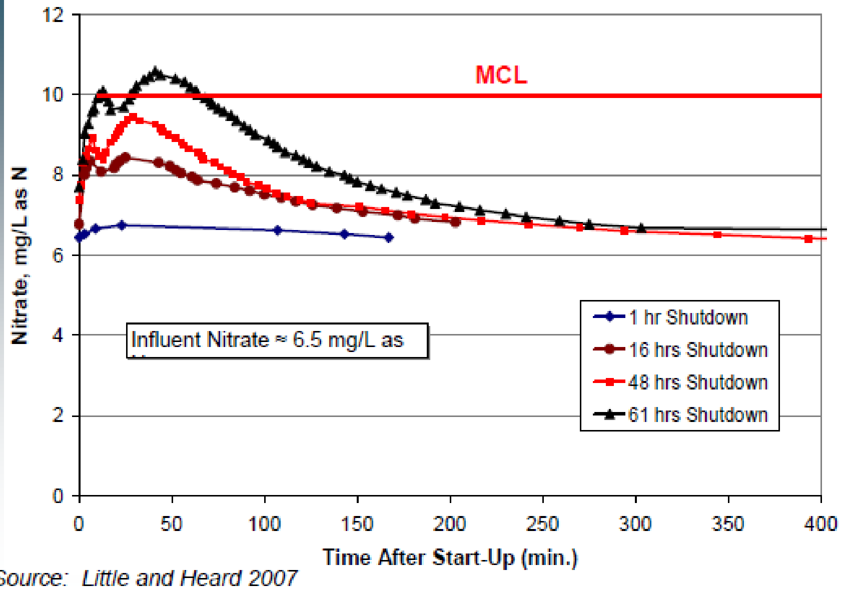
2 min EBCT

How do you pick your technology: Water Quality

GAC can slough contaminants: Nitrate, PFAS, and other TOC

Fresno, California 2002-03

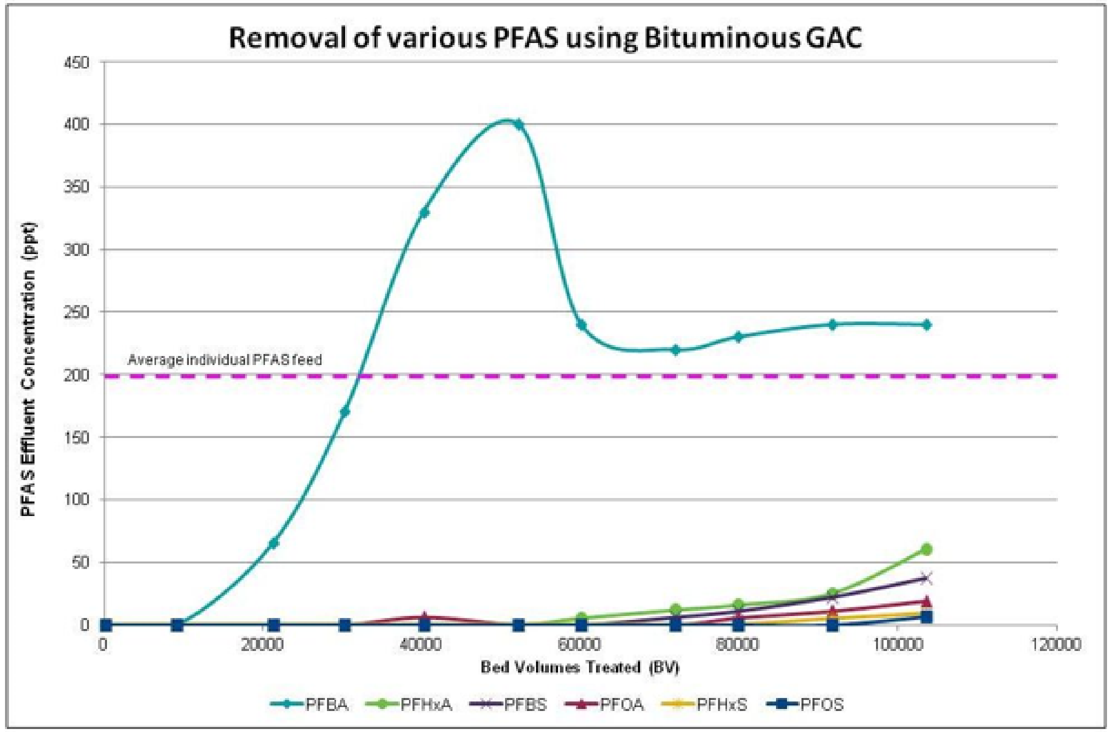
Of 29 treatment sites with GAC, 12 have exhibited nitrate peaking events over the years; peaking studied on well 297



- Nitrate peak occurs within the first two hours after bringing a well back online, regardless of the amount of time the well is offline
- A greater quantity of nitrate is able to desorb from the carbon when the well is left offline for a greater amount of time.

11

Source: Little and Heard 2007



Example GAC Removal Curves at Specific Influent Concentration (15 Minute EBCT).

Source: ITRC PFAS Manual, data provided by Calgon

How do you pick your technology: Water Quality

Coal based GAC has been shown to have naturally occurring arsenic.

Arsenic Content
"All coal contains some arsenic, which is present primarily within the mineral pyrite interspersed in the coal (USGS, 2005). This means that widely used bituminous and sub-bituminous products often contain arsenic."

Guest Column | July 6, 2021

Implementing Granular Activated Carbon Systems: Important Design And Start-Up Considerations

By Scott A. Grieco

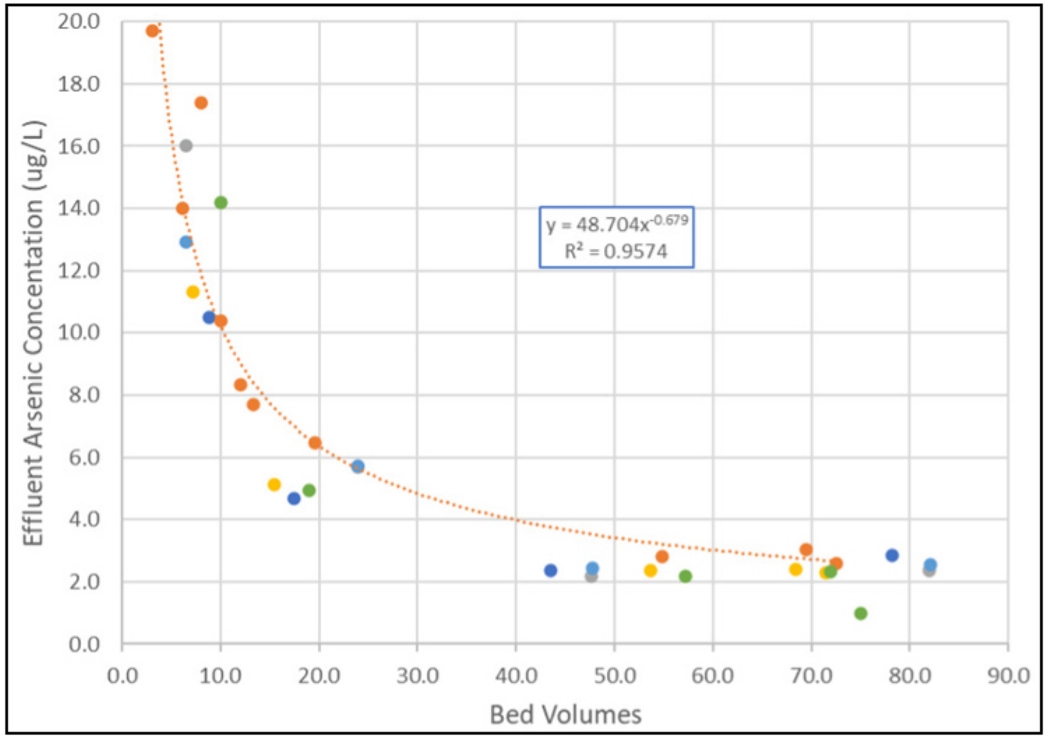
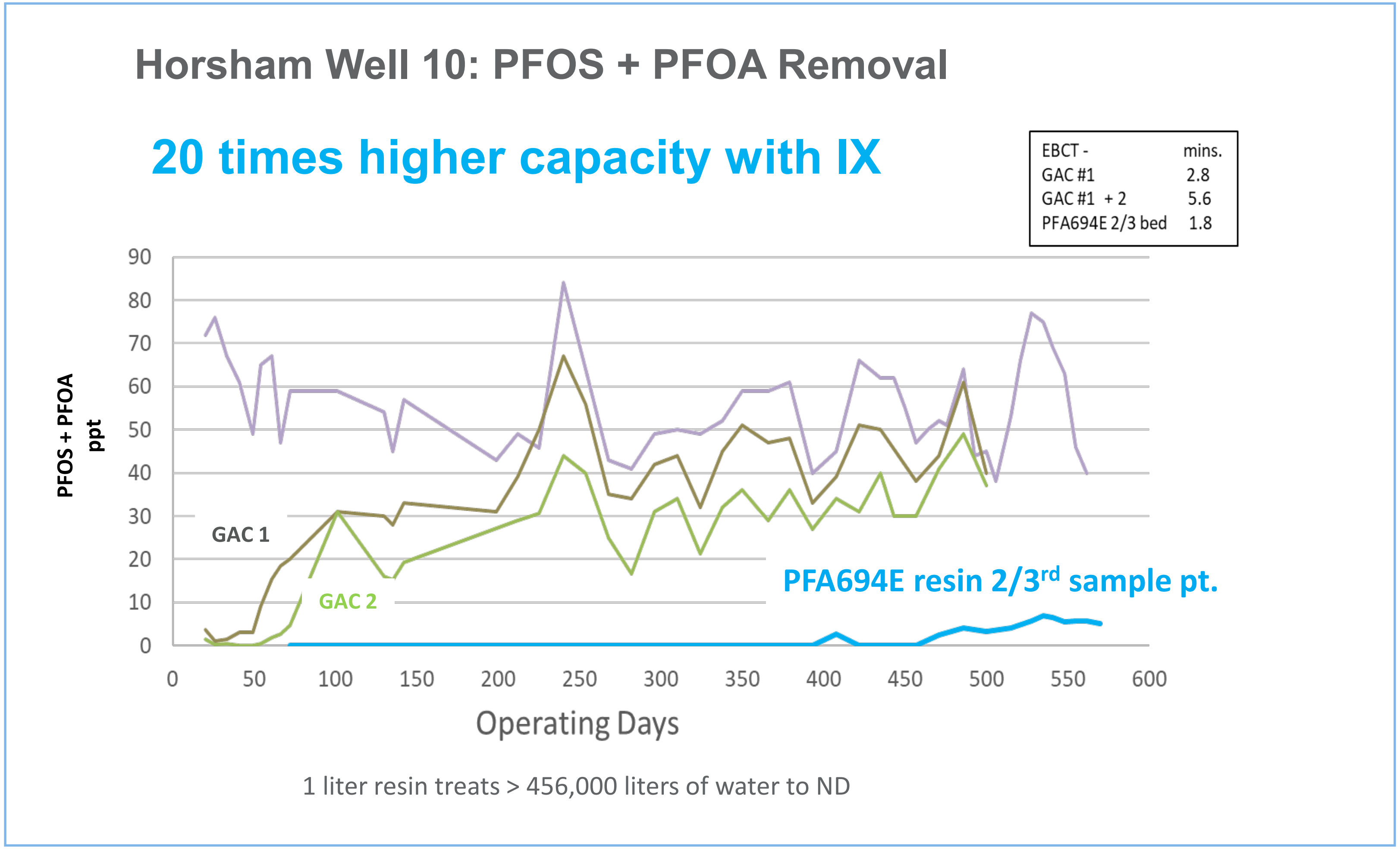


Figure 3. Arsenic concentration vs. bed volume from bituminous GAC startups (Source: Jacobs)

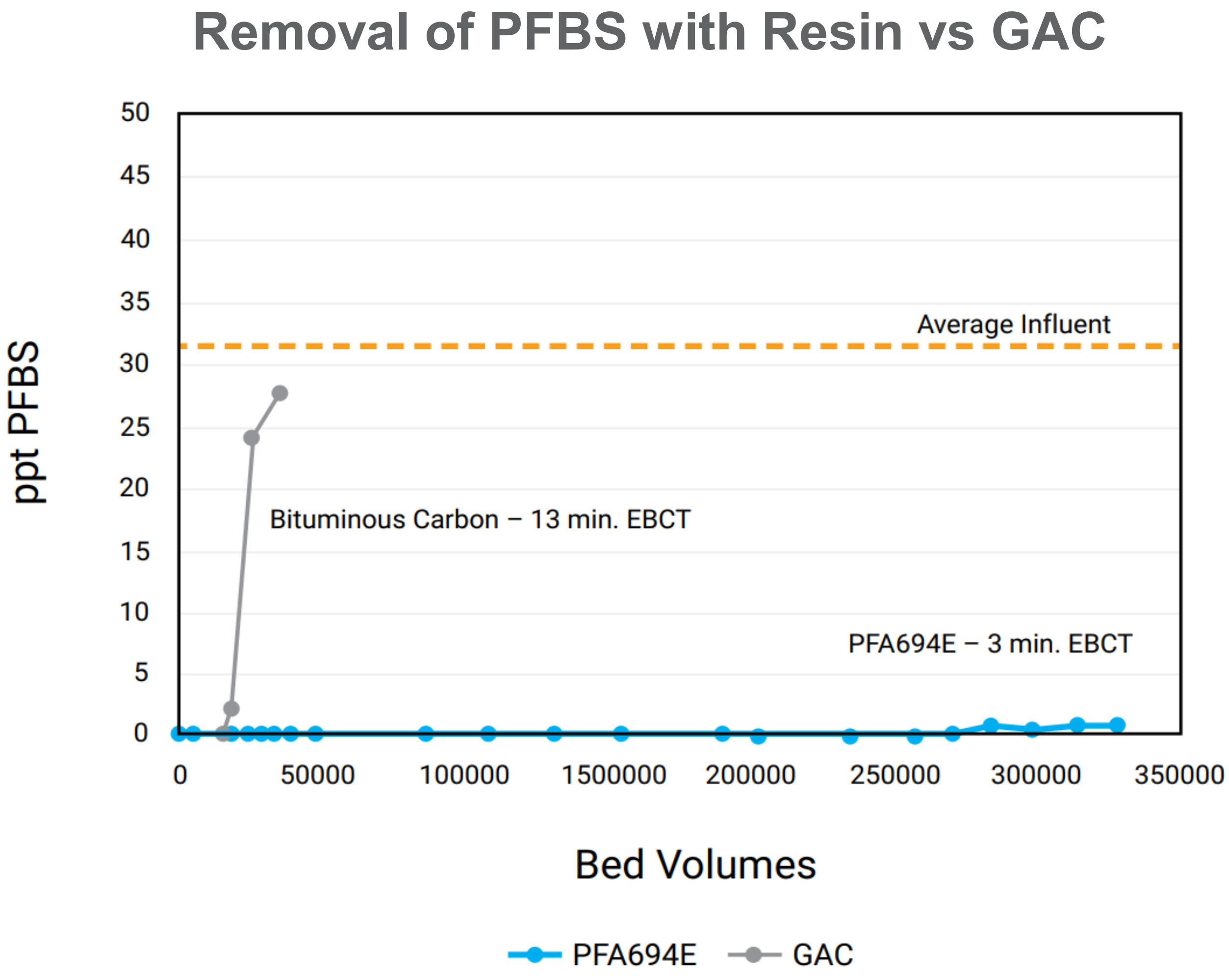
Source: https://www.wateronline.com/doc/implementing-granular-activated-carbon-systems-important-design-and-start-up-considerations-0001

PFOA & PFOS: GAC vs Resin



- Water Quality will drive bed life
- IX can be 5 to 20 times higher throughput than GAC
- Results in lower lifecycle cost for IX

Resin Outperforms GAC with Sulfonic Acid-PFAS



- PFBS is a 4-carbon length PFAS.
- Short chains are more difficult to remove.
- Resin lasted over two years removing PFBS to non-detect.
- GAC lasted 6 months.
- The trend is more dramatic with PFBS, but holds true for all sulfonic-acid PFAS like PFOS and PFHxS.

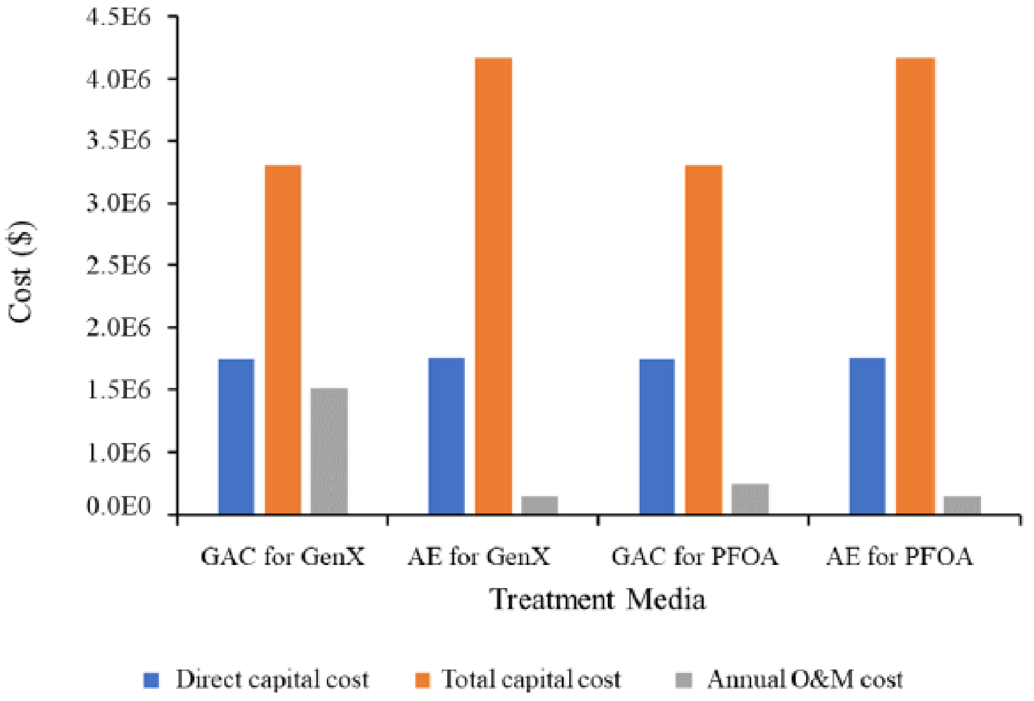
GenX: Resin outperforms GAC

"Both AC and AEs can treat GenX and PFOA, but AEs are a more promising choice with higher removal efficiency."

"It also showed that for AC, the estimated treatment cost for GenX is 4.4 times higher than that for PFOA, while the GenX treatment cost is approximately the same as PFOA for AEs."

AC = activated carbon, AE = anion exchange

Treatment cost of PFOA is approximately equal to the treatment of GenX with AE.



Source:

GenX is not always a better fluorinated organic compound than PFOA: A critical review on aqueous phase treatability by adsorption and its associated cost

Author: Hamed Heidari,Tauqeer Abbas,Yong Sik Ok,Daniel C.W. Tsang,Amit Bhatnagar,Eakalak Khan

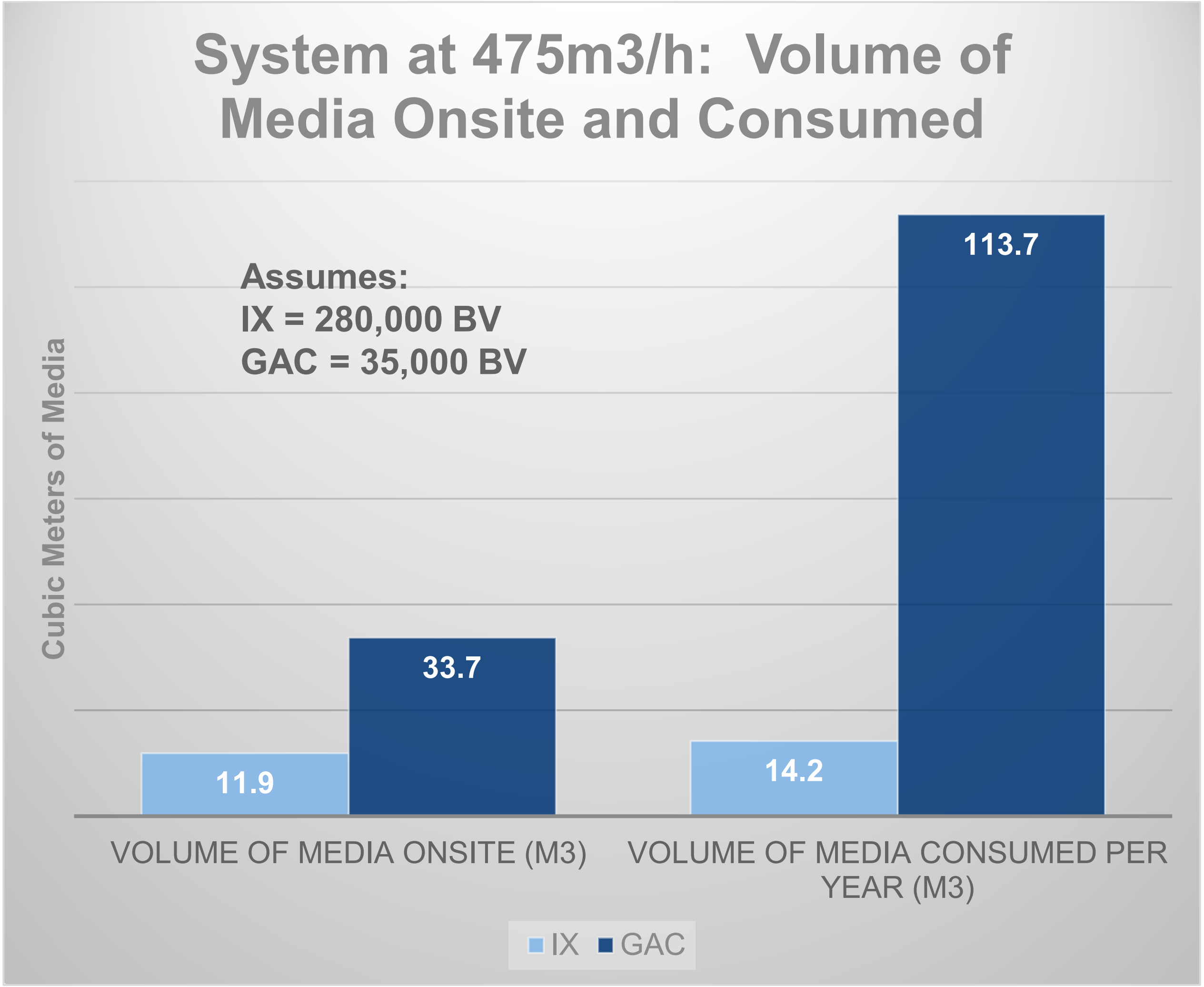
Publication: Water Research

Publisher: Elsevier

Date: 15 October 2021

Waste Generation

- Ion Exchange requires less media onsite and generates significantly less waste per year.
- PFAS waste will become designated as "hazardous substance in US."



PFAS Waste Management

Landfill
Incineration
Reactivation (GAC)

Currently commercial

Mechanochemical
Supercritical Water Oxidation
Electrochemical

Promising technologies

Chemical
Biological
Plasma
Sonolysis
Ebeam
UV

Technologies also being developed

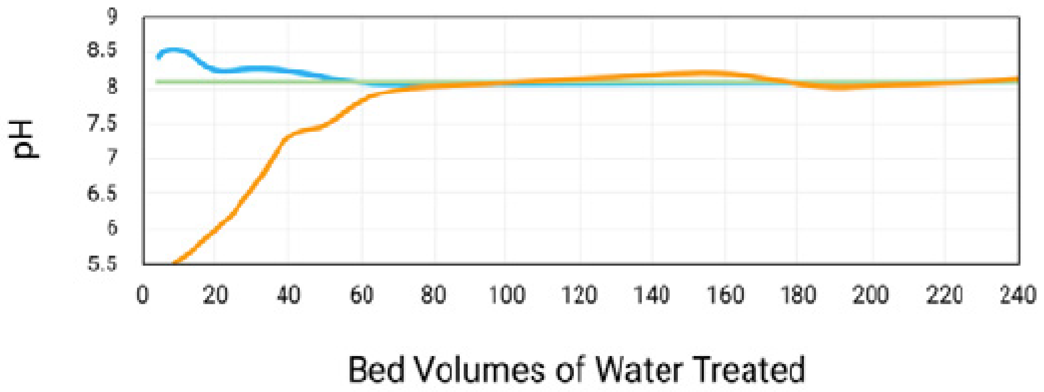
Deep Well injection
Sorption / stabilization
Land application

Less desirable

Flushing Requirements for Neutral pH: Startup Only

IX Resin vs GAC

- 20 BV Rinse per NSF/ANSI/CAN 61
- Buffered Resin to minimize if needed



GAC pH stabilization can take up to 400 BV

Activated Carbon Type	Initial Contact pH	Flushing Required (Bed Volumes)
Sub-bituminous	10.4	350
Bituminous	10.4	350 - 400
Reactivated Bituminous	10.6	400
Bituminous Acid-Washed	9.8	200 – 250
Coconut	10.3	200 - 250

Table 1. Activated carbon type, initial pH, and required rinse volumes for pH stabilization (Adapted from Farmer et. al., 1996)

Future Trends???

Regulatory Levels Drop

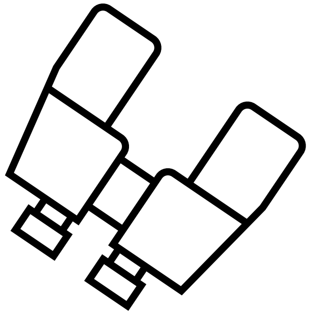
Short Chains become Greater Focus

- Will move into a combination of single use ion exchange resin followed by regenerable systems to capture short chain.
- Regenerable ion exchange will require a swelling agent (solvent or caustic) and a brine

Future-proof your PFAS Technology Choice

PFAS-Selective IX Resin provides the following advantages:

- Fast kinetics → Smaller footprint → Lower Capital Costs
- Higher selectivity → Long bed life → Lower Operational Costs
- Higher selectivity → better long-term performance than GAC with PFAS of concern → Future-Proof
- Higher selectivity → no sloughing of shorter chain PFAS or nitrate → Future-Proof
- Less Waste Generation → Lower Operational Costs



Thank You!