Treatment Technologies for PFAS Site Management

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Presentation Overview

- Summary of Available Technologies
- Pump and Treat
- Soil Treatment Technologies
- Wrap-Up

Summary of Available Technologies – Drinking Water Treatment

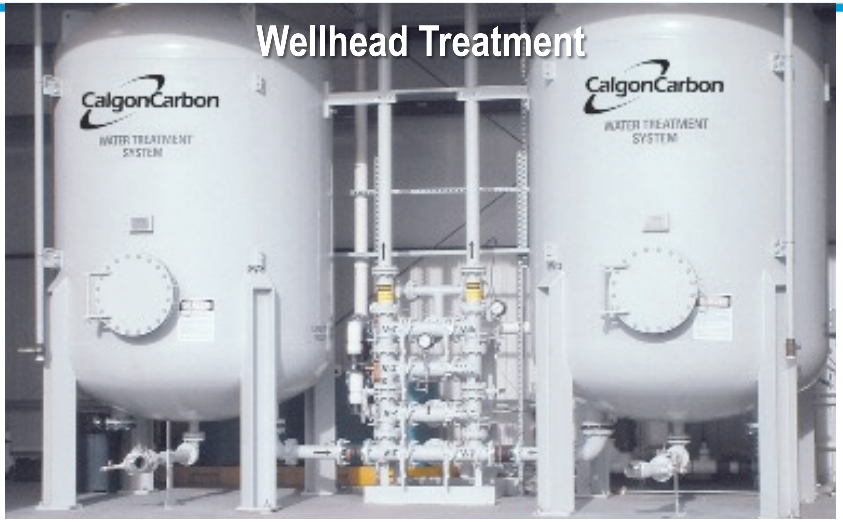
Technology Category	Technology	Maturity/Availability
Sorption	Activated Carbon*	Commercialized, can be purchased from vendors
	Anion Exchange Resin*	Commercialized, can be purchased from vendors
	Biochar	Field Pilot Scale, not commercially available
	Zeolites/Clay Minerals	Commercialized, can be purchased from vendors
Membrane Filtration	Reverse Osmosis and Nanofiltration	Commercialized, can be purchased from vendors
Coagulation	Specialty Coagulants	Full Scale application being conducted by researchers
Redox Change	Electrochemical*	Field Pilot Scale, not commercially available but underdevelopment
Other	Sonochemical	Field Pilot Scale, not commercially available

***** *Technologies that will be discussed*

Pump-and-Treat

- At drinking water wellhead
- At point of use
- To control plume size/spread
- At base boundary to prevent plume migration

Key Point Only practical treatment for groundwater available



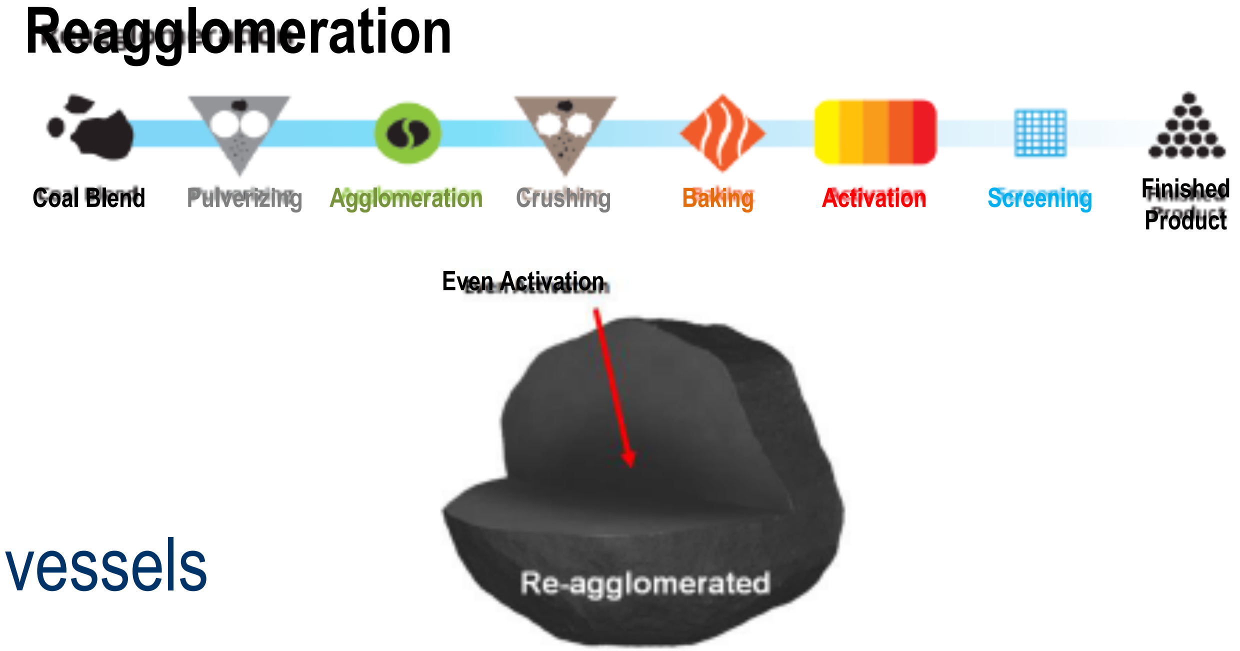
Granular Activated Carbon (GAC)

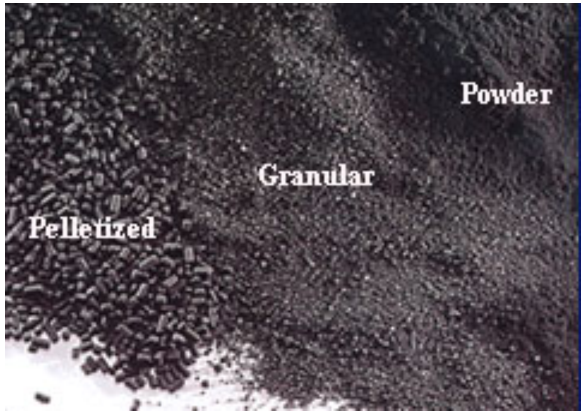
Material

- Made from bituminous coal or coconut
- Highly porous, large surface area

Application

- Typically used in packed-bed flow-through vessels
- Operate in series (lead-lag) or parallel
- Virgin or Reactivated GAC





http://store.ecologixsystems.com/detail/index.cfm?nPID=294

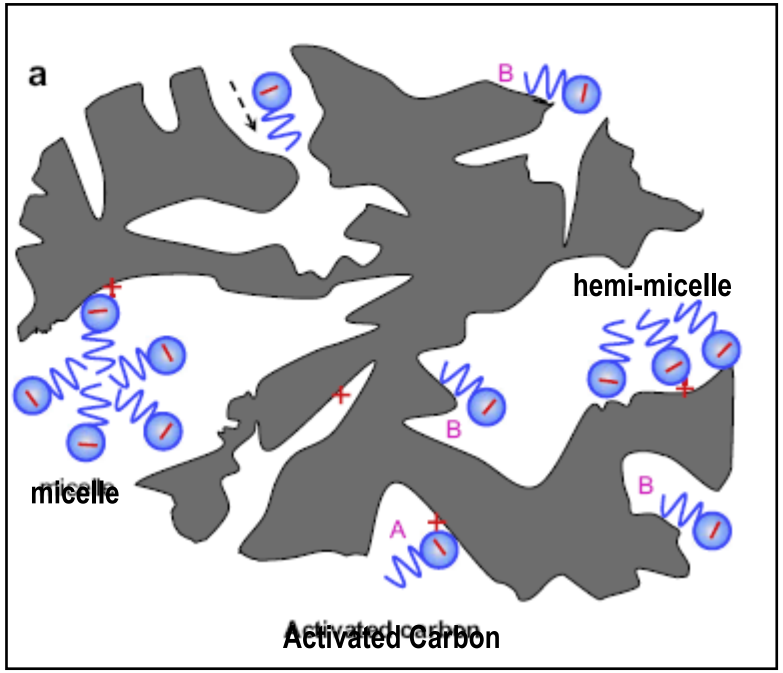
Granular Activated Carbon (cont.)

Mechanism

- Adsorption on surface process, physical mass transfer
- No chemical degradation or transformation

Effectiveness

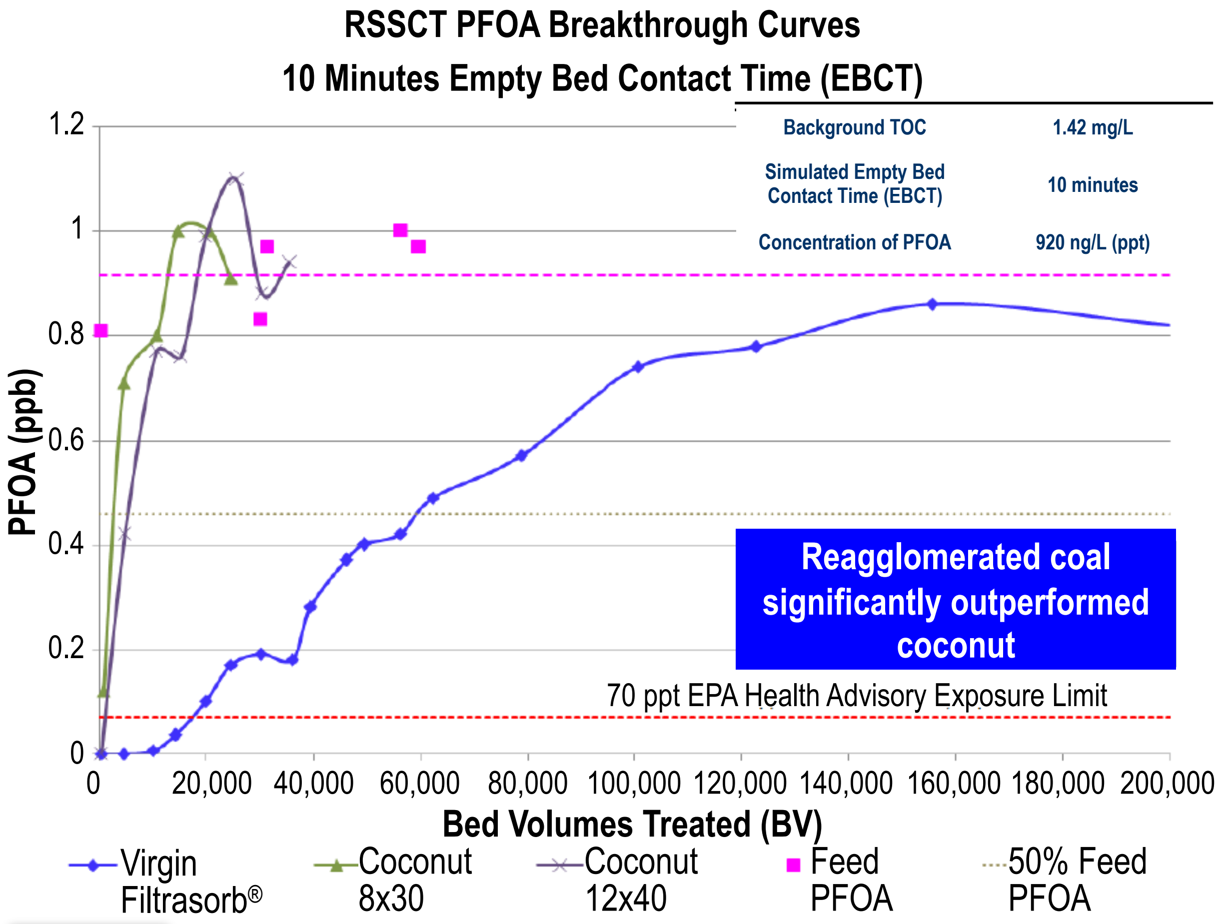
- Capable of 90 to >99% removal efficiency
- Individual PFAS have different GAC breakthrough times
  - e.g., GAC capacity for PFOS>PFOA
- Influent conc. for <5 Carbon PFAS typically lower
- High DOC reduces effectiveness

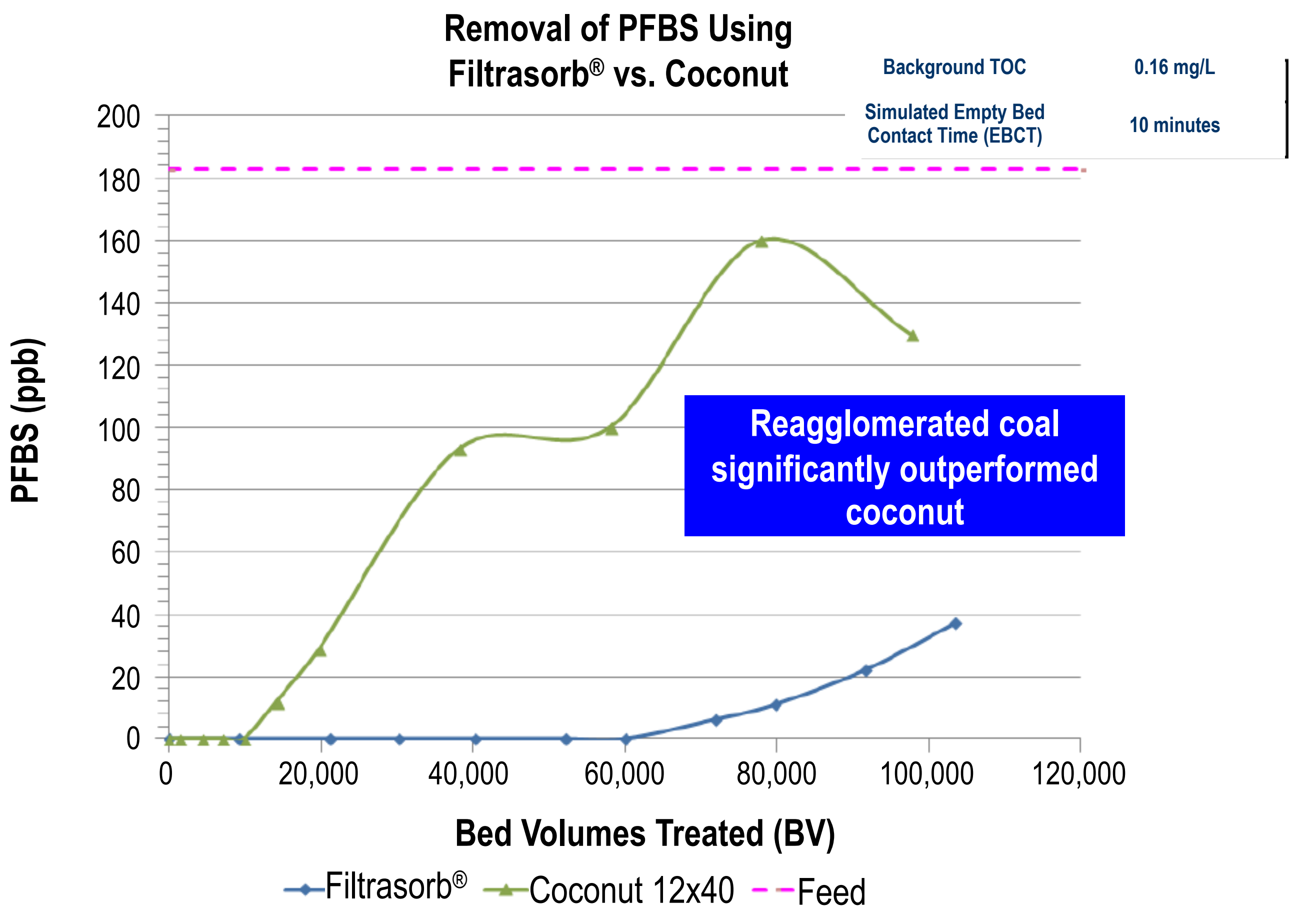


Reference -Yu, Q., R. Zhang, S. Deng, J. Huang, G. Yu, 2009. "Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study." *Water Research*, 43, 1150-1158.

Key Point — **PFAS <5 carbons shorter breakthrough times**

Bituminous vs. Coconut Carbon





Key Point

Bituminous carbon appears to perform better than coconut carbon on this specific water

NEWMOA PFAS Technical Workshop – Activated Carbon
Don Ivey and John Matthis May 2017

Reactivation of PFAS Contaminated Granular Activated Carbon

Thermal Reactivation Process

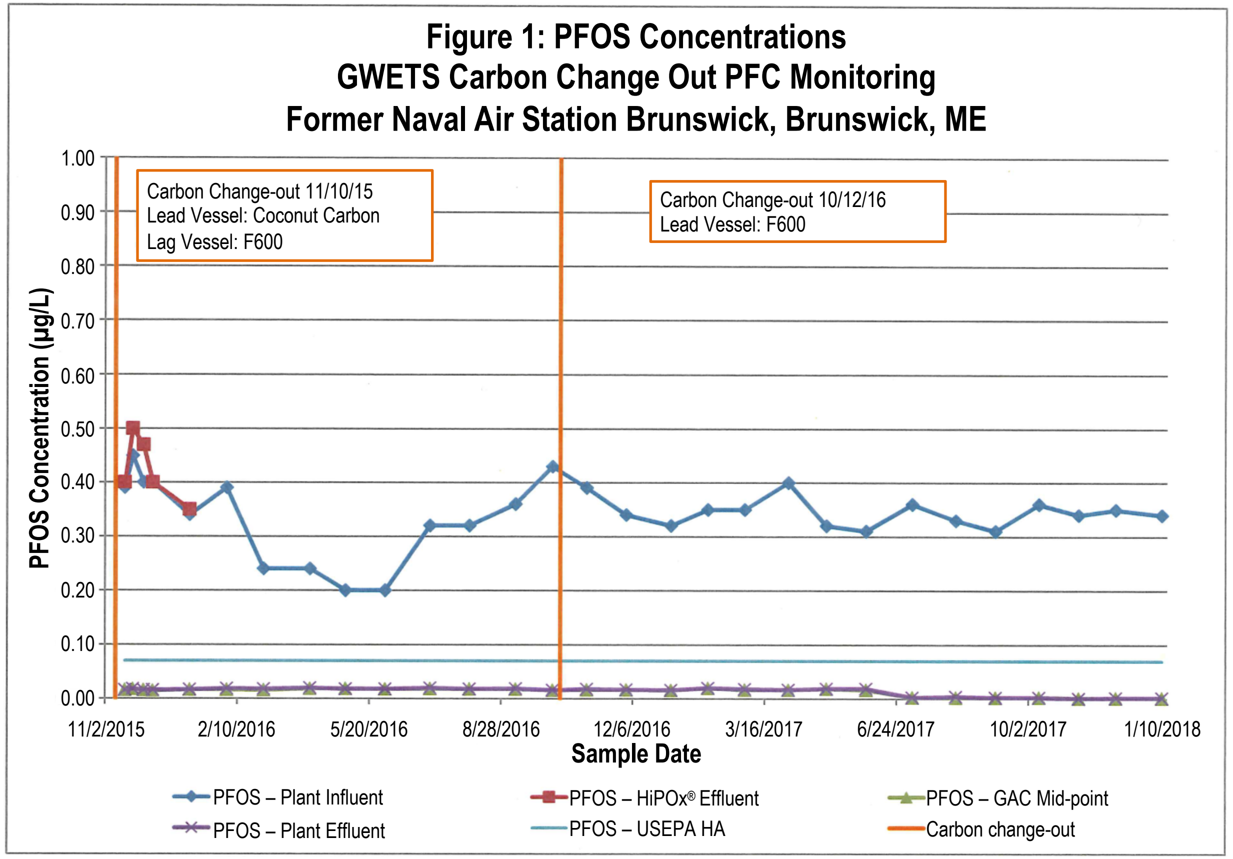
Reactivation furnace under negative pressure and nitrogen environment → Furnace off gas passed through after burn to destroy organics → Emission stream passed through chemical scrubber to remove acid gases → Final treatment through baghouse filters to remove particulate matter

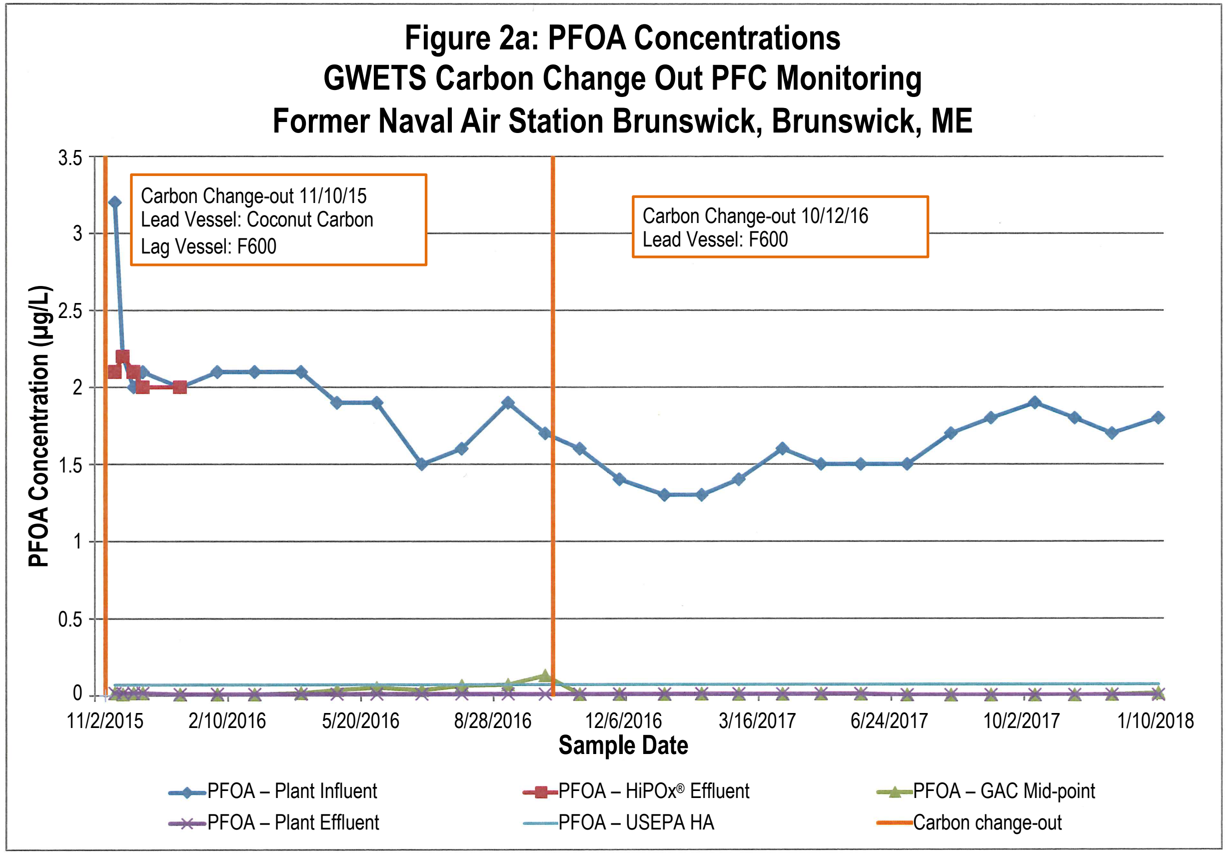
- Reactivation temperature 1,300°F to 1,700°F
- PFAS pyrolysed to carbon char
- Lower CO_2 footprint than making virgin GAC
- Reactivated carbon may be just as effective as virgin carbon

Case Study – NAS Brunswick, ME GWETS

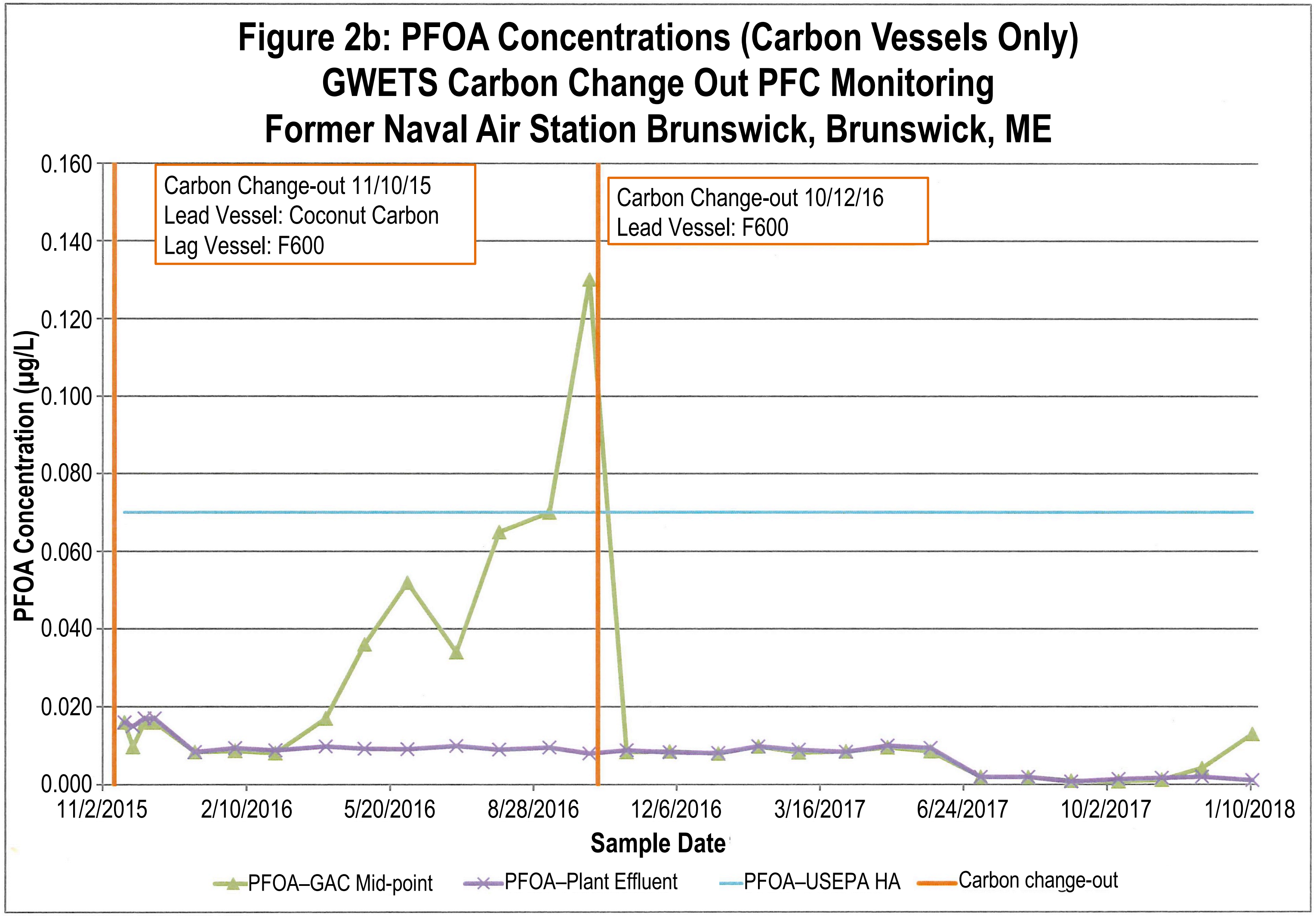
- Former Naval Air Station in Brunswick, ME, BRAC 2011
- Treating CVOCs at GWETS using air stripping and GAC (vapor and liquid phase)
- Recovered over 500 kg VOCs since 1995; removal now limited by back diffusion rate, asymptotic range
- 1,4-Dioxane addressed by addition of HiPOx® unit
- PFAS removed via liquid-phase GAC
  - PFOA breakthrough determines changeout
  - Shorter-chain PFAS, carboxylates, break through earlier

Case Study – NAS Brunswick, ME GWETS – Results

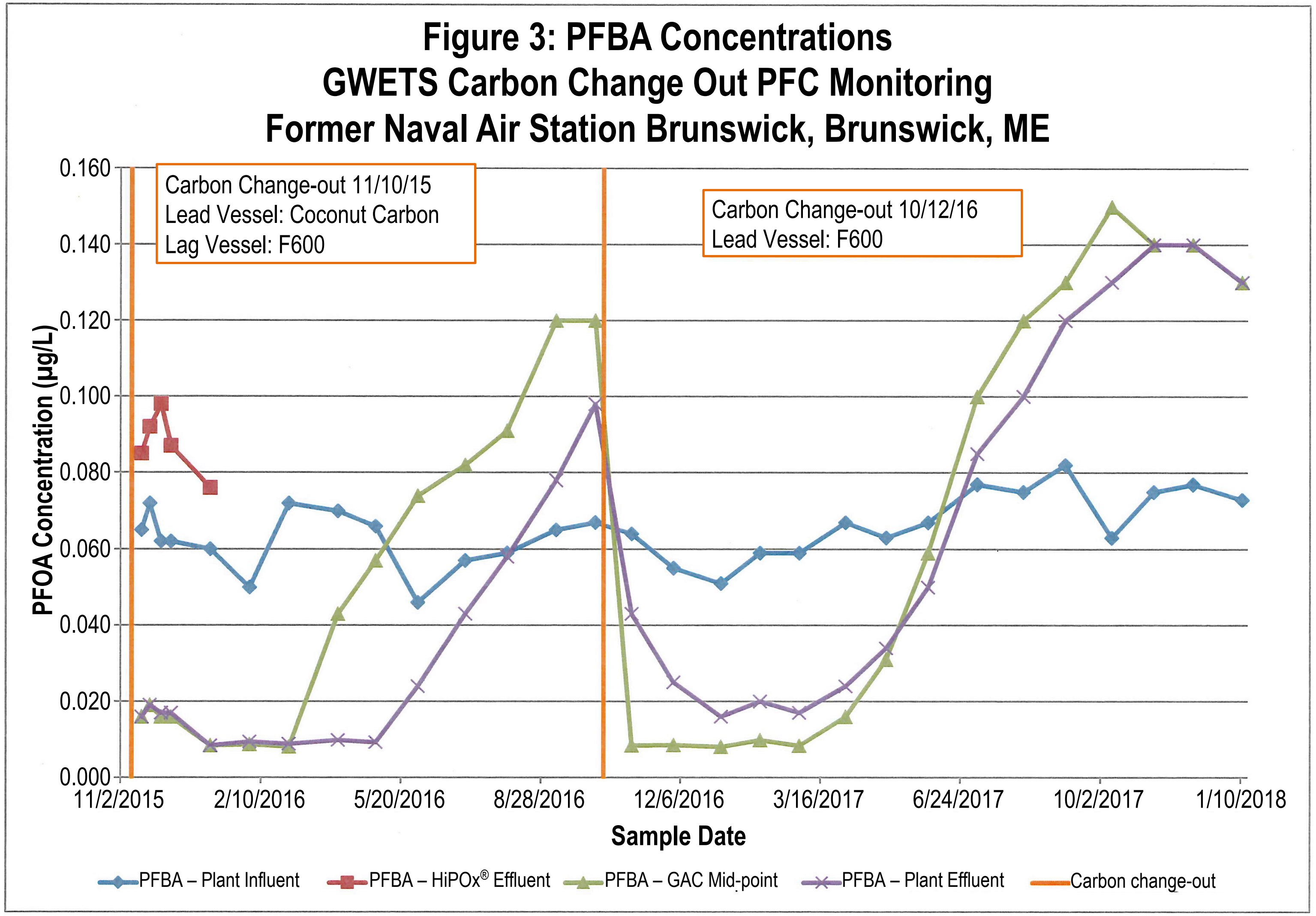




Case Study – NAS Brunswick, ME GWETS – Results (cont.)



Case Study – NAS Brunswick, ME GWETS – Results (cont.)



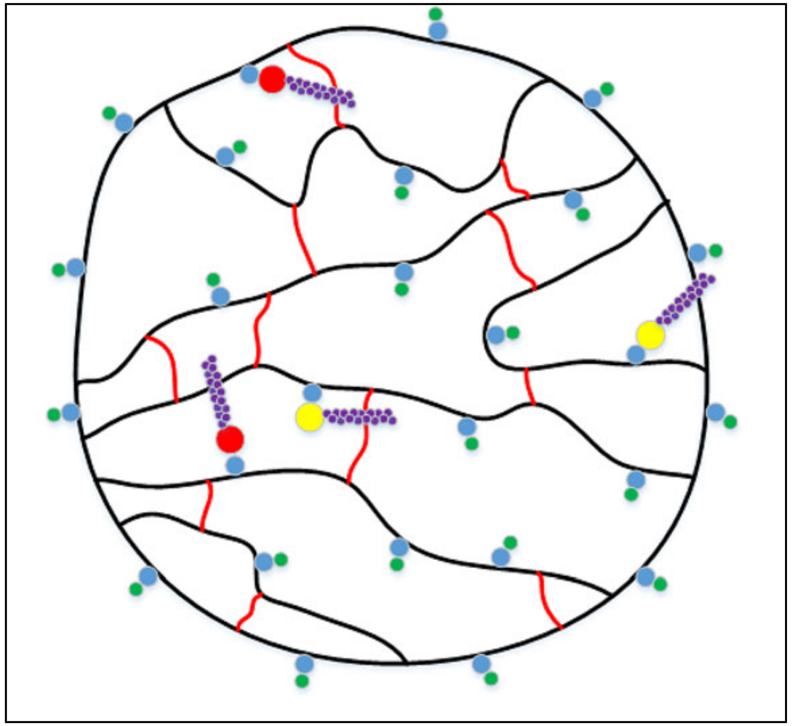
Ion Exchange

Material

- Synthetic neutral co-polymeric media (plastics) with positively-charged exchange sites
- Can be regenerated (produces waste stream) or single use (must be disposed of properly)

Application

- Removes anionic PFAS binding to negatively-charged functional group
- Lead-lag including combination of single use and regenerated



- Polystyrene polymer chain
- Divinylbenzene crosslink
- Fixed ion exchange group, e.g., quaternary ammonium, $—\equiv N^+$, for anion IEX
- Exchangeable counter ion, e.g., chloride ion, Cl-, for anion IEX
- Sulfonate group, $—SO_3^-$, of PFAS (e.g., PFOS), replacing exchangeable counter ion
- Carboxylate group, $—CO_2^-$, of PFAS (e.g., PFOA), replacing exchangeable counter ion
- PFAS carbon-fluorine tail adsorbing to polystyrene polymer chain or divinylbenzene crosslink via Van der Waals forces

Reference: Steve Woodward John Berry Brandon Newman. 2017. Ion Exchange Resin for PFAS Removal and Pilot Test Comparison to GAC. Remediation Journal Volume 27, Issue 3 Pages 19–27

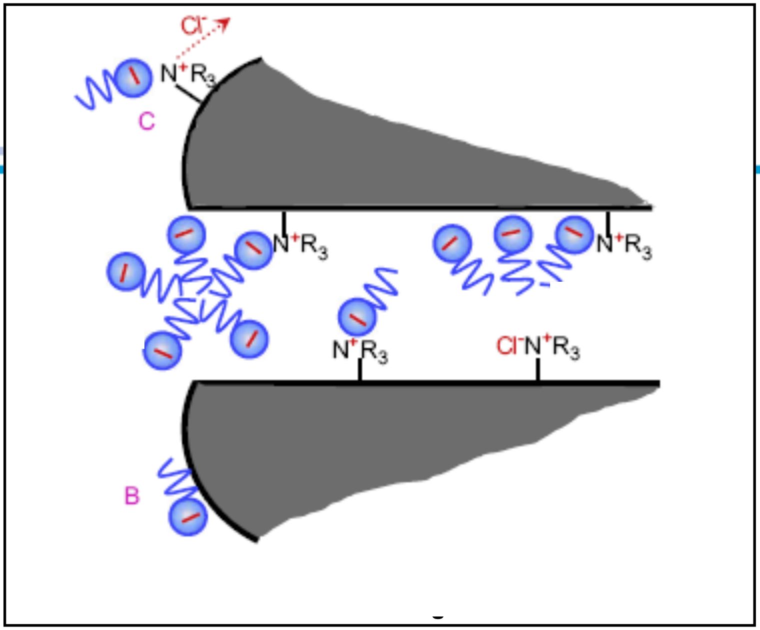
Ion Exchange (cont.)

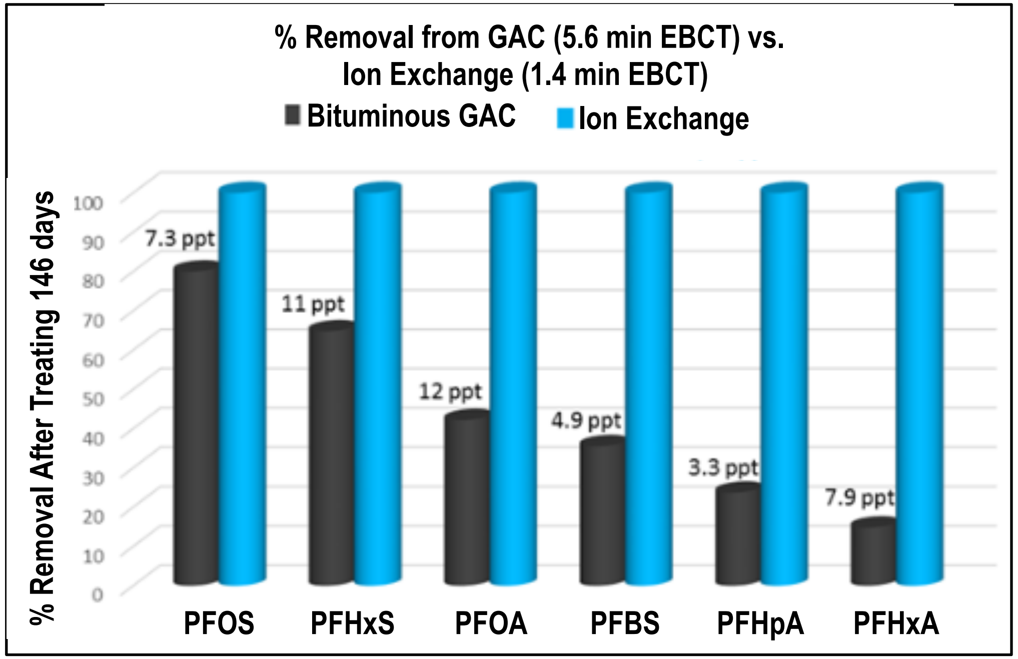
Mechanism

- Acts as ion exchange resin and adsorbent resin
- Positively charged anion exchange media
- Removes negatively-charged PFAS from water

Effectiveness

- Reaction kinetics faster than GAC
- Operating capacity higher than GAC
- Breakthrough varies for different PFAS
- Less frequent media change-outs





Considerations When Using Ion Exchange

- Type and concentration of inorganic ions in groundwater affect PFAS capacity of resin
- Bench-scale tests recommended to determine most effective resin
- More cost-effective at higher concentrations
- Organic matter may foul resin
- Co-contaminants compete for resin site
- Site-specific testing should be performed

Regeneration of Ion Exchange Resins

- Brine solution can desorb anionic head of PFAS from resin
- Organic solvent-like methanol or ethanol can desorb C-F tail
- Surfactants with both nonionic and anionic properties can be used as regenerants
- Most successful has been organic solvents and sodium chloride
- The solution used to regenerate may then need to be concentrated to minimize the volume of waste

Key Point — **Shipped back to vendor for regeneration**

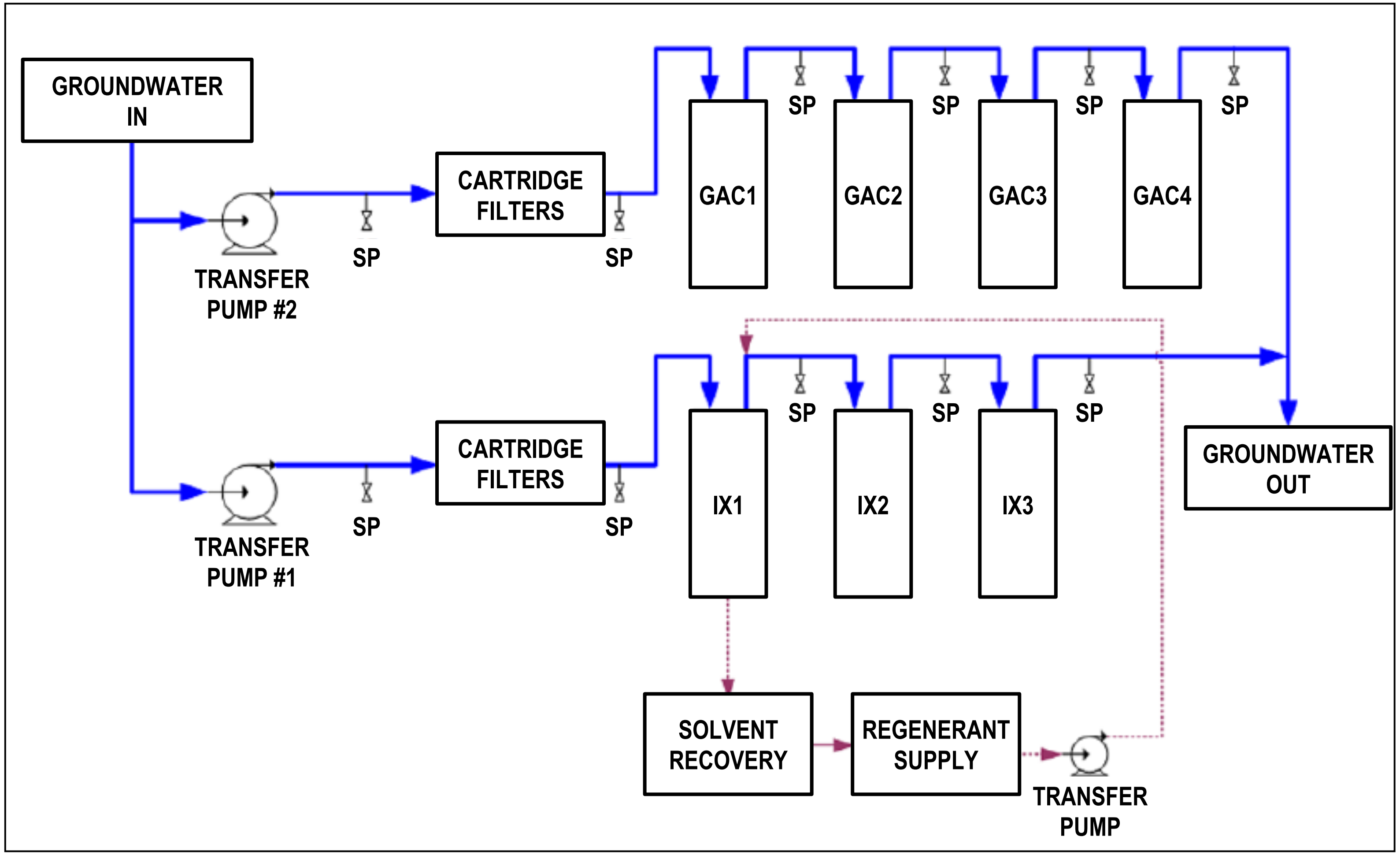
Case Study – Comparison of GAC with Ion Exchange at Pease AFB

- Historic use of AFFF for firefighting training
- Ion Exchange – ECT Sorbix A3F
- Note 6:2 FS 2nd highest concentration PFAS
- GAC – Calgon Filtrasorb® 400 (F400)

Analyte	Analyte Acronym	Influent Concentrations Observed During Pilot Test (μg/L)		
		Low	High	Average
6:2 Fluorotelomer sulfonate	6:2 FS	15	22	18
8:2 Fluorotelomer sulfonate	8:2 FS	0.055	0.3	0.23
Perfluorobutane sulfonate	PFBS	0.81	1.3	1.1
Perfluorobutanoic acid	PFBA	0.89	2.1	1.3
Perfluoroheptane sulfonate	PFHpS	0.85	1.4	1.1
Perfluoroheptanoic acid	PFHpA	1.6	2.2	1.9
Perfluorohexane sulfonate	PFHxS	18	25	22
Perfluorohexanoic acid	PFHxA	5.9	8.9	7.7
Perfluorooctanoic acid	**PFOA**	**9.1**	**13**	**12**
Perfluorononanoic acid	PFNA	0.046	0.082	0.054
Perfluorooctane sulfonate	**PFOS**	**4.2**	**32**	**26**
Perfluoropentanoic acid	PFPeA	3.1	5.1	4.2
Sum of observed PFAS	-	**65**	**112**	**94**

Reference: Steve Woodard John Berry Brandon Newman. 2017 Ion Exchange Resin for PFAS Removal and Pilot Test Comparison to GAC. Remediation Journal Volume 27, Issue 3 Pages 19–27

Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

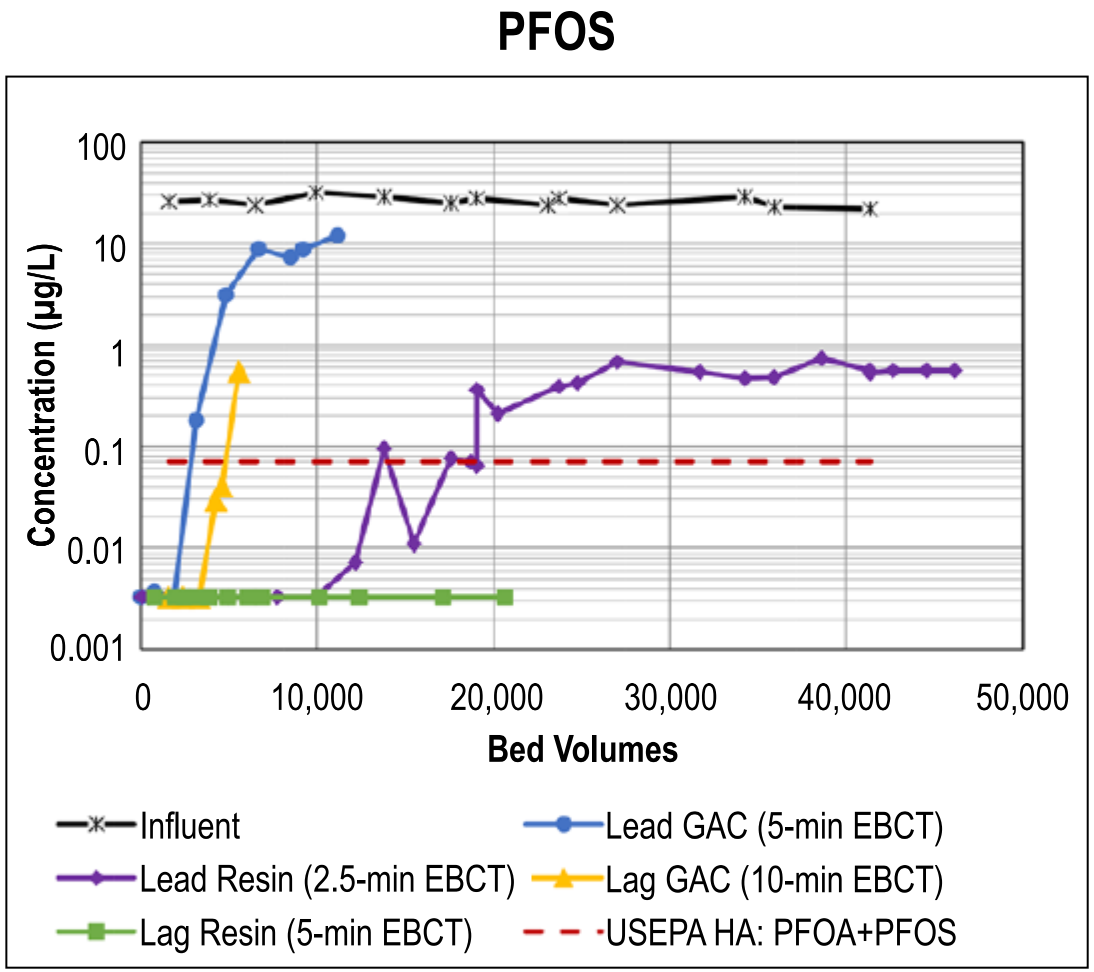


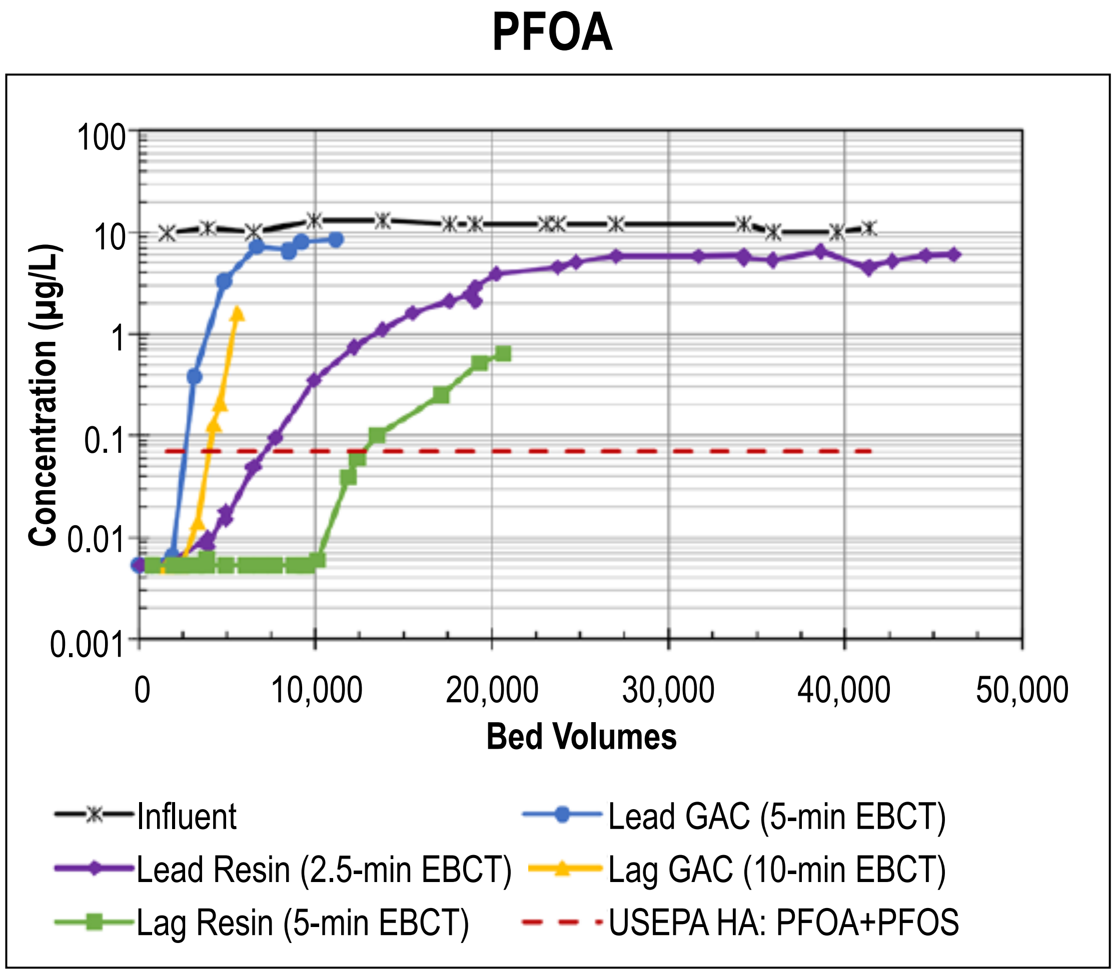
GAC
- 4 vessels in series
- Each containing 9 gal F400
- Each vessel 5 min EBCT, overall 20 min EBCT
- Samples collected at influent and after each vessel weekly for 8 weeks
- At 1.8 gpm treated 100,486 gal water (11,165 bed volumes)

Ion Exchange
- 3 vessels in series
- Each containing 9 gal resin
- Each vessel 2.5 min EBCT, overall 7.5 min EBCT
- At 3.6 gpm treated 422,645 gal water (46,961 BVs)
- Samples collected routinely at influent and effluent

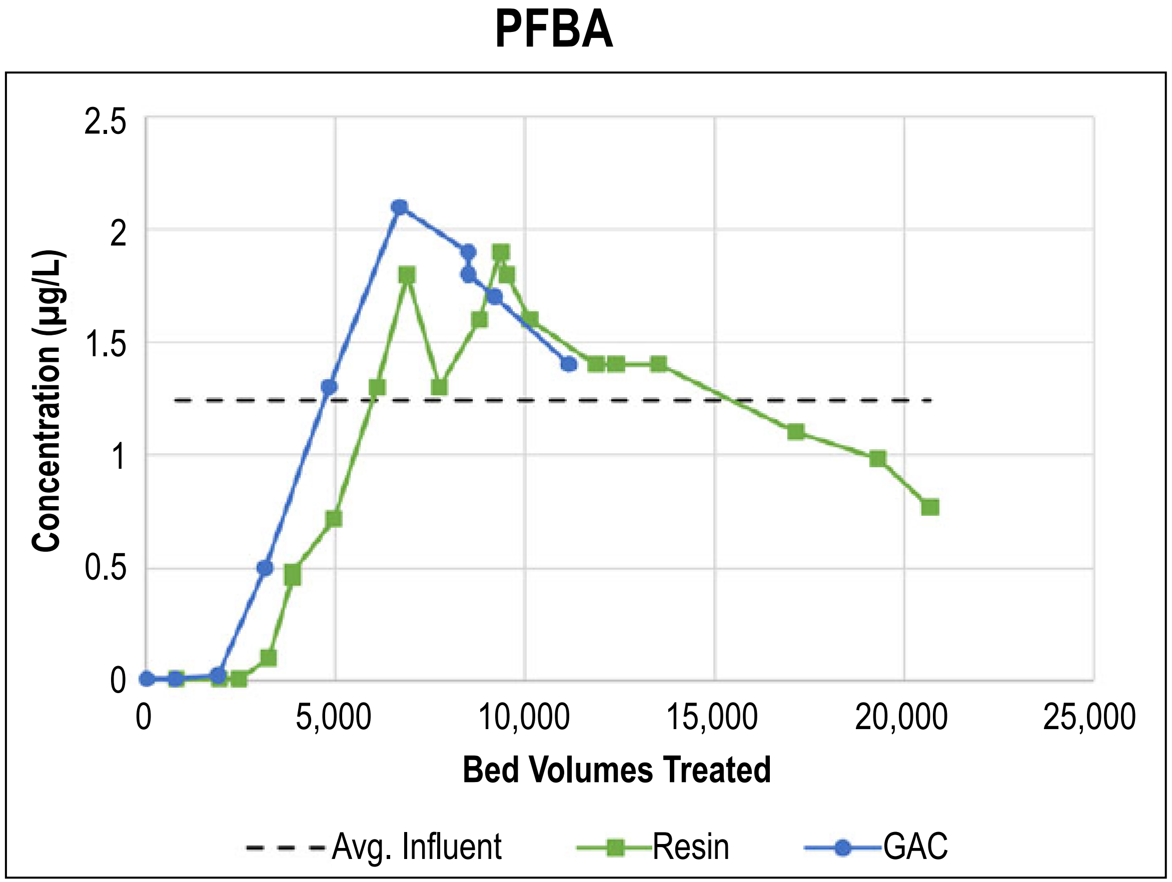
Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

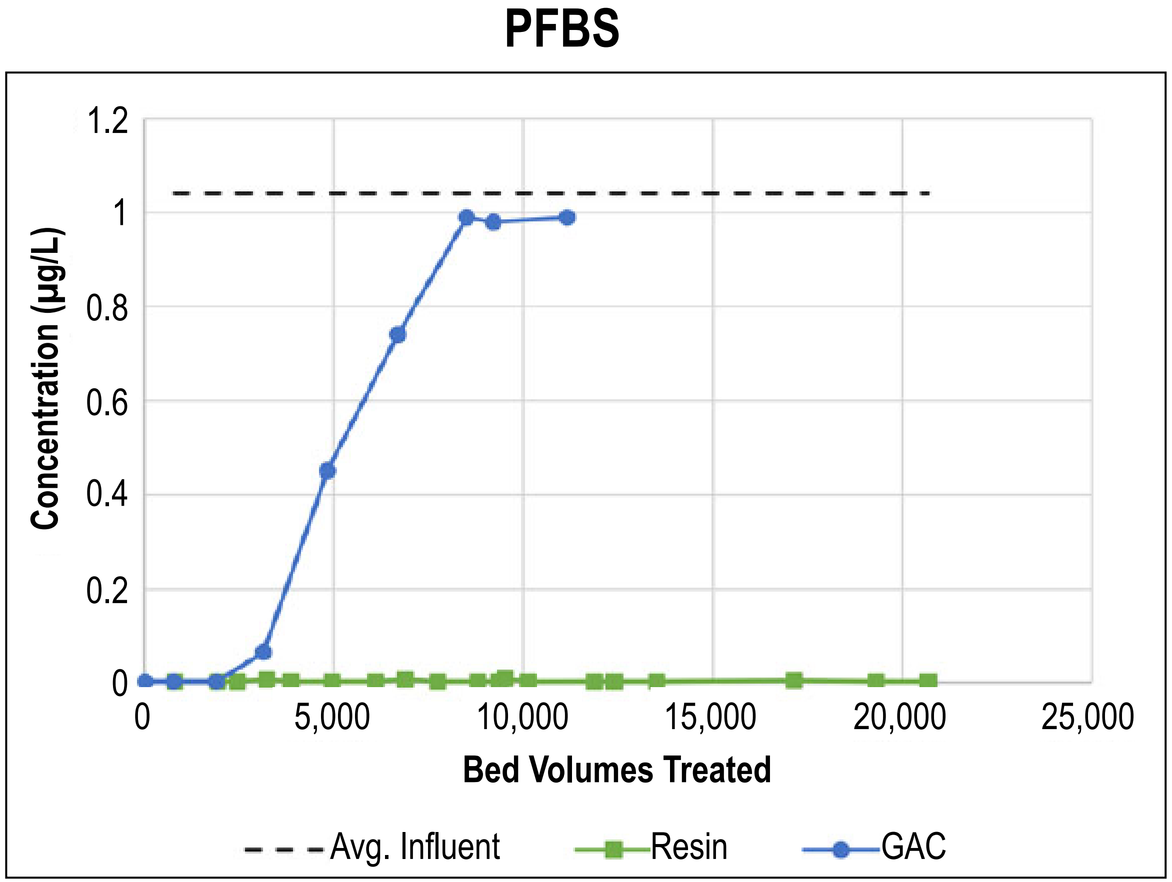
Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)





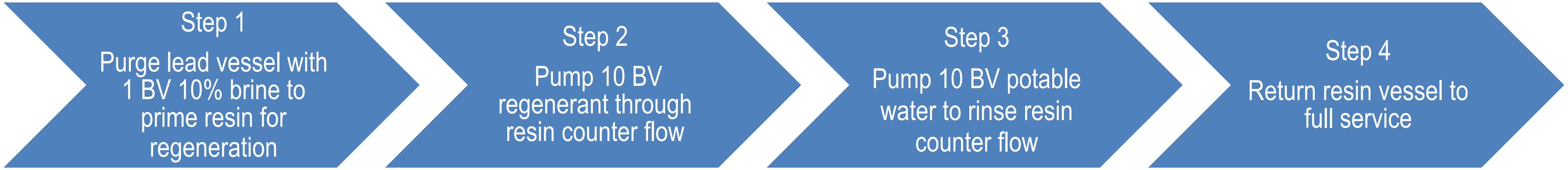
Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

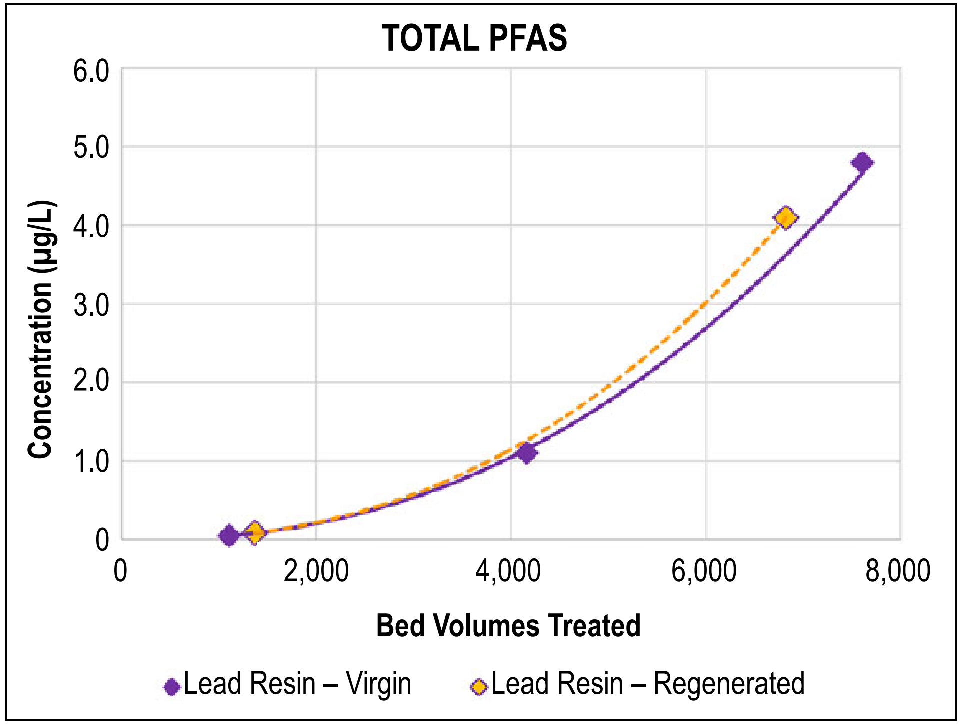




Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

- Three regeneration trials using proprietary blend of organic solvent and brine





Regenerant Solution Recovery

- Distill off solvent fraction into regenerant tank for reuse, left with concentrated brine PFAS fraction
- OR conduct superloading – process concentrated brine PFAS solution through adsorption media then recycle brine solution

Case Study – Comparison of GAC with Ion Exchange at Pease AFB (cont.)

- Both GAC and Ion Exchange Resin can remove PFOS and PFOA from groundwater to below EPA LHA

At 5 min. contact time

- Resin treated 8X more BV than GAC before breakthrough of PFOS observed
- Resin treated 6X more BV than GAC before breakthrough of PFOA observed
- Resin removed 1.66 mg PFAS per gram of resin whereas GAC removed 0.40 mg PFAS per gram GAC
- Resin could be regenerated in the field

Activated Carbon for *In Situ* Water Treatment – PlumeStop®

Material

- Colloidal activated carbon
- 1-2 µm sized particles of carbon suspended in water by organic polymer dispersion chemistry

Application

- *In situ* sorbent technology sorbs PFOS and PFOA from aqueous phase
- Treats dissolved-phase contaminants
- Applied by low-pressure injections

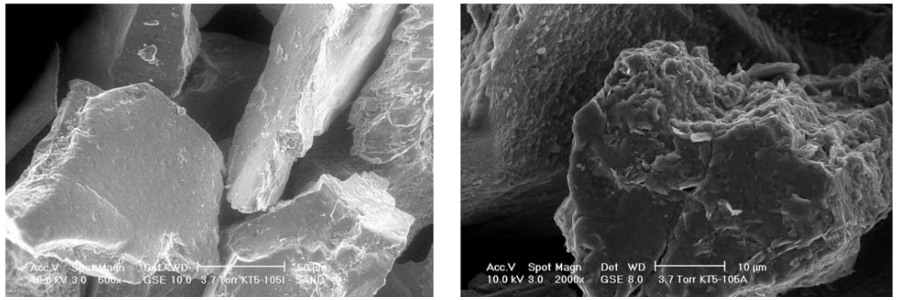
Activated Carbon for *In Situ* Water Treatment – PlumeStop® (cont.)

Mechanism

- Coats surface of soil
- Contaminants in dissolved phase then sorb to carbon
- Does not destroy PFAS, immobilizes PFAS in place
- Occupies just 0.1% soil pore volume

Effectiveness

- Reduces aqueous concentration to below 70 ng/L
- Radius of Influence can be up to 25 ft
- Can be applied as multiple barriers perpendicular to plume



A Scanning Electron Microscope (SEM) Image of Sand Grains With and Without a Coating of Carbon

Electrochemical for Water Treatment – DE-FLUORO™

Mechanism

- Electrochemical Oxidation
- Direct electron transfer on anodes

Application

- Complete mineralization of C4 to C8 perfluoroalkyl acids
- Tested on ion exchange regenerant
- Tested on PFAS impacted waste water

Summary of Available Technologies – Soil Treatment

Technology Category	Technology	Maturity/Availability
In Situ Stabilization	Modified Carbon*	Commercialized, can be purchased from vendors
	Minerals/Modified Minerals*	Commercialized, can be purchased from vendors
Excavation Disposal	To Landfill	Commercialized
	To Incinerator	Commercialized
Thermal		Field Pilot Scale, commercially available

** Technologies that will be discussed*

In Situ Stabilization (ISS)

- Use of amendments for adsorbing and stabilizing PFAS in soil and groundwater
- GAC, stabilizers, and modified minerals (organoclays)
- Commercially available
- Additional amendments being developed
- Critical to monitor soil leachate to determine treatment effectiveness
- Limited full-scale application in U.S. (more overseas)

In Situ Soil Treatment – Aluminum-Based Sorbent – Rembind Plus®

Material

- Aluminum hydroxide, activated carbon, organic matter, and kaolinite

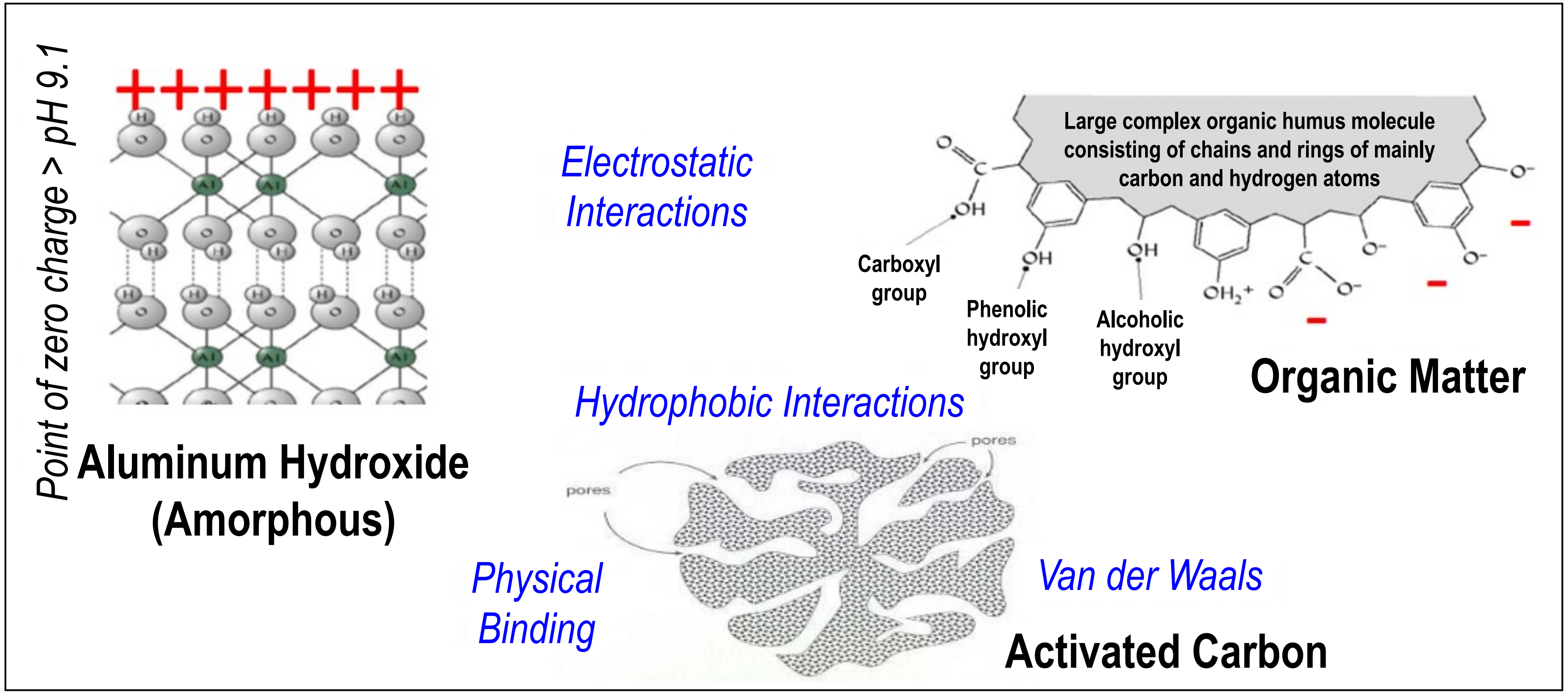
Application

- Apply to soil in ~2 to 5% by weight
- Adjust to 30% moisture content
- Binding occurs in 24 hours
- ***Pilot tested for water treatment***

In Situ Soil Treatment – Aluminum-Based Sorbent – Rembind Plus® (cont.)

Mechanism

- Aluminum hydroxide binds to functional head of PFAS by electrostatic interactions
- Activated carbon and organic matter binds to tail via by hydrophobic interactions and Van der Waals forces



Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study

- Airport contaminated with PFAS
- Replacing asphalt – excavated 900 tons of PFAS-contaminated soil

Aviation Rescue and Fire Fighting Services

Damaged Asphalt

Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

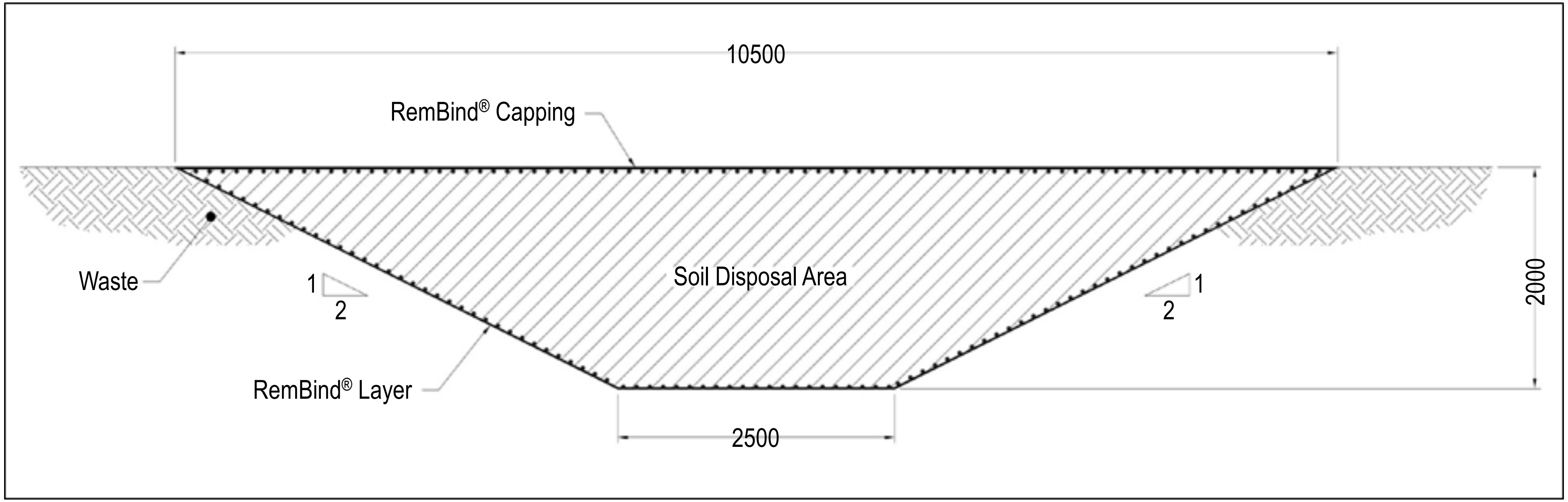
- 900 tons of contaminated soil
- PFOS total concentration <5.7 mg/kg
- PFOS leachable concentration <180 µg/L (by USEPA Method 1311)

Construction of New Apron

PFAS-Contaminated Soil
~900 tonnes

Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

- Transported 900 tonnes of soil to municipal waste landfill site
- Treated hotspots with 10% RemBind®
- Validated samples at accredited lab
- Obtained EPA approval for disposal in a purpose-built burial cell



Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

Laying the Amendment Capping Layer

Finished Lined Burial Cell

Aluminum-Based Sorbent for Full-Scale Soil Treatment Case Study (cont.)

- Soil Leachate after Treatment

	Hotspot 1 (µg/L)*	Hotspot 2 (µg/L)*	Compliance Limit (µg/L)*
PFOS	<0.01	<0.01	0.2
PFOA	<0.01	<0.01	
6:2 Fluorotelomer sulfonate	<0.1	<0.1	
8:2 Fluorotelomer sulfonate	<0.2	<0.2	

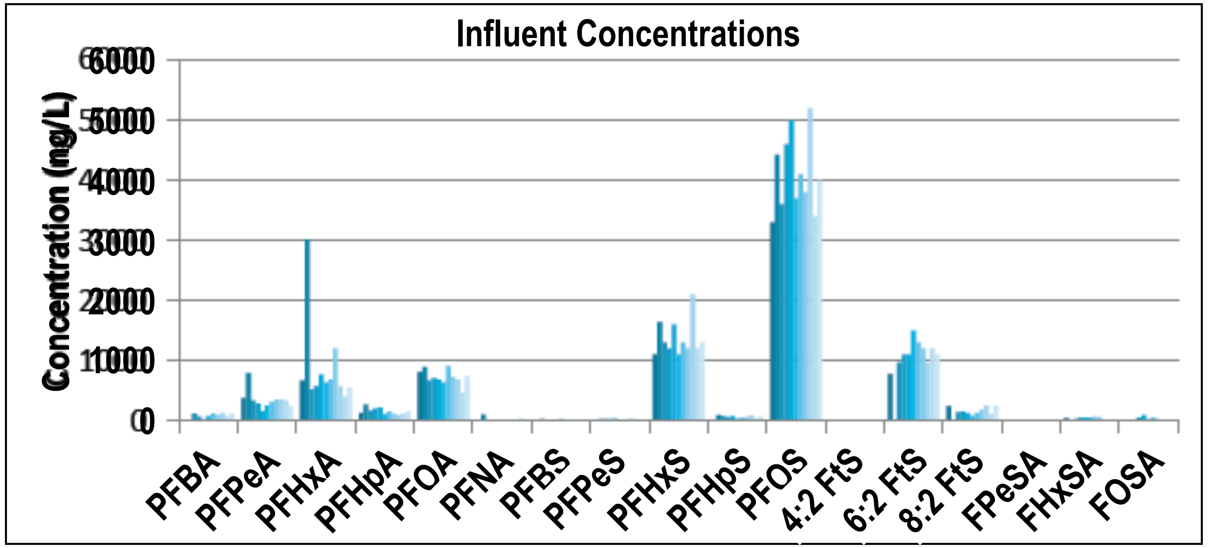
*Soil leachate concentrations as measured by TCLP at pH 5

- Project Costs

Activity	Approximate Cost (US)	Cost per Ton (900 Tons)
Landfill disposal fees	$63,500	$67
Investigation, bench trials, mixing, and reagent supply	$47,500	$50
Total	**$111,000**	**$117**

Aluminum-Based Sorbent for GW Case Study – Air Force Site

- Historical use of AFFF at site
- Full-scale GAC system: two 20,000-lb GAC vessels in operation to remove PFOS/PFOA from groundwater
- Goal of pilot study to evaluate sorption capacity of RemBind Plus®

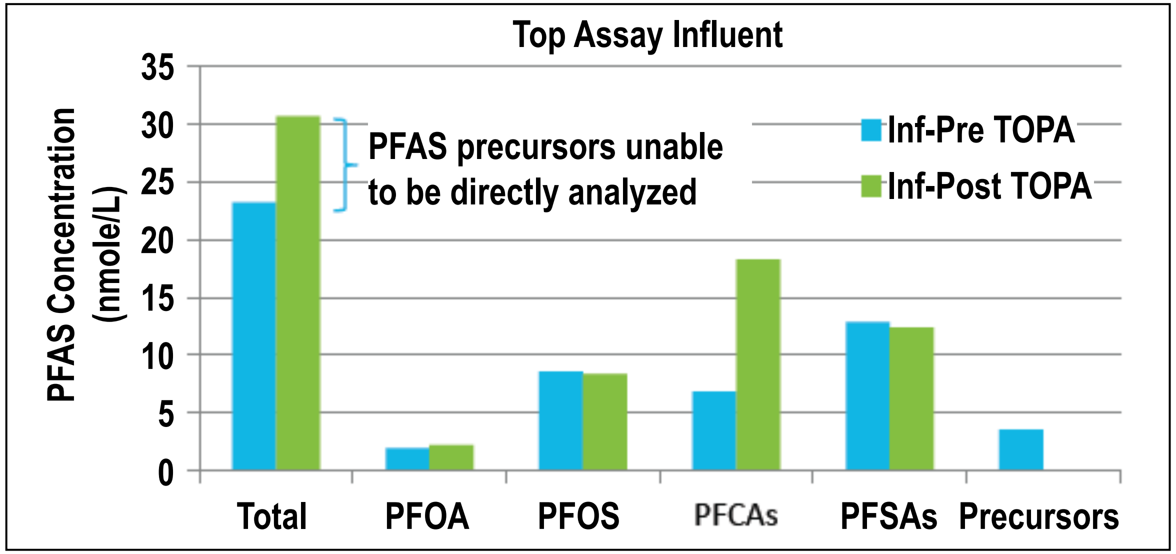


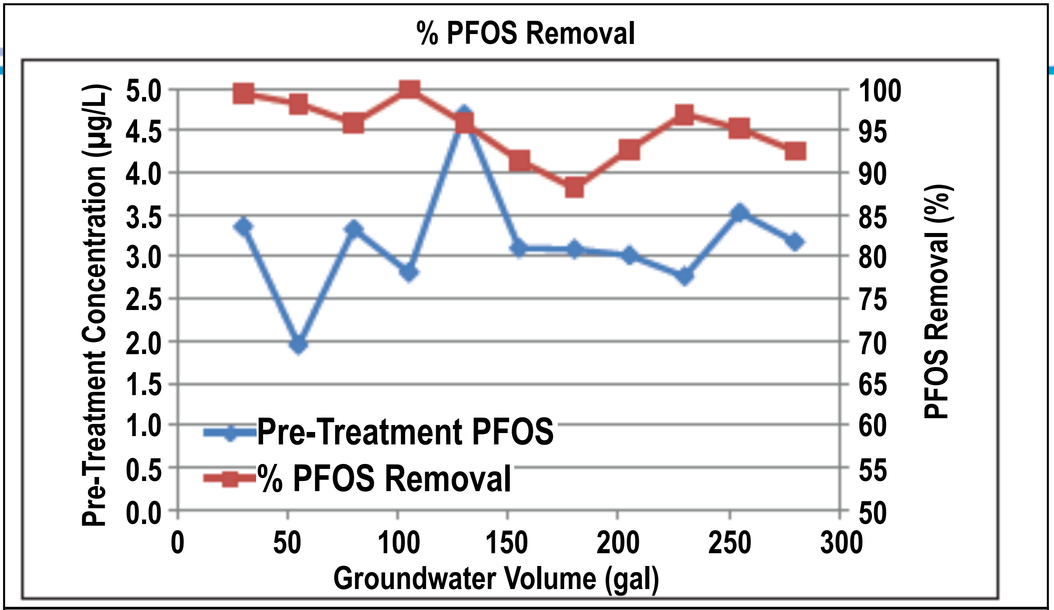
Aluminum-Based Sorbent for GW Case Study – Air Force Site (cont.)

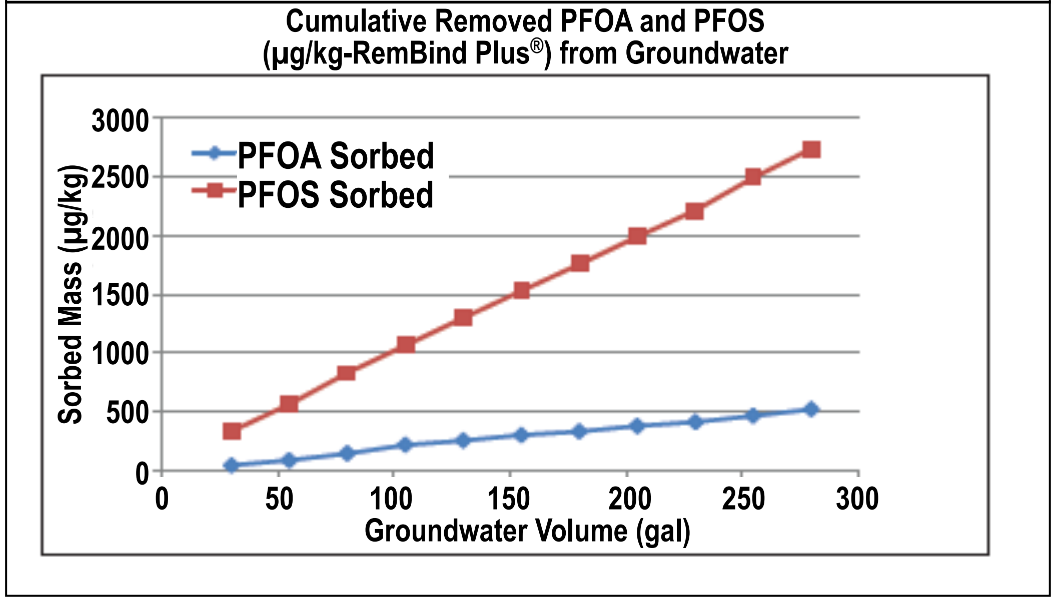
- 30-gal batch reactor pilot test set up next to GAC system
- 30 gal of contaminated water mixed 1.135 kg aluminum-based sorbent for one hour and allowed to settle overnight
- Next day treated GW moved to effluent tank and contaminated GW added to tank with amendment without replacing amendment
- Run for 2 weeks treating 280 gal water
- Monitored for 53 PFAS compounds and TOP assay
- TOC also monitored

Aluminum-Based Sorbent for GW Case Study – Air Force Site – Results

- 18 PFASs detected frequently
- Removal ranged from 80 to 100% after 155 gal
- Slight decrease in removal beyond 155 gal







Key Points

- GAC may be the only practical treatment for groundwater to date
- PFAS <5 carbons much shorter breakthrough times
- Bituminous carbon may perform better than coconut carbon but depends on site conditions
- Ion exchange resin may be better at removing PFAS and can be regenerated but may be more expensive
- *In situ* treatment technologies PlumeStop®, RemBind Plus® and MatCARE™ limited field demonstrations in U.S.

Select References

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Questions and Answers