

Exploring PFAS Treatment Options

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October 26, 2021



**CDM
Smith®**

North Carolina Pretreatment Consortium
October 25 – 27, 2021

Presentation Outline

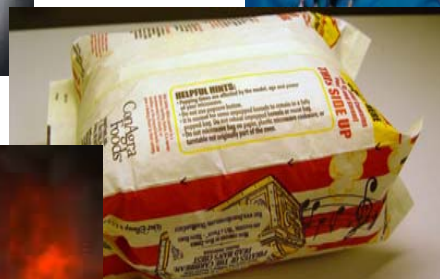
- PFAS Occurrence, Sources and Regulatory History
- PFAS Treatment Options
 - Conventional Treatment
 - Remediation
 - Destruction
- Next Steps



PFAS Occurrence, Sources, and Regulatory History

What are PFAS Compounds?

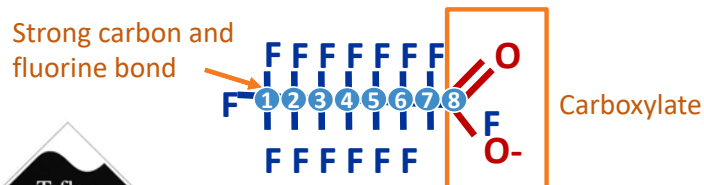
- Per- and Polyfluoroalkyl Substances (PFAS) are a large class of manufactured fluorosurfactant chemicals
- Unique chemical & physical properties that make many of them extremely persistent and mobile in the environment



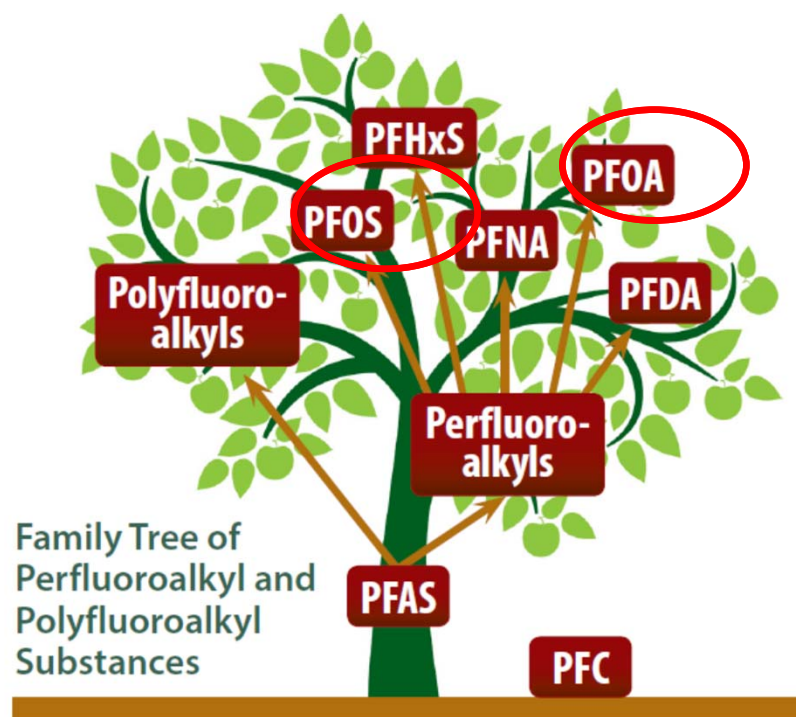
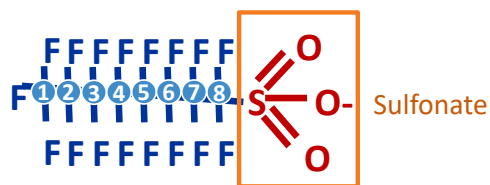
<http://www.defence.gov.au/Environment/PFAS/pfas.asp>

There are over 9,000 Different Per- and Polyfluoroalkyl Substances (PFAS)!

PerFluoroOctanoic Acid (PFOA)



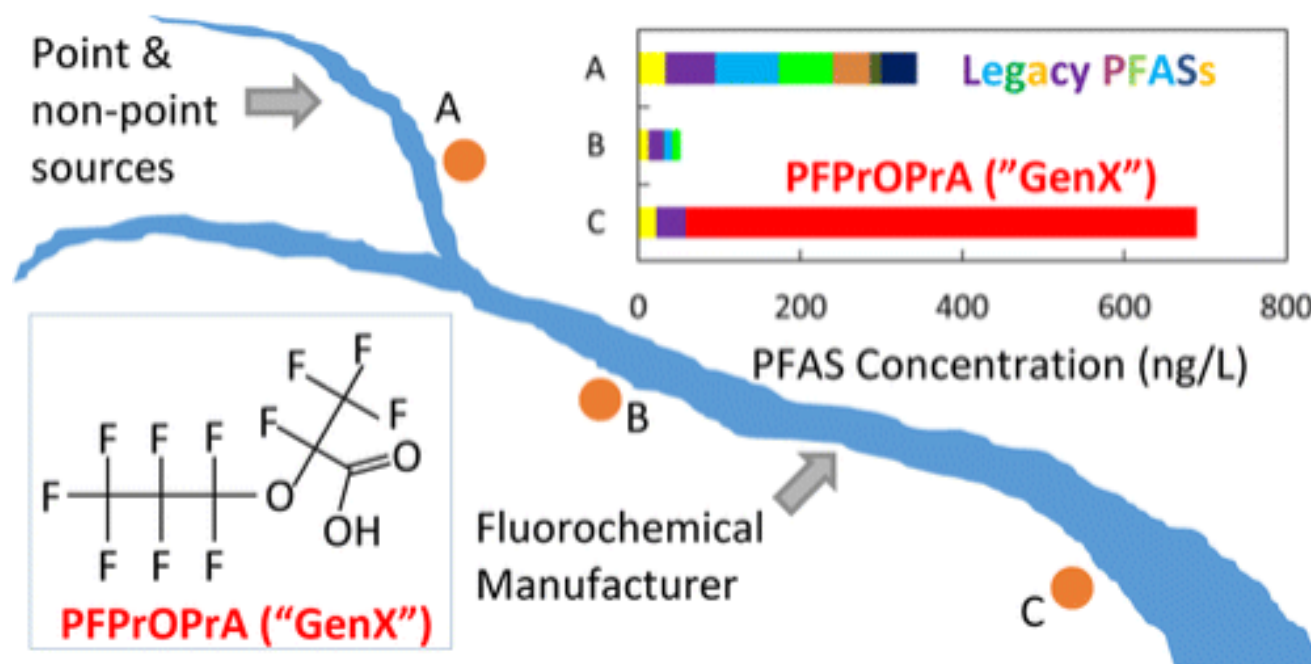
PerFluoroOctaneSulfonic Acid (PFOS)



https://www.atsdr.cdc.gov/docs/17_278160-A_PFAS-FamilyTree-508.pdf

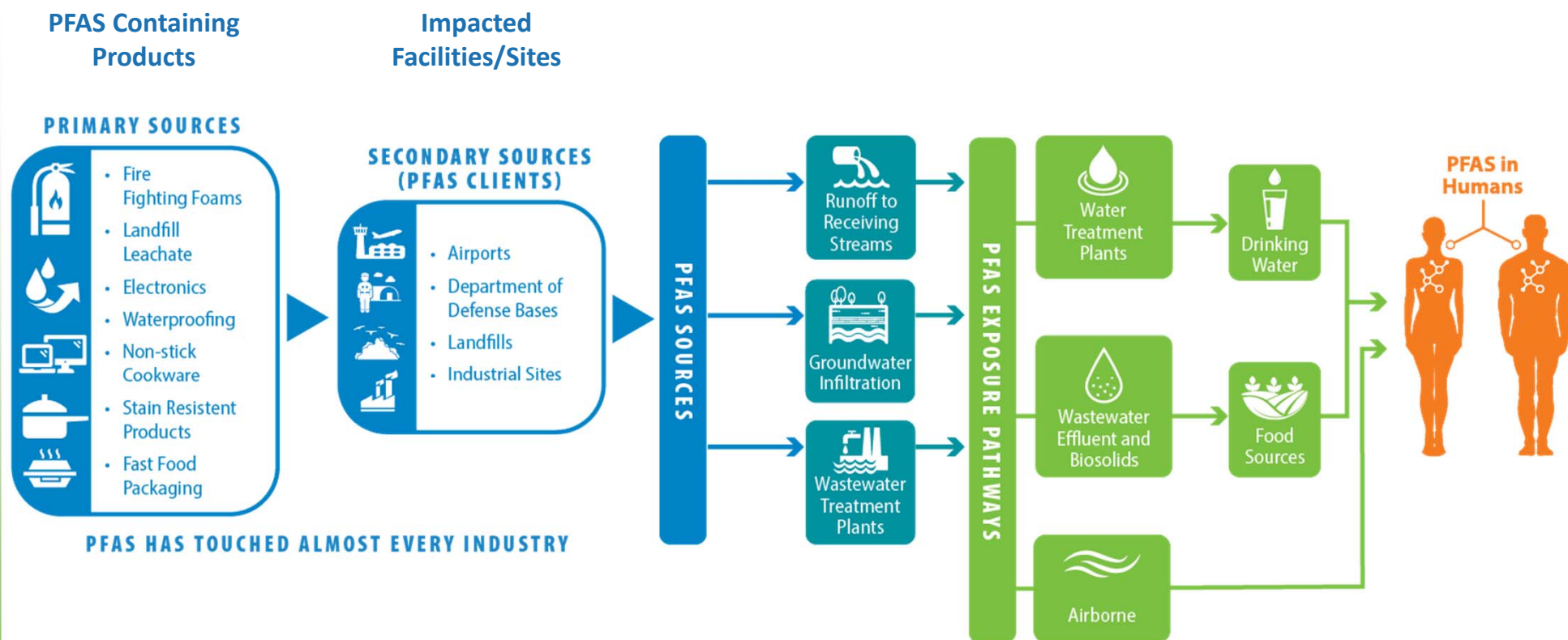
GenX

- Replaced PFOA (C8) in Fluorochemical Manufacturing.
- Nov 2016 article by Mei Sun et al.
- Utilities in the lower portions of the Cape Fear River in NC began removal studies.
- Now pursuing treatment to remove.
- NC Drinking Water Health Advisory = 140 ng/L

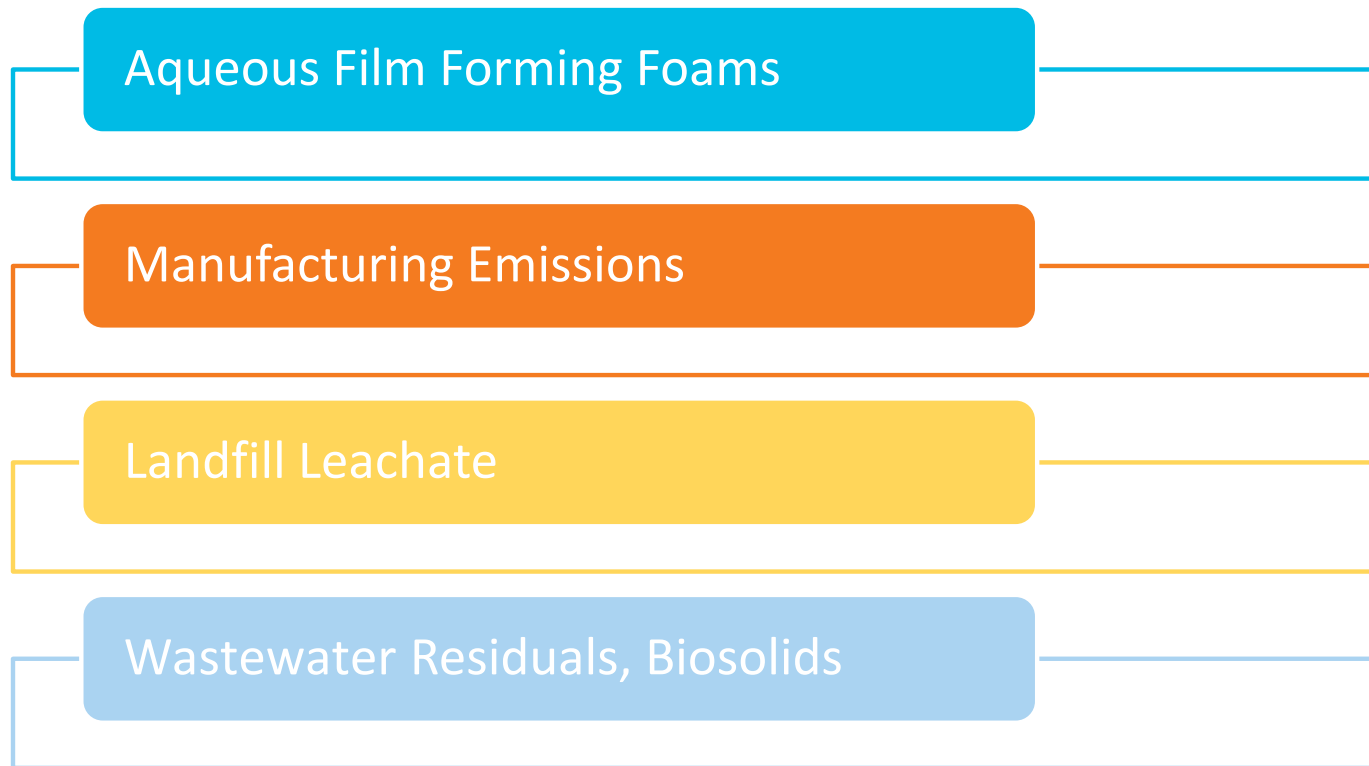


Source Mei Sun et al, ES&T Letters, Nov 2016

PFAS Lifecycle



How is PFAS Released to the Environment?



Aqueous film forming foam (AFFF)

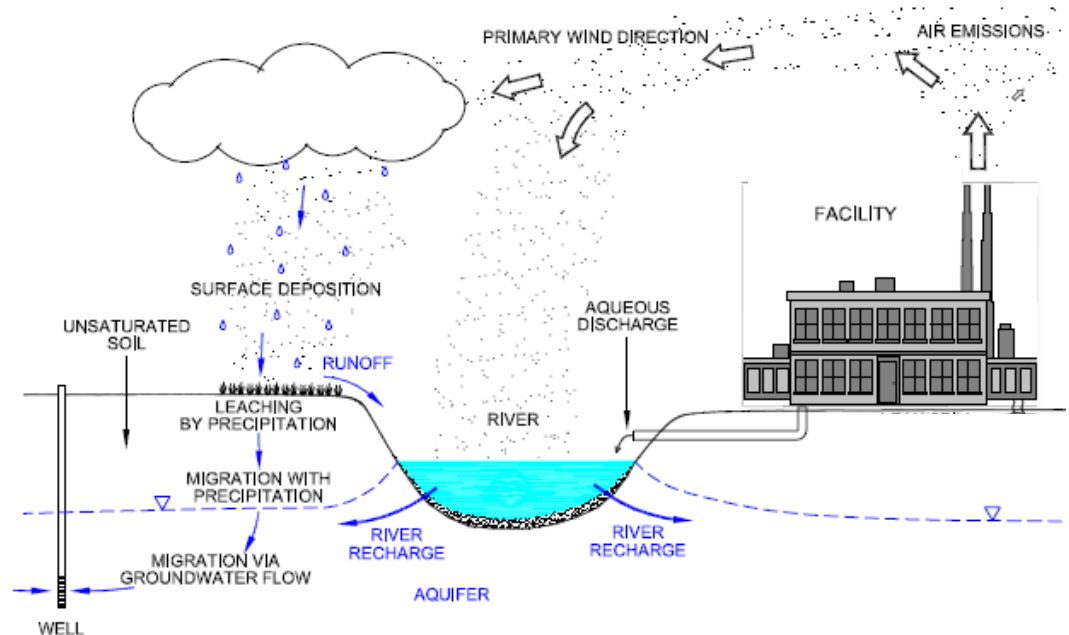
- DoD began use of AFFF in the 1970s to fight fuel fires
- Both military and civilian fire fighting training sites and emergency response sites
- Frequently directly released to the environment
- Complex, proprietary mixtures with high concentration of PFAS
- Georgia and Virginia recently passed bills to discontinue use of Class B firefighting foam (with some exceptions)



Source: Houston Chronicle (ITC Fire)

PFAS Emissions/Discharges from Manufacturing Sources

- Aqueous Discharges
- On-site Landfills or lagoons
- Air emissions
 - Wind directions and atmospheric deposition play key roles on transporting PFAS
 - PFAS can be detected in soil and water upgradient and downgradient from the manufacturing facility

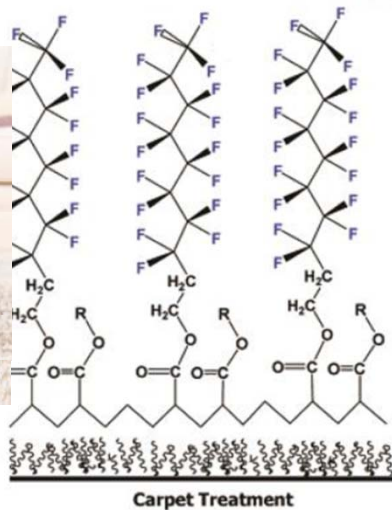


PFAS in Landfills

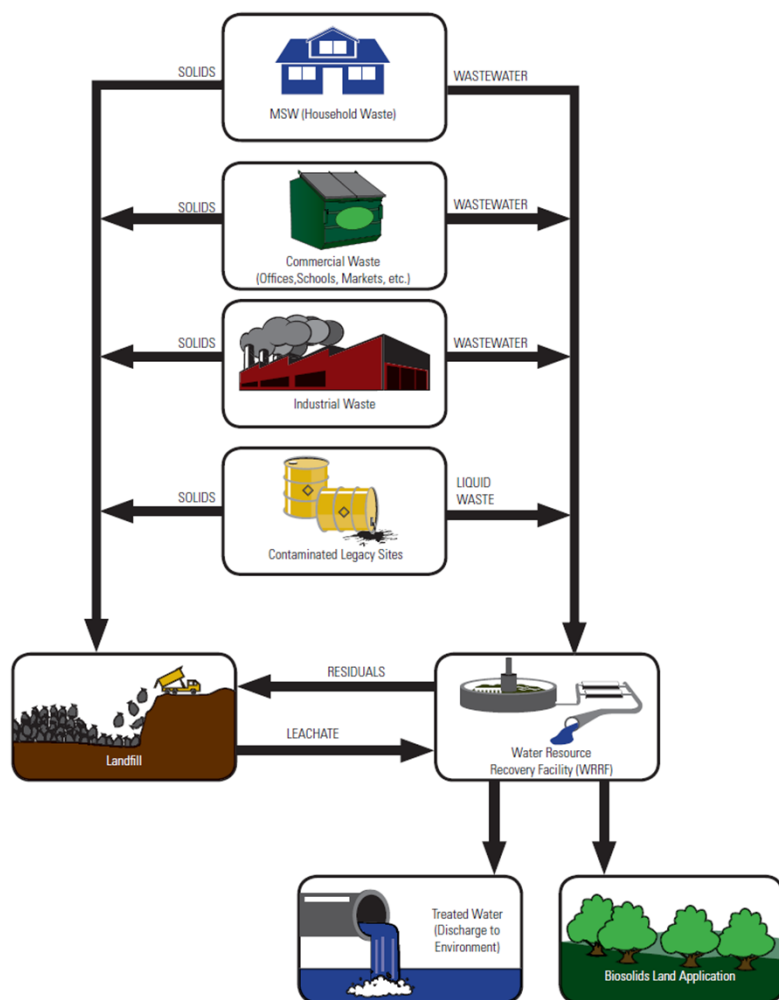


Fate of landfill leachates:

- Leach into groundwater with no treatment (if unlined)
- Recirculated back to landfill
- Discharged to POTW with or without pretreatment

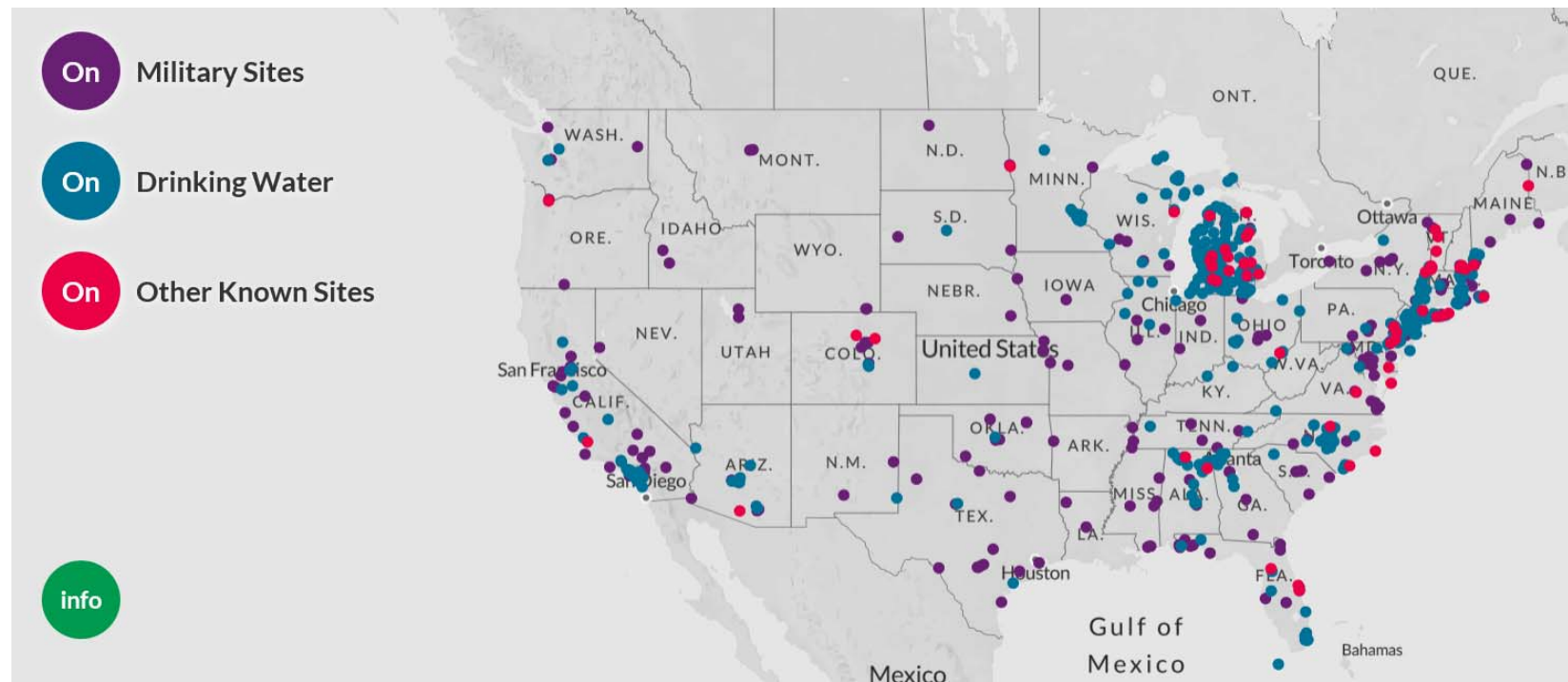


PFAS in Wastewater and Biosolids



- Significant research is on-going to understand fate of PFAS (and precursors) in wastewater and biosolids.
- **Most removal via sorption to wastewater sludge, particularly for long chain PFAS**
- Short chains get discharged into the environment
- Depending on influent compositions, typically effluent concentrations slightly lower than influent, but some documents effluent higher than influent

How Much PFAS Contamination Have We Found Today?



Source:



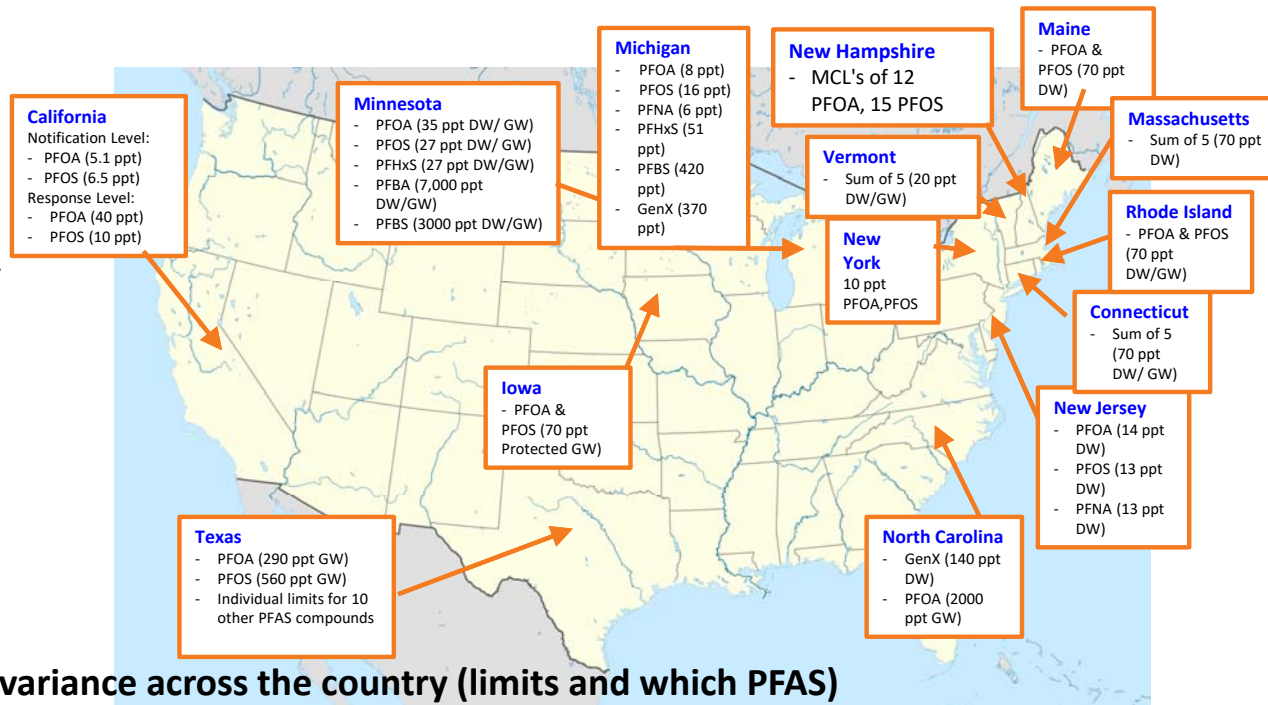
The Current Scientific Understanding of PFAS Health Impacts



- More research is needed to understand the link between exposure to PFAS and human health effects
- Having PFAS exposure or PFAS in your body does not mean you will necessarily have health problems now or in the future.
- Some health studies (primarily on animals) have found health effects linked to some PFAS such as:
 - Fertility issues and pregnancy induced hypertension and preclampsia
 - Increased risk of thyroid disease
 - Changes in immune system
 - Increased cholesterol levels
 - Increased risk of cancer, especially kidney and testicular cancers
- Overall scientific and medical evidence is currently inconclusive

PFAS Regulatory Landscape is Evolving and Is Currently Being Led at the State Level

- EPA has set HAL for PFOA + PFOA at 70 ng/L
- States Regulations (limits, HAs, goals) vary

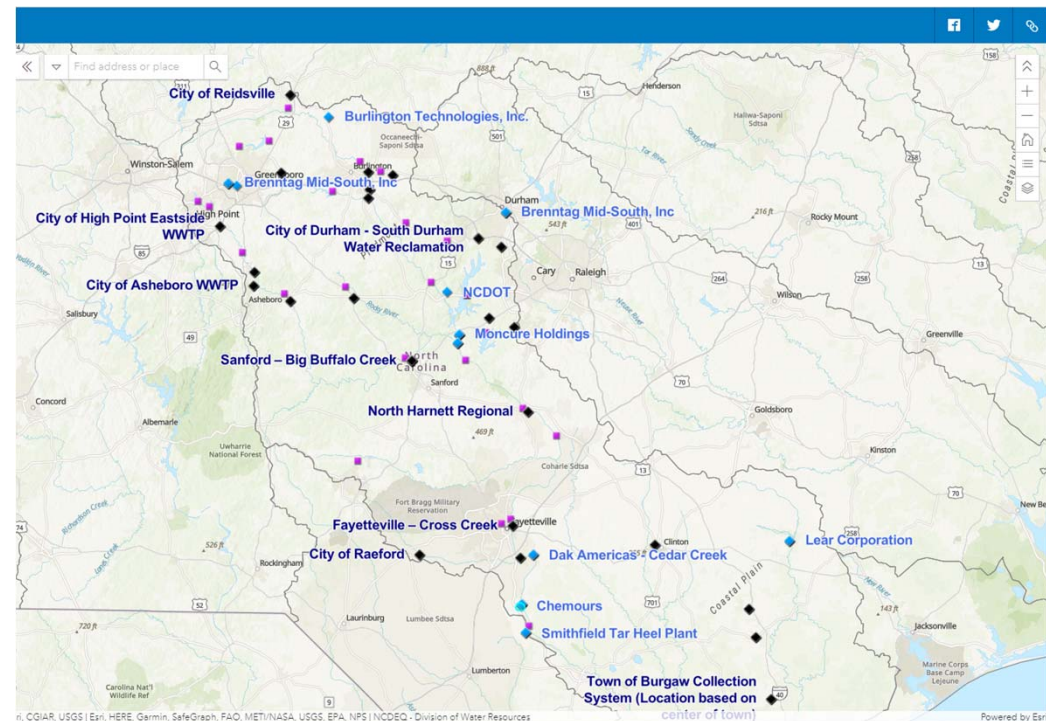


- Trends:
1. Wide variance across the country (limits and which PFAS)
 2. PFOS AND PFOA first, but more limits & States coming quickly
 3. States with lots of occurrence first and peer pressure of neighbor NE States
 4. Limits Keep Getting Lower!

NC DEQ – Wastewater Sampling 2019

- Cape Fear Basin NPDES dischargers with pretreatment programs
 - Influent testing for PFAS and 1,4 Dioxane
- Requirement could expand statewide
- Possibility to limit discharges of 1,4-dioxane and PFAS
 - Some NPDES permits include 1,4-dioxane

<https://deq.nc.gov/news/key-issues/emerging-compounds/managing-emerging-compounds-water#management-strategy-for-industrial-dischargers-and-pretreatment-facilities>



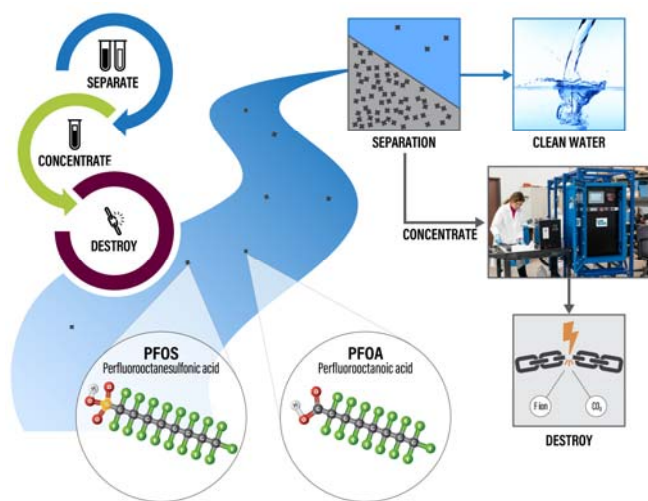
PFAS Monitoring Sampling and Analysis

	Method 537.1	SW-846 Method 8327	Method 533	Method 8328	ASTM 7979	ASTM 7968	Top Assay	ISO/CD 21675	Method 537M
Type of Sample	Drinking Water	Surface Water Groundwater Wastewater	Drinking Water	Surface Water Groundwater Wastewater	Surface Water Groundwater Wastewater Sludge (>0.2%)	Biosolids Soil	All PFAAs	Drinking Water Surface Water Groundwater Wastewater Sludge (>0.2%)	Surface Water Groundwater Wastewater
Pros and Cons	Limited capture of short-chain PFAS	Basic method already widely used	Effective capture of short-chain PFAS	Effective capture of long-chain PFAS	Higher minimum reporting limit	Suitable for biosolids and soil	Captures all PFAAs	Broad spectrum of PFAS can be analyzed	-Faster runs -Not validated -Inconsistent QC

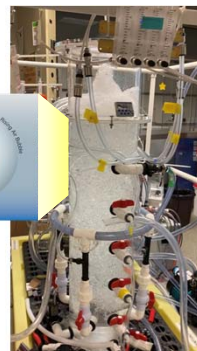


PFAS Treatment Options

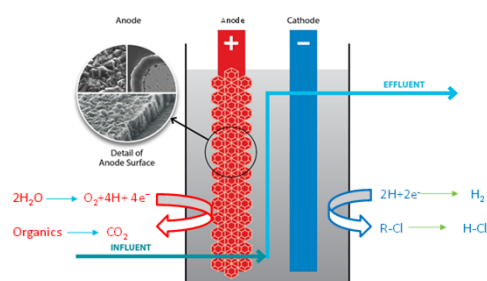
Separate-Concentrate-Destroy



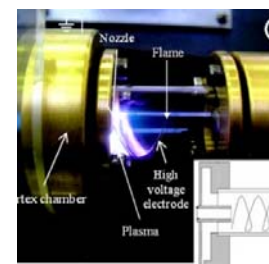
SAFF™



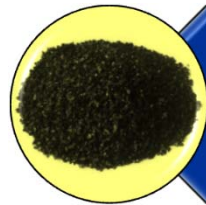
Electrochemical
Oxidation



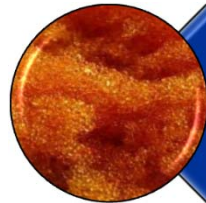
Plasma



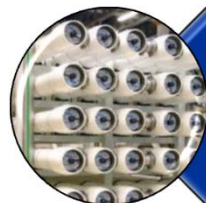
Three Mainstream PFAS Treatment Technologies



Granular Activated
Carbon (GAC)



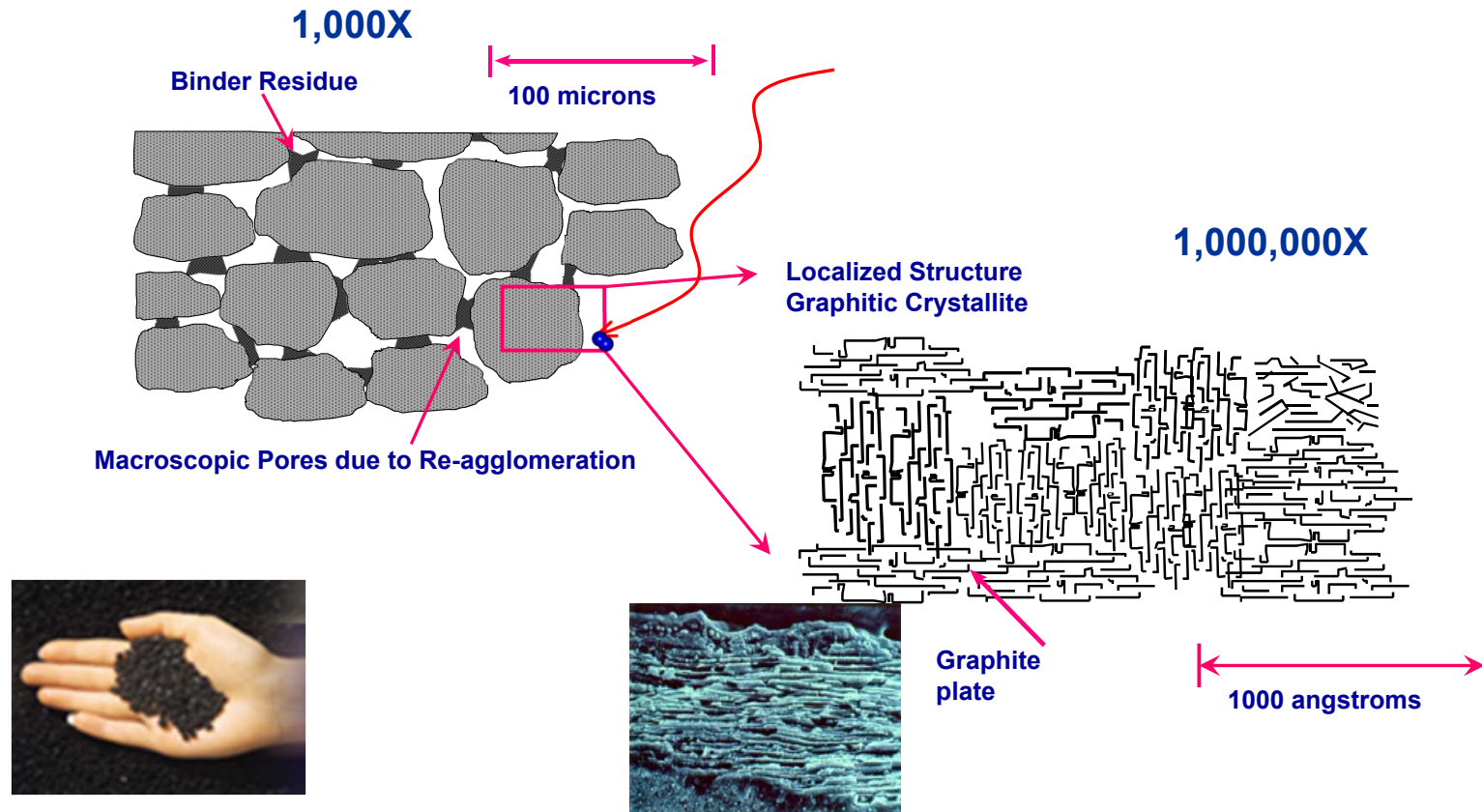
Ion Exchange Resin



Reverse Osmosis
Membranes

PFAS are NOT removed appreciably by conventional drinking water treatment

Granular Activated Carbon



Example GAC Contactors



Major Pros and Cons of GAC

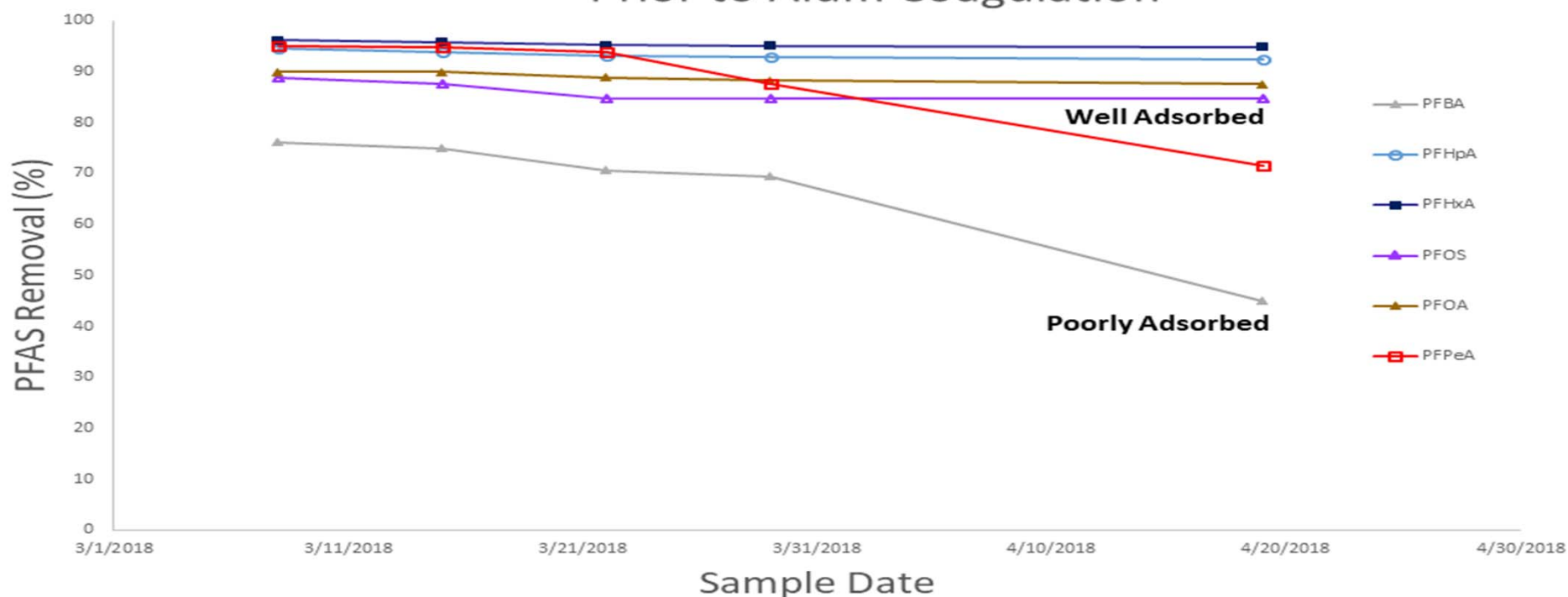
PRO

- Most Effective for Strongly Adsorbing Compounds - Many SOC/PPCPs/EDC such as Pesticides, PFOA, PFOs
- EPA termed BAT for many SOC
- Some bio-removal continues long after adsorptive sites are filled
- Typically lower capital cost

CON

- Much Less Effective (shorter life) for Gen-X and PFBA
- The amount removed decreases with time as adsorptive sites are filled
- Following a sudden large drop in concentration of a compound like Gen-X in the Influent, the GAC releases some of the compound as it seeks the new equilibrium
- Spent GAC requires disposal or reactivation

Fresh Norit 820 GAC PFAS Removal with 40-60 ppm Donau Standard Purification WC-800 Added to Jordan Lake Raw Water Prior to Alum Coagulation



Sample results below the method reporting limits (MRL) were approximated at the MRL for these calculations. This graph therefore represents a conservative depiction of removal percentages that may be at or above the levels shown. The MRL for all of these compounds is 2 ng/L with the exception of PFBA, which has an MRL of 5 ng/L.

Ion Exchange

- Removing undesirable ions in waters through a chemical reaction using an ion exchange resin.
- A substitution reaction is used to remove ions



Ion Exchange Resin

- Contained in columns 4 to 5 feet in depth
- 20 x 50 mesh area of bead-shaped particles – flow distribution
- Generally charged

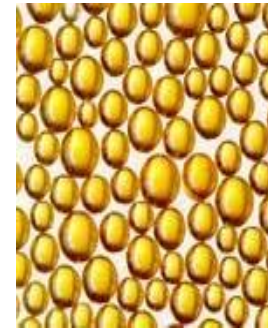
Anionic

- Exchange for negative ions
- Charged with hydroxide (OH^-) or chloride (Cl^-) ions



Cationic

- Exchange for positive ions
- Charged with hydrogen (H^+) or sodium (Na^+) ions



Grove Pond PFAS Treatment Facilities

- AIX for PFAS Removal with Resin 2
- Calcium thiosulfate for dechlorination & bag filters prior to IX
- Zinc orthophosphate for improved corrosion control



Major Pros and Cons of Ion Exchange (IX)

PRO

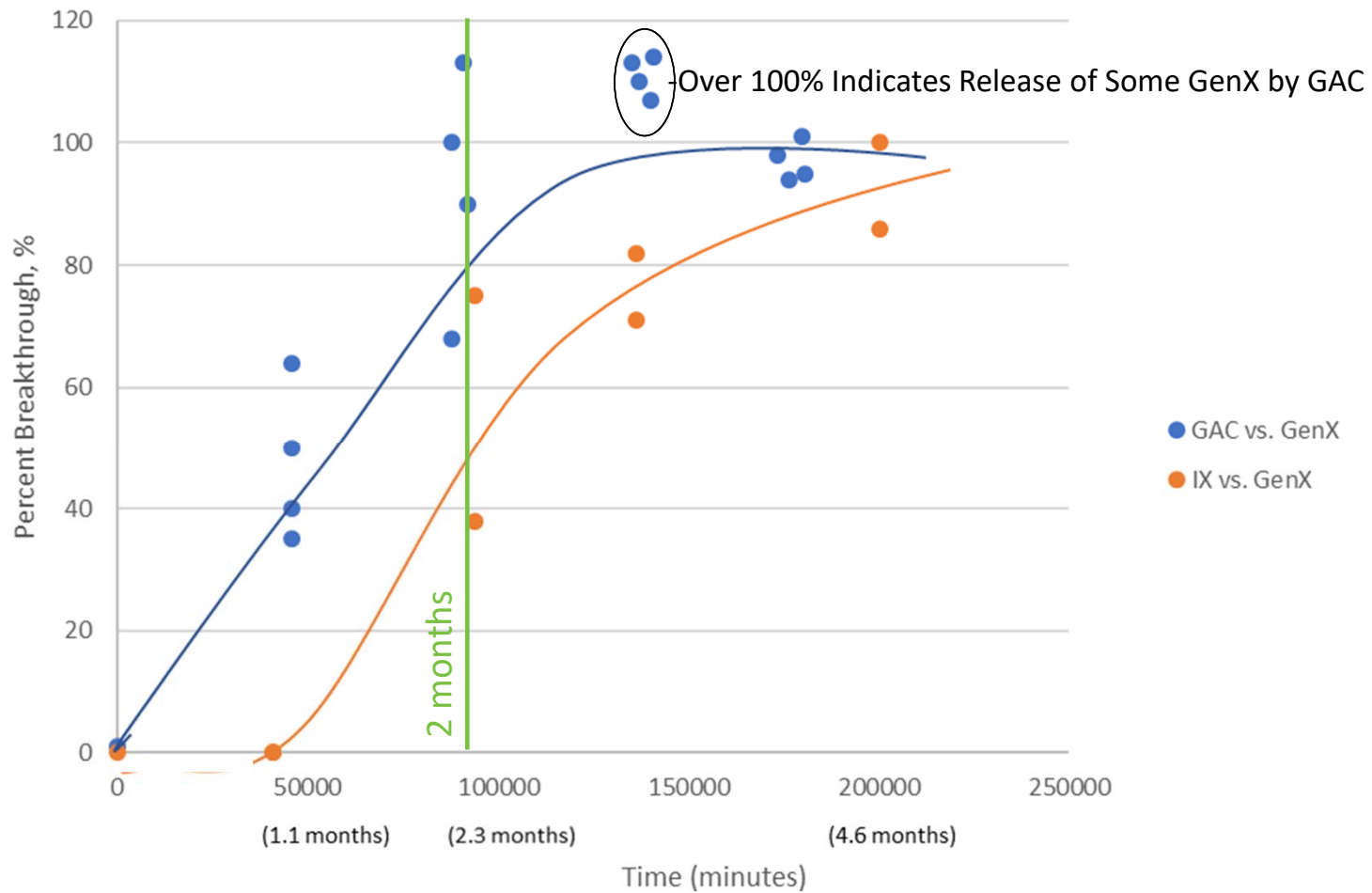
- Excellent Removal of Most PFAS – Better than GAC, especially for GenX
- Extra Barrier for Anions – PFAS, organics, bromide, etc.

CON

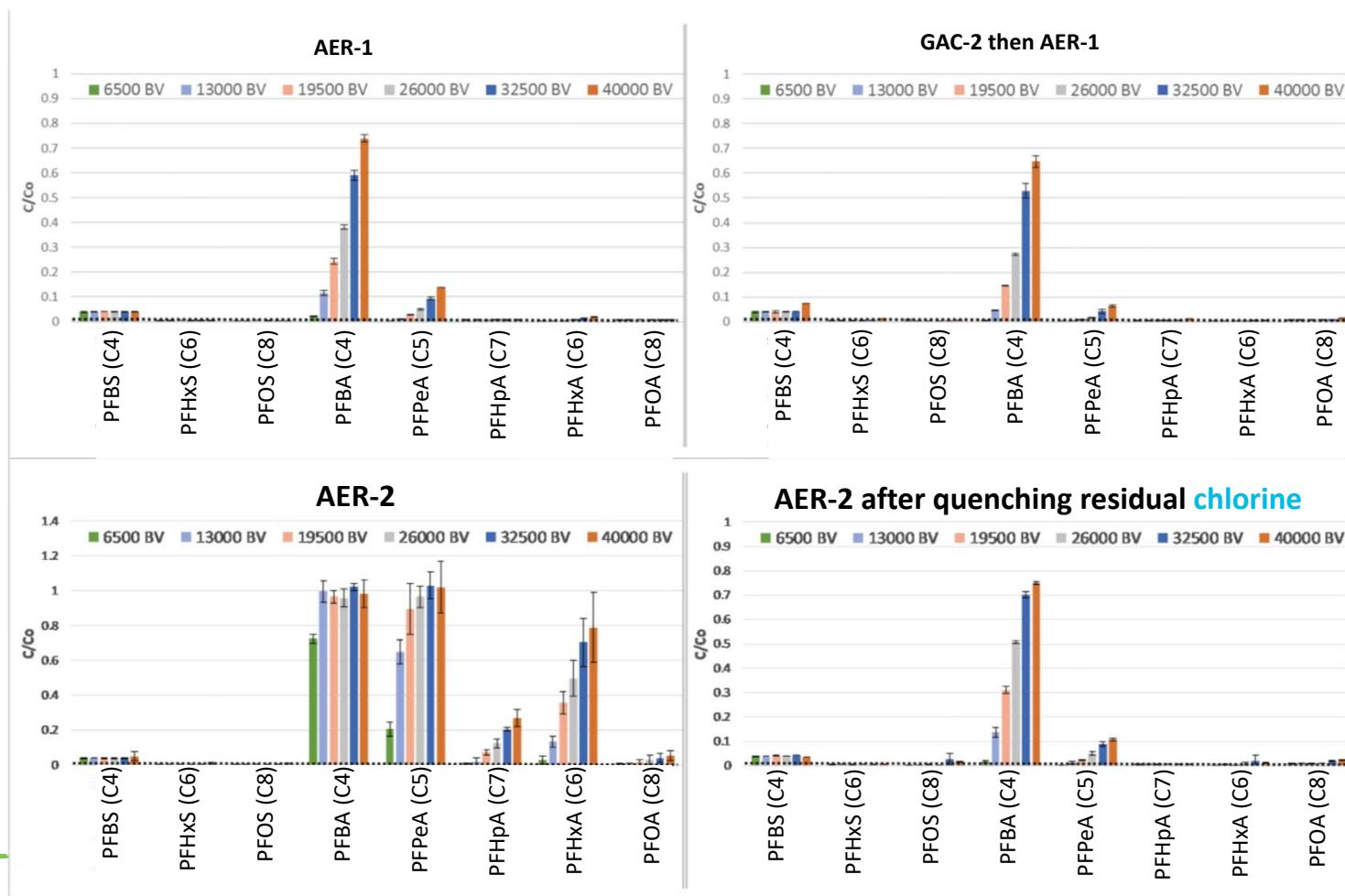
- Spent IX resin requires disposal



Example GenX Breakthrough Curves



Bench-scale validation of commercial products



GAC vs Ion Exchange Resin (IX-R)

 GAC	 Single Use IX-R
7 to 20 minute EBCT	2-3 minute EBCT
Larger infrastructure footprint	Smaller infrastructure footprint
Typical bed life: 50-120,000 bed volumes	Typical bed life: 250-300,000 bed volumes
GAC media is less expensive	IX-R media is more expensive
Less effective for short chain PFAS	Effective for a wider range of PFAS
Well established technology	Not as extensively practiced as GAC
Backwash is available	Backwash not recommended
• Life cycle costs for GAC and IX-R are often similar • Both generate spent media requiring off-site reactivation (GAC) or incineration (IX-R) • Pretreatment may be needed for both technologies to increase media life span	

Reverse Osmosis

- In Reverse Osmosis, water passes through a semi-permeable membrane in the direction opposite to that for natural osmosis by applying a hydrostatic pressure greater than the osmotic pressure.

Membranes – Types

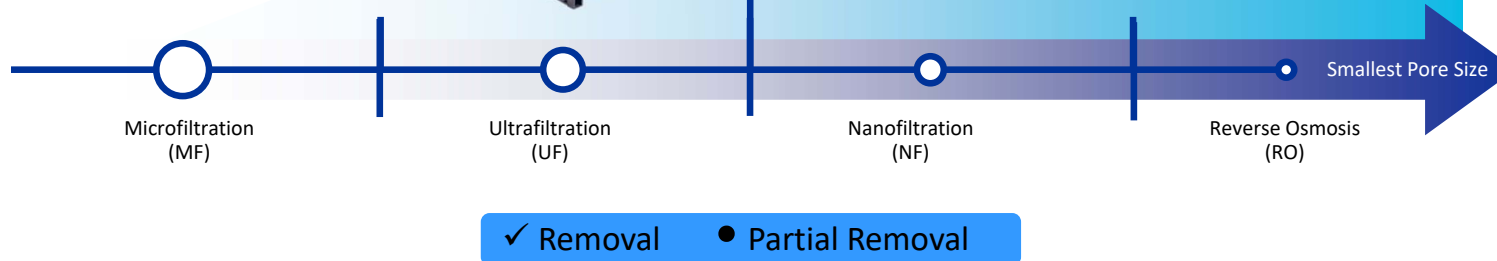
MF & UF Removes:

- ✓ Turbidity
- ✓ Viruses
- ✓ Bacteria
- ✓ Protozoa
- Organics

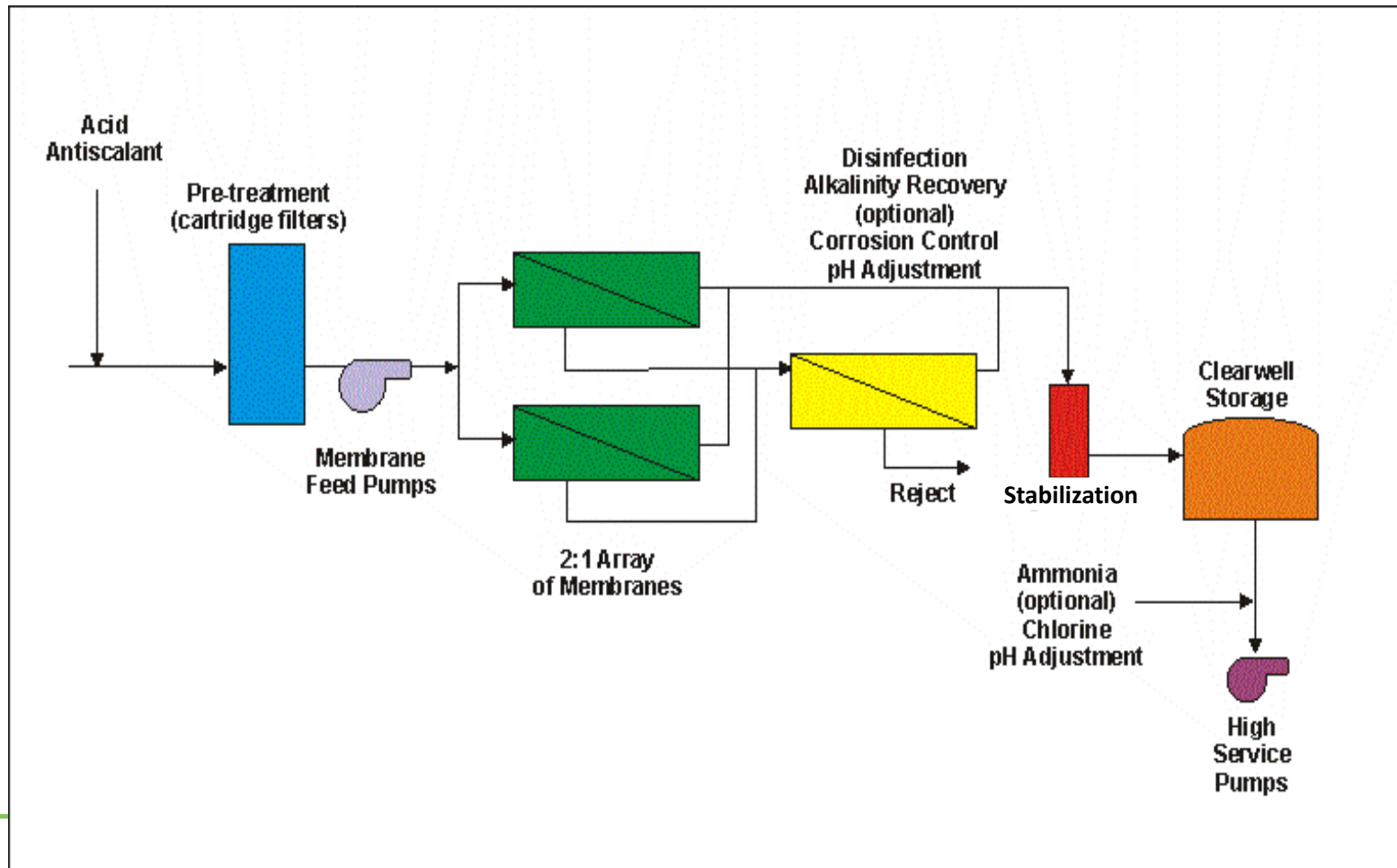


NF & RO Removes:

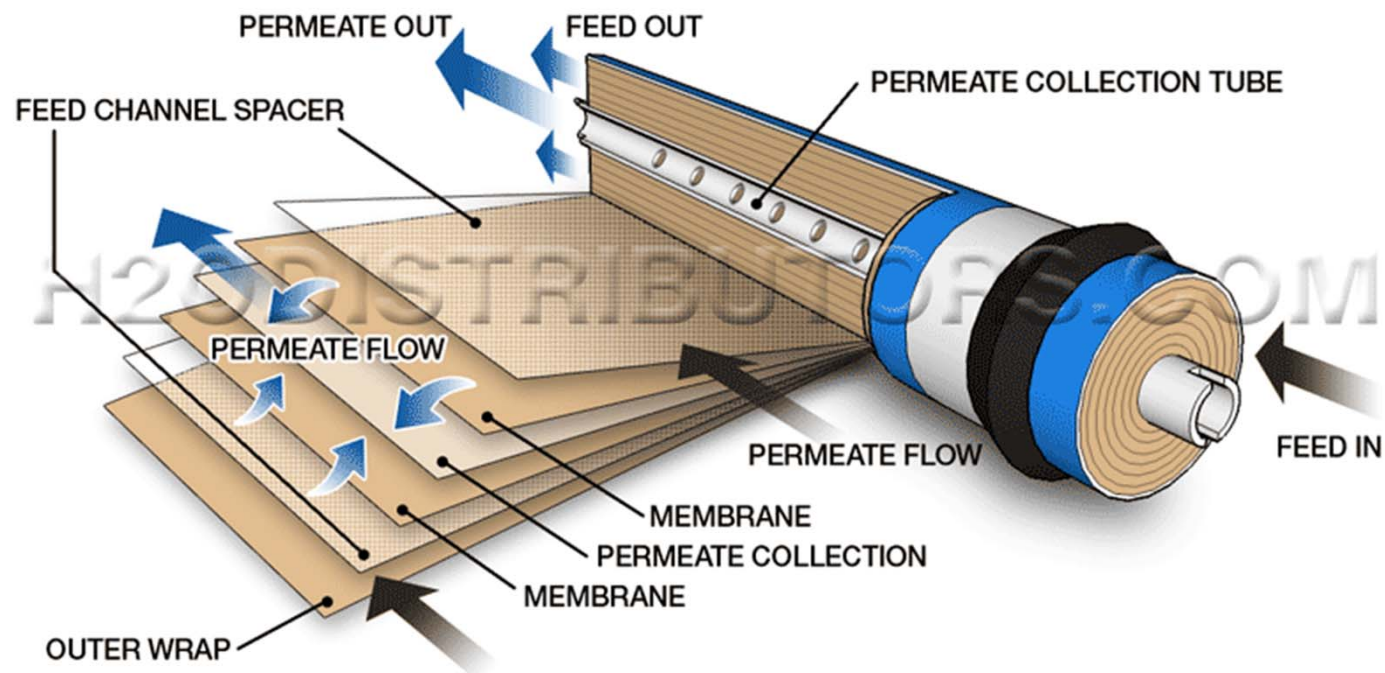
- ✓ Turbidity
- ✓ Inorganics
- ✓ Organics
- ✓ Virus, Bacteria, Protozoa
- ✓ RO for TDS
- ✓ RO for Best Removal of PFCs, PPCP/EDCs



Example RO Schematic



How does RO work?



RO Pilot Testing Update

- 16-Month Pilot, started February 2018
- Feed Water in Pilot Unit is Filter Effluent from Drinking Water Treatment Plant
- 18 sampling events



PFOS + PFOA Removal for RO Membranes



RO Technology Selection Example

Parameter	Filtered Water Concentration	RO Treated Water	Calculated Removal %
Gen X	7 – 12 ng/L	ND	--
Nafion Byproduct 1 & 2	ND	ND	--
PFMOAA	320 – 750 ng/L	ND – 11 ng/L	98%+
PFO2HxA	12 – 26 ng/L	ND	--
PFHxA	19 – 20 ng/L	ND	--
PFPeA	16 - 17 ng/L	ND	--
PFOS + PFOA	26 ng/L	ND	--
Sum (45) of PFAS Tested	423 – 892 ng/L	ND – 11 ng/L	--

Parameter	Filtered Water Concentration	RO Treated Water	Calculated Removal %
1,4-Dioxane (industrial chemical)	3.2 µg/L	0.2 µg/L	94%
Carbamazepine (seizure medicine)	13 ng/L	ND	--
Atrazine (herbicide)	58 ng/L	ND	--
Cotinine (metabolite of nicotine)	15 ng/L	ND	--
DEET (insect repellent)	44 ng/L	ND	--
Simazine (herbicide)	57 ng/L	ND	--
Tris (1,3 dichloro-2-propyl)phosphate (pesticide, flame retardant)	120 ng/L	ND	--

Economic Comparison of Advanced Treatment Options

	Low Pressure Reverse Osmosis (LPRO)	Ozone/BAF - GAC	GAC/IX/UV-AOP
Total Capital Costs	\$ 99 M	\$ 99 M	\$ 84 M
25-yr Present Worth of Annual Costs	\$ 59 M	\$ 95 M	\$ 93 M
Total 25-yr NPW (Capital + Annual O&M)	\$ 158 M	\$ 194 M	\$ 177 M

**** In some cases, RO cannot be chosen as a feasible option due to high capital costs and lack of options on managing rejected concentrates**

- Capital and O&M costs based on removal of >90% of each target contaminant

Major Pros and Cons of RO

PRO

- Best Available Technology for Removing Most Contaminants - will give Non-detect for the Largest Number of Parameters
- Barrier Approach – effluent contaminant concentrations will not rise with time of use or have bleed out potential as they do for GAC and IX
- Barrier to Pathogens



CON

- Higher Capital Cost than GAC or IX
- O&M Needs
- Need for Stabilization
- Concentrate Disposal/NPDES Permit

Limitations of “Conventional” PFAS Treatment



We are getting smarter on PFAS technology selection

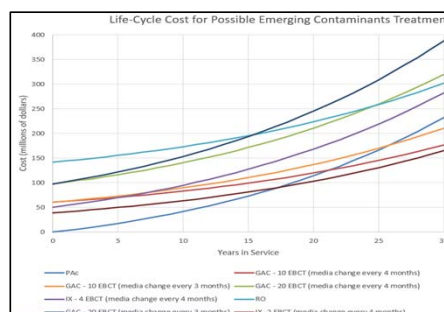


Engineering evaluation

- Treatment options
- New systems to remove PFAS



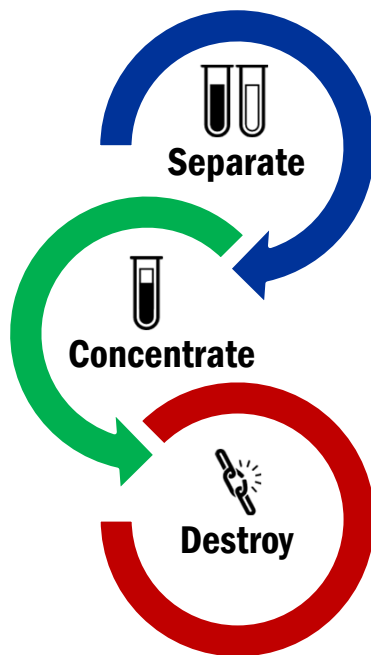
Check on PFAS treatability and compatibility with other existing treatment processes



System design, permitting, construction, operation, maintenance, monitoring
→ Life cycle success

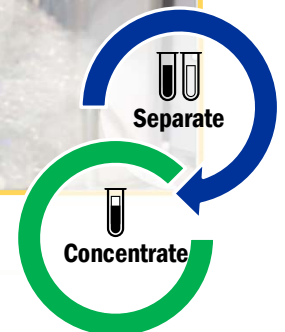
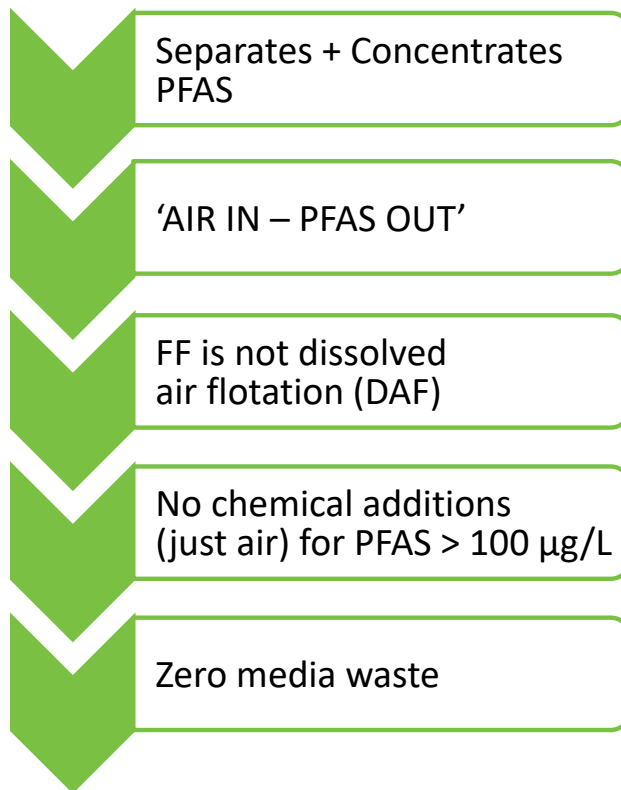
Pilot testing and life cycle assessment

Treatment Trains - PFAS Management Solution



Treatment Goals	Example Technologies
• Protect human health and the environment • Meet safe drinking water and discharge requirements • Reduce waste stream volume	• GAC, AIX, RO (demonstrated) • NF • Regenerable sorbents • Foam fractionation • Regenerable media → regenerant waste • Surfactant or coagulant separation → PFAS laden flocs • Foam fractionation → foam concentrate
• Zero PFAS waste discharge	• High temp thermal, electrochemical, plasma, sonolysis, others

SURFACE ACTIVE FOAM FRACTIONATION (SAFF™): *A Cost-effective, Green Technology*



PFAS Removal at the Air-Water Interface

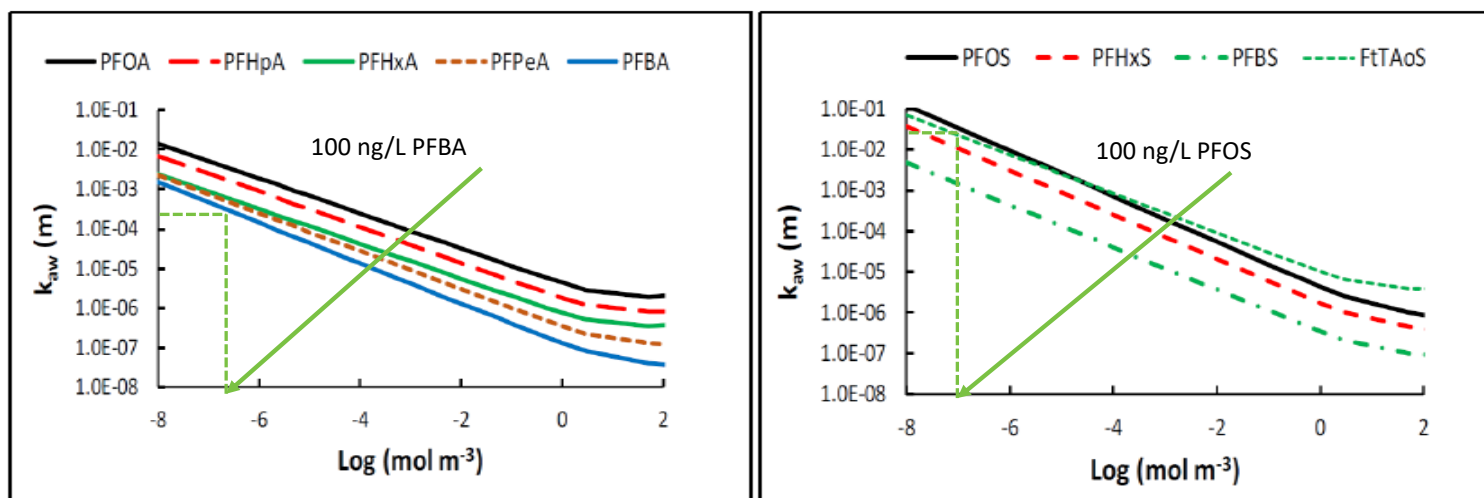
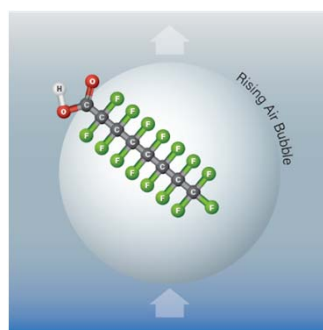


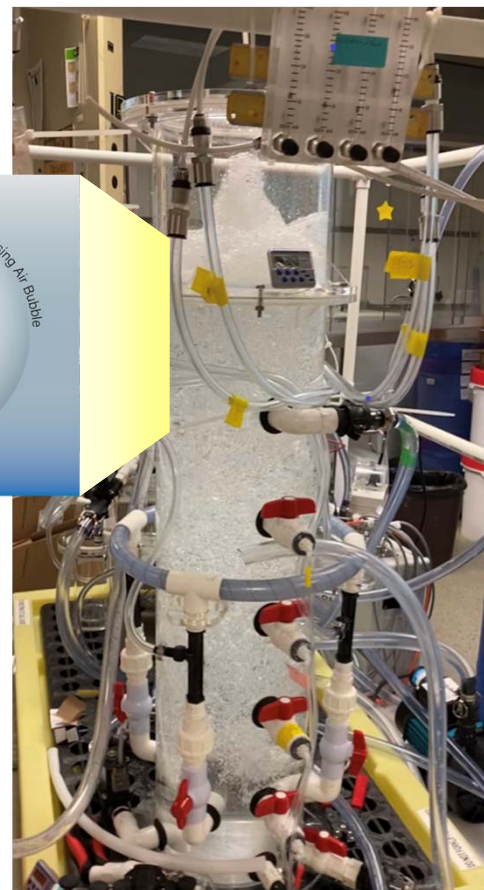
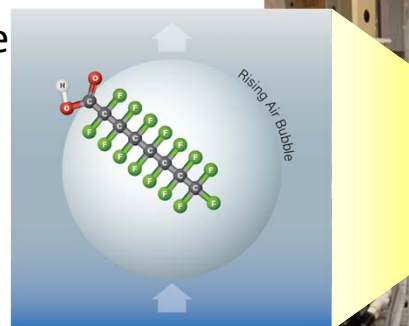
Figure courtesy of Schaefer et al., 2019



Surface Active Foam Fractionation (SAFF™)

Developed by OPEC in Australia

- Increase air-water interface and separate foam from water phase
- Creates PFAS foam concentrate
- Applicable for:
 - ✓ **Groundwater**
 - ✓ **Surface water**
 - ✓ **Wastewater**
 - ✓ **Leachate treatment**
- No sorbents or chemicals needed



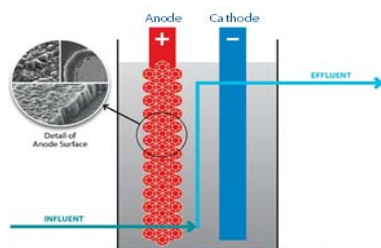
PFAS Treatment Summary

- PFAS treatment is a young practice: Do not generalize or assume and consider site specific conditions
- GAC, IX-R and RO are often effective but all generate waste streams
- Commercial products behave differently, pre-design studies should be considered for all cases
- PFOS and PFOA treatment down to below the 70 ppt HA is being achieved
- Removal of lower Molecular Weight PFAS compounds (C3 through C6) is generally more difficult than for PFOS and PFOA (C8)
- PFAS destruction technologies are under development

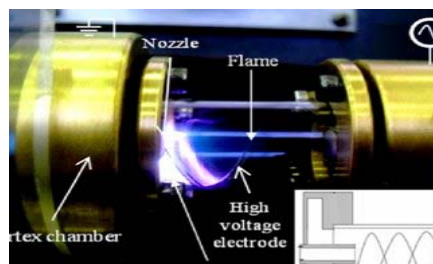


PFAS Destructive Technologies

**Demonstrated at the Bench:
Pilot and Field Scale**



**Electrochemical
Oxidation**



Plasma

**Research and Development:
Bench**

Sonolysis

UV – Hydrated Electrons

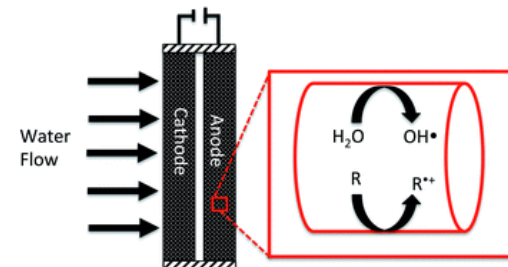
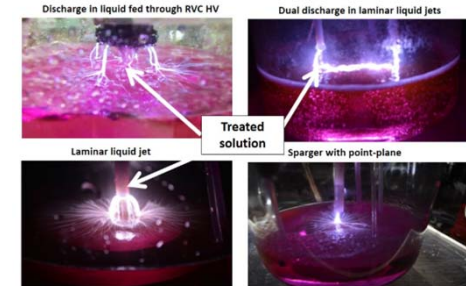
Photolysis/photochemical

Hydrothermal

Supercritical water oxidation

PFAS Destruction Is Possible but Under Development

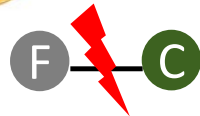
- PFAS are mineralized to F^- and CO_2
- It requires very high energy to break C-F bond
- Only makes sense for PFAS concentrates
- Most discussed destruction technologies
 - Plasma treatment
 - Electrochemical oxidation (EO)
 - Sonication
- Pilot scale studies were funded
- Significant progress has been made on understanding EO treatment effectiveness
- Major limitations
 - EO: slow kinetics, perchlorate generation
 - Plasma and sonication: less effective for short chain PFAS, operation safety, costs



PFAS Destruction vs. Transformation



Complete Destruction



Breaking C-F bonds to mineralize PFAS

Three lines of evidence

PFAS disappearance



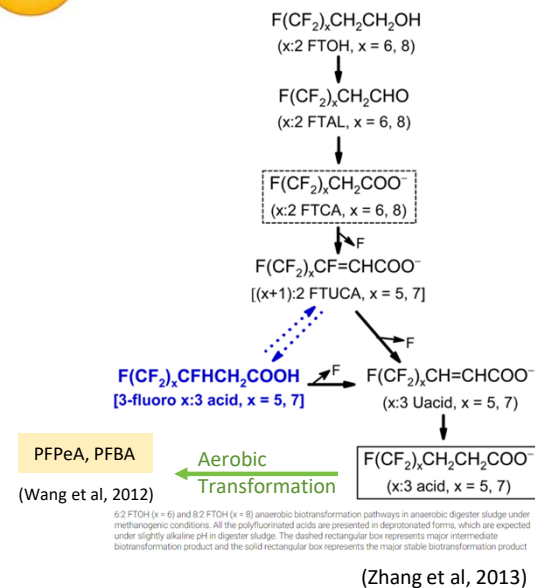
Fluoride generation



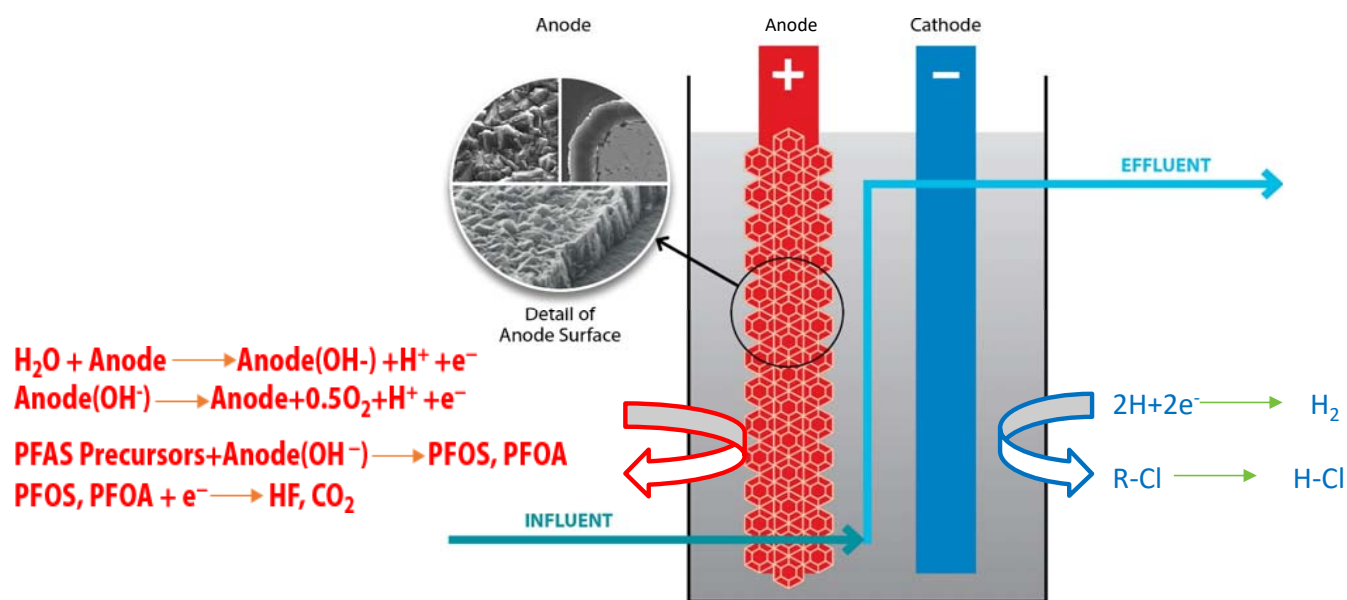
Total organic fluorine concentration reduction



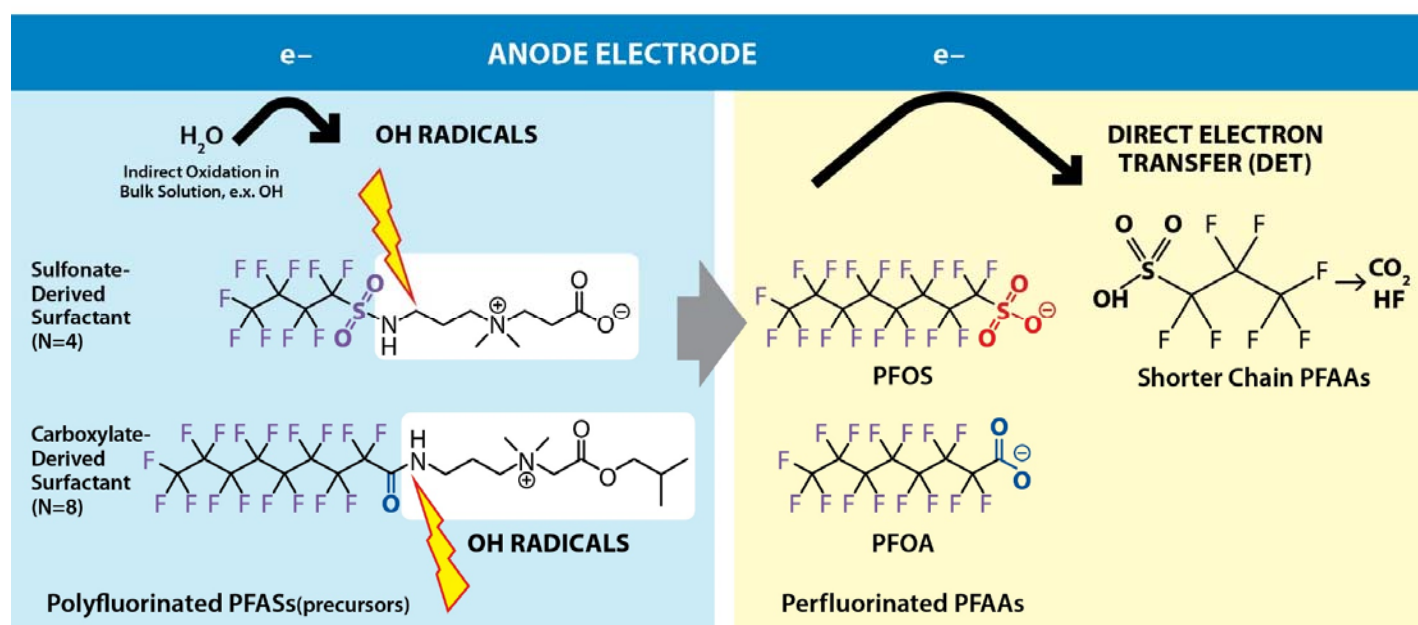
Incomplete Destruction



Electrochemical Oxidation (ECO) Water Treatment Can Degrade Virtually Any Organic Contaminant

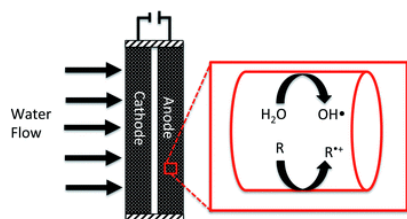


Degradation Mechanisms During ECO



Electrochemical Oxidation

- PFAS destruction requires high energy to break C-F bond
- PFAS are **mineralized** to F^- and CO_2
- Stainless steel anode and boron-doped diamond cathode
- 80% reduction of PFCAs and PFSA's after 8-hr treatment
- No transient increases in PFCAs or PFSA's
- 200 W power supply; 25 – 200 mA/cm^2

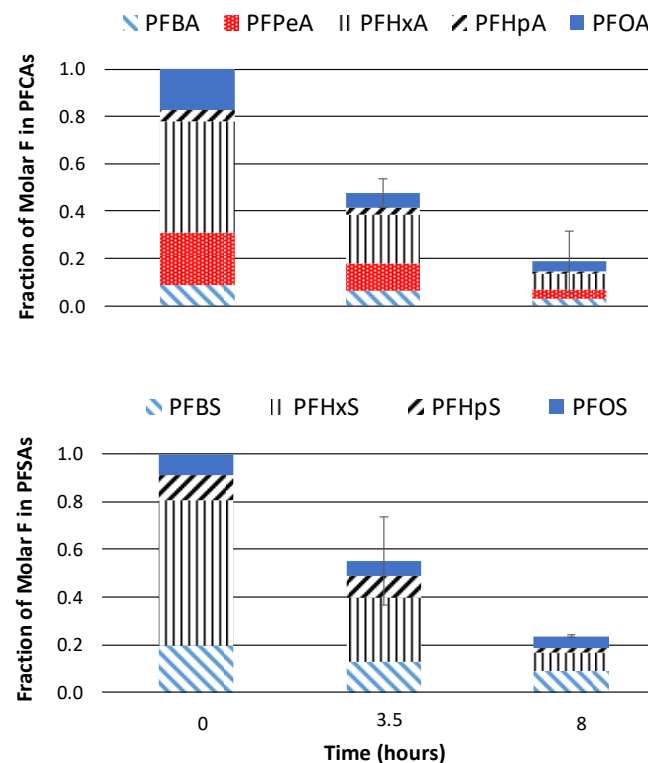


Environmental Science & Technology

Electrochemical Transformations of Perfluoroalkyl Acid (PFAA) Precursors and PFAAs in Groundwater Impacted with Aqueous Film Forming Foams

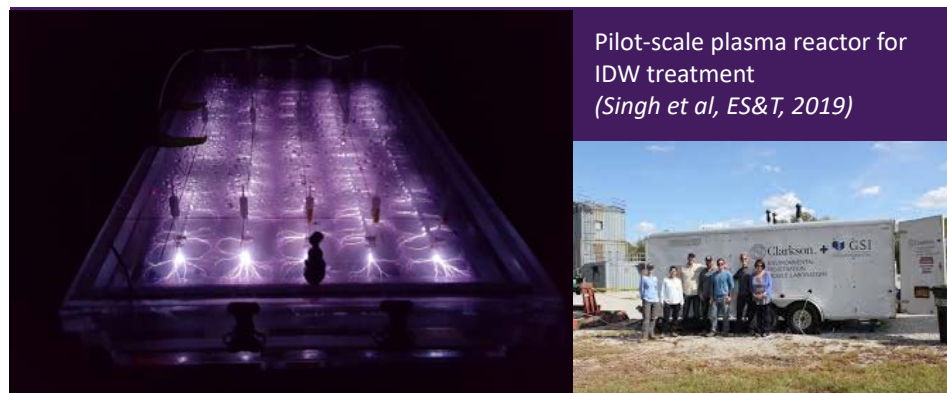
Charles E. Schaefer,^{1,*} Sarah Chivke,¹ P. Lee Ferguson,² Christina Andaya,¹ Aniela Burant,¹ Andrew Mair,¹ Timothy J. Strathmann,¹ and Christopher P. Higgins¹

1. Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6001; 2. Environmental Sciences Division, Lawrence Livermore National Laboratory, Livermore, California 94550

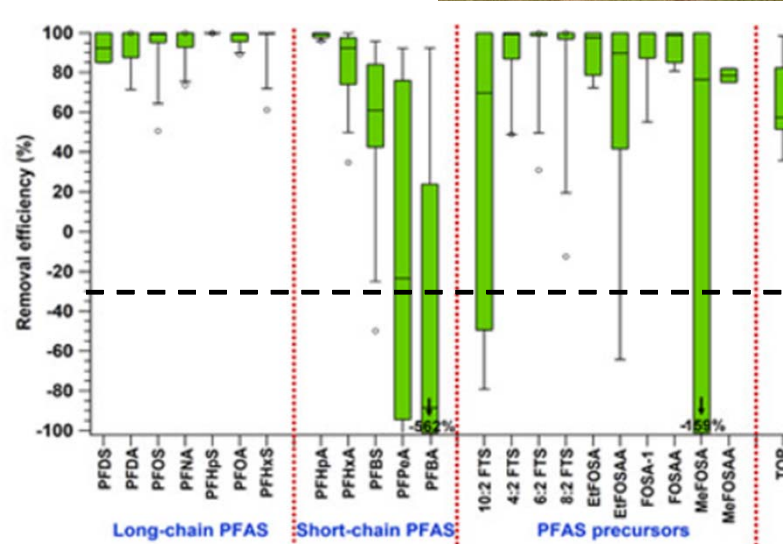


Plasma

- Groundwater; AFFF; regenerable AIX; regenerant waste; IDW
- Shorter (minutes) reaction time, not hours
- Not effective for shorter chain PFAS
- Partial destruction leads to accumulation of some PFAS
- Not yet ready to assess full-scale PFAS treatment life-cycle costs



Pilot-scale plasma reactor for IDW treatment
(Singh et al, ES&T, 2019)



Takeaways



Future PFAS solutions will focus on PFAS destruction with zero waste discharges



Most destructive technologies (ECO and Plasma) are impractical for dilute streams – best suited for low-volume, high-strength PFAS concentrates



Effective PFAS destruction that checks all the boxes for full-scale applications is going to be challenging and will take years to develop



More pilot-scale demonstrations for PFAS destruction in concentrates (waste streams) will be the interim solution



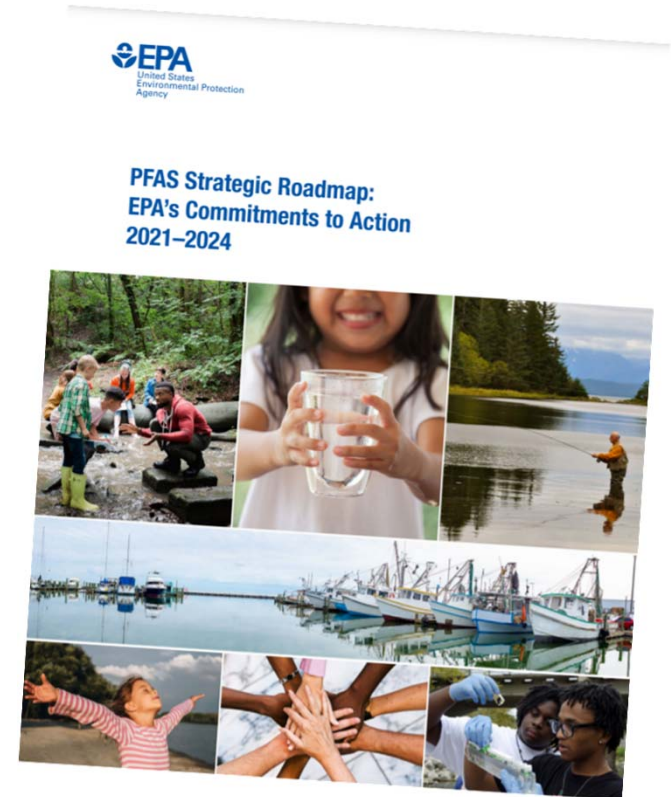
When water matrix is complex, shorter chain PFAS and precursors are present, complete defluorination remain problematic for nearly all destruction technologies



Next Steps

What's on the horizon

- Research
 - Toxicity assessments
 - Exposure pathways
 - Transport and fate in the environment
 - Remediation and control technologies
- Restrict
 - Minimize exposure (e.g., drinking water regs)
 - Prevent or minimize discharges
 - Source control
- Remediation
 - Address contamination
 - Monitor progress





Questions?

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