Los Angeles County Sanitation District
Industry Advisory Council

7 Habits of Highly Effective PFAS Source-Trackers

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carollo 90 YEARS

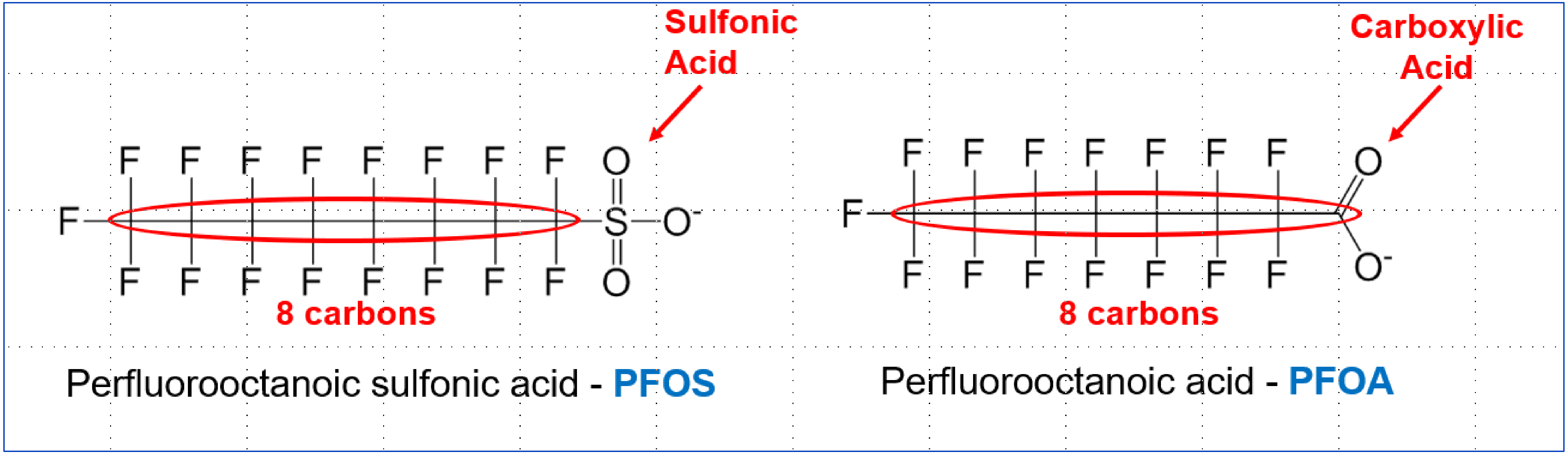
01 Background

Per- and Polyfluoroalkyl Substances (PFAS) are fluorinated chemicals with many uses and unique properties

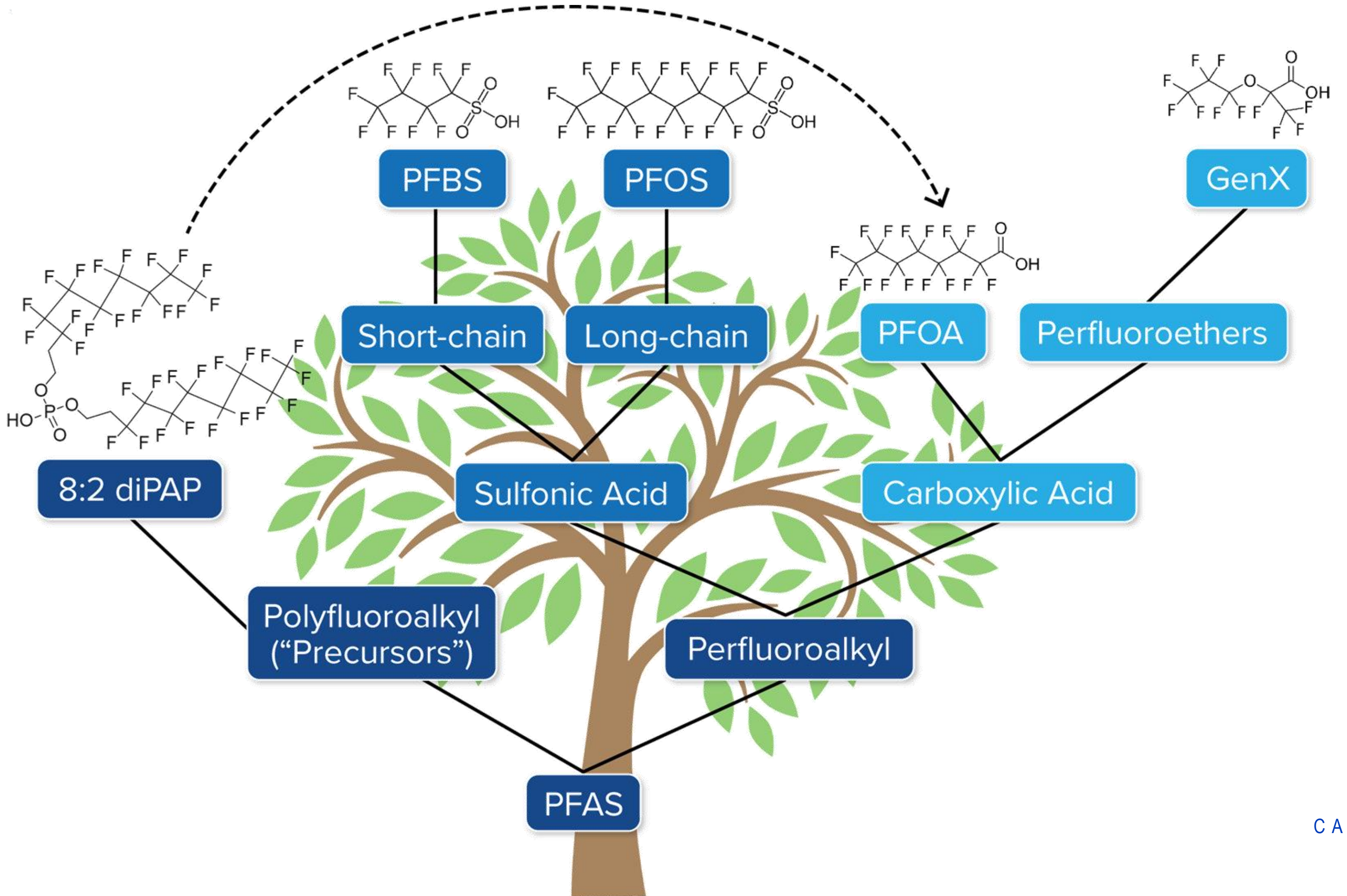
UNIQUE PROPERTIES

- Stain repellant
- Flame resistant
- Non-stick
- Water resistant
- Good for coatings

PFOA and PFOS are of the most concern in the PFAS family

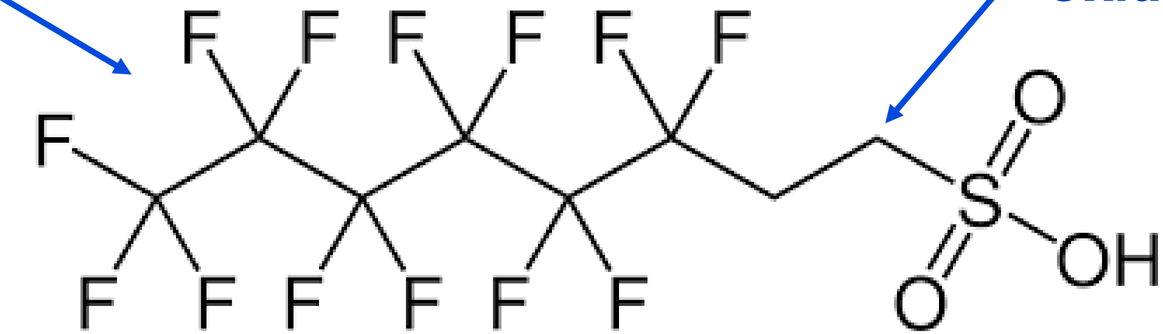


PFAS are a galaxy of compounds (~10,000)!



Polyfluoroalkyl substances or “precursors” have a fluorinated side and a non-fluorinated side

Fluorinated
Hydrophobic
Recalcitrant

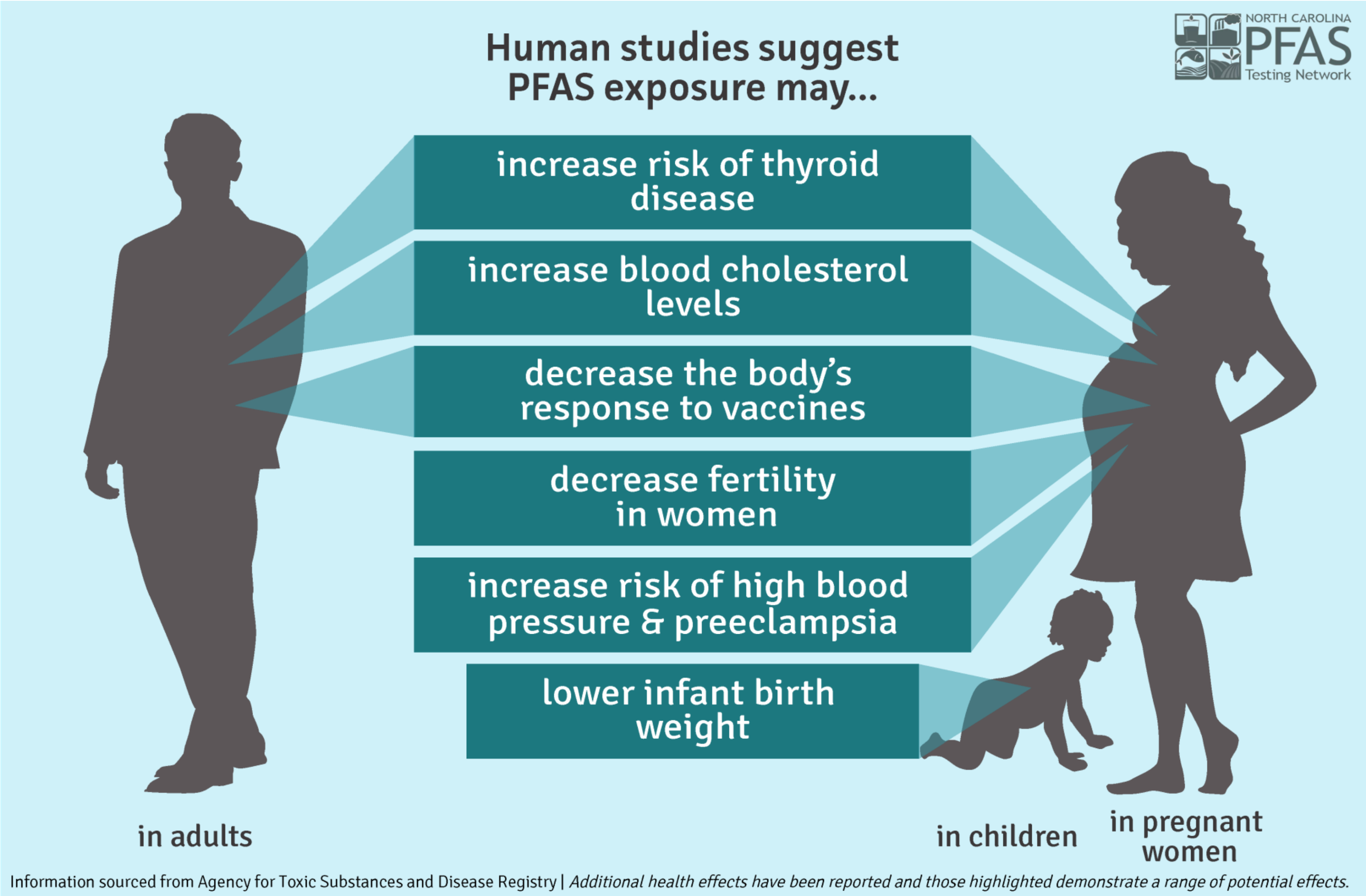


Non-Fluorinated
Biodegradable
Oxidizable

Polyfluorinated precursors can transform into perfluoroalkyl substances

Health Risks

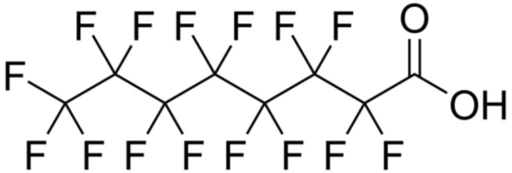
PFOA and PFOS have been linked to many adverse health effects



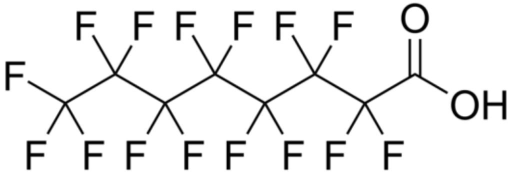
PFAS Occurrence

PFAS are everywhere

- **PFAS have been detected even atop Mount Everest and at the North Pole**



Miner et al. 2021. *Sci. Tot. Env.* 759, 144421.



Young et al. 2007. ES&T. 41, 3455-3461.

PFAS are detectable in all wastewater effluent, even without industrial sources

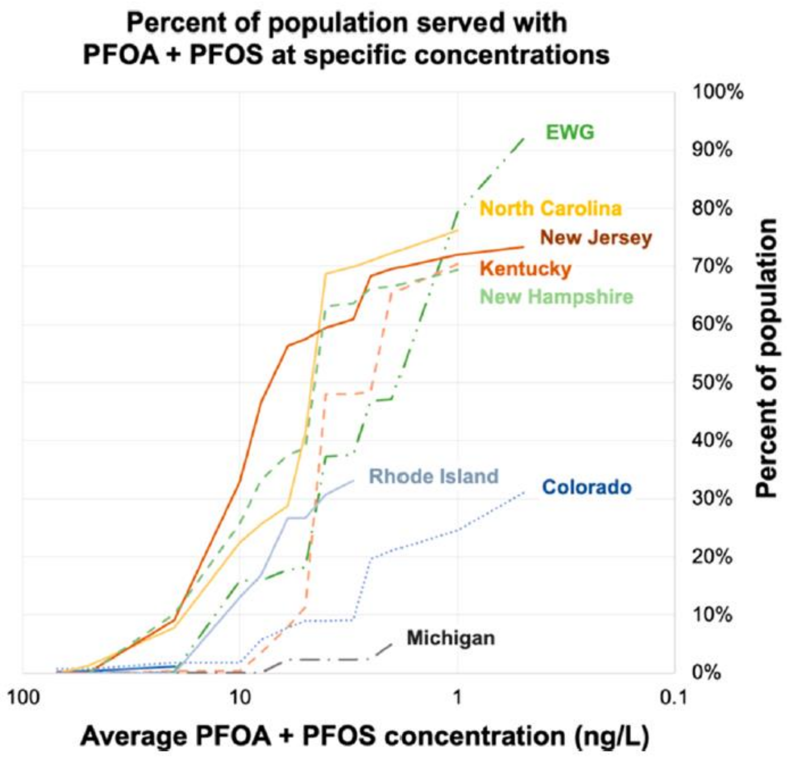
PFAS	All Data		No stated industrial sources		Recent (2013-2020)		No Outliers		Recent, No Outliers	
	n	DF	n	DF	n	DF	n	DF	n	DF
PFOA	129	**99%**	112	**99%**	68	**99%**	70	**99%**	58	**98%**
PFOS	129	**94%**	109	**96%**	68	**90%**	109	**93%**	59	88%
PFHxS	78	**92%**	62	**90%**	26	**96%**	69	**91%**	22	**95%**
PFNA	76	71%	61	70%	30	80%	62	65%	27	78%
PFHxA	71	**99%**	56	**98%**	30	**100%**	61	**98%**	24	**100%**
PFHpA	70	**96%**	55	**95%**	30	**100%**	60	**95%**	25	**100%**

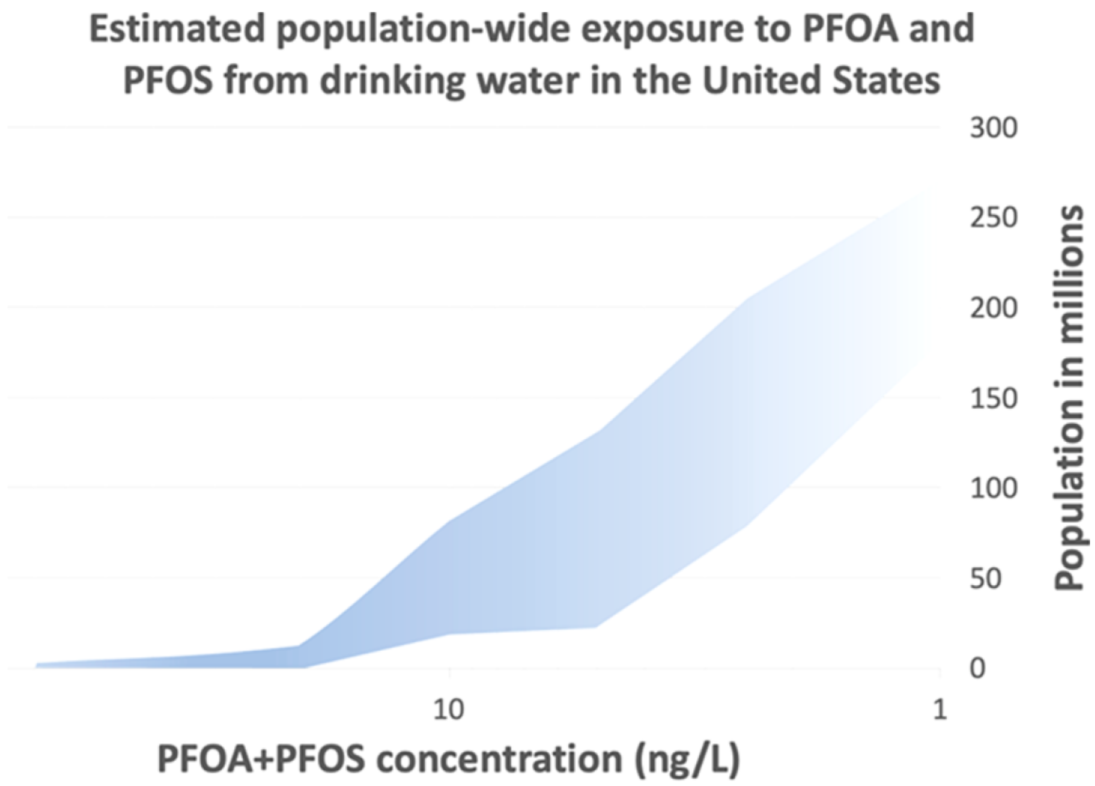
n = sample size
DF = Detection Frequency

Thompson, K. A. et al. ACS ES&T Water 2022, 2 (5), 690–700

Much of the US population likely has single digit ng/L PFOA or PFOS in their drinking water

- **AWWA estimates ~10% drinking water systems over 4 ng/L PFOA or PFOS**





Andrews, D.Q., Naidenko, O. V., 2020. Environ. Sci. Technol. Lett. 7, 931–936.

Regulations

National Primary Drinking Water Regulation (NPDWR) proposed for 6 PFAS

EPA's first regulatory action to safeguard communities from PFAS contamination.

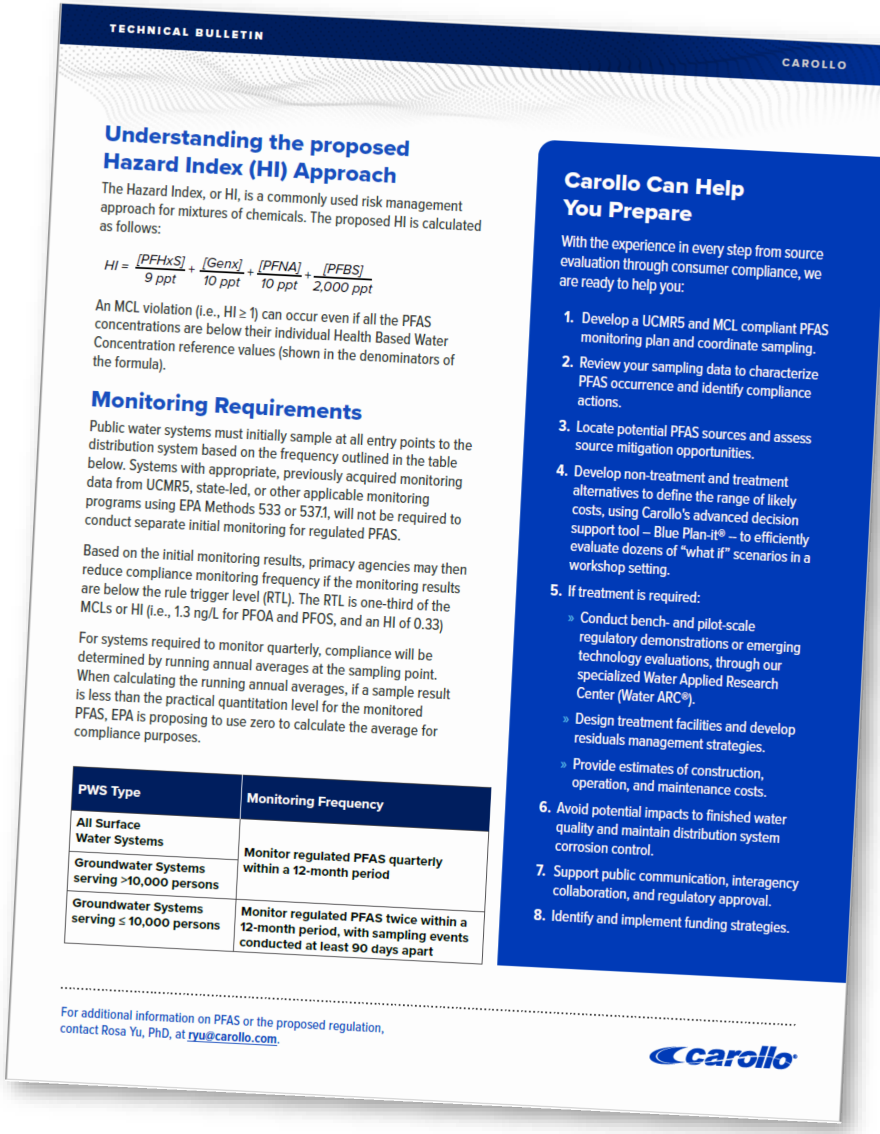
Public health protection is the main driver.

- PFOA MCL: 4.0 ng/L
- PFOS MCL: 4.0 ng/L
- PFHxS, HFPO-DA, PFNA, PFBS MCL:
  - » Hazard Index (HI) < 1.0

$$HI = \frac{[PFHxS]}{9\ ppt} + \frac{[GenX]}{10\ ppt} + \frac{[PFNA]}{10\ ppt} + \frac{[PFBS]}{2{,}000\ ppt}$$

C6 **C5** **C9** **C4**

Short-chain PFAS


TECHNICAL BULLETIN

CAROLLO

Understanding the proposed Hazard Index (HI) Approach

The Hazard Index, or HI, is a commonly used risk management approach for mixtures of chemicals. The proposed HI is calculated as follows:

$$HI = \frac{[PFHxS]}{9\ ppt} + \frac{[Genx]}{10\ ppt} + \frac{[PFNA]}{10\ ppt} + \frac{[PFBS]}{2{,}000\ ppt}$$

An MCL violation (i.e., HI ≥ 1) can occur even if all the PFAS concentrations are below their individual Health Based Water Concentration reference values (shown in the denominators of the formula).

Monitoring Requirements

Public water systems must initially sample at all entry points to the distribution system based on the frequency outlined in the table below. Systems with appropriate, previously acquired monitoring data from UCMR5, state-led, or other applicable monitoring programs using EPA Methods 533 or 537.1, will not be required to conduct separate initial monitoring for regulated PFAS.

Based on the initial monitoring results, primacy agencies may then reduce compliance monitoring frequency if the monitoring results are below the rule trigger level (RTL). The RTL is one-third of the MCLs or HI (i.e., 1.3 ng/L for PFOA and PFOS, and an HI of 0.33)

For systems required to monitor quarterly, compliance will be determined by running annual averages at the sampling point. When calculating the running annual averages, if a sample result is less than the practical quantitation level for the monitored PFAS, EPA is proposing to use zero to calculate the average for compliance purposes.

PWS Type	Monitoring Frequency
All Surface Water Systems	Monitor regulated PFAS quarterly within a 12-month period
Groundwater Systems serving >10,000 persons	
Groundwater Systems serving ≤ 10,000 persons	Monitor regulated PFAS twice within a 12-month period, with sampling events conducted at least 90 days apart

Carollo Can Help You Prepare

With the experience in every step from source evaluation through consumer compliance, we are ready to help you:

1. Develop a UCMR5 and MCL compliant PFAS monitoring plan and coordinate sampling.
2. Review your sampling data to characterize PFAS occurrence and identify compliance actions.
3. Locate potential PFAS sources and assess source mitigation opportunities.
4. Develop non-treatment and treatment alternatives to define the range of likely costs, using Carollo's advanced decision support tool – Blue Plan-it® – to efficiently evaluate dozens of "what if" scenarios in a workshop setting.
5. If treatment is required:
   - » Conduct bench- and pilot-scale regulatory demonstrations or emerging technology evaluations, through our specialized Water Applied Research Center (Water ARC®).
   - » Design treatment facilities and develop residuals management strategies.
   - » Provide estimates of construction, operation, and maintenance costs.
6. Avoid potential impacts to finished water quality and maintain distribution system corrosion control.
7. Support public communication, interagency collaboration, and regulatory approval.
8. Identify and implement funding strategies.

For additional information on PFAS or the proposed regulation, contact Rosa Yu, PhD, at ryu@carollo.com.

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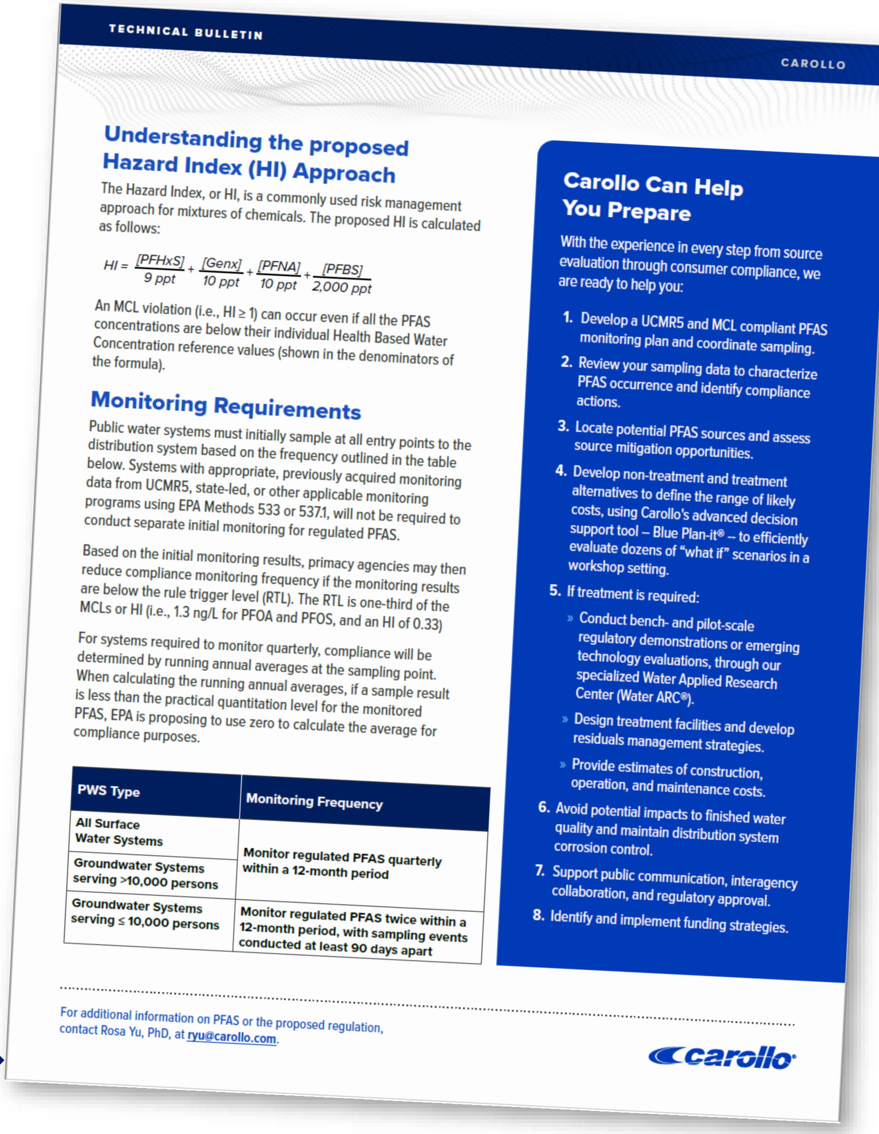

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2024	2027	2029
RULE FINALIZATION	ENFORCE MCLS	TWO-YEAR EXTENSION

EPA's planned actions on PFAS beyond drinking water regulation

Implementing upcoming PFAS regulations could be very expensive

Summary of estimated 20-year costs for managing PFAS in targeted waste streams in Minnesota

WASTE STREAM	ESTIMATED NUMBER OF FACILITIES	RANGE OF FLOWS	ESTIMATED 20-YEAR COSTS FOR MINNESOTA (millions of USD)
Municipal WRRF effluent	283	0.1-300 MGD	$12,000-$125,000
Municipal WRRF biosolids	1 regional facility, plus 50 on-site facilities	50 dry tons of wastewater solids per day (dtpd) regional facility, on-site for 1-10 dtpd	$1,600-$3,300
Mixed MSW landfill leachate	24	1-100 gpm	$77-$160
Compost contact water	9	1-100 gpm	$28-$60

MPCA, 2023. Evaluation of Current Alternatives and Estimated Cost Curves for PFAS Removal and Destruction from Municipal Wastewater, Biosolids, Landfill Leachate, and Compost Contact Water. Minnesota Pollution Control Agency, Minneapolis, MN, USA.

Treatment

Most common treatment processes for PFAS:

GRANULAR ACTIVATED CARBON

ION EXCHANGE

REVERSE OSMOSIS

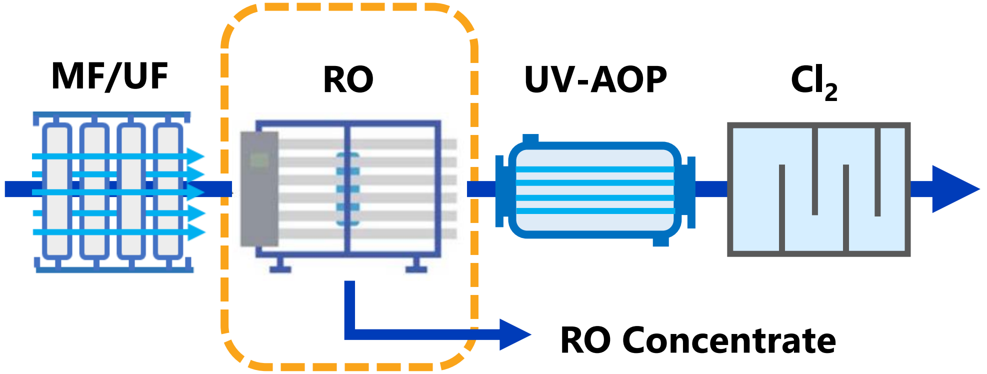
Advantages and disadvantages of PFAS treatments

	OPERATIONAL COMPLEXITY	FOOTPRINT	CAPEX	OPEX	SHORT-CHAIN REMOVAL
GAC	✓✓	✓	–	?water? ?quality?	✗
IX	✓	✓✓	–	?water? ?quality?	✗
RO	✗	–	✗✗	✗	✓✓

Two prevailing advanced treatment (AWT) approaches for potable reuse do address PFAS

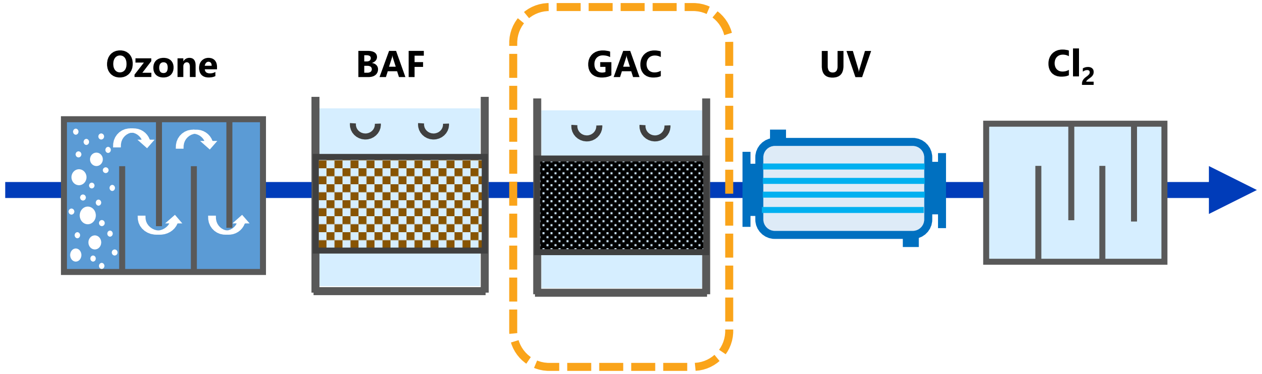
RO-Based Advanced Treatment (RBAT)

- Core processes:
  - MF/UF
  - RO
  - UV-AOP
  - Chlorine contact
- RO is a strong treatment barrier for PFAS but produces ROC



Carbon-Based Advanced Treatment (CBAT)

- Core processes:
  - Ozone
  - BAF/BAC
  - GAC
  - Disinfection (UV, UV-AOP, chlorine contact)
- GAC is a treatment barrier for PFAS, but short-chain species breakthrough early



PFAS merit source control despite RO removal

Name	Cancer Slope Factor $(mg/kg/day)^{-1}$	Risk Specific Dose (mg/kg/day)	Non-Cancer Reference Dose (mg/kg/day)	Lower Toxicity Metric (mg/kg/day)	RO-based Reuse Overall Removal	Screening Score $(mg/kgday)^{-1}$
PFOA	**0.07**	**1.4×10^{-3}**	**1.5×10^{-9}**	**1.5×10^{-9}**	**95%**	**33,300,000**
PFOS	**NA**	**NA**	**7.9×10^{-9}**	**7.9×10^{-9}**	**97%**	**3,800,000**
NDMA	51	2.0×10^{-6}	8.0×10^{-6}	2.0×10^{-6}	85%	76,500
NMOR	6.7	1.5×10^{-5}	NA	1.5×10^{-5}	99%	503
1,4-Dioxane	0.1	1.0×10^{-3}	3.0×10^{-2}	1.0×10^{-3}	89%	113
Cobalt	NA	NA	3.0×10^{-4}	3.0×10^{-4}	97%	100
PFBS	NA	NA	3.0×10^{-4}	3.0×10^{-4}	97%[b]	100
Uranium	NA	NA	6.5×10^{-4}	6.5×10^{-4}	95%	77
PFBA	NA	NA	1.0×10-3	1.0×10-3	97%[b]	35
Mercury	NA	NA	3.0×10^{-4}	3.0×10^{-4}	99%	34

Several start-ups offer pilot-scale PFAS destruction tech

Plasma – *Purafide*

Electrochemical Oxidation – *Aclarity*

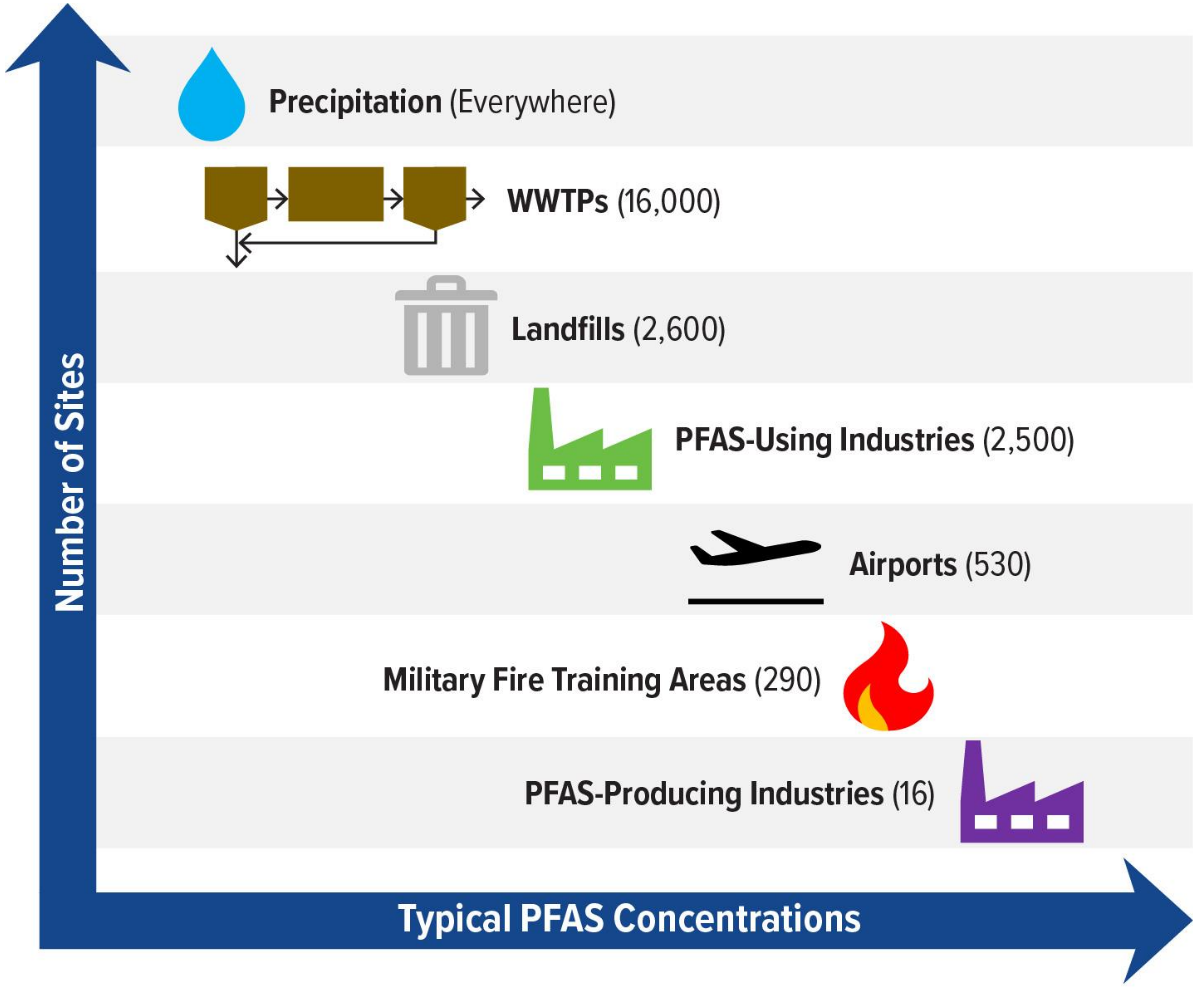
Supercritical Water Oxidation (SCWO) – *374Water*

UV / Advanced Reduction – *Enspired Solutions*

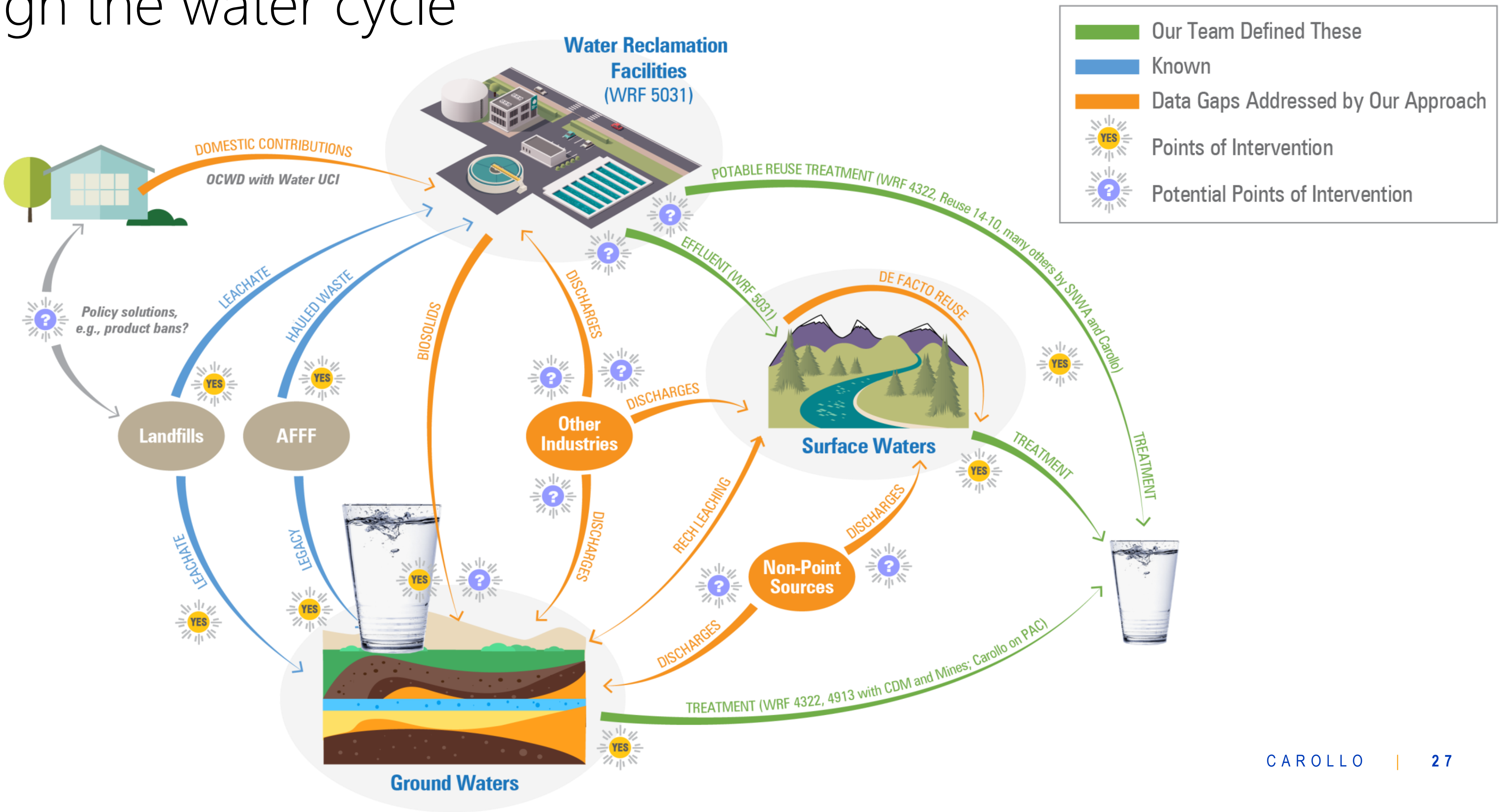
Hydrothermal Alkaline Treatment - *Aquagga*

PFAS Sources

Major PFAS sources include industrial sites, military fire training areas, and airports



Gaps remain in understanding PFAS movement through the water cycle



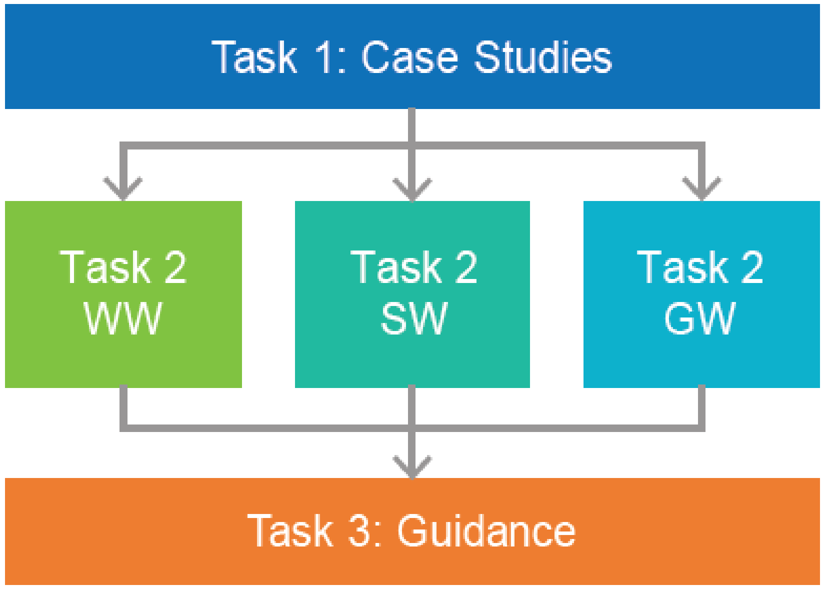
WRF #5082: Investigation of Alternative Management Strategies to Prevent PFAS from Entering Drinking Water Supplies and Wastewater

GOAL

- Provide utilities with practical, implementable, and cost-effective guidance on PFAS source evaluation and mitigation strategies.

APPROACH

- Gather utility data and experience,
- Strategically fill data gaps; and
- Develop guidance with practical, implementable solutions.



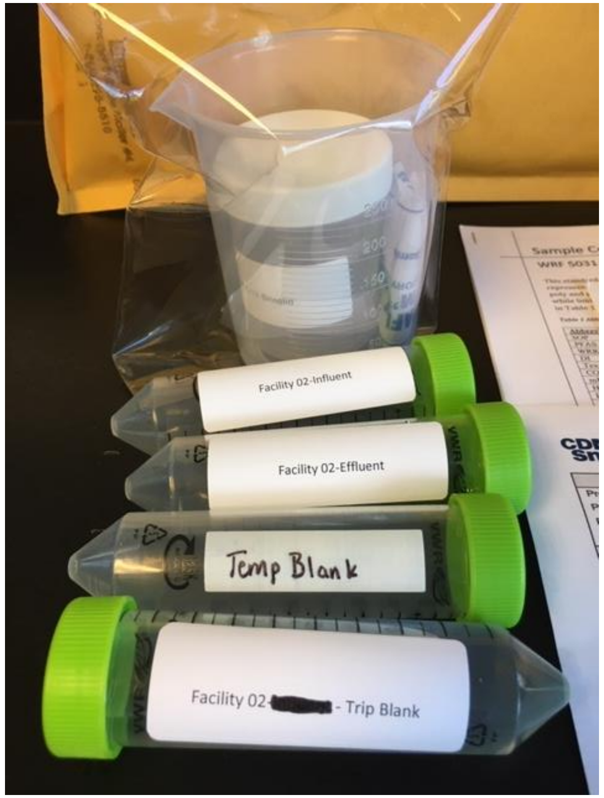
02

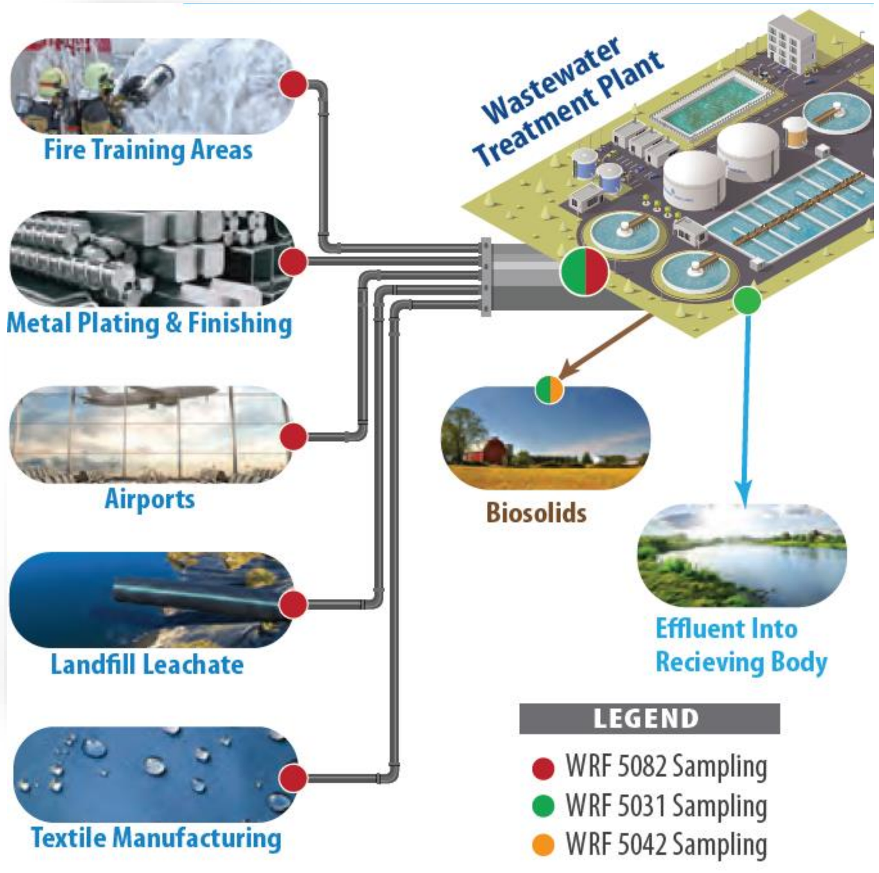
Wastewater Results

Five wastewater collection systems were sampled to investigate PFAS sources

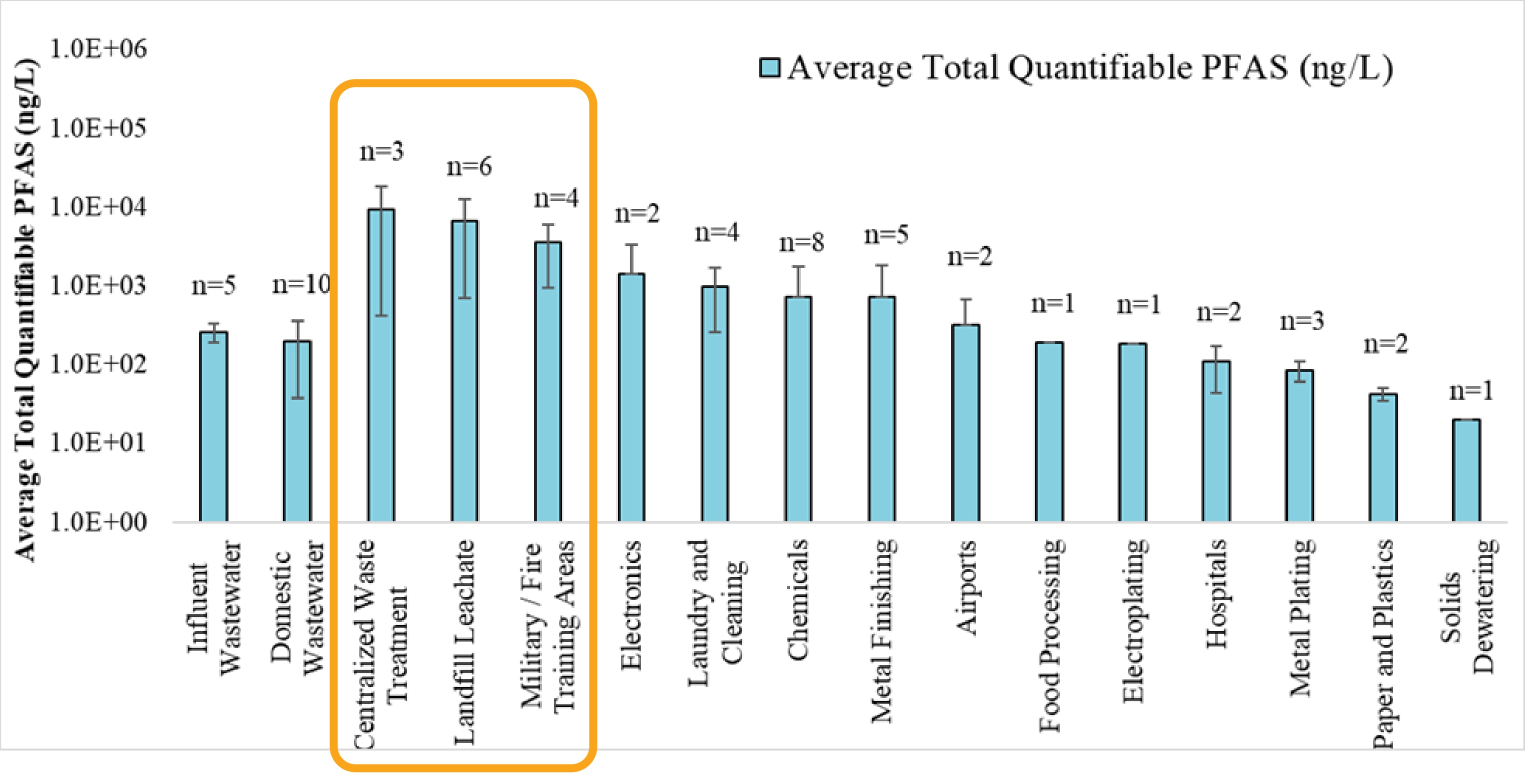
- Characterize PFAS signature at WWTP influents and collection system domestic and point sources
- Quantify point source mass flows relative to domestic dischargers

Facility ID	Design Flow (MGD)	Average Flow (MGD)
A	930	654
B	16	13
C	54	34
E	354	308
F	54	40

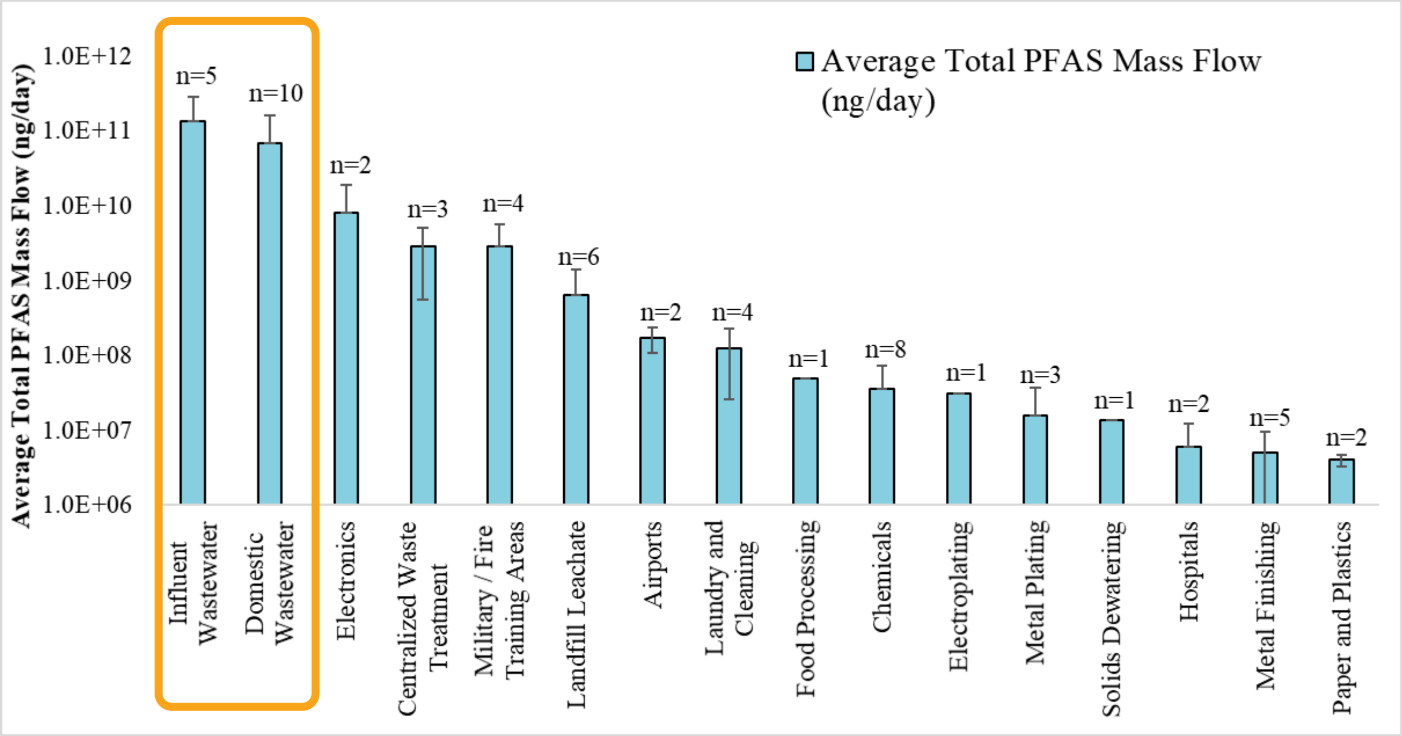




Across five wastewater collection systems, several industries had higher PFAS concentrations than domestic wastewater



However, more PFAS mass was measured in domestic wastewater due to flow



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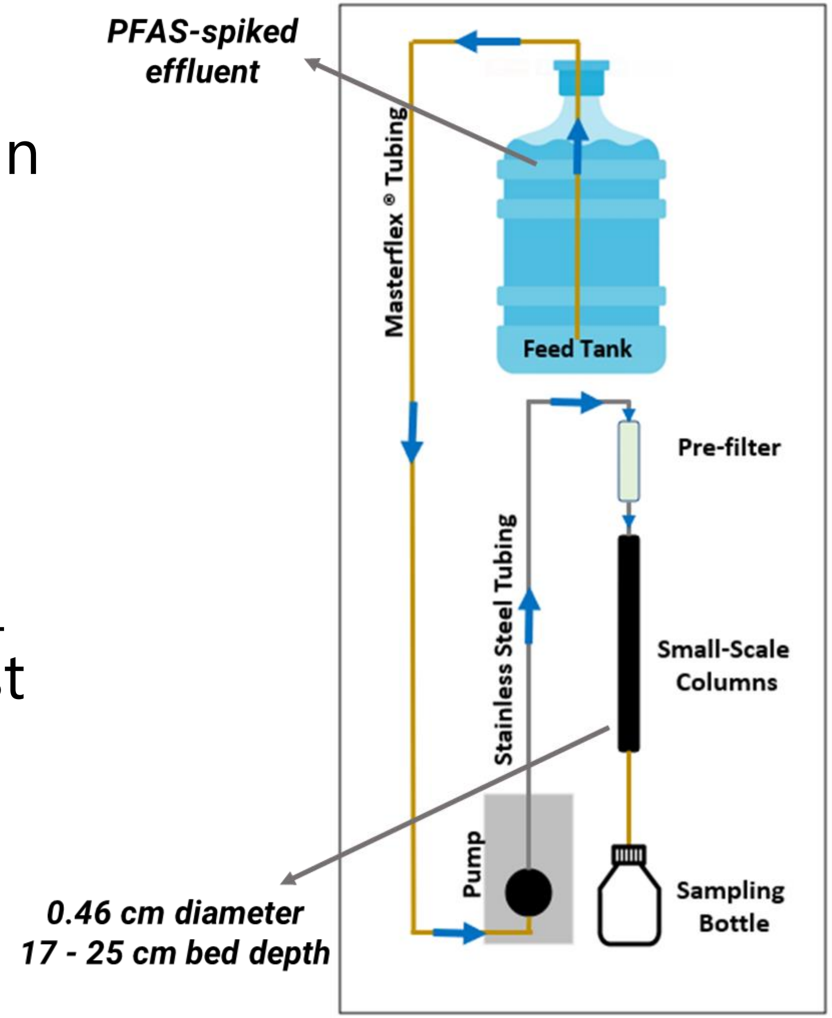
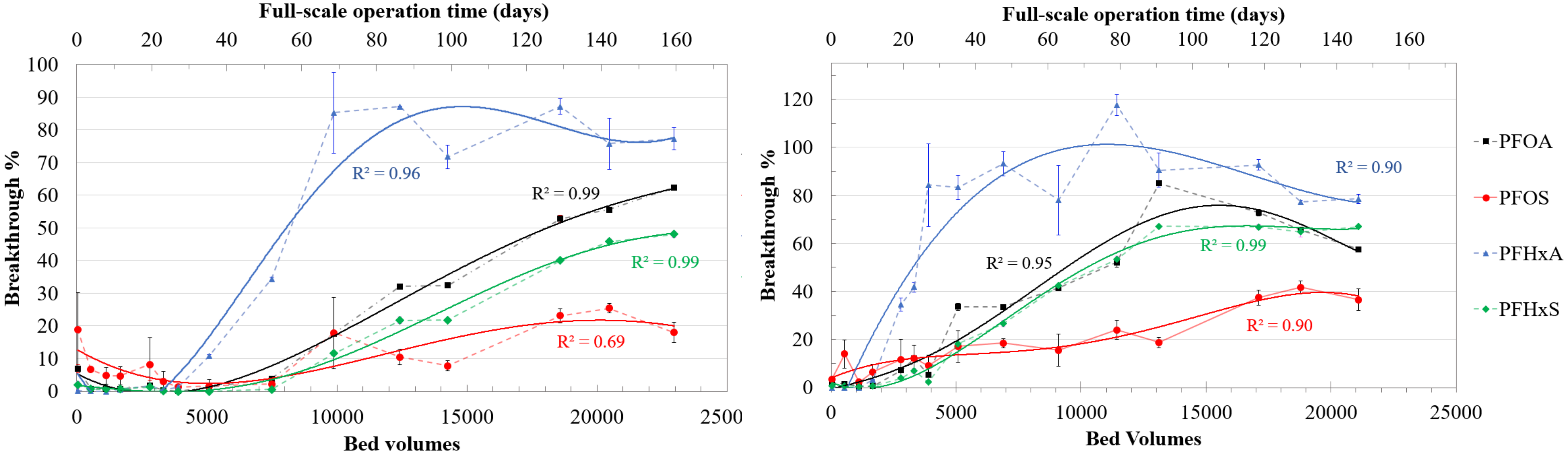
Evaluating GAC Efficacy in Secondary Effluent

- Collected secondary treated municipal wastewater effluents from two water resource recovery facilities in Ontario, Canada.
- Spiked the effluents with 200 ng/L of each individual PFAS, including **PFOA, PFOS, PFHxA, PFHxS,** and **PFBS.**
- Used two types of bituminous coal-based GAC and a commercial biochar in a rapid small scale column test (RSSCT) system to generate breakthrough curves.
  - » Simulated a full-scale EBCT of 10 min.
- Removal percentage calculated by comparing PFAS concentration in the feed tank and column filtrate.



GACs reached 50% breakthrough of PFOA or PFOS after ~10,000 to 20,000 BVs



- PFHxA was the least well-adsorbed compound on both GACs.
- Order of ease for PFAS sorption onto GAC:
  - » (easiest) **PFOS > PFHxS ≥ PFOA > PFHxA** (most difficult)

For cost estimation, we considered 50% breakthrough of PFOA or PFOS– whichever happens first– as our arbitrary treatment objective in this project

- Cost evaluations provided by Jennifer Hooper, PE, and Ibrahim Abusallout , Ph.D., EIT, at CDM Smith Inc. for implementing GAC adsorption units at three full-scale WTPs and WWTPs.
- Combined cost estimates provided by CDM Smith and our RSSCT results:

To use **Filtrasorb 400 GAC** in a **WWTP** for removing **50% of PFOA or PFOS** with an **EBCT of 10 min** and service life of **4 months**:

→

In 30 years: Total annual project cost ranges ~ **$900 - $1400 per million gallons treated ($/MG)**

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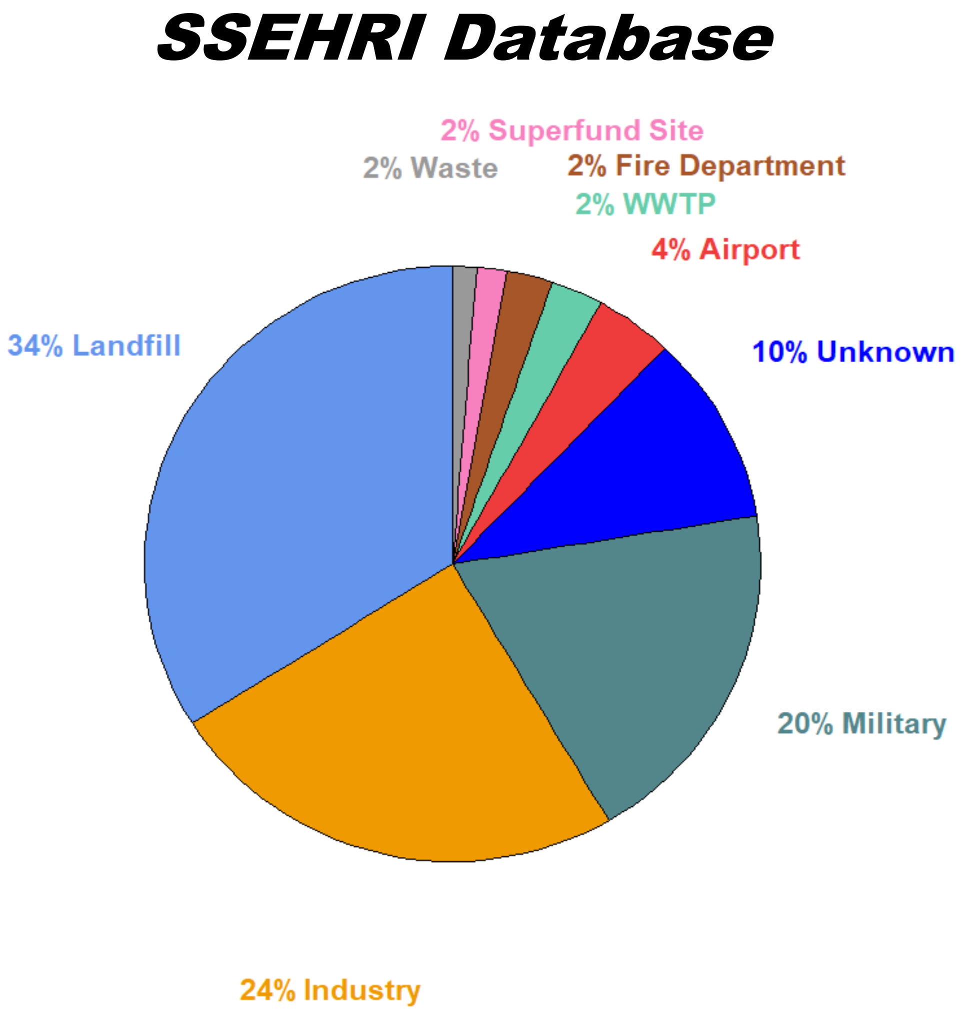
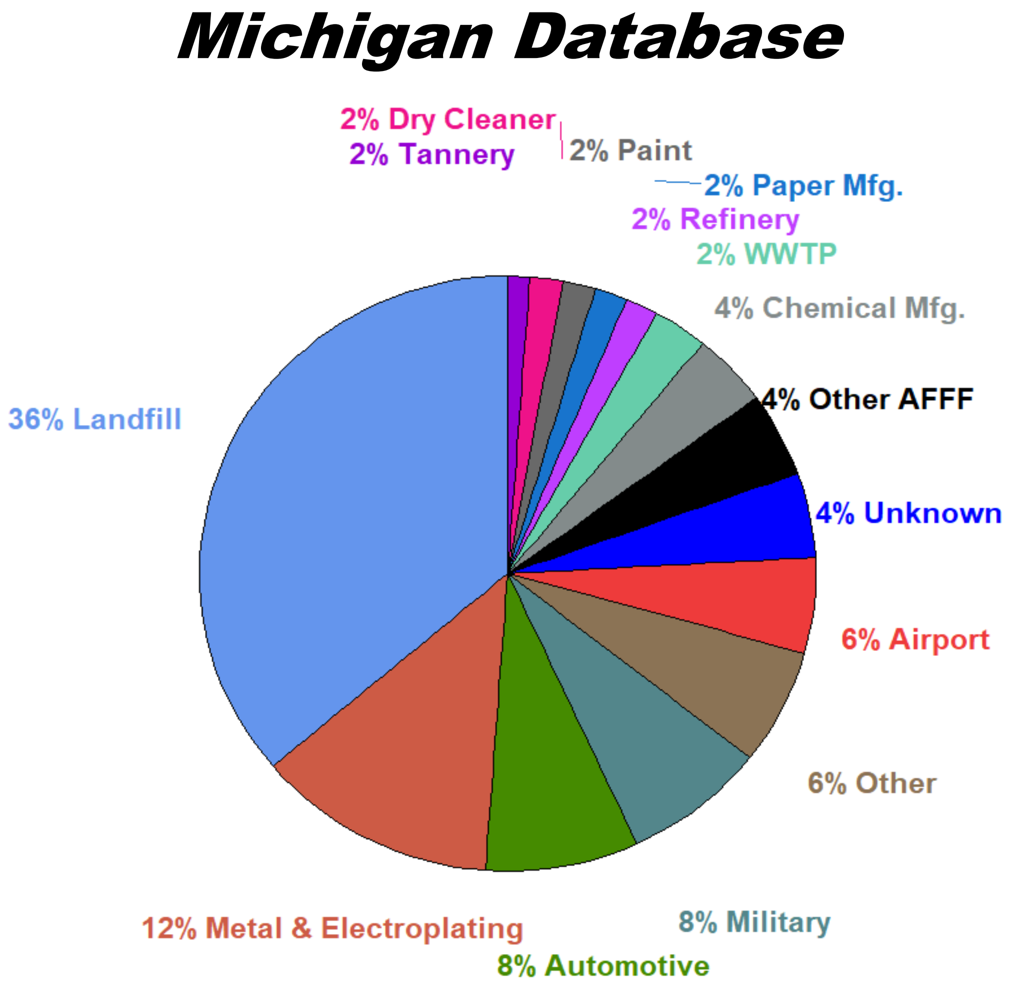
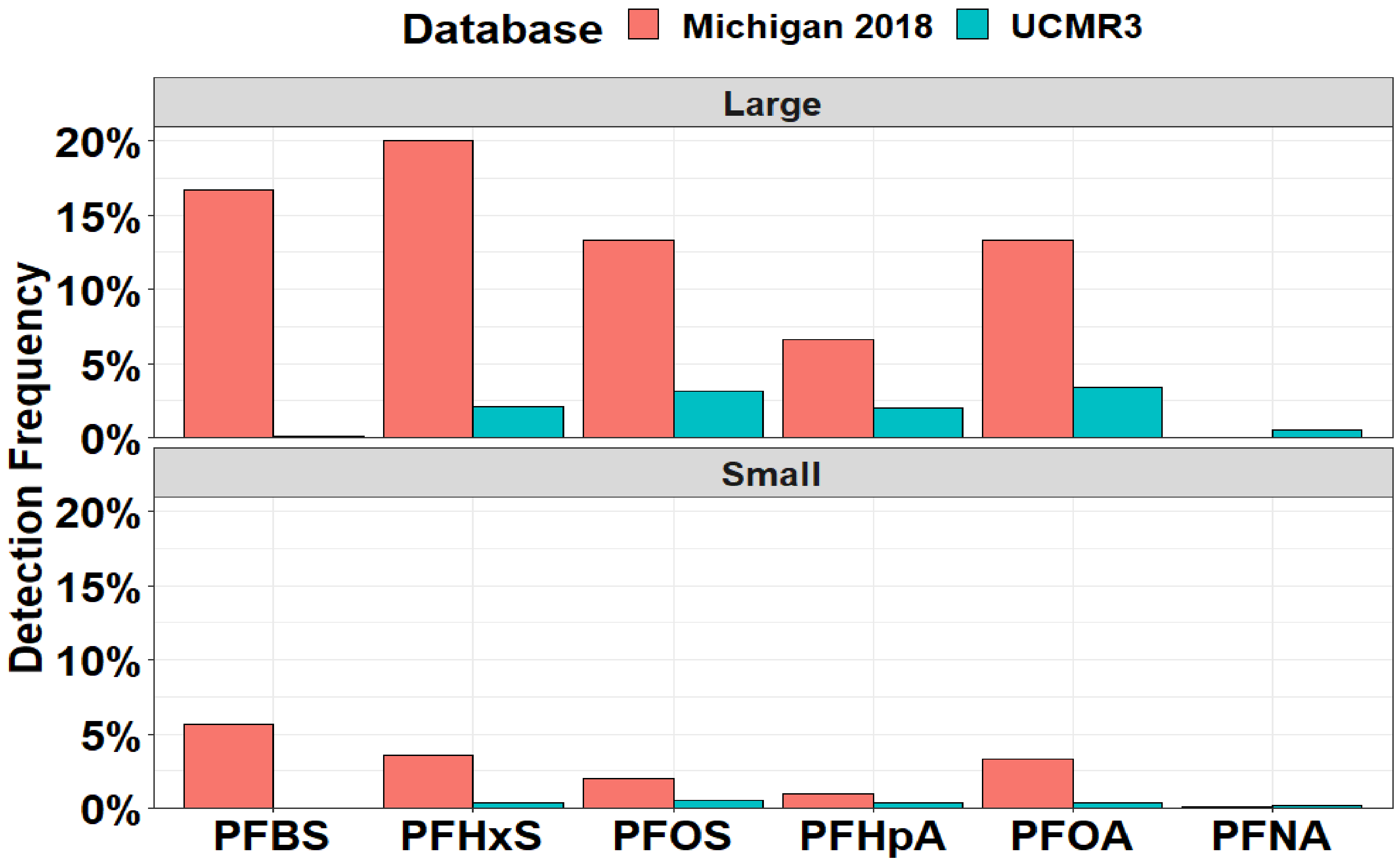
Groundwater Results

Landfills are frequent sources of PFAS to groundwater

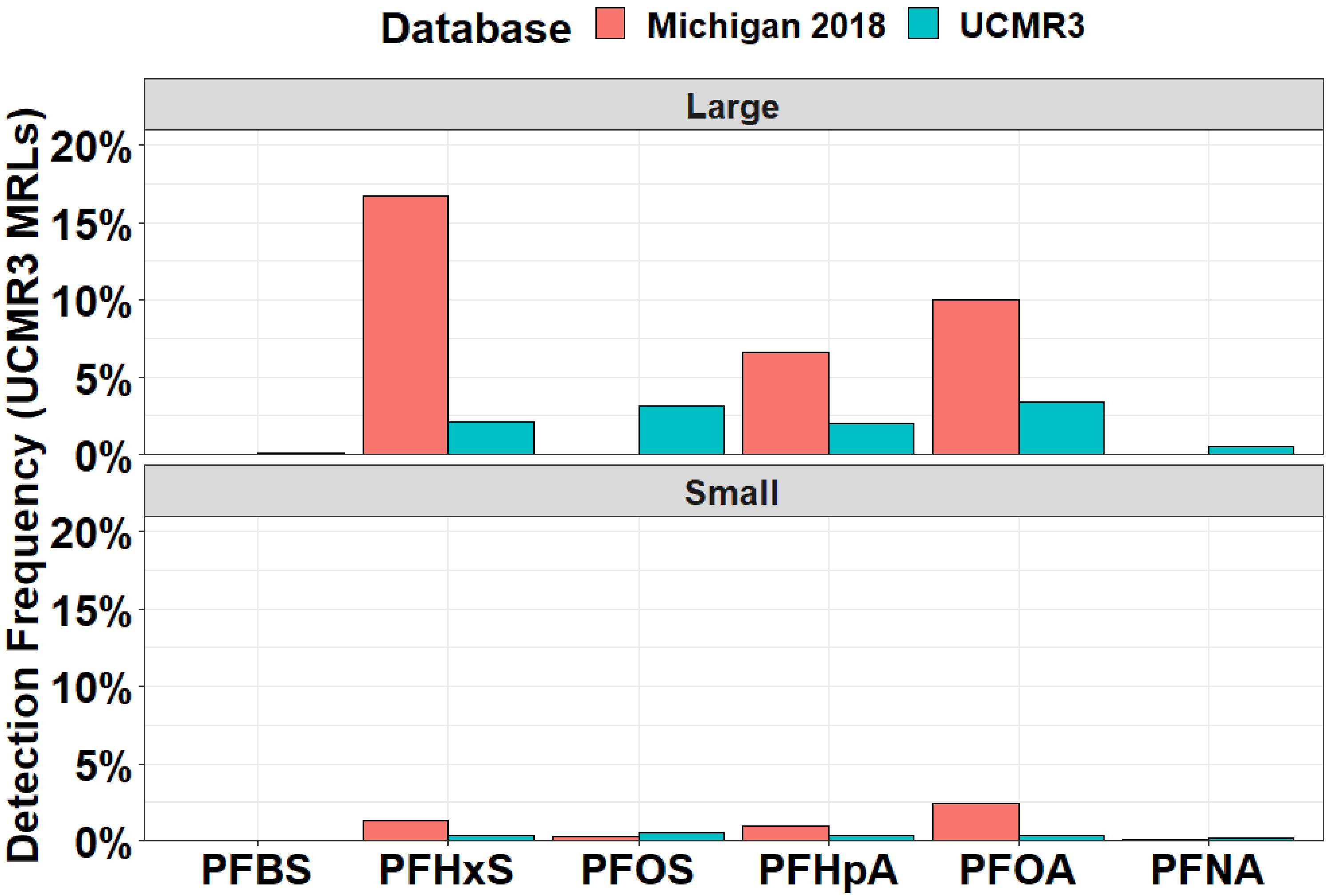




PFAS detection frequencies were higher in the Michigan database than UCMR3



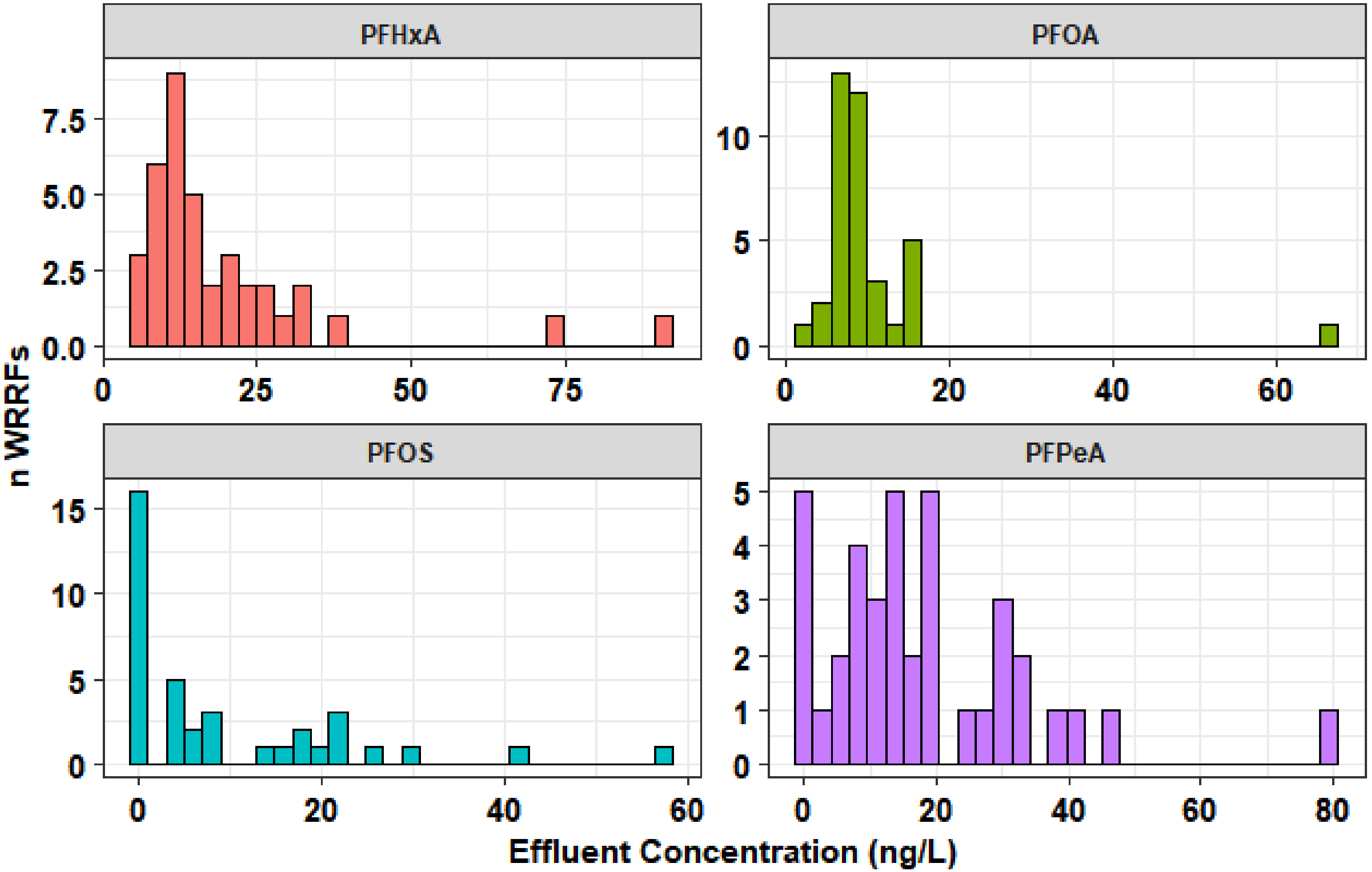
PFAS detection frequencies were higher in the Michigan database than UCMR3…even using the same MRLs



04

Wastewater Implications for Surface Water

Median PFOA and PFOS are around 8 ng/L and 4 ng/L respectively in wastewater effluent



Data from: Schaefer et al. 2022. *Occurrence of PFAS Compounds in U.S. Wastewater Treatment Plants* (WRF 5031).

Impact of Effluent PFAS on Surface Waters Across the US

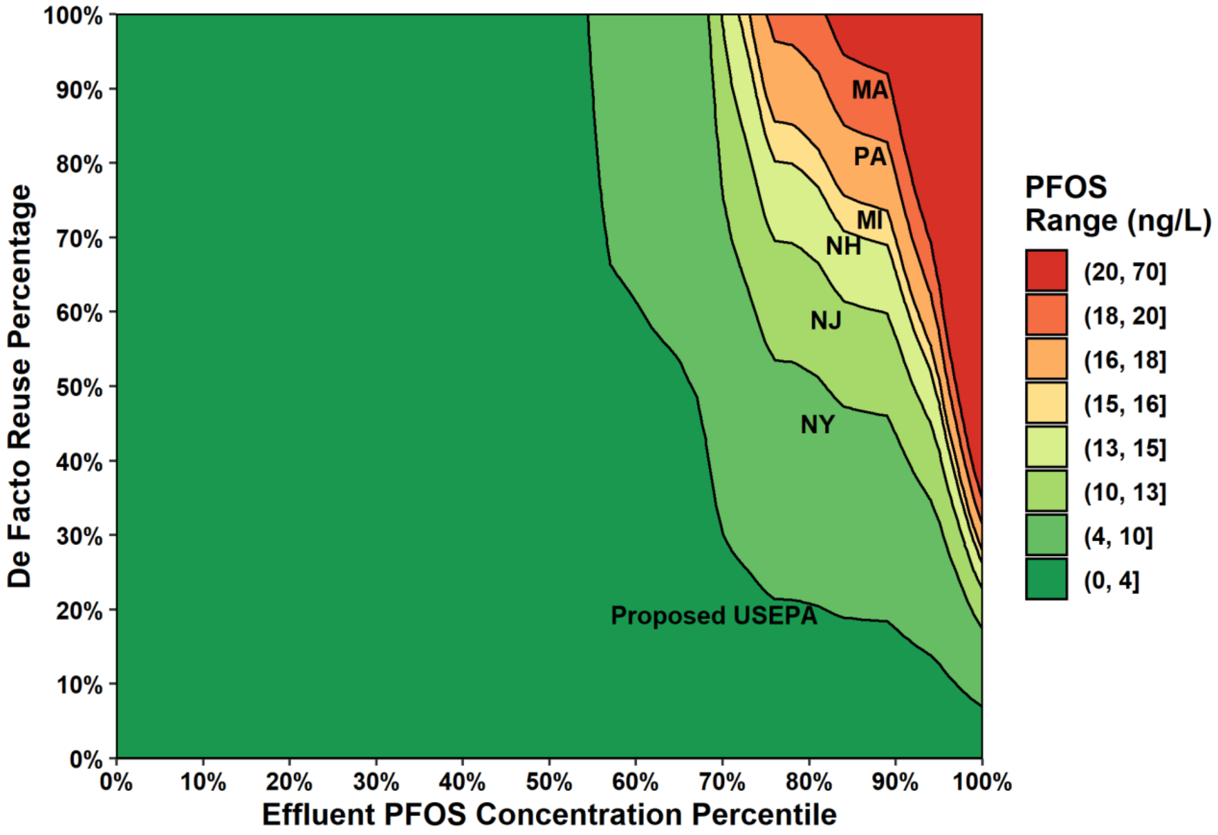
Example

Drinking water intake with:

- » Median WW effluent PFOA upstream and
- » 50% de facto reuse
- » PFOA ≈ 4 ng/L MCL

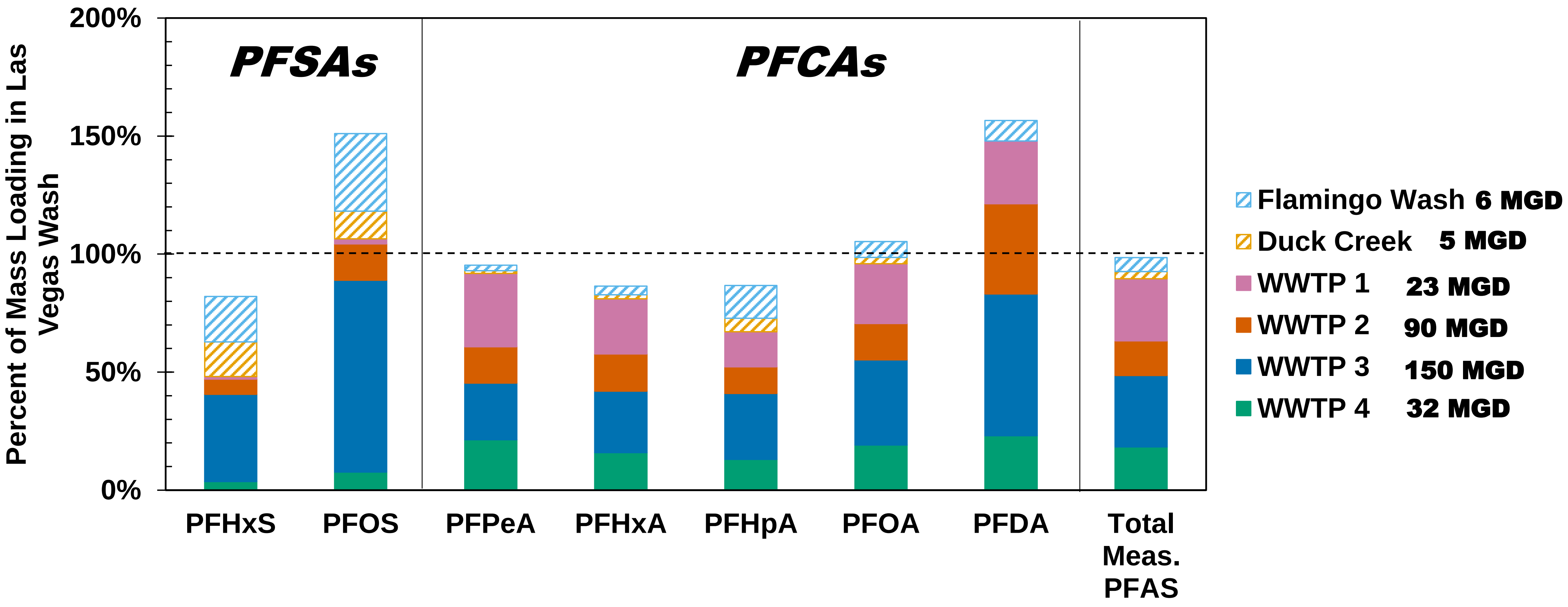
But remember:

WWTPs are not the original source of PFAS

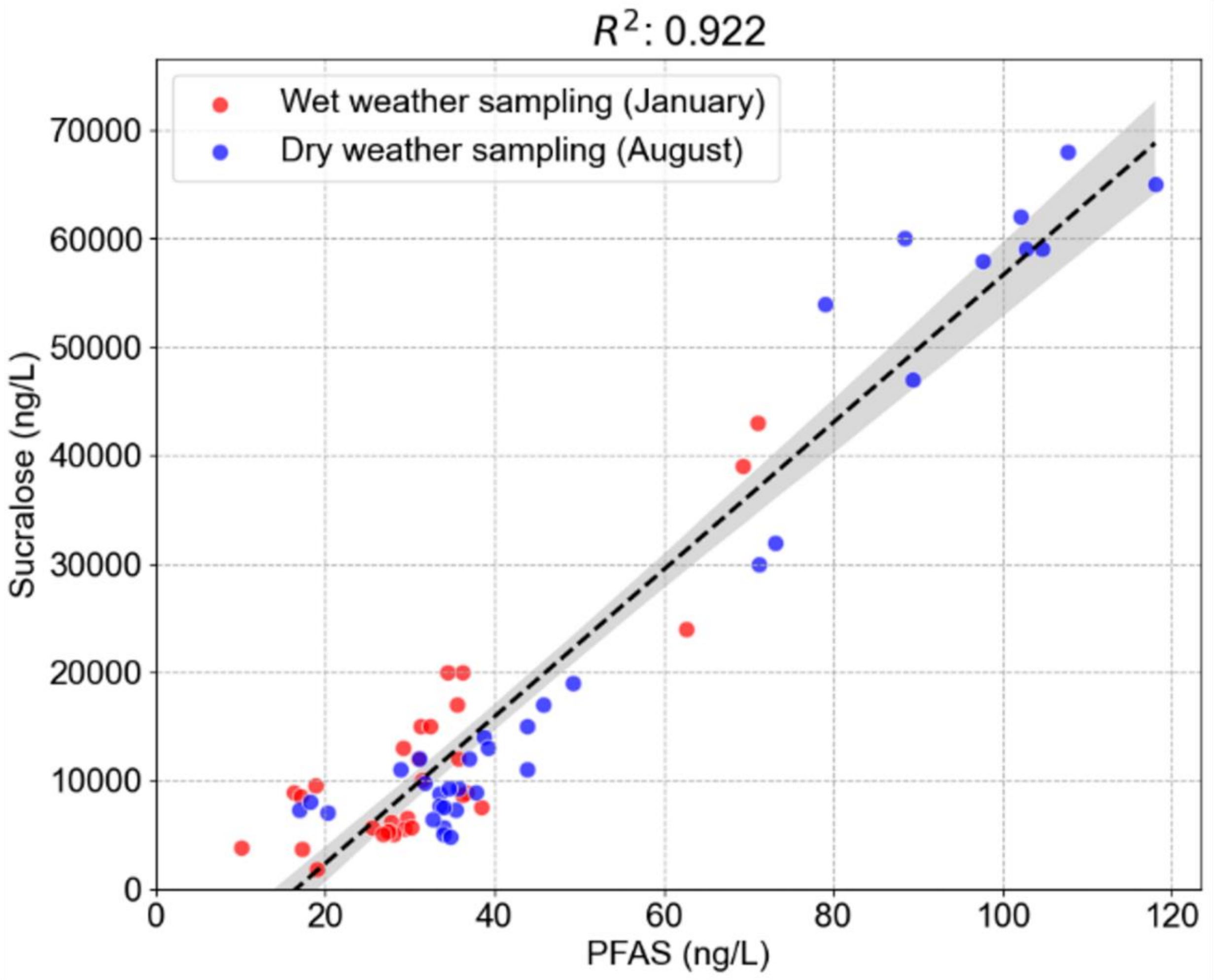


Data from: Schaefer et al. 2023. *Occurrence of PFAS Compounds in U.S. Wastewater Treatment Plants* (WRF 5031); analysis completed as part of WRF 5082.

Wastewater effluent accounted for 90% of the total measured PFAS in a watershed in Nevada



The sum of measured PFAS correlated strongly with sucralose (a wastewater indicator) in a watershed in Texas



05

Guidance

The Guidebook lays out a step-by-step process to find and mitigate PFAS sources

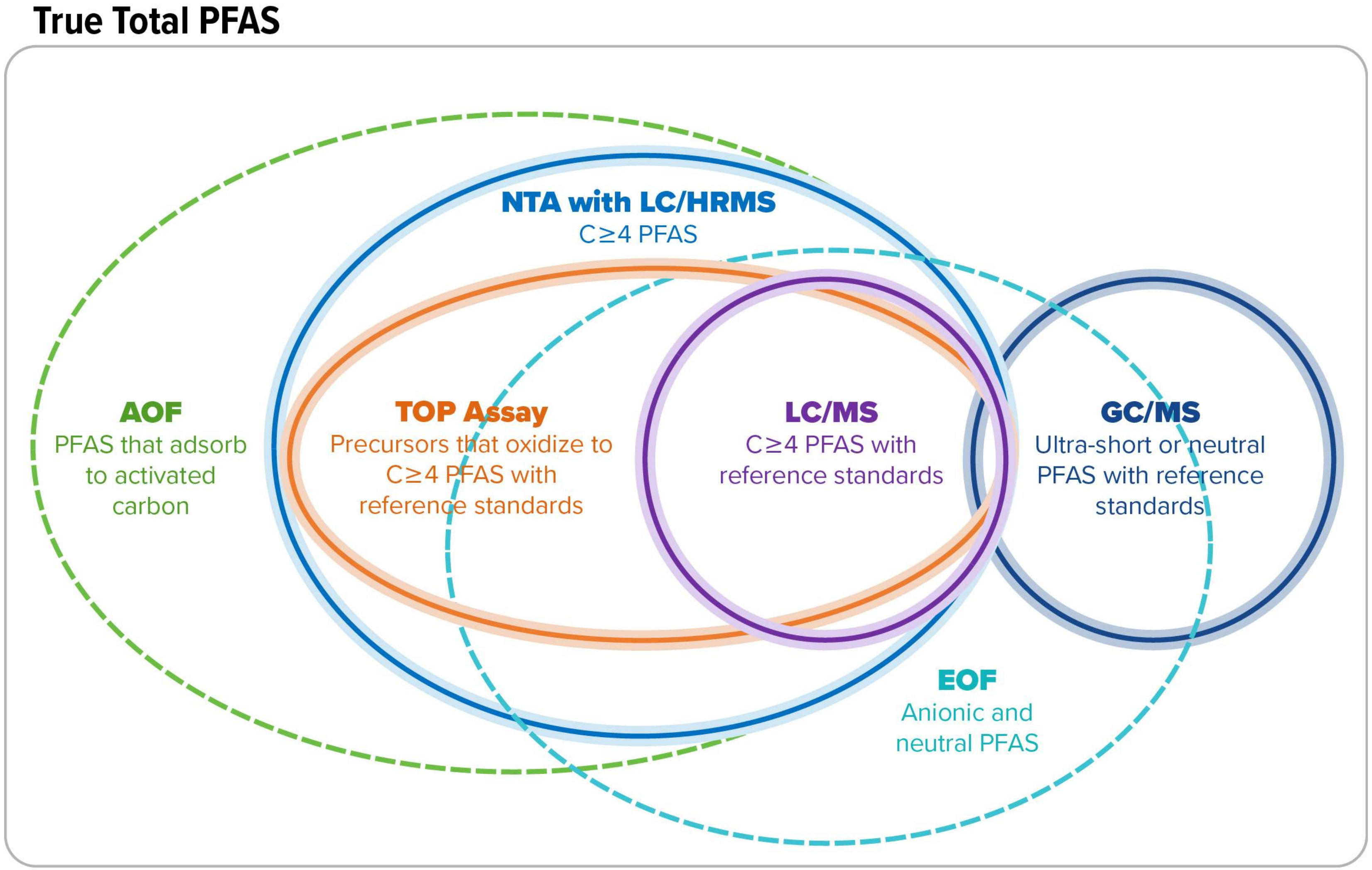
- **Guidebook for Preventing PFAS from Entering Drinking Water Supplies and Wastewater**

Bring everybody to the table

The Guidebook discusses benefits and limitations of analytical methods

Method	Cost $/sample	Sensitivity (MRL) How low of concentrations can it measure?	Selectivity Can it tell apart specific PFAS?	Inclusivity Can it measure a wide range of PFAS?
LC/MS	Low	High	High	Low
GC/MS	Low	High	High	Low
NTA	High	High	Medium-High	Medium-High
TOP Assay	Medium	Medium-High	Medium	Medium
AOF-PIGE	To Be Determined	Medium	Low	High
AOF-CIC	Low	Low	Low	High

Different methods detect different PFAS



We developed screening tools for levels of PFAS in wastewater effluent or biosolids indicating industrial sources

Effluent (ng/L)

PFAS	WRF 5031 Literature Data Outliers Removed			WRF 5031 New Data Outliers Removed		
	n	Median	Max	n	Median	Max
PFBA	40	8.2	21			
PFPeA	48	22	44	37	15	47
PFHxA	61	21	54	35	13	33
PFHpA	60	4.8	15			
PFOA	70	8.5	15	30	7.6	11
PFNA	62	4.2	10			
PFDA	56	1.3	5.3			
PFBS	53	2.9	13			
PFHxS	69	4.7	10			
PFOS	109	7.1	31	36	3.5	30
6:2 FTS	41	4.4	24			
EtFOSAA	30	1.3	11			

We developed screening tools for levels of PFAS in wastewater effluent or biosolids indicating industrial sources

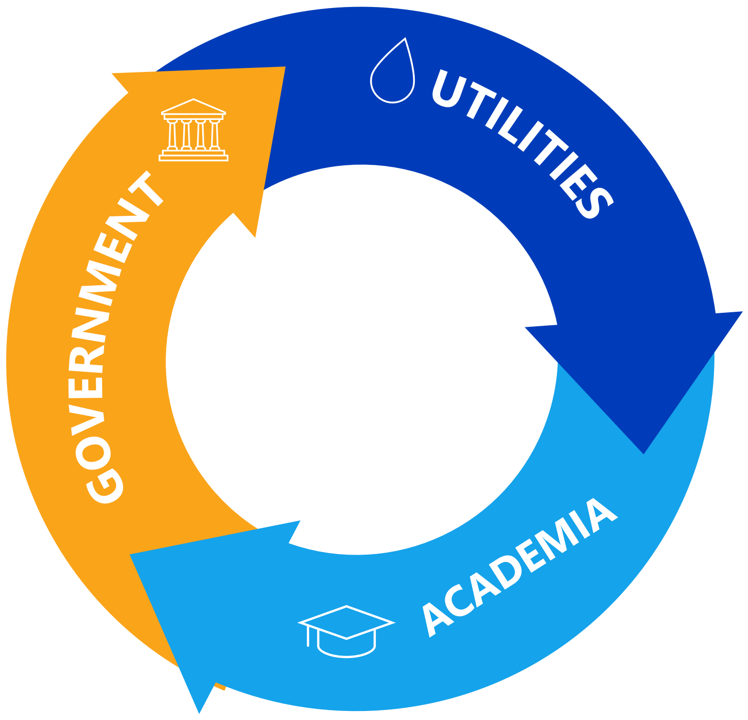
Biosolids (ppb)

PFAS	*n*	Median	Max Non-Outlier
8:2 FTSA	*33*	0.77	2.2
FOSA	*33*	0.86	2.2
MeFOSAA	*36*	4.5	12
PFBA	*36*	0.35	0.78
PFPeA	*36*	0.41	1.2
PFHxA	*32*	2.2	3.8
PFHpA	*37*	0.15	0.54
PFOA	*31*	2.2	4.8
PFNA	*34*	0.68	2.4
PFDA	*34*	3.6	14
PFUnDA	*35*	1.2	2.5
PFOS	*32*	10	26

Collaboration is key

BENEFITS OF COLLABORATION

- State governments or regional entities may be able to gather samples farther afield.
- Universities can offer cutting edge analyses.
- Utilities can work together to exchange information and protect their shared watersheds.
- Utility representatives can sit on state or federal panels guiding policy and regulations.



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