

## **Project Description**

### **a. Background and Statement of Need**

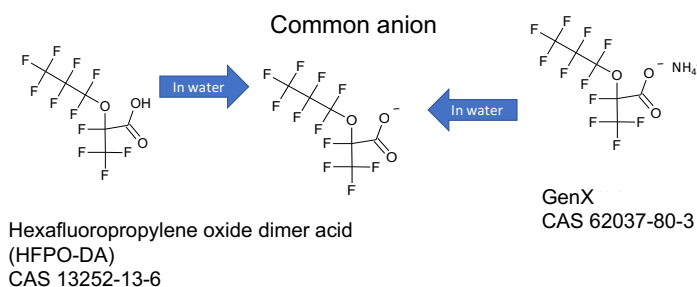
Poly- and perfluoroalkyl substances (PFAS) serve as processing aids in the production of fluoropolymers such as polytetrafluoro-ethylene (PTFE, aka Teflon) and are active ingredients in stain repellents (e.g. Scotchgard), firefighting foams, and food-contact paper coatings.

Perfluoroalkyl substances are aliphatic organic compounds in which all C-H bonds of a non-fluorinated analogue have been replaced by C-F bonds (Buck et al. 2011), while polyfluoroalkyl substances contain at least one perfluorinated carbon atom, but also one or more C-H bonds.

Until about 2000, use of long-chain PFAS chemistries, defined as perfluorocarboxylic acids (PFCA) with 7 or more carbon atoms (sometimes the cutoff is at 8, as written in the RFP) and perfluorosulfonic acids (PFSA) with 6 or more carbon atoms (Buck et al. 2011, OECD 2013), was dominant. The most well-studied examples of long-chain PFAS are perfluorooctanoic acid (C8) and perfluorooctane sulfonate (PFOS). Increasing evidence about ecotoxicological and human health effects associated with exposure to long-chain PFAS has led to efforts to eliminate their production and use. In May of 2016, the USEPA issued health advisory levels (HAL) for C8 and PFOS for drinking water at a sum concentration of 70 ng/L. On June 21, 2018, the Agency for Toxic Substances and Disease Registry (ATSDR) released for public comment Minimal Risk Levels for four long-chain PFAS: C8, perfluorononanoic acid (C9), perfluorohexane sulfonate (PFHxS), and PFOS (ATSDR 2018). Drinking water equivalent levels corresponding to the MRLs would be 11 ng/L for C8, 11 ng/L for C9, 74 ng/L for PFHxS, and 7 ng/L for PFOS. For PFOS and C8, the levels are substantially below the current HAL. Adoption of PFAS standards below the current HAL would greatly expand the number of drinking water providers that would need to consider PFAS treatment options (Guelfo and Adamson 2018).

As long-chain PFAS chemistries are being abandoned, industry is moving towards (1) short-chain PFAS chemistries and (2) fluorinated replacements (Wang et al. 2013, Scheringer et al. 2013). For example, the active ingredient of the stain repellent Scotchgard was changed from PFOS, an 8-carbon PFAS, to perfluorobutane sulfonate (PFBS), a 4-carbon PFAS, in 2003 (Renner 2006). The effect of global efforts to eliminate PFOS production/use is reflected in decreasing blood serum levels of PFOS in pregnant and nursing women in Sweden (Glynn et al. 2012). On the other hand, blood serum levels of PFBS and PFHxS have been rising since 2004 (Glynn et al. 2012). Similarly, Sun et al. (2016) showed that the PFAS fingerprint in the Cape Fear River basin of North Carolina shifted from long-chain PFCA dominance in 2006 to short-chain PFCA dominance in 2013.

While the move towards short-chain PFAS chemistries is tractable in a relatively straightforward manner, the move towards fluorinated replacements represents a much more complex challenge from a standpoint of drinking water safety as well as environmental and human health assessment. As noted in the Helsingør Statement, little information is available about production volumes, uses, properties, and biological effects of fluorinated replacements (Scheringer et al. 2014). For example, DuPont began to phase out the use of C8 to manufacture Teflon around 2009/10 and replaced C8 with GenX. GenX is the ammonium salt of hexafluoropropylene dimer acid (HFPA-DA) as shown in Figure 1. When dissolved in water both GenX and HFPA-DA form the same anion. For the purposes of this proposal, GenX generically refers to the common anion. At the time this switch occurred, almost nothing was known about the molecular structure of GenX, its production volume, environmental releases, and human health effects. Only through non-targeted analysis did Strynar et al. (2015) identify GenX and other poly- and perfluoroalkyl ether acids (PFEA) in the Cape Fear River downstream of a fluorochemical manufacturer. A



**Figure 1. GenX and HFPO-DA**

challenge for drinking water providers is that the presence of short-chain PFAS, fluorinated replacements, and fluorinated manufacturing by-products is typically unknown.

As highlighted by the UCMR3, PFAS occur in drinking water derived from both groundwater and surface water. Nationwide, the UCMR3 data highlight

that PFAS detection in finished drinking water was more commonly associated with contaminated *groundwater* sources - 76% of PFAS-positive UCMR3 samples were derived from groundwater. However, in some states, such as North Carolina, PFAS detection in finished drinking water is principally linked to contaminated *surface* water - 79% of PFAS-positive UCMR3 samples from NC were derived from surface water. Sources of PFAS contamination are manifold and include firefighting training activities involving storage and use of aqueous film-forming foams (AFFF) at military and civilian airports (e.g. Hu et al. 2016), industrial and municipal wastewater treatment plants (Sun et al. 2016), landfill leachate (Lang et al. 2017), land applied sewage sludge (Lindstrom et al., 2011; Sepulveda et al. 2011), and air emissions from fluorochemical production facilities (e.g. Davis et al. 2007). The multitude of sources has led to the contamination of drinking water sources with a wide range of background water characteristics (e.g. sources with low/moderate/high total organic carbon (TOC), sources with low/high hardness, sulfate, alkalinity, iron), and these background water constituents strongly impact the performance of treatment processes for PFAS removal. We *hypothesize* that selection of the most cost-effective PFAS removal process(es) is strongly dependent on background water matrix composition and targeted PFAS.

### **Data Gaps**

The research proposed herein is principally motivated by knowledge gaps associated with the selection of treatment approaches for the removal of short-chain PFAS, fluorinated replacements, such as GenX, and other perfluoroalkyl ether acids, and emerging PFAS associated with the use of AFFF. The **overarching goal** of the proposed research is to develop a **guidance manual** that allows water treatment professionals to select the most **cost-effective treatment options for short-chain PFAS removal**, recognizing the PFAS removal performance of individual treatment processes is strongly dependent on background water matrix effects.

### **Objectives**

1. Identify conventional and innovative sorbents for effective control of short-chain PFAS
2. Identify membrane properties for effective control of short-chain PFAS
3. Assess the impact of background water matrix parameters on short-chain PFAS removal
4. Identify pre-treatment options that enhance PFAS removal in downstream processes; e.g. enhance TOC removal prior to granular activated carbon (GAC) adsorption
5. Develop scale-up protocol to estimate full-scale sorbent use rates
6. Develop information for residuals management (e.g., treatment of spent ion exchange regenerant by electrochemical oxidation)

7. Develop a quantitative structure-property relationship to predict the removal of structurally diverse PFAS by adsorption, anion exchange, and membrane processes.
8. Develop information for life-cycle cost and environmental impact models. These models are being developed in a separate, recently funded research project (Department of Defense, ESTCP) that will be conducted by co-PIs Knappe and Bellona.

To meet the above objectives, we have assembled a research team that has broad PFAS expertise. We have developed an ambitious research plan that builds on past and ongoing work of each team member as well as past and existing collaborations among team members. The experience of our team and the roles of each team member in this admittedly ambitious effort are described in the Project Management Plan. The effort is also made possible by additional cash contributions the team was able to raise – in particular a >\$130,000 cash contribution by the North Carolina Policy Collaborative, which is available without overhead cost to support the laboratory and modeling work at NCSU. As a result, we are able to support substantial additional research efforts by the organizations of each co-PI [Colorado School of Mines (CSM), Hazen and Sawyer (HS), Southern Nevada Water Authority (SNWA), American Water (AW), the City of Ann Arbor (AA), and CDM Smith (CDM)].

Research objectives will be met by completing the following tasks:

1. Literature review and review of existing data (led by NCSU and CSM)
2. Analytical method validation among participating laboratories (NCSU, CSM, SNWA, AW)
3. Evaluation of short-chain PFAS removal in full-scale water treatment plants (led by NCSU, CSM, SNWA, AW with support from HS and CDM)
4. Systematic evaluation of established and innovative treatment approaches for short-chain PFAS removal at the bench-scale (led by NCSU and CSM with significant support from SNWA and CDM)
5. Validation of promising treatment approaches at the pilot scale (led by CSM, AW, and AA)
6. Development of quantitative structure-property relationships to predict PFAS removal by activated carbon and anion exchange treatment processes (led by NCSU with support from CSM)
7. Comparison of treatment approaches using life cycle analysis and cost models (led by CSM with support from NCSU, Hazen, CDM, and SNWA)
8. Development of a decision support tool for treatment process selection (led by HS)

## **b. Research Approach**

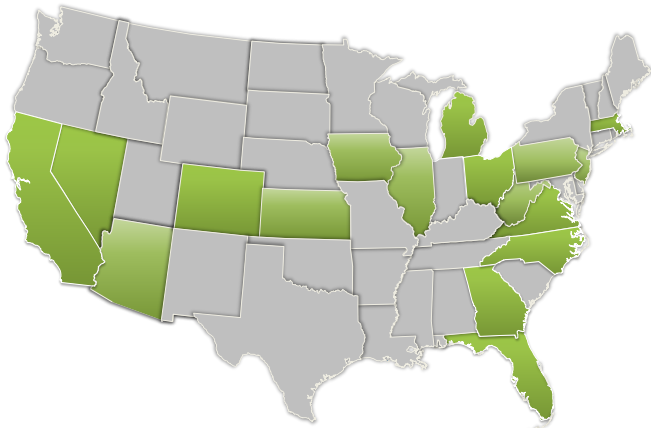
**Overview.** In this study, we propose to investigate short-chain PFAS removal at multiple scales, from bench-scale to full-scale. To maximize the value of our study, we have recruited 39 utilities, who will either share existing data or collect new data during the course of the project, some at multiple scales. Table 1 summarizes the utility participants, the scale(s) at which PFAS removal data have been or will be collected, and the treatment processes that have been or will be investigated. Participating utilities from 16 states, stretching from the Pacific to the Atlantic coasts, are represented (Figure 2). The selection of utility participants was based on the type of source water (groundwater, surface water, treated wastewater for reuse), known presence of

short-chain PFAS, and impact by a variety of PFAS sources (e.g. manufacturing sites, military facilities, airports, etc.). Named participants include utilities in known PFAS hotspots, such as Plainfield Township, MI (impacted by waste disposal from the Wolverine shoe factory), the City of Fountain, CO (impacted by firefighting training activities with AFFF at an Air Force base), and the Cape Fear Public Utility Authority in Wilmington, NC (impacted by GenX and related compounds that originated from a fluorochemical manufacturer).

**Table 1. Confirmed utility participants**

Utility	State	Source Water	Study Scale			Treatment Trains Evaluated							
			Bench	Pilot	Full-scale	GAC	PAC	IX	O3	BAC	MF/UF	RO	UV-AOP
A	CA	WW			●						●	●	●
B	CA	GW			●	●							
C	CA	GW			●								
D	CA	WW	●	●		●			●	●	●	●	●
E	CO	GW			●			●					
F	CO	GWUDI			●	●				●			●
G	CO	GW		●	●	●		●					
H	FL	WW		●					●	●	●	●	●
I	FL	WW		●		●			●	●			●
J	GA	WW		●	●				●	●	●		
K	IA	SW			●					●			
L	IL	SW			●					●			
M	IL	SW			●					●			
N	IL	SW(+GW)			●					●			
O	IL	SW			●					●			
P	KS	GW			●								
Q	MA	GW	●			●							
R	MA	GW	●			●		●					
S	MI	GW+SW	●	●	●	●		●	●				
T	MI	GWUDI			●	●							
U	NC	SW		●								●	
V	NC	SW		●	●	●	●	●				●	
W	NC	SW+ASR	●	●	●	●		●	●	●			
X	NJ	GW			●	●							
Y	NJ	SW+GW			●	●							
Z	NJ	SW+GW			●	●							●
AA	NJ	SW+GW			●	●							
AB	NJ	SW+GW			●	●							
AC	NJ	SW+GW			●	●							
AD	NJ	GW			●								
AE	NJ	GW			●	●							
AF	NV	SW+WW		●		●			●	●			
AG	NV	WW	●	●		●			●	●			
AH	OH	SW		●		●				●			
AI	PA	GW			●								
AJ	PA	SW(+GW)			●	●							
AK	VA	WW		●	●	●			●	●			
AL	VA	WW		●		●			●	●			
AM	WV	SW			●	●							

GW: groundwater, SW: surface water, WW: wastewater, GWUDI: groundwater under the direct influence of surface water, ASR: aquifer storage and recovery



**Figure 2. Locations of utility participants**

database of documents, search for new literature, and then continue to track ongoing work through participation in conferences such as WQTC, ACS, and the Gordon Research Conference on emerging contaminants (2018). We do not envision a formal literature review as a deliverable to the Foundation and the PAC; rather, the information collected and discussed throughout the project will ultimately become part of the guidance document and will be used to support statements and guidelines developed as part of that document. Should the Foundation and PAC request updates on this task or information on new data/findings from outside sources, our Project Team can provide those on-going updates as part of the Quarterly Reports. We are also aware that US EPA is conducting a thorough review of the PFAS treatment literature and is planning to submit the review for publication in a peer-reviewed journal. Should enough new information be collected, the NCSU team will lead the development of a review article for a journal such as *Water Research* or *JAWWA*.

During this task, we will also assemble and analyze existing data that will be shared by named utility participants, participating AW utilities, and clients of Hazen and Sawyer and CDM Smith. As shown in Table 1, full-scale, pilot-scale, and bench-scale data are available for a wide range of treatment processes and water matrices (groundwater, surface water, wastewater). These data will be analyzed together with new data that will be collected in Tasks 2-4.

**Task 2: Analytical Method Validation among participating laboratories (NCSU, CSM, SNWA, AW)**

The objective of Task 2 is to assess whether each of the four participating laboratories (NCSU, CSM, SNWA, and AW) produces comparable PFAS results in a blinded round-robin analysis. All four participating labs have ongoing PFAS projects and the ability to determine PFAS concentrations in aqueous samples at drinking water-relevant concentrations (method reporting limits are in the <2-5 ng/L range for most targeted compounds). While each lab follows elements of EPA Method 537 for finished drinking water and/or EPA standard operating procedures 113.0 and 114.2 (EPA 2009, EPA 2016) for collection and analysis of environmental waters (i.e. groundwater and surface water), each lab has made modifications that increase the number of targeted PFAS analytes and enhance method performance, especially for short-chain PFAS. The team has analytical methods in place that follow the EPA Method 537 workflow closely (solid-phase extraction, analysis by LC-tandem mass spectrometry, LC/MS-MS), but other methods suitable for bench-scale studies are in place as well (e.g. large-volume direct injection, analysis by LC-quadrupole time of flight, LC/QToF-MS). Details of available analytical methods and

**Task 1: Literature Review and Review of Existing Data (NCSU and CSM)**

While our team is already at the forefront of many PFAS projects currently underway, it is critical that our study builds upon past and on-going studies in order to fill existing knowledge gaps. To that end, a literature review will be conducted as a continuous process throughout this project. Project personnel, supported by graduate students and postdocs at NCSU, CSM, and SNWA will conduct an initial review of our existing

quality control/quality assurance (QA/QC) protocols are presented in the QA/QC document of this proposal.

**Target Compounds.** The focus of the proposed research is on developing treatment solutions for short-chain PFAS and fluorinated replacements such as GenX, ADONA, and other PFEA. As shown in Table 2, 16 short-chain PFAS will be targeted along with understudied precursor compounds such as fluorotelomer sulfonic acids. In addition, overlooked longer-chain PFAS will be included. In total, >35 PFAS, including 18 perfluoroalkylether acids (PFEA), were selected. The majority of the compounds shown in Table 1 were chosen because they are known to occur in drinking water sources. It should be noted that NCSU is one of very few laboratories that has authentic standards for a number of PFEA that are not commercially available. As a result, we will be able to accurately determine concentrations for a large number of PFEA and conduct controlled PFEA experiments by spiking them into aqueous matrices as described in Task 4.

Table 2 also includes a few PFAS we included because of our interest to develop quantitative structure property relationships describing PFAS removal by adsorption, anion exchange, and membrane treatment processes. Some PFAS shown in Table 2 were chosen because they (1) are members of homologous series with increasing numbers of perfluorinated methylene groups and/or ether groups, (2) exist in branched and linear forms, and (3) are available in pure form at NCSU. The list of target compounds will be finalized based on feedback from the project advisory committee should our proposal be selected for funding.

**Round Robin Analysis.** To conduct the round-robin analysis, each laboratory will receive three sets of samples in triplicate. These samples will be prepared by Dr. Mark Strynar at the US EPA in Research Triangle Park, NC and will include use of NIST standard reference materials. The number of PFAS analytes and their concentrations in the round-robin samples will not be known to the analysts in each of the four participating laboratories. Results from the round-robin analysis will be submitted directly to Dr. Mark Strynar, who will tabulate the results and distribute them to the research team along with the known concentrations contained in each sample. The research team will review the results and assess whether results of the round robin analysis are acceptable (i.e. within 30% of true values) or whether corrective actions are needed by one or more teams. Corrective action would lead harmonization of procedures among the four participating laboratories. An outcome of Task 2 will be a set of recommendations for the accurate analysis of short-chain PFAS.

### **Task 3: Evaluation of short-chain PFAS removal in full-scale water treatment plants**

**Overview.** The objectives of this task are to (1) evaluate the behavior of short-chain PFAS (as well as long-chain PFAS) in utilities using diverse water sources (groundwater, surface water, treated wastewater) and treatment processes (PAC, GAC, anion exchange, membranes, (advanced) oxidation processes, biofilters) and (2) to conduct full-scale experiments to support optimization of GAC adsorption processes. Results from this Task will demonstrate the effectiveness of full-scale treatment processes for PFAS removal. In addition, we will explore whether oxidation/ disinfection processes have the potential to increase the concentrations of PFAS we are targeting (Table 2).

**Table 2.** Proposed List of Target Compounds

PFAS Name (Abbreviation)	MW	PFAS Name (Abbreviation)	MW
<b>Perfluoroalkylcarboxylic acids (C<sub>n</sub>HF<sub>2n-1</sub>O<sub>2</sub>)</b>			
Perfluoroacetic acid (PFAcA=C2) <sup>+</sup>	114	Perfluoroheptanoic acid (PFHpA=C7)*	364
Perfluoropropanoic acid (PFPrA=C3) <sup>+</sup>	164	Perfluorooctanoic acid (PFOA=C8)*	414
Perfluorobutanoic acid (PFBA=C4)*	214	Perfluorononanoic acid (PFNA=C9)*	464
Perfluoropentanoic acid (PFPeA=C5)*	264	Perfluorodecanoic acid (PFDA=C10)*	514
Perfluorohexanoic acid (PFHxA=C6)*	314		
<b>Perfluoroalkyl carboxylic acids with one ether group (C<sub>n</sub>HF<sub>2n-1</sub>O<sub>3</sub>)</b>			
Perfluoro-2-methoxyacetic acid (PFMOAA)	180	Perfluoro-2-ethoxypropanoic acid (PFEOPrA branched)	280
Perfluoro-2-methoxypropanoic acid (PFMOPrA branched)	230	Perfluoro-3-methoxybutanoic acid (PFMOBA linear)	280
Perfluoro-3-methoxypropanoic acid (PRMOPrA linear)	230	Perfluoro-2-propoxypropanoic acid (PFPrOPrA) = hexafluoropropylene oxide-dimer acid (HFPO-DA = "GenX")*	330
<b>Per- and polyfluoroalkylcarboxylic acids with one or more ether groups (C<sub>n</sub>HF<sub>2n-1</sub>O<sub>4</sub>)</b>			
Perfluoro-4-dimethylmethoxybutanoic acid (PFDMMOBA)	380	Perfluoro-4,8-dioxa-3H-perfluorononanoic acid (ADONA parent acid)	378
Perfluoro-3,5-dioxahexanoic acid (PFO2HxA)	246	Perfluoro(3,6,9-trioxatridecanoic) acid (PFO3TDA)	446
Perfluoro-3,5,7-trioxaoctanoic acid (PFO3OA)	312	Perfluoro(3,6-dioxadecanoic) acid (PFO2DA)	412
Perfluoro-3,5,7,9-tetraoxadecanoic acid (PFO4DA)	378	Nafion by-product 4	442
<b>Perfluoroalkylsulfonic acids (C<sub>n</sub>HF<sub>2n+1</sub>SO<sub>3</sub>)</b>			
Perfluoroethane sulfonic acid (PFETs) <sup>+</sup>	200	Perfluorohexane sulfonic acid (PFHxS)*	400
Perfluorobutane sulfonic acid (PFBS)*	300	Perfluoroheptane sulfonic acid (PFHpS)	450
Perfluoropentane sulfonic acid (PFPeS)	350	Perfluorooctane sulfonic acid (PFOS)*	500
<b>Per- and polyfluoroalkylsulfonic acids with one or more ether groups</b>			
NVHOS	298	Nafion by-product 1	444
F-53B	533	Nafion by-product 2	464
<b>Precursor compounds</b>			
4:2 fluorotelomer sulfonic acid (4:2 FtS)*	328	6:2 fluorotelomer unsaturated carboxylic acid	358
6:2 fluorotelomer sulfonic acid (6:2 FtS)*	428	8:2 fluorotelomer unsaturated carboxylic acid	458
4:2 fluorotelomer unsaturated carboxylic acid	258		

<sup>+</sup> percent removal measurements, but no quantitation of concentrations

\* matched mass-labeled internal standard available

**Approach.** The occurrence and removal of short-chain PFAS across full-scale water systems treating a wide variety of water sources that are located downstream and/or the vicinity of known sources of PFAS will be evaluated in this task. At the time of this writing, we have received commitments from 39 utility participants (Table 1), and we anticipate that, with input from the PAC and TWRP, additional utilities will be added to this Task. The division of labor for this Task will be as follows: AW will analyze samples from 19 AW participants, and SNWA will analyze the 9 water reuse systems (indicated by WW source in Table 1). Of the remaining plants, CSM will analyze samples from plants located in CO and to the west and NCSU from plants located to the east of CO. For this task, we propose to evaluate removal (or production, Xiao 2018) of PFAS (Table 2) by sampling the raw and finished water from all participants twice,

once ~4 months after the project start date, and once ~6 months thereafter. Collection of finished water samples will take into account the hydraulic residence time (HRT) of the plant. E.g. if a plant has an HRT of 24 hours, the finished water sample will be collected 24 hours after the raw water sample. In addition, more intense monitoring will be conducted at utilities that, based on the first sampling campaign, exhibit elevated short-chain PFAS levels in their raw water, operate processes capable of PFAS removal, and/or exhibit an increase in PFAS levels across the plant. At the latter plants, we will sample the raw and finished water as well as the influent and effluent of individual treatment processes capable of PFAS removal (or production) quarterly during four consecutive quarters. A more comprehensive full-scale testing will also be performed for the Hampton Road Sanitation District's GAC process, i.e., to capture breakthrough behavior for PFAS after fresh GAC has been implemented (reflected in cash contribution to SNWA to support additional analyses). In addition to PFAS analyses, selected water quality parameters (e.g. pH, TOC, turbidity, alkalinity, TDS) will be determined during the course of the study.

#### **Task 4: Systematic evaluation of established and innovative treatment approaches for short-chain PFAS removal at the bench-scale**

**4.1. GAC Introduction (NCSU leads)** – GAC is used extensively for PFAS removal from drinking water sources because it effectively adsorbs certain PFAS, such as long-chain PFAS. However, relatively early breakthrough has been observed for short-chain PFAS. Pilot data collected by a NC utility participant treating coagulated surface water showed that GenX and other short-chain PFAS broke through within 5,000 bed volumes for two GAC products (Hopkins et al. 2018). The performance of GAC for PFAS removal depends on numerous factors including GAC characteristics, source water PFAS species and concentrations, source water chemistry (e.g., presence of background organic matter, co-contaminants) and design/operating parameters (e.g. empty bed contact time, EBCT). GAC pilot data collected by co-PI Bellona on contaminated groundwater illustrated that GAC selection is of critical importance as certain products exhibited much earlier short- (and long-) chain PFAS breakthrough than other products. Currently, there is minimal guidance on GAC selection for short-chain PFAS removal as well as the treatment and life cycle costs associated with GAC compared with competing technologies. The latter is important as exhausted GAC must be disposed of, or shipped to a regeneration facility periodically for energy-intensive thermal regeneration.

The *goal of the proposed bench-scale testing program* is to answer the following questions: (1) Is there adsorption competition among co-existing PFAS and, if so, do the competitive effects manifest themselves in terms of earlier breakthrough and/or peaking (GAC effluent concentrations > GAC influent concentrations), (2) Can bench-scale RSSCT data be used reliably for (a) GAC selection and (b) prediction of GAC service life, (3) what GAC properties are associated with effective short-chain (and other) PFAS removal, (4) how does the background water matrix affect PFAS removal (groundwater, coagulated surface water, treated wastewater), and (5) what opportunities exist to enhance GAC service life for short-chain PFAS removal by optimizing pretreatment (e.g. PAC, MIEX)?

**Task 4.1.1 - Select most appropriate RSSCT design for scale-up and subtasks 4.1.2-4.1.5.** Scale-up of RSSCT data to estimate field-scale GAC service life for micropollutant removal is challenging as RSSCTs overpredict field-scale GAC service life (Summers et al. 2014). The reason for the overprediction is that the smaller GAC particles used in RSSCTs are less impacted by background organic matter fouling than the larger GAC particles used in field-scale adsorbers. Intraparticle diffusivity controls adsorption kinetics. However, studies conflict about



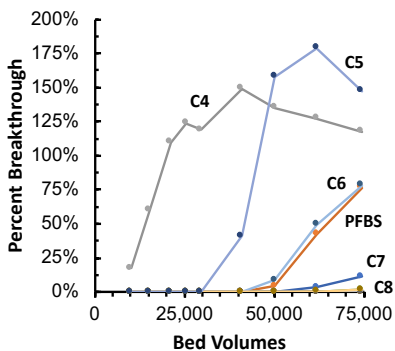
whether intraparticle diffusivity is independent or linearly related to particle size, leading to the design of constant diffusivity RSSCTs (CD-RSSCTs) or proportional diffusivity RSSCTs (PD-RSSCTs), respectively (Crittenden et al. 1991; Summers et al. 2014). Nevertheless, CD-RSSCTs are more commonly used for GAC selection and estimation of GAC service life because CD-RSSCTs can be completed in a shorter time than PD-RSSCTs. Given the many objectives of the project proposed herein, perfecting a scale-up approach that permits estimation of field-scale GAC service life for short-chain PFAS removal from RSSCT data is likely not feasible. What is feasible, however, is to identify the RSSCT design that is most appropriate for GAC selection for short-chain PFAS removal. For this purpose, linking RSSCT data to pilot-scale data in this study is of critical importance. We will also explore whether fouling factors, as proposed by Summers et al. (2014), can be used to scale RSSCT data for estimation of GAC service life.

**Approach.** In PI Knappe's lab, we have evaluated three types of RSSCT designs: (1) mini-column CD-RSSCTs that permits rapid completion of the experiment (< 1 week) (Knappe et al. 1997), (2) conventional CD-RSSCTs that permit relatively rapid completion of the experiment (< 1 month) and (3) PD-RSSCTs that require a longer time to complete the experiment, ~3 months for long-chain PFAS in groundwater at a simulated EBCT of 20 minutes. In this subtask, we will complete RSSCTs with waters from utilities W (coagulated SW with moderate TOC) and Z (GW with low TOC). Matching pilot data are available (utility W, EBCT = 10 min, bituminous coal-based GAC and enhanced coconut GAC) or will be collected during the project (utility Z, EBCT = 10 min, bituminous coal-based GAC). Utility W is impacted by PFAS discharged by a fluorochemical manufacturer and contains a range of PFEA, including GenX, while utility Z is impacted by AFFF-derived PFAS. If needed, PFAS will be spiked into the RSSCT influents to match concentrations present during the pilot study.

For each water/GAC combination, a set of three RSSCTs will be completed: (1) mini-column CD-RSSCT, (2) conventional CD-RSSCT, and (3) PD-RSSCT. For the SW utility (W), RSSCTs will be conducted with both GACs, for which pilot data exist, to more robustly assess which RSSCT design is most appropriate for GAC selection and estimation of service life for short-chain PFAS removal. Resulting RSSCT breakthrough curves will be compared to pilot data, and we will assess how well RSSCT data describe pilot-scale PFAS adsorption kinetics (shape of the breakthrough curve) and adsorption capacity (position of RSSCT breakthrough curves relative to pilot-scale breakthrough curves). We currently have six RSSCT setups (see methods section), and a total of 9 RSSCTs will be completed in this sub-task. This sub-task is expected to take 3 months to complete.

**Task 4.1.2. Effect of co-existing PFAS on onset of PFAS breakthrough and PFAS peaking.** A second key knowledge gap is whether there is adsorption competition among PFAS that co-occur in drinking water sources. PFAS generally occur at ng/L levels in drinking water sources, and it is generally assumed that background organic matter constituents are primarily competing with PFAS for adsorption sites while adsorption competition among co-existing PFAS is negligible. However, this assumption has not been validated for GAC adsorption systems. Similarly, the impacts of background organic matter type and concentration on the extent of GAC fouling and the peaking of short-chain PFAS has not been quantified. By peaking, we mean that the concentration of a PFAS in the GAC effluent is higher than in the GAC influent as a result of its displacement by one or more strongly adsorbing constituents. Peaking for short-chain PFAS is expected to occur (based on existing bench-scale and pilot-scale data) when the GAC

replacement or regeneration frequency is based on breakthrough levels of longer-chain PFAS, as illustrated in Figure 3 for C4 and C5 when breakthrough exceeds 100%.



**Figure 3.** PFAS breakthrough curves obtained with enhanced coconut GAC in GW with low TOC. PD-RSSCT, EBCT = 15 min

**Approach:** Using the most appropriate RSSCT design selected in Task 4.1.1, we will conduct RSSCT as follows: using “PFAS-free” GW with low TOC (<0.5 mg/L) and coagulated SW with moderate TOC (2-3 mg/L), we will conduct a pseudo-single-solute RSSCT with C6 only, a pseudo-bisolute experiment with two PFAS of similar adsorbability (C6 and PFBS, see Figure 3), and a bi-solute experiment containing a more weakly adsorbing short-chain PFAS (C6) and a more strongly adsorbing long-chain PFAS (C8). All compounds will be spiked into “PFAS-free” water matrices at a level of 100 ng/L. RSSCTs will be conducted with bituminous coal-based GAC and will simulate a field-scale EBCT of 10 min. Results will show whether or not co-existing PFAS affect onset of PFAS breakthrough as well as PFAS peaking in low TOC GW and in coagulated surface water with moderate TOC. A total of 6 RSSCTs will be conducted in this subtask, which will require 2 months to complete.

**Task 4.1.3. Linking PFAS removal performance to GAC properties.** Using the most appropriate RSSCT design determined in Task 4.1.1, we will evaluate the effect of GAC properties on PFAS removal. We will include at least six well-characterized GACs prepared from different starting materials (2 bituminous coal, 1 coconut/coal blend, 1 enhanced coconut, 1 coconut, 1 lignite) with widely different pore size distributions. Experiments in this sub-task will be conducted with the same waters as in 4.1.1 (low TOC GW, coagulated SW with moderate TOC), but in this sub-task, we will spike all compounds shown in Table 2 into the RSSCT influent at a level of 100 ng/L each. RSSCTs will simulate an EBCT of 10 min. Results of this subtask will show whether GAC selection is influenced by the background water matrix (i.e. is the best GAC for GW different than the best GAC for SW?) and whether GAC selection is influenced by PFAS type (is the best GAC for C4 removal different than the best GAC for GenX removal?). One of the bituminous coal GACs and the enhanced coconut GAC will be the same as in 4.1.1. As a result, RSSCTs results for the two GAC obtained in this subtask can be compared to those in 4.1.1, which will allow us to assess whether the addition of PFAS beyond those present in the pilot study impacted onset of PFAS breakthrough and/or PFAS peaking. Finally, the results obtained in subtask 4.1.3 will serve as a basis for QSPR development (Task 6). Completion of this subtask (12 RSSCTs) is expected to take 3 months.

**Task 4.1.4. Effect of background water matrix and EBCT.** One important knowledge gap is how the character and concentration of background organic matter in the GAC influent affects GAC service life for PFAS removal. In this subtask, we will conduct RSSCTs with a wide range of water types as follows:

- GW with high TOC (utility G)
- Coagulated SW with low (utility AF) and high (Utility K) TOC
- GW/SW blend (utility S), GWUDI (utility T), ASR (utility W)
- Treated WW (utility AF)

RSSCT influent will be spiked with the PFAS shown in Table 2 (100 ng/L each). RSSCTs in this sub-task will be conducted with a GAC that performed well in subtask 4.1.3 at simulated EBCTs of 10 and 20 minutes. For this purpose, two RSSCT columns will be operated in series with an additional sampling port between the two columns. All RSSCT influents will be characterized in terms of their organic and inorganic composition. Based on prior results (Dudley et al. 2015), we do not expect pH and ionic strength (total dissolved solids) to affect PFAS removal by GAC. In contrast, background organic matter will likely have a strong effect. We will characterize background organic matter by its dissolved organic carbon (DOC) concentration, UV absorbance spectrum, and excitation-emission matrix. Data collected in this subtask will answer how background matrix characteristics impact PFAS removal and whether selection of the “best” GAC depends on the background water matrix. Also, the data will illustrate how carbon use rates are impacted by EBCT. Results of this subtask will be used for model development (Task 6).

**Task 4.1.5. Effect of pretreatment.** A final important question we plan to explore is whether GAC influent can be pretreated in a manner that extends GAC service life for PFAS removal. Three pretreatment options that will remove or alter background organic matter will be explored: PAC adsorption, MIEX treatment, and ozonation. PAC and MIEX pretreatments will be explored with coagulated surface water with high TOC from utility K. PAC and MIEX treatment conditions will be chosen such that either treatment lowers the RSSCT influent TOC by ~25%. Subsequently, all PFAS shown in Table 2 will be spiked into the pretreated RSSCT influent to match levels in non-treated controls. RSSCT results for utility K will be compared to those obtained in 4.1.4. To assess the effect of ozonation, coagulated surface water from utility W will be evaluated. It should be noted that water from utility W for subtasks 4.1.1 and 4.1.3 will be collected at the plant following raw and settled water ozonation. In this subtask, we will collect raw water from utility W and coagulate it prior to conducting the RSSCT to avoid the full-scale ozonation step. Raw water for this subtask will be collected on the same day as the coagulated, settled, ozonated water for 4.1.1 and 4.1.3 to assure comparability. RSSCT results for utility W in this subtask will be compared to those obtained in 4.1.3. Results from this sub-task will highlight to what extent PAC, MIEX, and ozone pre-treatment change carbon use rates for the control of short-chain (and other) PFAS.

**4.2. IX Introduction (NCSU leads)** – Although used less extensively than GAC, anion IX has garnered recent attention as an alternative to GAC. Several studies have evaluated the removal of long- and short-chain PFASs by anion-exchange resins (McCleaf et al. 2017, Woodard et al. 2017, Zaggia et al. 2016, Dudley et al. 2015). For example, Woodard et al. (2017) showed that the number of bed volumes to the onset of PFAS breakthrough was larger for anion exchange than for GAC treatment. Differences were more pronounced for longer-chain PFASs compared with shorter-chain PFASs, and more pronounced for sulfonic acids compared with carboxylic acids with the same number of perfluorinated carbons. To evaluate PFEA removal, a pilot study evaluating anion-exchange resins at a utility in the lower Cape Fear River basin is ongoing. Pilot columns (EBCT = 1.5 min) showed that GenX was removed to below the method reporting limit of 5 ng/L for at least 27,400 BV, and GenX removals for the two tested resins were 38 and 75% after treating 62,500 BV (CFPUA, 2017). Also, no detectable breakthrough was observed for Nafion byproduct 2, PFOA, or PFOS after 62,500 BV of water had been treated. The latter data were collected in coagulated surface water with moderate TOC and low total dissolved solids (TDS) concentrations. Results from controlled laboratory studies suggest that background organic matter does not appear to substantially impact IX resin performance for PFAS removal (Dudley et al. 2015). In contrast, we do expect that IX resin performance is adversely impacted

by increasing concentrations of competing anions, especially sulfate and nitrate (Dudley et al. 2015). While these results are encouraging, further evaluation is needed before life cycle costs of anion exchange and GAC treatment options can be compared. Management of spent anion-exchange resin requires careful consideration. Spent resin can be regenerated on site, landfilled, or incinerated. On-site resin regeneration would require the development of a suitable regeneration strategy that may require both brine and an organic solvent (McCleaf et al. 2017, Woodard et al. 2017, Zaggia et al. 2016, Dudley et al. 2015) and management of the spent brine that contains high levels of PFASs. Currently, there are several related projects evaluating IX regenerant treatment including non-thermal plasma (NTP), electrochemical processes, UV-persulfate, UV-bisulfite, and distillation. Methods to address the IX regenerant stream will also be examined in a new SERDP Project (ER18-1063), on which co-PI Schaefer is involved.

**Task 4.2.1. Selection of bench-scale approach.** To date, there is little experience with scale-up of bench-scale IX data for PFAS removal. Guidance is therefore needed for a suitable bench-scale test that can be used for IX resin selection and for estimating resin service life in different background water matrices. Ongoing work in co-PI Schaefer's lab is evaluating CD-RSSCTs with crushed IX resin for scaleup, and ongoing work in PI Knappe's lab is evaluating a small column test conducted with as-received resin at the same EBCT as a corresponding pilot column, but with a lower hydraulic loading rate. In this subtask, we will build on ongoing work and also explore mini-column CD-RSSCTs for their suitability to more rapidly complete bench-scale evaluations. Since background organic matter does not appear to substantially impact IX resin performance for PFAS removal (Dudley et al. 2015, CFPUA 2017), we do not anticipate that the PD-RSSCT approach needs to be evaluated for IX resins.

**Approach.** In this subtask, we will complete bench-scale experiments with waters from utilities W (coagulated SW with moderate TOC and low TDS) and Z (GW with low TOC and high TDS). Matching pilot data are available (utility W, EBCT = 1.5 and 3 min, IX resins A and B) or will be collected during the project (utility Z, EBCT = 3 min, IX resin A). Utility W is impacted by PFAS discharged by a fluorochemical manufacturer and contains a range of PFEA, including GenX, while utility Z is impacted by AFFF-derived PFAS. If needed, PFAS will be spiked into the bench-scale column influents to match concentrations present during the pilot study.

For each water/IX resin combination, a set of three bench-scale tests will be completed: (1) mini-column CD-RSSCT, (2) conventional CD-RSSCT, and (3) bench-scale column with as-received IX. For the SW utility (W), bench-scale data will be conducted with two resins, for which pilot data exist, to more robustly assess which bench-scale approach is most appropriate for GAC selection and estimation of service life for short-chain PFAS removal. PFAS breakthrough curves will be compared to pilot data, and we will assess how well RSSCT data describe pilot-scale PFAS adsorption kinetics (shape of the breakthrough curve) and adsorption capacity (position of RSSCT breakthrough curves relative to pilot-scale breakthrough curves). A total of 9 RSSCT/column tests will be completed in this sub-task. This sub-task is expected to take 3 months to complete. This sub-task will be conducted in parallel with 4.1.1 experiments to assure that identical influents will be used for IX and GAC experiments.

**Task 4.2.2. Effect of co-existing PFAS on onset of PFAS breakthrough and PFAS peaking.** Using the most suitable test identified in 4.2.1, NCSU will conduct bench-scale studies to evaluate the effect of co-existing PFAS on resin performance using the experimental approach described for GAC in 4.2.2. Experiments will be conducted in parallel with 4.1.2.

**Task 4.2.3. Linking PFAS removal performance to IX properties.** Using the most suitable test identified in 4.2.1, up to five strong base anion exchange resins will be assessed for their PFAS removal effectiveness. Resins that have shown promise in previous studies will be included in the selection process as well as effective resins that are currently being evaluated at our utility participants and at DoD sites. The experimental design will be similar to that proposed for GAC in 4.1.3 (same waters, but different EBCTs) and will include evaluation of all PFAS listed in Table 2. Experiments will be conducted in parallel with 4.1.3

**Task 4.2.4. Effect of background water matrix (and EBCT).** An important knowledge gap is how the background water matrix affects PFAS removal by IX. In contrast to GAC, we anticipate that PFAS removal by IX will be more strongly impacted by competing inorganic anions (e.g. sulfate, nitrate) than by background organic matter (Dudley et al. 2015). A testing matrix will be developed to assess the impact of water chemistry on IX performance for PFAS removal. Through participating utilities our team has access to different background matrices with a range of sulfate, nitrate, hardness, total dissolved solids, and TOC concentrations, as well as a wide range of water sources (groundwater, surface water, treated wastewater). We will also evaluate the effect of EBCT (1.5 and 3 min at the field scale) in this subtask by operating to IX resin columns in series.

**Task 4.3. GAC/IX Introduction (NCSU leads)** - Our team has hypothesized that a GAC/IX treatment train may be advantageous as longer-chain PFAS will be preferentially removed by GAC, along with other organic micropollutants and disinfection by-product (DBP) precursors, leaving the adsorption of short-chain PFAS as the treatment objective for the IX resin. Key benefits of a treatment train approach are (1) **Lower GAC replacement frequency by focusing GAC treatment on removal of long-chain PFAS**, while allowing short-chain PFAS to break through the GAC for subsequent removal by IX, and (2) **Effective removal of short-chain PFAS by IX and the possibility for on-site IX resin regeneration**, which is more readily accomplished for short-chain PFAS than for long-chain PFAS (Dudley et al. 2015). While a GAC/IX treatment train approach may facilitate on-site regeneration of IX resins, we expect that utilities with multiple treatment objectives (pharmaceuticals, DBP precursors, etc.) may benefit from the treatment train approach even with single-use IX resins if GAC service life can be substantially prolonged by relying on the IX resin for short-chain PFAS removal.

**Approach.** Using the most effective bench-scale testing approaches identified in Task 4.2, we will explore possible benefits of operating a GAC/IX resin treatment train for short-chain PFAS removal. Experiments will be conducted with waters from utilities W (coagulated SW with moderate TOC and low TDS) and S (softened GW/SW blend with moderate TOC and high chloride and sulfate). Bench-scale columns will be operated with the most effective GAC and IX resin identified in Task 4.2 and will simulate field-scale EBCTs of 10 min for the GAC and 1.5 min for the IX resin. Results from the GAC/IX treatment train will be compared to results obtained for individual GAC and IX columns obtained in Tasks 4.1 and 4.2 to assess the impact of a treatment train approach on carbon and resin use rates. Data obtained here will also be used in Task 7, where we will explore optimization of GAC and IX treatment operations using models. For example, we will explore whether a GAC/IX treatment train offers benefits relative to a GAC lead/lag design.

**Task 4.4 – Powdered Activated Carbon (PAC) and Innovative Sorbents Introduction (SNWA leads, NCSU supports).** This task will focus on the evaluation of innovative sorbents and index their PFAS removal performance to that of PAC. Many innovative sorbents have been

proposed for PFAS treatment, but have not yet been systematically evaluated for short-chain PFAS in relevant water matrices. One such class of innovative sorbents contains cyclodextrins. Typical cyclodextrins consist of six to eight glucose monomers in a ring. Contaminants such as PFOA form host-guest inclusion complexes, with the contaminant bound inside the cyclodextrin ring (Karoyo et al., 2011). By selecting different sizes of cyclodextrin rings (Weiss-Errico et al., 2017a), or choosing different monomers to cross-link cyclodextrin polymers (Xiao et al., 2017), cyclodextrin can be “tuned” for specific contaminants. Cyclodextrin polymers with fluorinated cross-linkers appear especially effective (Xiao et al., 2017), possibly due to C-F to C-F fluorophilic interactions (Du et al. 2017). One of these cyclodextrin polymers became recently commercially available as CycloPure CD-PFAS (CycloPure, 2018).

Another promising class of innovative sorbents is organoclays. Synthetic organoclays are “swellable” and so have greater, faster adsorption than natural minerals (Martin et al., 2018). These sorbents can be resilient to competition or pore blockage: organo-functionalized swelling mica achieved 68-78% removal of PFBA in aqueous solution, tap water, surface water, raw wastewater, and treated wastewater with the same sorbent dose (Martin et al., 2018). It is expected that more mesoporous sorbents will perform better for PFAS removal by promoting hemi-micelle self-aggregation (Du et al., 2014) and reducing pore blockage (Newcombe et al., 2002). Preliminary data suggest mesoporous organosilica may be even more effective for PFBA than PFOA at concentrations in the ppb range (Horst et al., 2018). Mesoporous organosilicas are commercially available as both a bulk adsorbent (Osorb) and a coated filtration sand medium (PuraSorb) (Horst et al., 2018).

Hydrophobic polymers constitute a third category of innovative sorbents for PFAS. One such hydrophobic polymer, PA-F 2600, had higher adsorption capacity for PFOS than activated carbon or anion exchange resins in the environmentally relevant  $\mu\text{g/L}$  range (Schuricht et al., 2017). This is because adsorption in water requires replacement of the previously adsorbed species – water, in the case of activated carbon, or monovalent ions in ion exchange resins. At low concentrations, the driving force of PFOS adsorption may be too weak to displace the water or ions effectively. However, due to the high hydrophobicity PA-F2600, water molecules are easily replaced by PFOS. PA-F 2600 is also more mesoporous than activated carbon (Schuricht et al., 2017), which has benefits for PFAS sorption as described above. This innovative sorbent has not yet been tested to determine if its superior performance at environmentally relevant concentrations of PFOS extends to short-chain PFAS.

**Approach.** Three innovative sorbents (CD-PFAS, Osorb, and PA-F 2600), will be compared to a reference PAC for short-chain PFAS removal from groundwater, surface water, and wastewater effluent. Selected waters will span a range of TOC concentrations to probe competitive effects. Each water will be spiked with 200 ng/L of each PFAS (Table 2). Batch tests will be conducted to determine the dose of each sorbent required to remove all short-chain PFAS by at least 90% in both wastewater effluents. Samples will be collected after 0.5 hours and 24 hours of mixing time, representative of PAC contact times in conventional treatment and superpulsators. To the extent possible, equal particle diameters will be used for all sorbents so that any differences in sorption rate reflect different properties among the sorbents and not merely differences in particle diameter. If results from batch tests are promising, innovative sorbents will also be evaluated in bench-scale column tests using the most challenging of the above water matrices. Breakthrough bed volumes will be determined for each sorbent and PFAS, and the rank order of most effective

sorbents will be compared between batch and column testing. Results from column tests will be compared to those obtained with GAC in Task 4.1.4.

**4.5. SPAC/MF Introduction (CSM leads)** - Super-fine powdered activated carbon (SPAC) has the potential to be a superior adsorbent due to an increased quantity of mesopores and macropores on wet milled carbons as well as a smaller particle size that enhances PFAS adsorption kinetics (Dudley, 2012). These advantages could result in a lower quantity of activated carbon being used for PFAS adsorption as well as faster adsorption kinetics requiring shorter contact times (Yu et al., 2009). Adsorbability of PFAS is often chain-length dependent with short-chained PFAAs (<C6 for sulfonic acids; <C8 for carboxylic acids) being more resistant to treatment compared to longer-chained PFAS (Appleman et al., 2014; Sun et al., 2016; Buck et al., 2011) Factors associated with the preferential adsorption of longer-chained PFAS and natural organic matter present in source water can lead to a faster breakthrough of the shorter-chained PFAS (Appleman et al., 2014). In addition, there is currently little understanding of the removal mechanisms of additional intermediate PFAS that have received limited attention, including polyfluorinated precursor chemicals. The purpose of this task is to evaluate SPAC/MF on a variety of source waters for the removal of short-chained PFAS as well as longer-chained PFAS including PFAAs, GenX and precursors.

CSM has been conducting experiments with a SPAC/MF product from Aqua-Aerobics (subsidiary of METAWATER) for treatment of contaminated groundwater and fire-fighting training area run-off. Wood-based SPAC was compared to bituminous coal based GAC for treating PFAS from a contaminated groundwater sample. Results indicate that the SPAC/MF system provided a significantly higher adsorption capacity (based on PFAS adsorbed/mass carbon to 10% breakthrough) than the best performing GAC product (F400, Calgon Carbon Corporation; Table 3). Additional testing on highly contaminated fire-fighting training area water showed that SPAC was approximately 100 times more effective than GAC.

**Table 3.** Adsorption mass loading rate ( $\mu\text{g}$  PFAA/g activated carbon) for SPAC/CMF and GAC tested with contaminated groundwater.

	PFOS	PFHxS	PFBS	C8	C7	C6	C5	Sum PFAAs
GAC	$\geq 2.4$	2.2*	0.015*	0.86*	0.0033*	0.43*	0.12*	6.2
SPAC/CMF	$\geq 3.8$	3.3	0.043*	1.5	0.49	1.2	0.90	11.0

\*Indicates that 10% breakthrough was observed

**Task 4.5.1 – Identification of best PAC/SPAC product.** Work to date has been performed with a wood-based SPAC (Aqua-Aerobics); however, SPAC sourced from other materials may provide better adsorbability. The research team will work with activated carbon vendors to obtain additional SPAC samples for PFAS removal during the course of the proposed project.

**Task 4.5.2 – Evaluation of operating conditions.** Limitations associated with the SPAC/MF system include energy requirements associated with cross-flow filtration, limited understanding of the exhausted SPAC wasting rate, and critical permeate flux to minimize fouling. Once a promising SPAC product has been identified for short-chain PFAS removal, experiments will be conducted to determine the optimal cross-flow velocity and permeate flux to minimize energy requirements while estimating the SPAC wasting rate based on exhaustion. This information will be used to develop a cost comparison between GAC and IX, and SPAC/MF.



**Approach.** Water samples used for this task will be based on Tasks 4.1 and 4.2 to compare use rates of SPAC to those of IX and GAC for removal of PFAS with a wide range of properties (Table 2). For this work, a lab-scale ceramic MF (CMF) system will be used for experimentation. Approximately 80 L of source water will be fed into a 10-L conical feed SPAC adsorption tank at the rate of CMF permeate flux. SPAC doses between 100 – 1,000 mg/L will be evaluated, and experiments will be performed to evaluate effective cross-flow velocities and permeate flux set-points on membrane operation, as well as long-term PFAS/SPAC adsorbability. If required, short-chain PFAS and fluorinated replacements will be spiked into source water at 200 ng/L. PFAS adsorption capacity at breakthrough (e.g.,  $\mu\text{g-PFAS/g-SPAC}$ ) will be used as a metric of comparison to GAC and IX treatment systems.

**4.6. Nanofiltration (NF) and Reverse Osmosis (RO) Introduction (CSM leads)** - High-pressure membrane technologies can provide an efficient PFAS barrier and are commonly used for treatment of a variety of water resources (Appleman et al., 2014). Prior bench-scale results from co-PI Bellona show that NF and RO membranes effectively reject short-chain PFAS, such as C4 (Appleman et al., 2014), and a recently completed pilot study at one of our utility participants shows that RO membranes also reject PFEA, including GenX and PFMOAA, the PFEA with the lowest molecular weight in Table 2. However, there are discrepancies regarding the rejection of short-chain PFAS based on past research (Appleman et al., 2014; Steinle-Darling and Reinhard, 2008). The main drawback to RO and NF is the continuous production of a retentate or concentrate stream requiring treatment and/or disposal. NF provides a significant advantage over RO as it can operate at significantly lower pressure and generally does not result in inorganic scaling. Fouling of membranes and requirements for high operating pressures can lead to high costs and energy needs. The ultimate goal of this task is develop a robust dataset with the goal of reporting on the removal of short-chain PFAS by NF and RO membranes for a variety of source waters.

For this work, we will leverage an ongoing project funded by the Air Force Civil Engineering Center (AFCEC) entitled: ‘Sequential nanofiltration with UV destructive treatment’ (AFCECBAA 16-001-031). In this project, we are testing a variety of NF and RO products for the removal of a broad-range of PFAS (including short-chain PFAS and PFAS with the potential to adsorb to membranes) from several different source waters at both the bench- and pilot-scale. Pictures of CSM bench- and pilot-scale membrane testing systems are provided in Figure 4.



Figure 4. (Left) bench-scale membrane system at CSM, (middle) pilot-scale membrane system at CSM, (right) rejection of PFAS as a function of time by NF270.



We diluted an AFFF formulation to 30 µg/L PFOS and evaluated the effectiveness of NF (NF270, Dow/Filmtec) and RO (ESPA2, Hydranautics) for PFAS removal at the pilot-scale. Greater than 97% removal of the quantified PFAS was achieved (Figure 4, right). For this project, we will build on our ongoing research to further investigate removal of short-chain PFAS, including fluorinated replacements by NF and RO.

Work being conducted at CSM in conjunction with an AFCEC project has been evaluating commercially available NF and RO products for the removal of short- and long-chain PFAS, including precursors. Outcomes of this task include (1) treatability data and (2) a protocol (step-by-step instructions) for laboratory-scale treatability testing. This protocol will assure accurate and comparable treatability tests. Based on past membrane-based projects, the team has selected the NF-270 (NF; Dow/Filmtec) and the ESPA2 (RO; Hydranautics) as promising membrane products. Based on ongoing and future work, the team may evaluate additional membrane products if necessary.

Currently, the team is evaluating the influence of operating parameter on PFAS rejection, including permeate flux, recovery and water chemistry (e.g., pH, ionic strength). In particular, CSM has been diluting AFFF formulations, adding it to our NF/RO system feed container and running experiments evaluating permeate flux and recovery for the identified NF and RO membranes. Removal of short-chain PFAS during this work will be summarized and included in the final report for this project.

**Approach.** Beyond AFCEC sponsored work, effectiveness of NF/RO for removal of short-chain PFAS will be evaluated in this study with up to three PFAS-impacted waters (preliminarily, utilities G, W and AF; groundwater, surface water impacted by GenX, and treated wastewater, respectively). The rejection of PFAS including short-chain compounds and fluorinated replacements will be evaluated using the aforementioned bench-scale membrane testing system. PFAS (Table 2) will be spiked into feed solutions at 200 ng/L each. Membrane experiments will be conducted to evaluate the influence of operating parameters including permeate flux (10, 20, 30 LMH) and recovery (up to 85%) on PFAS removal. Operating parameters will be continually monitored by a SCADA system to evaluate flux decline due to fouling and energy requirements for filtration. Long-term filtration experiments will also be conducted to evaluate the rejection of solutes with potential solute-membrane interactions.

**4.7. IX Resin Regeneration and PFAS Destruction in Spent Regenerant Brine (CDM leads, CSM supports)** - While several studies have demonstrated that IX resins can be effective for PFAS removal, short-chain PFAS (e.g., PFBS, C4) break through long before long-chain PFAS (Zaggia, 2016; Woodard, 2017). Thus, if short-chain PFAS are present, the longevity of the IX resins will be greatly diminished, resulting in frequent and costly changeouts. ZagNessgia (2016) showed that use of a brine solution consisting of NH<sub>4</sub>OH + NH<sub>4</sub>Cl was effective for regenerating IX resins impacted by C8, PFOS, C4, and PFBS, thus substantially increasing their treatment lifetime. However, more comprehensive testing of IX regeneration using a wide range of PFAS in natural waters has not, to our knowledge, been performed. Our approach is to investigate IX resin regeneration using brine for a wide range of PFAS, thereby serving as a means to extend IX resin lifetime when short-chain PFAS are present.

**Task 4.7.1 – IX resin regeneration.** Spent IX resin used in both the pilot- and bench-scale tests (described in Task 5.2 and 4.2) will be regenerated using a caustic brine solution. Based on previous studies (Zaggia et al., 2016), such solutions are expected to be effective for removing

short-chain PFAS from the IX column. Here, we will focus on using both conventional chloride salt brine solutions, as well as carbonate-based solutions (Ness and Boyer, 2017), as the carbonate-based solution will not facilitate the formation of chlorate and perchlorate during subsequent electrochemical treatment. It is expected that regeneration will require approximately 10 bed volumes of flushing, followed by 5 bed volumes of clean water flushing. A mass balance approach will be used to determine the percentage removal of PFASs from the resin, and the regenerated resin will be subsequently tested to confirm its capacity for PFAS treatment in further pilot and bench-scale testing.

***Task 4.7.2 – Efficiency of selected destruction methods for short-chain PFAS destruction.***

After assessing IX resin regeneration using the various brine solutions, electrochemical treatment will be used for destruction of the PFAS in the regeneration fluid. Electrochemical treatment is ideally suited for the high PFAS concentrations and high salinity expected in the regeneration fluid, as confirmed in preliminary studies performed by Liang et al. (2018). A bench-scale electrochemical system (Schaefer et al., 2017) using commercially-available electrochemical cells will be used to evaluate treatment of the IX regeneration fluids. Boron doped diamond anodes, as well as other commercially available anode materials currently being evaluated in SERDP Project ER-2424 (e.g., magneli phase  $Ti_4O_7$  anodes), will be tested with respect to their ability to treat PFASs mixtures in IX regenerant solutions. PFAS removal and defluorination, as well as treatment energy demand, will be carefully evaluated using experimental methodology we have previously developed (Schaefer et al., 2017). Our own experiments (Schaefer et al., 2017) show effective oxidation of PFOA and PFOS in solutions amended with sodium sulfate, although the concentrations added were still much lower than the 0.5-10 wt% solutions expected for regenerant brines.

**Task 5: Validation of promising treatment approaches at the pilot-scale and full-scale**

Pilot-scale validation of promising treatment approaches for short-chain PFAS removal will be conducted through several approaches: 1) collecting and summarizing short-chain PFAS removal data from existing pilot-scale systems, 2) summarizing data from project team's past pilot-scale projects, and 3) performing additional pilot-scale testing during the course of the project. In addition, limited full-scale experiments will be conducted. Table 1 includes a list of utilities that will contribute pilot-scale data. PFAS removal data from these systems will be summarized during the course of this project; when possible, additional samples will be collected to probe whether PFAS (Table 2) are present that are not monitored for currently. The following sections highlight pilot-scale projects that will be conducted during this project. During the course of the project, the team will search for additional opportunities to collect pilot-scale data on short-chain PFAS removal by a variety of treatment processes.

**Task 5.1 - American Water Pilot-Scale Studies.** We will compare the performance of a single-use IX resin and GAC for the removal of PFAS, with focus on short-chain PFAS. Single-use resins eliminate the regeneration step once the PFAS removal capacity of the material is exhausted. The economic feasibility of single-use IX resins for full-scale operations treating various water qualities needs to be evaluated. AW is working with Purolite to assess the efficiency of single-use ion exchange resin (PFA694E) and compare its performance against two types of GAC typically used by AW. Pilot units will be installed at two utilities (X and Z in Table 1) operated by AW. For the latter, matching bench-scale tests will be conducted in Task 4. The wells at the two utilities present similar alkalinity but different TDS concentrations and PFAS fingerprints. Elevated concentrations of PFAS, most likely released from different types of

sources, have been consistently detected in both systems. The pilot-units will be operated for approximately 12 months. During this time, column flow will be monitored at least every three (3) days and adjusted as needed. Pre-filters will be changed out every two (2) weeks or more frequently if excessive solids build-up is observed. To prevent the development of biological activity, the pilot columns will be covered from sunlight. Background water quality parameters (e.g. pH, TOC, turbidity, alkalinity, TDS) and PFAS will be analyzed in the influent and effluent from the columns (resin and two types of GAC). Flow rate and cumulative throughput at the time of sampling will be also recorded. The research team will establish the sampling frequency prior to the start-up of the pilot-units.

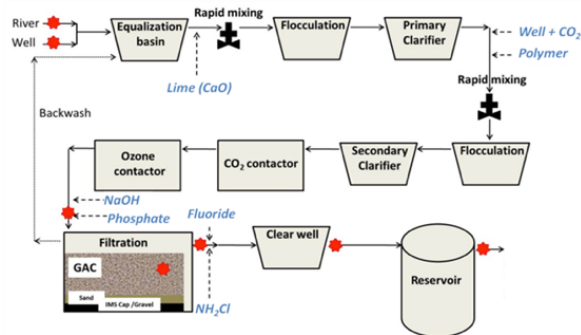
**Task 5.2 - CSM Pilot-Scale Studies.** Researchers at CSM have several opportunities to compile pilot-scale short-chain PFAS removal data. Systems include a pilot-scale GAC/IX system operating at the City of Fountain, CO, a pilot-scale SPAC/CMF project at the City of Fountain, and a pilot-scale NF system with concentrate PFAS destruction at Peterson Air Force Base. While these studies are ongoing, CSM is collecting data regarding the efficacy of short-chain PFAS removal. In addition, CSM has recently constructed a modular column system to side-by-side test established and emerging adsorbents, which will be deployed to treat contaminated groundwater at the City of Fountain. Depending on results from laboratory-scale testing, CSM will select best performing GAC and IX resin products for pilot-scale testing for the removal of short-chain as well as additional PFAS. In addition, one goal is to test not only novel adsorbents but also novel configurations including GAC followed by IX as well as mixed-media beds (GAC with IX). Additionally, spent IX resin will be regenerated through various methods (e.g., bicarbonate brine, brine with methanol) to assess the option of treating IX brine with destructive technologies (see Task 4.7).

### **Task 5.3 - Ann Arbor Pilot-Scale and Full-Scale Studies**

***Task 5.3.1 – Pilot-scale.*** In 1999, the City of Ann Arbor Water Treatment Plant commissioned construction of six pilot-scale filters to replicate performance of its full-scale filters. The pilot plant was recommissioned in 2017 for WRF4743 and is fully functional. This project will use the 6 pilot filter columns to test promising GAC and IX media as identified in Task 4. While the pilot filters were designed to mimic the operational parameters of the City’s full scale filters, they also have the flexibility to operate at greater media depths. The work proposed will take advantage of this feature to evaluate the effects of EBCT (5, 10, and 20 minutes for GAC; 1.5, 3, and 6 minutes for IX) on sorbent use rates. Pilot-scale testing will be conducted in two rounds. In round 1, the pilot columns will receive settled water to mimic GAC performance in filter adsorber mode. In round 2, pilot columns will receive filtered water from a full-scale adsorber containing spent GAC to mimic GAC performance in post-filter adsorber mode. These results will show whether filter adsorber performance for PFAS removal is impacted by higher influent turbidities and a greater backwash frequency. Also, if GAC/IX process trains show promise in Task 4, the City will evaluate the effectiveness of a GAC/IX treatment train at the pilot scale. Using a pilot-scale ion exchange columns built by NCSU, the City will install the IX column in series after the GAC columns. This scenario will quantify the improved media life of the ion exchange resins resulting from the reduced loading by following GAC.

***Task 5.3.2 Full-scale.*** The City of Ann Arbor, MI operates a 50 MGD lime softening water treatment plant that serves 125,000 people in Ann Arbor and its surroundings. The treatment plant was built in 1938 and modified over the years to its current treatment configuration illustrated in Figure 3. One key feature of the City’s water treatment plant is the blending of two

water sources prior to treatment. The primary source of water for the City is the Huron River where the City has detected C4, C5, C6, C7, C8, PFBS, and PFOS at combined concentrations up to approximately 60 ppt. The City also has a series of wells that comprise approximately 15% of the source water requirements to the plant. The City has not detected any PFAS in its groundwater supply.



**Figure 3. City of Ann Arbor Water Treatment Plant**

The City has been experimenting with different filter configurations to address removal of PFAS from its source water. The City has 26 filters, with different combinations of GAC and sand that range from 24 to 28 in. deep, with 18 to 24 in. comprising GAC and the remainder sand. Two of the 26 filters are full bed GAC with no sand. Five of the filters use Calgon F400 GAC and the remainder have Calgon F300. The City typically replaces GAC every 5 years in its filters, but is evaluating the impact on effective life if the media is used for PFAS removal. As

part of this proposal, the City intends to dedicate two to five of its filters to explore the impact empty bed contact time (EBCT) and GAC type on PFAS removal. The City normal loads its filters at 1.5 gpm/ft<sup>2</sup>, but can operate up to 3.0 gpm/ft<sup>2</sup> to explore the effect of EBCT (5-10 min) at the full scale. These EBCTs are typical for utilities considering GAC filter adsorbers for PFAS removal.

**Task 6: Development of quantitative structure-property relationships to predict PFAS removal by activated carbon, anion exchange, and membrane treatment processes (NCSU leads, CSM supports).** The proposed research is designed to provide a comprehensive understanding of the removal of short-chain PFAS by state-of-the-science treatment approaches. The resulting data sets provide an opportunity to fill a significant need: to develop approaches to predict treatment performance *a priori*. The research team has developed, and through this project will continue to develop treatment databases to develop structure-activity relationships to aid in the selection of treatment processes. We will build on our past research and findings from this project to develop multi-linear regression models that link short- (and long-)chain PFAS removal to PFAS properties, background water matrix constituents, and treatment process parameters. For example, in a prior TWRP study (Summers et al. 2014, Kennedy et al. 2015), we developed a model to predict GAC service life to 10% breakthrough for a diverse set of micropollutants. In this model, micropollutant properties that determined adsorbability included the pH-dependent octanol:water partition coefficient (log D) and two Abraham solvation parameters (S, representing the compound's polarity/polarizability and V, representing the compound's molecular volume). In addition, the influent DOC concentration to the GAC contactor was an important factor controlling the volume of water that could be treated to 10% breakthrough. By developing data sets for a large number of PFAS and background water matrices, we expect to identify PFAS properties, background water characteristics, and process operating conditions that are strong predictors of PFAS removal. We expect to develop models describing PFAS removal by GAC, IX, and high-pressure membrane treatment processes. For GAC and IX treatment processes, bench- and pilot-scale data will first be described by the pore-surface diffusion model to develop breakthrough curves and estimates to targeted levels of breakthrough. Resulting model input parameters will also serve to quantitatively discuss factors

that influence PFAS removal performance in different background water matrices and by different sorbents.

**Task 7: Comparison of treatment approaches using life cycle analysis and cost models (CSM leads with significant support from NCSU, Hazen, CDM, and SNWA).** Work performed on life-cycle analysis (LCA) and life-cycle costing (LCC) will build on several ongoing projects, including our recently funded ESTCP project comparing treatment technologies, as well as several projects evaluating the costs of individual treatment technologies. To evaluate the benefits and identify possible tradeoffs and disadvantages of different treatment technologies, we will employ a life cycle and systems-based analysis approach. Direct and indirect impacts (costs, environmental and human health impacts, etc.) will be quantified and compared for each treatment technology. Our team will work with technology development companies to develop cost matrices. Each sub-model or treatment system model will characterize the material and energy inputs and outputs as required to operate the entire treatment system over 20 years (all technologies will be normalized by the same timeframe and account for differences in chemical and energy use as well as material and system lifetimes), and it will include: chemical type and mass, energy type and mass, material (e.g., steel reactor) type and mass, and waste type, mass, and treatment/disposal requirements. The technology sub-models will all be combined into one meta-analysis systems model that will then be evaluated using multiple life cycle metrics. Fundamental development of this model is taking place in a separately funded ESTCP project, and this work will be leveraged and expanded upon to address the needs of the water treatment community for short-chain PFAS removal.

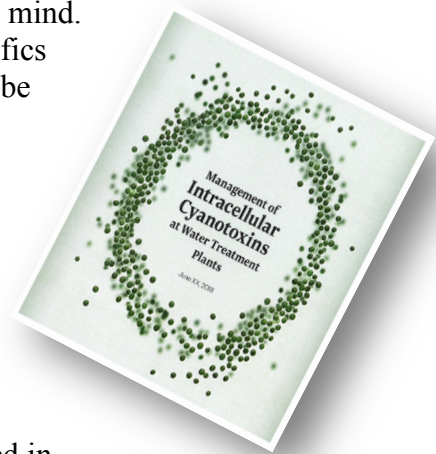
**Task 8. Development of a decision support tool for treatment process selection (led by Hazen)**

To most effectively assist water providers with developing effective strategies for PFAS treatment, it is critically important to effectively disseminate the results of this study to multiple audiences, including utility managers, engineers, regulators, and communications staff. Data surrounding treatment strategies for PFAS is often incomplete and sometimes inconclusive. For example, the impacts of water quality on PFAS treatment via common sorbents such as GAC and IX remains poorly understood. Some studies have reported substantial impacts of DOC on PFAS removal (e.g., Yu et al., 2012) while other studies have not shown a strong correlation between DOC levels and PFAS removal (e.g., McCleaf et al., 2017). In addition, recent studies have shown that several PFAS compounds not routinely monitored are poorly removed by GAC (Xiao et al., 2017), leading to questions from regulators and the public about effective removal strategies.

To clarify these and other concerns, the results of this study will be used to develop general guidelines for evaluating treatment effectiveness. Specific areas that will be addressed include:

- Up-to-date PFAS analyte list (including short-chain) and analytical reproducibility
- Effectiveness of potential treatment approaches based on background water quality
- Clarity regarding conflicting information focused on GAC and IX treatment technologies
- Guidelines on appropriate bench scale testing methods for potential treatment strategies
- Applying results from bench-scale testing
- Determining representativeness of water used for testing, within natural variability
- QSAR to extend the result of the study to unmonitored PFAS
- LCA and cost models to evaluate feasibility of treatment

The results of the study will be presented with two audiences in mind. The tools provided in the final report will include detailed specifics gleaned from the research performed within the study, and will be presented in appropriate detail to meet the needs of design engineers and researchers interested in advancing technologies. A second document, a summary guidance manual, will be targeted to utility manager and communications staff. This document will present high level concepts from the study, suitable for garnering public and regulatory trust in the evaluation, design, and implementation process undertaken by utilities in determining their best treatment options. Hazen will lead the effort of developing this second document, utilizing an approach similar to that currently being implemented in TWRP 4692: Release of Intracellular Cyanotoxins during Oxidation of Natural and Lab Cultured Cyanobacteria.



### **Evaluation Criteria**

The project can be evaluated relative to specific project objectives and the ability of the Project Team to provide data and deliverables associated with each objective. Thus, corresponding with each objective, the Foundation and PAC can use these benchmarks and/or deliverables to evaluate project progress:

1. Objective 1: We will identify effective sorbents by completing (1) a literature review and a review of existing bench-, pilot-, and full-scale data (Task 1), (2) completion of bench-scale tests in a wide range of water matrices (Task 4), and (3) pilot- and full-scale experiments (Task 5). The resulting treatment database will highlight effective sorbents as well as limitations that may be associated with certain background water quality parameters.
2. Objective 2: Similar to the first objective, we will identify effective membranes by developing a treatment database through completion of a literature review and review of existing data (Task 1) and (2) completion of bench-scale and pilot-scale tests (Tasks 4 and 5).
3. Objective 3: The effectiveness of short-chain PFAS removal will be evaluated through the completion of full-scale sampling of utilities with a wide range of background matrices (Task 3) as well as bench- and pilot-scale experimentation with water from selected utility participants (Task 4 and 5).
4. Objective 4: Through completion of bench-scale tests in Task 4, we will explore the effects of PAC, MIEX, and ozone on carbon use rates for short-chain PFAS removal
5. Objective 5: We will explore several bench-scale testing approaches for GAC and IX (Task 4) and compare results to matching pilot-scale tests (Tasks 1 and 5). These comparisons will allow us to identify suitable bench-scale testing approaches for sorbent selection and scale-up.
6. Objective 6: Through completion of a literature review (Task 1) and experimentation in Tasks 4 and 5, we will develop information about residuals management (spent resin and GAC through Task 1, destruction of PFAS in brine through Tasks 4 and 5).
7. Objective 7: Through completion of Task 6, we will develop predictive models for short-chain PFAS removal by adsorption, anion exchange, and membrane processes
8. Objective 8: Using models being developed in a separately funded ESTCP project, we will develop life-cycle cost and environmental impact information for short-chain PFAS treatment alternatives (Task 7). This information will be summarized in a guidance manual for water treatment professionals.