Effectiveness of point-of-use/point-of-entry systems to remove per- and polyfluoroalkyl substances from drinking water

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INTRODUCTION

The widespread use of per- and polyfluoroalkyl substances (PFAS) over the last half century has resulted in these compounds being detected in environmental media. Although much is unknown, certain PFAS are toxic, resistant to degradation, and bioaccumulate in the food web and, subsequently, in animals and humans. At many sites, it is also likely that PFAS precursors and their degradation products are present; however, limited occurrence data are available due to the lack of comprehensive analytical method capabilities.

Recently, this has been a growing concern for the U.S. Environmental Protection Agency (USEPA)'s Superfund program as these compounds have been identified in groundwater at many high-profile sites across the country, including the Widefield aquifer near Colorado Springs, Colorado. At this site, perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorohexanoic acid (PFHxS), perfluorobutane sulfonate (PFBS), perfluoromethylcyclohexane sulfonic acid (PFHxS), and perfluoromonomeric acid (PFNA) have been detected in the groundwater. Three large water utilities, seven smaller state-regulated utilities, and hundreds of private wells are currently under investigation. At the three large water utilities, nonimpacted surface water from the Pueblo Reservoir is being blended with impacted groundwater sources to meet USEPA’s health advisory level (HAL) for combined PFOA and PFOS concentrations. The seven smaller systems and numerous private well owners use the impacted aquifer as source water.
their sole source of drinking water. On the basis of concentrations found in the Widefield aquifer and USEPA’s 2016 HAL of 70 ng/L of combined PFOA and PFOS concentrations (Federal Register, 2016), these Widefield aquifer systems are at risk.

Private well owners and small municipalities, where the presence of PFAS is known, are subject to multiyear or even decades-long site-specific investigations, source determinations, risk assessments, and remedial designs and constructions. In addition, many challenges exist at sites managing PFAS contaminants, including the lack of USEPA analytical methods, for the detection of PFAS, their precursors and degradation products, the unknown toxicological impact of many PFAS, and remediation or treatment technologies.

Many private well owners are seeking information on commercially available resources to treat PFAS-contaminated drinking water. Dissemination of the knowledge of the capabilities of commercially available reverse osmosis (RO) and granular activated carbon (GAC) point-of-use (POU) and point-of-entry (POE) treatment systems on PFAS removal would be valuable to those well owners. To match their needs, the PFAS removal systems that were selected for this study were designated to be in accordance with NSF International’s Standard P473 (2016).

2 | METHODS AND MATERIALS

To assess the removal effectiveness of the target PFAS present in the Widefield aquifer region, treatability studies were conducted using three commercially available RO treatment systems and two GAC media at the USEPA Test and Evaluation (T&E) facility in Cincinnati, Ohio. RO systems and GAC media were tested using test water simulating the PFAS composition and water quality in the Widefield aquifer region. PFAS samples were analyzed using liquid chromatography/mass spectrometry (LC/MS/MS) at the USEPA Region 5 Chicago Regional Laboratory (CRL) in Chicago, Illinois.

Before RO system and GAC media tests, initial PFAS stability tests were conducted using the same test water to determine the stability of the PFAS compounds in the test water in the 5,000-gal stainless steel RO feed tank and the 55-gal stainless steel GAC media feed drum used in the study. On confirmation of stability, subsequent studies were completed on three RO POU/POE treatment systems, which were tested on the basis of aspects of NSF Standard P473 (NSF International, 2016). In addition, two GAC media were evaluated using rapid small-scale column tests (RSSCTs) per American Society for Testing and Materials D6586-03 (ASTM, 2008).

2.1 | Test water preparation

The feed water was prepared to simulate the PFAS contamination of the Widefield aquifer by adding the PFAS concentrations shown in Table 1. These six PFAS target concentrations are worst-case (maximum) concentrations compiled from historic records (2013–2016) of Widefield aquifer region water samples (Colorado Department of Public Health and Environment [CDPHE], 2016). To align with the NSF P473-specified 2:1 PFOS:PFOA ratio, the PFOA feed concentration was increased from 200 to 800 ng/L.

Cincinnati tap water was added to a 5,000-gal stainless steel tank equipped with a mixer, recirculation pump, and a chiller with a shell-and-tube heat exchanger to control feed water temperature. Sodium thiosulfate (1 mg/L) was added to dechlorinate the test water. The target water quality characteristics specified in Table 2 were maintained throughout the RO and GAC test runs to adhere to the requirements of NSF P473. The test water targets for pH (8.2), total dissolved solids (TDSs) (500 mg/L), and hardness (300 mg/L) were maintained to align with the historic maximum Widefield aquifer well water sampling results (1992–2016) to determine their impact on the longevity and removal capabilities of RO membranes and GAC media.

After the feed water additives dissolved overnight, the target PFAS were measured, mixed, and dissolved in 1 L of deionized water. The PFAS were then added to the 5,000-gal tank and allowed to mix for 3 h for use in the RO treatability study. Before the start of the RO study, approximately 50 gal of the feed water was drained into a 55-gal stainless steel drum equipped with a mixer for use in the GAC RSSCT evaluations. Dehydrated natural organic matter (NOM) of Ohio River water was rehydrated, filtered, and added to the 55-gal drum to increase the total organic carbon (TOC) of the water to above 1 mg/L for the GAC media studies (Pressman et al., 2012).

2.2 | Stability study

A PFAS stability test was run without the RO system and GAC adsorbents over an 8-day period to assess PFAS degradability and sorption in the test apparatus. The

| CAS number | PFAS compounds | Carbon chain length | Target concentration (ng/L) |
|------------|----------------|---------------------|---------------------------|
| 375-95-1   | PFNA           | C9                  | 200                       |
| 335-67-1   | PFOA           | C8                  | 800                       |
| 1763-23-1  | PFOS           | C8                  | 1,600                     |
| 375-85-9   | PFHpA          | C7                  | 200                       |
| 3871-99-6  | PFHxS          | C6                  | 1,000                     |
| 375-73-5   | PFBS           | C4                  | 300                       |

Note. CAS: Chemical Abstracts Service; PFBS: perfluorobutane sulfonate; PFHpA: perfluoroheptanoic acid; PFHxS: perfluorohexane sulfonic acid; PFNA: perfluorononanoic acid; PFOA: perfluorooctanoic acid; PFOS: perfluorooctane sulfonate.
concentrations of the six target PFAS remained stable in both the 5,000-gal tank and the 55-gal drum over the 8-day test period. The PFOS concentration was significantly lower than the target concentration due to a lower spike amount inadvertently used when adding the quantity of PFOS to the test water. The PFOS spike amount was corrected in the following test runs. The PFBS concentration was below the detection limit possibly due to the stock solution used during the stability test. A different source of PFBS was secured for the follow-up test runs. These adjustments resolved the concentration discrepancies of PFOS and PFBS during the actual test runs. Although no PFAS degradation or sorption was noted in the stability study, the initial target PFAS concentrations were increased by 25% for the treatability studies as a safety factor to ensure adequate PFAS concentrations for the tests.

### 2.3 Analytical methods

PFAS analysis was performed following the USEPA Region 5 standard operating procedure (SOP) for the analysis of polyfluorinated compounds of interest to the Office of Superfund Remediation and Technology Innovation in water, sludge, influent, effluent, and wastewater by multiple reaction monitoring LC/MS/MS (USEPA, 2017). Per the USEPA Region 5 PFAS analytical SOP, 15-mL polypropylene sample containers were weighed before and after sample collection to allow the laboratory to determine the exact sample amount used during analysis. The target volume of a sample per polypropylene container was 5 mL. Because all of the 5-mL sample volumes were analyzed, triplicate samples were collected from both influent and effluent for additional quality assurance/quality control analyses. With a 28-day sample holding time, grab water samples for PFAS analysis were shipped for overnight delivery to the USEPA Region 5 CRL in Chicago, Illinois. All other water quality analyses were performed at the USEPA T&E facility in Cincinnati, Ohio.

### 2.4 Analytical sampling plan

Six target PFAS compounds were analyzed in both RO system and GAC media influent and effluent water samples to determine PFAS removal efficiency. The sample plan included analysis of 188 PFAS samples at the CRL in USEPA Region 5 from one stability run and three test runs. Samples were collected from the 5,000-gal stainless steel mix tank and the 55-gal stainless steel drum and analyzed for PFAS, TOC, TDS, hardness, turbidity, pH, temperature, and free available chlorine. Only one free chlorine sample (influent and effluent) was collected at the beginning of each test to ensure that the test water was adequately dechlorinated. Additional information on methods and materials is provided in Appendix S1 (Supplementary Information).

### 2.5 RO system design

The installation of each unit was very straightforward. Each of the RO systems was preassembled by the manufacturer before shipment and used quick connects to attach inlet and outlet tubing. The RO systems only required connections to feed water and discharge points for operation. Specifications

| TABLE 3 | Summary of reverse osmosis (RO) system specifications |
|-----------------|-----------------|-----------------|
| **RO system**   | iSpring RCSOT  | HydroLogic Evolution RO1000 |
| Rated capacity* | 500 gpd (0.35 gpm) | 1,000 gpd (0.7 gpm) |
| Filters included | Sediment filter | Carbon prefilter |
|                 | Carbon prefilter | 2 RO membranes |
|                 | CTO filter      | Carbon postfilter |
|                 | RO membrane     | Carbon postfilter |
| System recovery*| 50%             | 50%, using 1:1 fitting |
| Booster pump    | Yes             | No |
| Connections     | 3/8” inlet      | 1/4” inlet |
|                 | 3/8” outlet (tubing not included) | 3/8” outlet (tubing included) |
| Self-supporting | Yes             | No |
| Size (L × W × H) | 8.5” × 15” × 18.5” | 20.5” × 11” × 10” |
| Weight          | 31 lb           | 16 lb |

*The systems' rated pressure and efficiency are a function of the temperature and pressure of the feed water.
for the three RO systems tested are summarized in Table 3. Table 4 shows the replacement part numbers, replacement frequency, and prices for the replacement filters and membranes in each of the three RO systems.

### 2.5.1 iSpring RO system

The five-stage iSpring RO system (iSpring Water Systems, LLC, Alpharetta, GA) was free standing and was preplumbed with a booster pump and color-coded feed and discharge tubing when it was removed from the box. Except for the RO membrane, the filters and cartridges described in Tables 3 and 4 were preinstalled. Wrenches were included to install replacement membranes and filters.

### 2.5.2 HydroLogic RO system

The two-stage HydroLogic RO system (HydroLogic Purification Systems, Santa Cruz, CA) was free-standing and included fittings for a 2:1 (green) or 1:1 (orange) waste to pure water ratio. The instructions stated that using the 1:1 fitting (chosen for this study) would provide a higher flow rate but could require more frequent replacement of the RO membranes. Three 90° elbow push fittings, the carbon prefilter, and two RO membranes were installed with wrenches before use. Inlet and outlet tubing was color-coded, and a ball valve at the end of the discharge line was provided for use when water was not needed. A booster pump had to be purchased separately and was installed in front of the HydroLogic RO system.

### 2.5.3 Flexeon RO system

The four-stage Flexeon RO System (AXEON Water Technologies, Temecula, CA) was preplumbed with filters when it was removed from the box. The Flexeon RO system was not self-supporting and did not come with a booster pump or inlet and outlet tubing. Except for the RO membrane, the filters and cartridges described in Tables 3 and 4 were preinstalled. A booster pump was purchased separately and was installed in front of the Flexeon RO system.

### 2.5.4 Booster pumps

The iSpring unit included an integrated booster pump to create a stable working environment for the RO membrane for situations in which the water feed pressure was not sufficiently high (40–50 psi). A booster pump was purchased separately for the HydroLogic and Flexeon RO systems (HydroLogic Booster Pump Model No. HL29014). The booster pump was installed and included tubing, a pressure gauge, and switches that turned the pumps off when the water supply was stopped or when the discharge line was closed (by a faucet or valve). This would not be needed in a home setup if system pressure is available.

### 2.5.5 Modifications for POE use

By themselves, the RO systems tested do not constitute a whole-house POE system; however, with some additional components, each of these RO systems could be part of a POE system. The RO systems tested were designed to produce 500–1,000 gpd (0.35–0.70 gpm), a flow rate that is not suitable for many household activities (bath water, showers, washing machines, dishwashers). In addition, the RO systems do not produce water at a significant pressure. However, it could serve as a POE system with the addition of a 200–500-gal storage tank, a delivery pump, and a 20-gal bladder tank. The storage tank would provide the necessary purified water to the home, and the delivery pump and booster tank would supply the necessary pressure. These RO systems would then be able to refill the storage tank to meet household water demands in real time. However, watering of lawns and gardens and filling swimming pools with treated water would not be a viable option without a much larger GAC or RO system.

### TABLE 4 Reverse osmosis (RO) system replacement filters and membranes

| RO system     | iSpring RCS5T  | HydroLogic Evolution RO1000 | Flexeon LP-700 |
|---------------|----------------|-----------------------------|----------------|
| Sediment filter | #FP15 (3–6 months) | Not part of system #200627 (12 months) | #FP15 (3–6 months) |
| Carbon prefilter | #FG15 (6 months) | #2043 (2,000 gal of purified water) | #200658 (12 months) |
| Carbon block filter | #FC15 (6 months) | Not part of system #208802 (24 months) (requires 2) | Not part of system |
| RO membranes | #MS5 (24 months) | #20445 (6–24 months) (requires 2) | #208802 (24 months) (requires 2) |
| Carbon postfilter | #FT15 (12 months) | Not part of system #200658 (12 months) | Not part of system |

### TABLE 5 Reverse osmosis (RO) system sampling plan

| Day # | Day of week | Time of day | Sample (h) | Time of day | Sample (h) | Time of day | Sample (h) |
|-------|-------------|-------------|------------|-------------|------------|-------------|------------|
| Day 1 | Tuesday     | a.m.        | Startup*   | Noon        | 4          | p.m.        | 8          |
| Day 2 | Wednesday   | a.m.        | 24         | Noon        | 30         | p.m.        | 36         |
| Day 3 | Thursday    | a.m.        | 48         | Noon        | 54         | p.m.        | 60         |
| Day 4 | Friday      | a.m.        | 72         | Noon        | 78         | p.m.        | 84         |
| Day 5 | Saturday    | 2-day stagnation period* | | | | | |
| Day 6 | Sunday      | a.m.        | 144        | p.m.        | 148        | p.m.        | Shutdown* |

*No samples collected.
2.5.6 | RO system sampling plan
The RO systems were originally planned to operate continuously for 4 days, shut down for 2 days, and then operate for another day per NSF P473, as shown in Table 5 (NSF International, 2016). Because of the high use of water from the 5,000-gal tank, the Flexeon and HydroLogic units were operated for 2 days, shut down for 4 days, and then operated for another day. Sampling occurred normally during the period when the units were operating.

The RO systems received test water from a 5,000-gal stainless steel tank. The tank included a mixer and a recirculation pump that recycled the feed water from the bottom to the top of the tank. The feed to the RO system came off the recirculation line. A chiller with a shell and tube heat exchanger was located on the recirculation line to maintain the temperature of the tank at approximately 25°C. A schematic of the RO test system is shown in Figure 1. Figures 2–4 show photographs of the iSpring RCS5T, HydroLogic Evolution RO1000, and the Flexeon LP-700 RO systems, respectively, at the USEPA T&E facility.

Grab samples were collected from each of the RO systems twice or thrice per day during the test period. Grab samples from the influent to the RO system were collected from the recirculation line on the 5,000-gal tank. Grab samples from the effluent of the RO system were collected from the end of the permeate tubing. The flow rate of both the reject (concentrate) and the permeate water was measured throughout the test using a graduated cylinder. This allowed the calculation of the recovery, or efficiency, of the RO system.

2.6 | GAC system design
Two types of GAC media were evaluated using test water: (1) Calgon Filtrasorb 600 AR+ (Calgon Carbon Corporation, Pittsburgh, PA), manufactured from select grades of bituminous coal, and (2) Evoqua 1230CX (Evoqua Water Technologies Pittsburgh, PA), a coconut-based GAC as shown in Table 6. The two GAC media were tested separately using RSSCT methods described in ASTM D6586-03 (2008). Samples were collected every 30 min over an 8-h period.

The representative POE system for GAC filter was an H₂O Filter Warehouse Model FT-1-GAC-20, 4–5 gpm non-backwashing whole house carbon water filter (Omni Filter, Rexford, MT). This filter uses a 35⁰ (H) × 9⁰ (D) tank, 30 lb (1 ft³) GAC, and is rated for 4 gpm with a treatment volume of 150,000 gal. The RSSCT data were scaled up to approximate the use of GAC in this unit.

RSSCTs are based on fixed-bed mass transfer models. The mass transfer models are scaled down from the full-scale adsorber to a small column (SC). Similarity of operation to that of large-scale adsorbers is ensured by properly selecting the particle size, hydraulic loading, and empty bed contact time (EBCT) of the small adsorber. The RSSCT allows the tests to be conducted much more quickly and with less water than full-scale POE tests. Figure 5 shows a schematic of the RSSCT system. Figure 6 shows a photograph of the GAC RSSCT system at the USEPA T&E facility.
The EBCTs of the large-scale adsorber and the small-scale adsorber are related to the particle sizes of the GAC within the columns according to the following equation (Crittenden et al., 1991):

\[
\frac{EBCT_{SC}}{EBCT_{LC}} = \left(\frac{d_{p,SC}}{d_{p,LC}}\right)^{2-x} = \frac{t_{SC}}{t_{LC}},
\]

where \( EBCT \) is the empty bed contact time; \( d_p \) is the GAC particle size; and \( t \) is the elapsed time to conduct the tests for the RSSCT SCs and the POE large columns (LCs), respectively. \( X \) defines the dependence of the intraparticle diffusion coefficient on particle size. In this case, it is assumed that the intraparticle diffusivities do not change with particle size, so \( X = 0 \). Therefore, the time (minutes) of operation in the LC is proportional to the square of the ratio of the particle sizes in the large and SCs multiplied by the time of operation in the SC.

Other equations relating the large and SC operation include the following:

\[
\frac{V_{SC}}{V_{LC}} = \frac{d_{p,LC}}{d_{p,SC}}
\]

where \( V \) is the velocity in the LC and SC, and

\[
M_{SC} = EBCT_{LC} \left(\frac{d_{p,SC}}{d_{p,LC}}\right)^{2-x} Q_{SC} \times \rho_{LC},
\]

where \( M \) is the mass of GAC in the SC, \( Q \) is the flow rate in the SC, and \( \rho \) is the GAC density in the LC.

The RSSCT evaluation for this study used a 55-gal stainless steel drum with a mixer as a holding tank for the feed water in a temperature-controlled laboratory. The feed water was pumped through the GAC column using a Masterflex® gear pump (Masterflex, Gelsenkirchen, Germany) at approximately 10 mL/min. The flow rate was measured by collecting water in a graduated cylinder, and it was adjusted to maintain 10 mL/min throughout the study. One-quarter-inch stainless steel tubing was used throughout the system. The inside diameter of the RSSCT column was 4.76 mm. Each type of GAC was ground to a particle size between 170 and 200 mesh with a mortar and pestle. Carbon fines were washed off the crushed GAC with deionized water, and the crushed GAC was dried in a 150°C oven for 4 h. After weighing the crushed GAC for use in the RSSCT, it was added to 40 mL of deionized water and boiled for 10 min to replace the air in the GAC’s pores with water. Fiberglass wool was placed in the bottom of the column to keep the GAC inside the column.

On the basis of discussions with GAC vendors offering systems for PFAS removal, an EBCT of 10 min and a GAC RSSCT study duration of 8 h were selected, with a 30-min sample collection frequency. An EBCT of 10 min was selected to provide adequate time for PFAS to absorb GAC and to allow for reasonable GAC replacement frequencies for homeowners. Grab samples from the influent to the RSSCT were collected from the 55-gal drum (Figure 5). Grab samples from the effluent of the RSSCT were collected from the end of the ¼-in. stainless steel tubing every 30 min over an 8-h test period.
RESULTS AND DISCUSSION

3.1 RO system studies

Three RO systems were tested: RO#1, iSpring RCS5T 500 gpd (0.35 gpm); RO#2, HydroLogic Evolution 1,000 gpd (0.7 gpm); and RO#3, Flexeon LP-700 gpd (0.5 gpm).

3.1.1 RO#1 test

The first RO POU/POE system, the iSpring RCS5T (RO#1), was tested over a 7-day period at an average flow rate of 2,285 mL/min. RO#1 was operated on Tuesday through Friday of the first week, shut down over the weekend, and restarted on Monday morning of the following week for the Day 7 samples.

All PFAS in the effluent were reduced below detection for the entire test period. RO#1 also reduced the turbidity, TOC, TDS, and hardness in the effluent. The average permeate flow rate from this unit was approximately 1,020 mL/min, and the average concentrate (reject) flow rate from this unit was approximately 1,265 mL/min.

3.1.2 RO#2 test

The second RO POU/POE system, HydroLogic Evolution RO1000 (RO#2), was tested intermittently over a 7-day period. Because of the increased water volume necessary to test this unit at an average flow rate of 4,895 mL/min, the unit was only operated on Tuesday and Wednesday of the first week before being shut down for the weekend. RO#2 was then restarted on Monday morning of the following week for the Day 7 samples.

Most of the PFAS samples were below the detection limit for the test. However, 6 of 42 RO#2 PFAS sample results were above the detection limit as shown in Table 7 and Figure 7. Five of the PFAS were detected after startup on Day 7.

RO#2 reduced the turbidity, TOC, TDS, and hardness in the effluent as shown in Table 8. Other than a slightly higher effluent turbidity after startup on Day 7, the RO membranes appear to be intact as exhibited by the consistent removal of TOC, TDS, and hardness. Because of the demineralization of the RO-treated water shown in Table 8, a remineralization cartridge may be required to improve taste and to control corrosion in household premise plumbing.

The PFAS compounds found in the effluent may have resulted from the limited number of treatment barriers (activated carbon pre- and postfilters) in the two-stage HydroLogic RO system or a leaking membrane seal because the breakthrough does not correlate to molecular size, as might be expected with a strictly membrane system. However, even the breakthrough of the GAC from the activated carbon pre- and postfilters does not fully match the adsorption properties of the compounds. In addition, it is unclear whether this was a one-time event or whether it is to be expected for the days following Day 7.

The average permeate flow rate from this unit was approximately 2,165 mL/min, and the average concentrate (reject) flow rate from this unit was approximately 2,285 mL/min.
2,730 mL/min. The recovery of the RO#2 system was approximately 44%.

### 3.1.3 | RO#3 test

The third RO POU/POE system, Flexeon LP-700 (RO#3), was tested over a 7-day period. Because of the increased water volume necessary to test this unit at an average flow rate of 4,560 mL/min, the unit was only operated on Tuesday and Wednesday of the first week before being shut down for the weekend. RO#3 was then restarted on Monday morning of the following week for the Day 7 samples.

All PFAS in the effluent were reduced below the detection limit for the entire test. RO#3 also reduced the turbidity, TOC, TDS, and hardness in the effluent. The average permeate flow rate from this unit was approximately 1,260 mL/min, and the average concentrate (reject) flow rate from this unit was approximately 3,300 mL/min. The recovery of the RO#3 system was approximately 28%.

### 3.2 | RO discussion

The three RO systems were similar in many respects. They were each designed to be installed by a homeowner with basic “handyman” skills or a plumber, if necessary. The RO systems were all equipped with the required filters, membranes, and tools to install and replace these parts. However, the specifics of what was included varied (types of filters, tubing, booster pump, etc.). RO#1 and RO#2 (iSpring and HydroLogic) were self-supporting, while RO#3 (Flexeon) had to be mounted to a wall. Filters and membranes require replacement by the homeowner or plumber on a regular schedule, and all three RO systems generated more reject water than purified water during this study.

Because RO systems tend to increase water corrosivity without additional processes, care should be taken to evaluate potential lead and copper corrosion from the posttreatment premise plumbing for any POE systems. A remineralization cartridge may be required to improve the taste of RO-treated water and for corrosion control in household plumbing. Disposal of reject water via sewer or septic systems may be allowed under a homeowner exemption in many communities; however, special considerations should be made if there is a possibility of contaminating the aquifer.

### 3.3 | GAC media studies

Two GAC media were tested using the test water: GAC#1; Evoqua 1230CX, a coconut-based GAC, and GAC#2; Calgon Filtrasorb 600 AR+, manufactured from select grades of bituminous coal.

#### 3.3.1 | GAC#1 test

The first RSSCT was conducted using Evoqua 1230CX (GAC#1), a coconut-based GAC. The target flow rate was 10 mL/min, and the flow rate was checked every 30 min before samples were collected. Each time, the flow rate was adjusted to maintain 10 mL/min. The flow rate was maintained within 9.6–10.1 mL/min over the course of this test.

No PFAS were detected in the RSSCT effluent for the first 1.5 h of testing. Individual PFAS began to break through the GAC at 2 h and increased with time. The breakthrough time for each PFAS was dependent on the specific compound adsorption properties and its influent concentration. PFOA

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### Table 8: Water quality results from reverse osmosis (RO)#2 test

| Date       | Day | Hours | Turbidity (ntu) | TOC (mg/L) | TDS (mg/L) | Hardness (mg/L) |
|------------|-----|-------|----------------|------------|------------|-----------------|
|            |     |       | Influent       | Effluent   | Influent   | Effluent        | Influent | Effluent |
| Start-up   | March 13, 2018 | 1    | 4              | 0.38       | 0.12       | 1.2             | 0.48     |
|            | March 13, 2018 | 1    | 8              | 0.40       | 0.19       | 1.2             | 0.18     |
|            | March 14, 2018 | 2    | 24             | 0.31       | 0.17       | 1.2             | 0.21     |
|            | March 14, 2018 | 2    | 30             | 0.33       | 0.11       | 1.2             | 0.16     |
|            | March 14, 2018 | 2    | 36             | 0.30       | 0.12       | 1.2             | 0.16     |
| Shutdown and start-up | March 19, 2018 | 7    | 144            | 0.34       | 0.54       | 1.3             | 0.19     |
|            | March 19, 2018 | 7    | 148            | 0.39       | 0.12       | 1.3             | 0.12     |

Note. TDS: total dissolved solid; TOC: total organic carbon.

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FIGURE 8 | Per- and polyfluoroalkyl substances (PFAS) concentrations versus time for granular activated carbon (GAC)#1. PFBS: perfluorobutane sulfonate; PFHpA: perfluorohexanoic acid; PFHxS: perfluorohexane sulfonic acid; PFNA: perfluorononanoic acid; PFOA: perfluorooctanoic acid; PFOS: perfluorooctane sulfonate
and PFOS were the first compounds detected in the RSSCT effluent, and PFNA was the last compound detected. All PFAS were detected within 5.5 h of testing. By the end of the 8-h testing period, the PFOS and PFBS had the highest concentrations in the effluent, and the PFNA had the lowest concentration in the effluent. Figure 8 shows the PFAS concentrations as a function of time for GAC#1. These results do not match the general results seen by others (Appleman, Dickenson, Bellona, & Higgins, 2013; Dickenson & Higgins, 2016; McCleaf et al., 2017), where the smaller PFAS (e.g., PFBS) generally break through before the longer-chain PFAS (e.g., PFOA and PFOS). However, the PFBS concentration in the test water (260 ng/L) was much lower than the PFOS (1,600 ng/L) and PFOA (800 ng/L) concentrations. The data suggest that, in this case, the combined PFOS + PFOA results may be conservative for controlling the other PFAS. Care must be taken in translating these results to other waters and carbons.

On the basis of the USEPA PFOS and PFOA HAL, GAC#1 lasted for approximately 4 h before the total PFOS and PFOA concentration exceeded 70 ng/L. Using the RSSCT scaling factor for this test (194.3, as shown in Table 6), the simulated life of a GAC filter using GAC#1 with 10 min EBCT would be approximately 800 h (33 days). After this time, the total PFOS and PFOA concentration in the effluent would be expected to exceed the USEPA HAL. GAC#1 treated approximately 4,800 bed volumes of water before exceeding the USEPA PFOS and PFOA HAL. These results suggest that the HAL level of 70 mg/L for combined PFOA and PFOS concentrations is protective when evaluating the breakthrough of the other PFAS studies; however, this is a function of the experimental design chosen in terms of water quality and PFAS studies. Others have shown different results, as mentioned earlier. Aside from a reduction in TOC, no other changes were evident in the water quality parameters for GAC#1.

3.3.2 | GAC#2 test

As a comparison with the coconut-based GAC from Evoqua, a second RSSCT was conducted using Calgon Filtrasorb 600 AR+ (GAC#2), a coal-based GAC. The target flow rate was 10 mL/min, and the flow rate was checked every 30 min before samples were collected. Each time the flow rate was adjusted to maintain 10 mL/min. The flow rate was maintained at 9.5–10.8 mL/min over the course of this test.

No PFAS were detected in the RSSCT effluent for the first hour of testing. Individual PFAS began to break through the GAC at 1.5 h and increased with time. As with GAC#1, PFOA and PFOS were the first compounds detected in the GAC#2 effluent, and PFNA was the last compound detected. All PFAS were detected by 3.5 h of testing. By the end of the 8-h testing period, the PFOA and PFOS had the highest concentrations in the effluent, and the PFNA had the lowest concentration in the effluent. After 8 h of testing, compared with GAC#1, GAC#2 had higher concentrations of each of the PFAS except for PFBS. GAC#2 PFBS reached 70 ng/L 1.5 h later than GAC#1 PFBS. Figure 9 shows the PFAS concentrations as a function of time for GAC#2. These results are similar to those seen for GAC#1 (Evoqua 1230CX). The caveat that the HAL level for PFOA and PFOS may not be protective for PFAS removal made in the GAC#1 discussion also holds true for GAC#2.

On the basis of the USEPA PFOS and PFOA HAL, the GAC#2 lasted for approximately 3 h before the total PFOS and PFOA concentration exceeded 70 ng/L. Using the RSSCT scaling factor for this test (165.9, as shown in Table 6), the simulated life of a GAC filter using GAC#2 with 10 min EBCT would be approximately 480 h (20 days). After this time, the total PFOS and PFOA concentration in the effluent would be expected to exceed the USEPA HAL. GAC#2 treated approximately 2,900 bed volumes of water before exceeding the USEPA PFOS and PFOA HAL. Aside from a reduction in TOC, no other changes were evident in the water quality parameters for GAC#2. The projected life of GAC#1 and GAC#2 is based on the operation of the filters 24 h/day and should be adjusted to account for actual household water usage patterns. Tables of RO and GAC media study results are provided in Appendix S1.

3.4 | GAC media discussion

The representative POE system selected for the GAC filter used a 35° (H) × 9° (D) tank, 30 lb (1 ft³) GAC, and was rated for 4 gpm with a treatment volume of 150,000 gal. This size unit would only have an EBCT of 2 min, much smaller than a tank with an EBCT of 10 min (as recommended by GAC vendors for PFAS removal).

To meet the EBCT of 10 min, one alternative would be to use two tanks in series that are 65 in. high by 16 in. in diameter, with approximately 240 lb (8 ft³) GAC. However, scaling up the RSSCT data estimated that the coal-based
Calgon F-600 GAC would have a lifetime of 20 days (2,900 bed volumes) compared with the coconut-based Evoqua GAC lifetime of 33 days (4,800 bed volumes) before requiring replacement based on maximum day PFAS concentrations tested before exceeding the USEPA’s HAL of 70 ng/L for PFOS and PFOA. Modeling the results for a lower concentration (average daily concentration) gave bed lives of 545 days (79,000 bed volumes) for the Calgon F-600 GAC and 791 days (115,000 bed volumes) for the Evoqua coconut carbon before requiring replacement as described in Section 4.

Increasing the size of the GAC filter tank or placing two filter tanks in series to lengthen the lifetime of the GAC media for PFAS removal would require additional plumbing and access to drainage lines for backwash wastewater. Replacing wet, contaminated GAC with dry GAC in the home is labor-intensive and requires backwashing to precondition and sort out GAC particle sizes and to remove air. The larger carbon filter tanks will also require additional space that may need to be heated depending on the local environment.

3.5 RO and GAC residuals management

Residual streams from home residences are exempt from federal regulations as solid/hazardous wastes under the Resource Conservation and Recovery Act. Therefore, homeowners can discharge RO reject water to the publicly owned treatment works. The RO reject wastewater concentrations from RO#1, RO#2, and RO#3 were calculated to own treatment works. The RO reject wastewater concentrations tested before exceeding the USEPA’s HAL of 70 ng/L for PFOS and PFOA. Modeling the results for a lower concentration (average daily concentration) gave bed lives of 545 days (79,000 bed volumes) for the Calgon F-600 GAC and 791 days (115,000 bed volumes) for the Evoqua coconut carbon before requiring replacement as described in Section 4.

4 Modeling of GAC Results

To investigate the impact of PFAS influent concentrations on GAC (bed volumes to breakthrough at 70 ng/L PFOS + PFOA), a model was used to predict GAC lifetime based on average PFOA (43 ng/L) and PFOS (137 ng/L) concentrations based on historic records (2013–2016) found in Widefield aquifer region water samples (CDPHE, 2016). Adsorption Design Software (AdDesignSTM, Houghton, MI) version 1.0, distributed as part of the ETDOT suite, developed by Michigan Technological University (Hokanson, Hand, & Crittenden, 1999; Mertz, Gobin, Hand, Hokanson, & Crittenden, 1994), was used to model the adsorption of PFOA + PFOS compounds.

4.1 Parameter estimation process

Adsorptive capacity was estimated by calculating the area (integrating) between the influent and effluent concentrations and dividing the resulting value by the mass of carbon in the test apparatus. Any extrapolation of effluent concentration data needed to calculate the total breakthrough point was performed using a line fit for nonzero effluent concentrations and determining the intersection of that line with the average influent concentration. The capacity calculated in this step was used to estimate the Freundlich parameters. The Freundlich isotherm formula is

\[ q = K \cdot C^{(1/n)} \]

where \( q \) is the adsorptive capacity (\( \mu g/g \)), \( C \) is the average influent concentration (\( \mu g/L \)), and \( K \) (\( (\mu g/g)/(L/\mu g)^{(1/n)} \)), and \( n \) (unitless) are isotherm fitting parameters. The exponential term \((1/n)\) was set to 0.45 for all models on the basis of past experience with PFAS modeling. The \( K \) estimated in this step was used by the PSDM (pore surface diffusion model) code, as described below.

4.2 Pore surface diffusion model

The PSDM module from AdDesignS was used to model the adsorption of PFAS onto each carbon (Crittenden, Hutzler, Geyer, Oravitz, & Friedman, 1986; Mertz et al., 1994). AdDesignS uses input information about the adsorption column (diameter, length, flow rate, carbon mass), the adsorptive material/carbon (particle radius, apparent density, porosity), and the adsorbing species (molecular weight, molar volume, and so on). The calculated Freundlich isotherm parameters as described above were used as inputs to AdDesignS. Additional adsorption kinetics parameters were also required by the model. The film diffusion coefficient was calculated by the Gnielinski correlation (Mertz et al., 1994; Sontheimer, Crittenden, & Summers, 1988). The pore diffusion coefficient was calculated from the Hayduk and Laudie correlation (Mertz et al., 1994, Sontheimer et al., 1988). The surface diffusion coefficient was calculated by AdDesignS using the Sontheimer correlation (Mertz et al., 1994, Sontheimer et al., 1988). The surface and pore diffusion and film transfer coefficients were varied to produce a good fit to experimental data. The influent concentrations recorded during GAC RSSCTs 1 and 2 were input into the model. The surface and pore diffusion coefficients were varied to minimize the sum of squared (SSQ) difference between the modeled and experimental effluent concentrations. The minimum SSQ values were recorded with the associated pore and surface diffusion coefficients. PFAS AdDesignS model input parameters are provided in Table 30 of Appendix S1.
4.3 | Application of the model

Adsorption kinetics parameters that resulted in the best match to experimental values were recorded. These were used to model configurations or operating schemes that were not directly tested in the GAC RSSCTs. Specifically, the influent concentrations were reduced from the worst-case (maximum) to average-day concentrations seen in the Widefield aquifer (CDPHE, 2016). Figures 10 and 11 show the model results of effluent concentrations for PFOS and PFOA for both RSSCT experiments using the worst-case (maximum, tested, shown in green) and average-day concentrations (shown in blue) supplied to each carbon. The PFOS + PFOA concentration in the influent was approximately 3,000 ng/L for the worst-case scenario and 180 ng/L for the average day (a $16\times - 17\times$ reduction). For the maximum day, the model predicted an exceedance of the PFOS + PFOA HAL (70 ng/L) after approximately 3,400 bed volumes for Evoqua GAC#1 and approximately 2,700 bed volumes for Calgon GAC#2, which is consistent with the experimental values. Reducing the influent maximum-day concentrations to the average-day concentrations resulted in exceedances of the HAL after approximately 115,000 bed volumes (2.2 years of operation) for GAC#1 and approximately 79,000 bed volumes for GAC#2 (1.5 years of operation). For the $16\times - 17\times$ reduction in influent concentration, the model predicted about $34\times$ (Evoqua) and about $29\times$ (Calgon) improvements in the number of treatable bed volumes before exceedance of the 70 ng/L HAL. This modeling has a number of assumptions (see Table 30 in Appendix S1) on the scale-up approach made in the model fitting, and therefore, it should not be relied on by homeowners. GAC performance should be monitored to determine the bed volumes and time to PFOA + PFOS breakthrough based on the actual well water quality conditions that will vary on the basis of distance from contamination source and source water hydrology.

5 | CONCLUSIONS

In this study, RO and GAC technologies were evaluated to determine their ability as household POU/POE systems to remove PFAS from contaminated groundwater. The RO system and GAC media effluent results were compared for PFOA and PFOS at individual and combined concentrations with the current 70 ng/L USEPA HAL. Both GAC and RO POU/POE systems were shown to have the potential to remove PFAS to below detections under specific water quality conditions, PFAS concentrations, and operational conditions, studied here. However, performance will vary as these conditions vary both spatially and temporally. In addition, long-term performance of these systems, particularly the membrane system, was not tested.

Specifically, each of the three RO systems that was tested successfully removed PFAS from the influent water to below analytical detections for the majority of the sampling events. RO#1 and RO#3 (Flexeon and iSpring) did not show any PFAS in the treated water, while RO#2 (HydroLogic) showed low levels of PFAS in the treated water after shutdown and startup.
The GAC POE systems were evaluated using RSSCT studies to save experimental time. Two different GAC materials were tested in this treatability study: one manufactured from coconut shells and the other manufactured from bituminous coal. While each of the GAC materials tested during this evaluation produced water with little or no PFAS in the effluent, it was found that the coconut-based carbon would treat more water than the coal-based carbon before requiring a replacement. However, the GAC materials may react differently to variations in source water characteristics within the Widefield aquifer region, and additional pilot tests should be performed to ensure the use of the best-performing GAC for each application. In addition, more GAC materials are available that should be considered for testing.

Although this study suggests that using the HAL of 70 ng/L for the combined concentrations of PFOA and PFOS was protective when compared with the breakthrough of the other PFAS, other water qualities may not yield the same results. Differences in water quality, both in terms of PFAS concentrations and background water characteristics, can change this result. Other PFAS are also known to have weaker adsorption characteristics and would break through well before PFOA and PFOS.

If a POU/POE system is correctly designed on the basis of the source water’s characteristics and the PFAS found therein, POU/POE water systems can provide relatively inexpensive treatment barriers for PFAS removal in the home. However, analysis of PFAS samples is costly for homeowners and can be a major hurdle in effective removal of PFAS from household water supplies. Proper operation and maintenance and conservative replacement of POU/POE components and media may be one way to circumvent the high cost of monitoring treated household drinking water.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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